Evaluation of Catalysts as Automotive Exhaust Treatment Devices (1973)

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EVALUATION OF CATALYSTS
AS AUTOMOTIVE EXHAUST TREATMENT DEVICES

Report of the
Catalyst Panel
to the

COMMITTEE ON MOTOR VEHICLE EMISSIONS
NATIONAL ACADEMY OF SCIENCES

Revised March 28, 1973

NOTICE

The Committee on Motor Vehicle Emissions has evaluated the technological feasibility of meeting the light-duty motor vehicle emissions standards as prescribed by the Clean Air Amendments of 1970. This study was performed under the sponsorship of the National Academy of Sciences and with the express approval of the Governing Board of the National Research Council.

The Committee obtained much of its information from eight panels of consultants, each panel dealing with a particular subject area of importance in the Committee deliberations. Panel members were selected by the Committee on the basis of recognized competence in specific areas.

The panel reports are reports of the panels to the Committee. Before publication, each panel report was reviewed by appointed members of the Committee. The views represented by the panels are one of the sources of information provided to the Committee and were used as a partial basis for the Committee judgments.

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PREFACE

In legislating the Clean Air Amendments of 1970, the Congress asked the Environmental Protection Agency to contract with the National Academy of Sciences to conduct a comprehensive study and investigation of the technological feasibility of meeting the motor vehicle emissions standards prescribed in accordance with the law. In responding to this request, pursuant to a contract with the Environmental Protection Agency, the Academy established a Committee on Motor Vehicle Emissions and charged it with the conduct of this study. The Committee published the results of its work in a report to the Environmental Protection Agency dated February 12, 1973.

As a means of providing itself with authoritative information and expertise in the various critical aspects of the problem it undertook to study, the Committee appointed specialist panels to undertake investigations and report their findings. The following report, Evaluation of Catalysts as Automotive Exhaust Treatment Devices, presents the findings of one of those panels.

Taken together, the special panel reports constitute a very substantial accumulation of data and analysis brought together by many specialists in many investigations in a very fast-moving area of technological development. In its published report, the Committee on Motor Vehicle Emissions has, of course, brought together that part of all this information and analysis required to fulfill its stated obligation to the Environmental Protection Agency. The separate reports of the specialist panels are published for the public record and to complete the documentary record.

The Catalyst Panel was charged with analyzing the activity and durability of both oxidation and reduction catalysts for emission control systems. The availability of catalytic materials and possible toxicity problems associated with the use of certain catalysts also were investigated. During this period of study, the Panel on Catalysts for Automotive Emission Devices and Petroleum Refining (of the Committee on Technical Aspects of Critical and Strategic Materials of the National Materials Advisory Board of the National Academy of Sciences) was first, assessing the technological potential of catalysts other than platinum as economic and efficient substitutes for platinum in petroleum refining and automobile emission devices for control of atmospheric pollution and, second, indicating areas for further research. With the urgency for the automobile companies to comply with the standards established for 1975 and 1976, a state of flux existed and voluminous data were generated continuously, outmoding existing data practically overnight. Accordingly, the reader should peruse this report with the knowledge that this report is an interim step in evaluating catalysts as automotive exhaust treatment devices.

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1. INTRODUCTION AND SUMMARY

The Panel on Catalysts was organized in February 1972; the first meeting of the panel took place on March 31. Its responsibilities included investigations into the availability of catalysts for oxidation and NO_x reduction with sufficient activity and stability, the causes of aging, the interaction of catalysts with hardware modifications, raw material availability and toxicology of debris, and manufacturing and maintenance problems. The panel cooperated with the Panels on Emission Control Systems, Manufacturing and Production, and Maintenance.

The modes of operation of the panel included reading the relevant literature, sending out questionnaires to automobile and catalyst manufacturers, and visiting manufacturers. The panel visited seven automobile manufacturers in the U.S., West Germany, and Japan, and seventeen catalyst manufacturers in the U.S., England, and West Germany. The companies visited varied in the degree of cooperation from the most reticent -- who would not either reveal the scale of their research efforts or give a rudimentary description of their most promising products -- to the more cordial, who gave us a good deal of laboratory data as handouts and showed us their laboratories. The panel feels confident in evaluating the knowledge and ability of researchers, the quality of the research program, and the adequacy of resources. The panel has had no opportunity for independent verification of the accuracy of the company data collection and reduction, or for the completeness of the information given to it.

There are several unsolved problems in evaluation efforts:

1. While several catalysts have adequate initial activities, only vehicle testing under rigidly specified conditions can show whether they have adequate durability. Such vehicular tests are virtually always conducted by automobile manufacturers on catalysts submitted by would-be vendors. Since the usual secrecy agreement forbids the automobile manufacturers to examine the catalyst structure or composition, he has no knowledge about the chemical damage to the

catalysts consequent to aging and he can offer no related suggestions as to how to improve the next catalyst formulation. On the other hand, when the aged or damaged catalyst is returned to the catalyst maker, a complete history of the temperature and exhaust gas composition in the catalyst bed is often not available, so he cannot always determine the main cause of catalyst aging or how to make a better catalyst next time. Both automobile and catalyst manufacturers frequently claim that they are not able to show us all the relevant information in deference to the other party. In the future, it might be advisable to require auto manufacturers to report to the Committee the name of the manufacturer and the serial number of the most promising catalysts, together with the vehicle endurance test data, providing this information can be kept confidential.

2. None of the catalyst manufacturers were willing to tell us the elemental composition of their best catalysts, despite our need for this information in order to evaluate the adequacy of raw material supply and toxicology of debris. After hearing from the automobile manufacturers that a catalyst has done very well on a vehicular endurance test, it may be desirable to require the catalyst manufacturer to provide us with this information, providing this information can be kept confidential.

3. Vehicular endurance tests are very time-consuming, so there is often a 6-month delay between a new catalyst formulation and durability results. The Committee should institute a program of frequent updating of vehicular test results, so that the results contained in the Committee report on February 12, 1973, would not be grossly out of date.

4. The EPA endurance test does not encompass the range of conditions encountered in many road uses; there is a need to develop a more complete endurance test to evaluate catalyst life and failure rate in the hands of the public.

PROSPECTS FOR 1975-76

Oxidation catalysts have a longer history of development than NO_x reduction catalysts and the Clean Air Act requires their use a year sooner. Several catalyst companies have products with an initial catalytic activity that should permit a typical U.S. automobile (above 350 cubic inch displacement engine) initially to meet the 1975 standards of emission without extraordinary hardware modifications. The products of four companies are repeatedly cited by automobile manufacturers as having the best durability: Engelhard, Johnson Matthey, Grace, and Universal Oil Products (UOP). The first two have good results with platinum on monoliths, and the last two are inclined toward the use of noble or base metal promoted with noble metal on pellets. Even these products appear marginal for warranty purposes under the demanding and unpredictable everyday use and would probably require either a less severe interim standard or more frequent maintenance and replacement than every 50,000 miles. Other attractive candidates are predominantly base metal on pellets from Houdry, Oxy-Cat, and Monsanto.

NO_x catalysts are in a far more primitive state of development. While there are several products having sufficient initial activity when used in combination with exhaust gas recirculation, modified carburetion, and a very rich mixture, there is little vehicular aging data under the AMA or EPA endurance tests. Among the most promising products are the Gulf noble metal deposited on pellets or monoliths, which appears to have substantial lead resistance, and the Gould Gem catalyst, which is an open-mesh copper-nickel alloy reinforced by ceramic or stainless steel backing. Other candidates are from Johnson Matthey (noble metal on monolith) and Degussa (base metal on pellet). (See Table 1.)

A one-bed catalyst that will simultaneously reduce NO_x and oxidize CO and HC is under development at several companies, but it requires very precise balance in exhaust gas composition between oxidizers (O_2 and NO_x) and reducers (CO, HC, and H_2). This balance requires an air/fuel ratio control within $\pm.1$, which is difficult to attain.

Table 1 Vehicle Aging Data on NO_x Catalysts

Ford Emission Package AC

-EGR 10-15%

-thermal reactor

-dual bed pellet catalysts (147 $in.^3$ NO_x catalyst, 204 $in.^3$ HC/CO catalyst)

-fuel 0.03 gm/gallon of lead, 0.033 weight % S, .002 weight % P.

Mileage	HC	CO	NO_x gm/mile	Hot Start NO_x Efficiency (%)
low	0.26	1.72	0.55	75
18000	0.51	3.92	1.83	7
18000	0.33	1.88	0.54	(replace NO_x catalyst)

Ford Emission Package D

-metallic NO_x monolith

-EGR

-unleaded fuel

Mileage	HC	CO	NO_x	NO_x Efficiency (%)
low	0.3	1.50	0.56	77
3000	0.33	1.54	0.49	80
6000	0.48	2.63	0.70	71

Table 1 (continued)

Ford Emission Package D

-monolithic dual bed

Mileage	HC	CO	NO_x	NO_x Efficiency (%)
low	0.30	1.50	0.56	78
3000	0.33	1.54	0.49	80
6000	0.48	2.63	0.70	71
9000	0.72	1.92	0.89	63
12000	0.68	3.68	0.86	63
15000	0.69	5.40	1.29	46

General Motors ES 61322

-dual bed, Gulf NO_x catalyst on beads, HC/CO bead catalyst

-EGR, engine NO_x emission 0.7-1.0 grams/mile

-AMA durability miles

Mileage	NO_x Emission (gm/mile)	
low	0.22	
1000	0.42	
2000	0.41	
3000	0.43	
4000	0.58	
4000	0.49	(repeat run)
6800	0.44	
8800	0.48	
11700	0.70	
12900	0.72	

Table 1 (continued)

General Motors ES 61315

-dual bed, Johnson Matthey platinum and ruthenium on monolith

-EGR

-clear fuel

Mileage	NO_x Emission
low	0.21
1000	0.31
2100	0.33
3300	0.48
4400	0.59
5500	0.59
6600	0.59

(R. M. Campau _et_ _al_, SAE paper 720488, May 1972)

Such a catalyst would not perform well under conventional carburetion with a transient engine, and it has received relatively little vehicle testing. If precise carburetion can be attained in production, such as with an oxygen sensor and a feedback mechanism, a greater effort toward the development of a one-bed catalyst would be forthcoming.

The advantages claimed for monoliths over pellet beds are lower pressure drop through the bed, easier packaging, freedom of choice in the direction of gas flow, and lower attrition in road usage. The advantages claimed for pellet beds are higher resistance to melting, proven technology for large-scale manufacture, greater ease in changing catalysts, and a greater surface area, which enables base metals to function effectively. It is likely that two pellet beds in series would result in too large a pressure drop.

The size, shape, and location of converter are usually restricted by such space as can conveniently be allotted in an automobile; the basic chassis design was arrived at years ago when pollution was not a main concern. The converter design and location that is best for the performance of the catalysts has received inadequate attention and priority.

The greatest problems of catalyst deterioration in road use arise from over-temperature and poisons. The catalysts must be protected from these hazards as far as possible and must be replaced promptly upon failure. Protection may require a fast-acting, over-temperature bypass for the exhaust gas. The available test data are inadequate at this time to permit specification of maximum contaminant levels in fuels for the following reasons: (1) Test data are scanty, (2) Present variability in testing requires a large test fleet to give statistically significant sample size, (3) The identity of the catalyst that will be employed is not clear, and (4) The degree to which catalytic activities can recover from lead, sulfur, and phosphorus contamination after a high-temperature operation is imperfectly understood. Similar problems prevent any adequate evaluation at this time of any poisoning effects of additives in lubricating oil.

A signaling device to indicate catalyst failure would be needed, but this panel has not heard of any device that is simple, accurate, and durable.

Most catalyst makers are aware of raw material supply problems, and they are avoiding rare materials such as iridium. There appears to be no problem of supply for base metals and for the supports. The two noble metals of greatest promise are platinum and palladium; for oxidation alone, a car of 350 cubic inch displacement would need up to 0.15 ounces of either metal. This figure would be doubled if the requirement for the NO_x catalyst is similar. Thus, there would be an initial demand of as much as 3 million ounces per year in the United States, a figure comparable to the world production in 1970. Ruthenium is the most promising NO_x catalyst, although it is in short supply. The recovery of platinum contained in spent catalyst delivered to the door of precious metal refiners should be above 99 percent; the efficiency of scavengers in collecting spent noble metal catalysts is difficult to estimate. The value of the recovered metal would be of the order of $15 - 20 per car. In comparison, copper costs 50¢ per pound, and 61 percent of scrap copper is recycled in the United States. Most base metal catalysts are promoted with precious metals at less than 0.01 ounce per car. There would be less incentive for scavengers to collect the promoted base metal catalysts.

Although most of the materials projected for use in automobile exhaust catalysts have some toxicity, the dangers to humans from use in exhaust controls is minimal. Only during manufacture and installation of the catalyst is one likely to contact the material in concentrations sufficiently high to be potentially harmful. Techniques can be developed that will avoid such hazards.

INTEGRATION OF THE ENGINE-CONVERTER-CATALYST SYSTEM

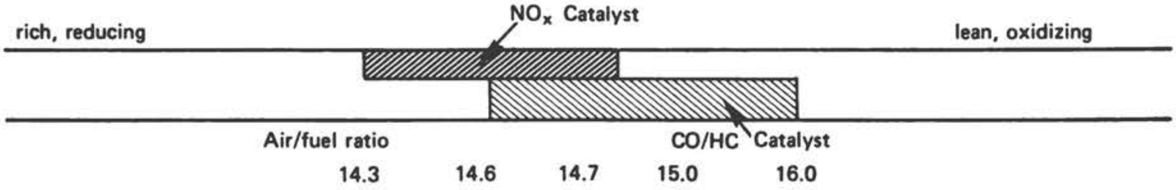
Proper functioning of the system requires adequate integration of the engine and auxiliary equipment, the converter, and the catalyst. Each component has historically been associated with a different industry and a different academic discipline. The performance of a catalyst depends on whether it is matched to hardware configurations that will bring out the best in the catalyst and whether the proper fuel and lubricant are used. There is no tradition in designing a hardware system to fit a given catalyst in the automotive industry. This fragmented and poorly coordinated research effort has retarded progress but is now improving.

Catalysts have a long history of success in the petroleum and chemical industries; the major processes in these industries employ steady-state conditions of temperature, pressure, flow rate of gases, and careful exclusion of poisons. Many of the automobile catalysts that have been developed would work well and probably last at least 50,000 miles if they were operated within narrowly defined operating ranges (or "windows") in four variables: temperature, gas composition, gas flow, and poison concentrations. Catalysts can tolerate occasional excursions from these windows, but prolonged excursions invariably lead to slow chronic aging or to quick massive failures, as shown in Figure 1.

In actual practice, an automobile is always in a transient condition: The catalyst is too cold during start-up and too hot during a long downhill cruise; the air/fuel ratio is too rich on idle and too lean at high speed; the exhaust gas flow is slow during idle and fast during upgrade cruise. The catalysts are also exposed to repeated cycles of heating and cooling, evaporation and condensation of water, pulsating flow from exhaust gases, vigorous shaking on the road, and a variety of poisons including lead and sulfur. The excursions from the optimal operating conditions lead catalysts in automobiles to deteriorate prematurely.

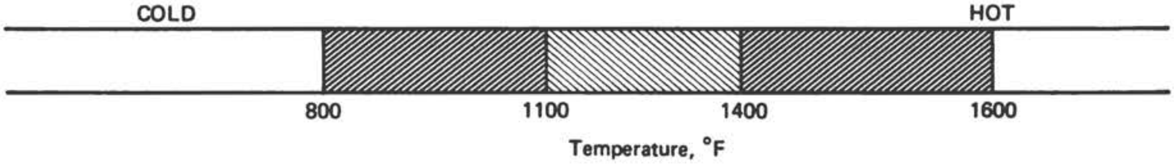
Much progress has been made in widening the operating windows. Stabilized supports have been developed that can tolerate occasional temperature excursions to 2000°F, but even this temperature may be exceeded in long downhill cruises. Recently some low-density catalysts have been developed that warm up quickly from a cold start but are apt to give dangerously high temperature excursions. No great breakthrough is anticipated in the simultaneous widening of all four windows to embrace all driving conditions in road use; it will be necessary to design hardware systems so that the catalysts are protected from long

Exhaust Gas Composition Window

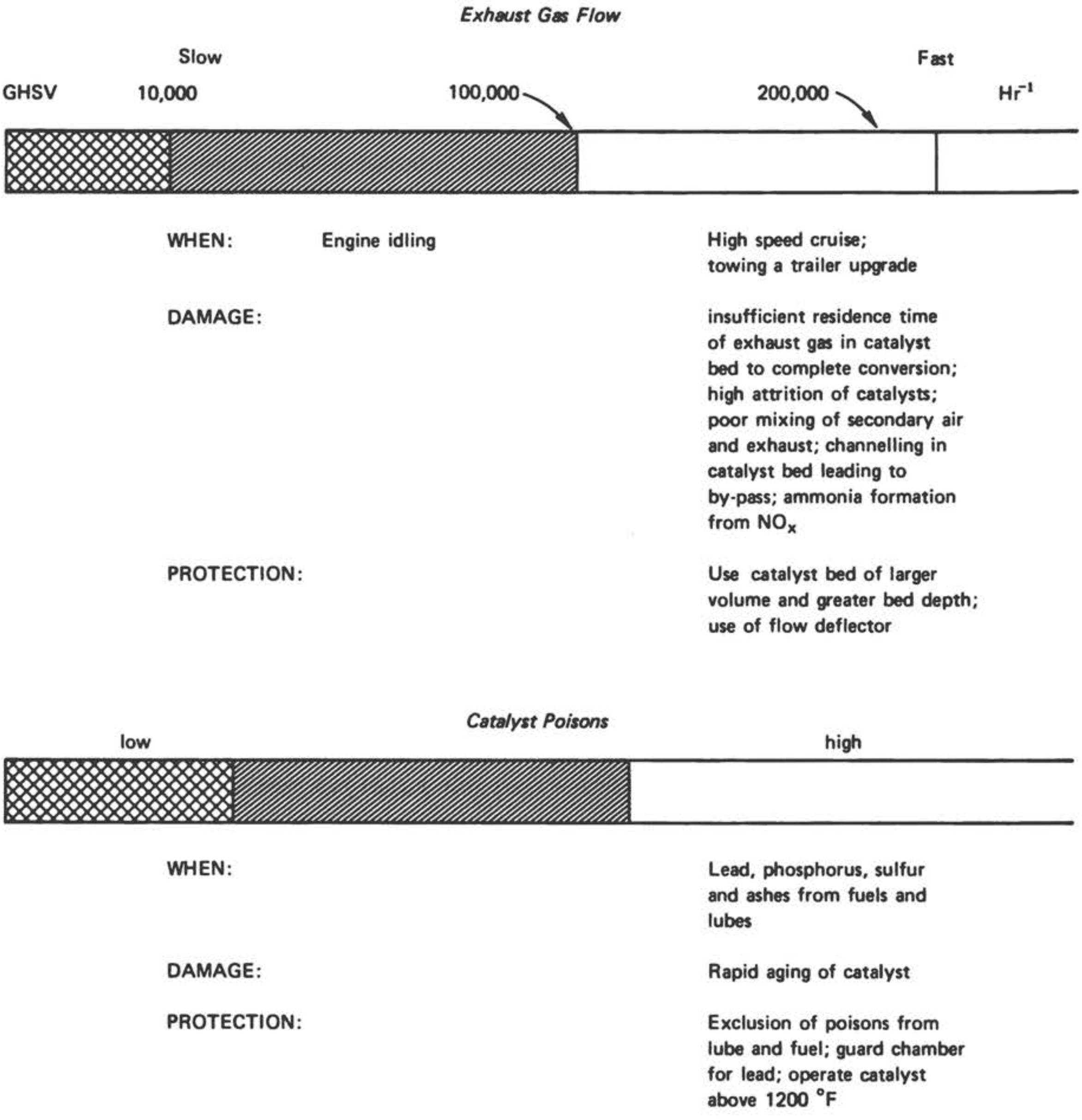


WHEN:	Engine idling, deceleration	High speed cruising
DAMAGE:	Low oxygen, inadequate conversion of HC and CO; Low oxygen and high CO or H_2 leads to ammonia	Too much oxygen, damage NO$_x$ catalyst; insufficient CO and H_2 means inadequate NO$_x$ reduction
PROTECTION:	fuel injection; oxygen probe and feedback control	

Catalyst Temperature Window



WHEN:	Warm-up from cold start	Sparkplug misfire; downhill cruise
DAMAGE:	Inadequate removal of exhaust; ammonia formation; sulfur poisons catalysts	Burn out and shrinkage of catalysts; rapid aging of catalysts and support, loss of active ingredients, metal container failure
PROTECTION:	Rapid warm-up devices; catalyst with smaller thermal mass, locate converter nearer exhaust manifold	Over-temperature by-pass; use catalyst with larger thermal mass, and place converter farther from exhaust manifold



WHEN:	Engine idling	High speed cruise; towing a trailer upgrade
DAMAGE:		insufficient residence time of exhaust gas in catalyst bed to complete conversion; high attrition of catalysts; poor mixing of secondary air and exhaust; channelling in catalyst bed leading to by-pass; ammonia formation from NO_x
PROTECTION:		Use catalyst bed of larger volume and greater bed depth; use of flow deflector

WHEN:		Lead, phosphorus, sulfur and ashes from fuels and lubes
DAMAGE:		Rapid aging of catalyst
PROTECTION:		Exclusion of poisons from lube and fuel; guard chamber for lead; operate catalyst above 1200 °F

FIGURE 1 Operating "Windows" for Catalysts.

excursions from these windows.

ADEQUACY OF CATALYST RESEARCH PROGRAMS

Although the catalyst is the key element in the success or failure of 1975-76 automotive exhaust control technology, its cost will be less than 1 percent of that of an automobile. At present, research in automotive catalysts is not a top-priority program in many great catalyst laboratories with proven ability. The anticipated annual gross sale and profit margin of automotive catalysts are not enough to support a greater research effort. The catalyst industry is also apprehensive about delays in the use of automotive catalysts and about changes in automotive power plants that might eliminate the need for catalysts after 1978. As long as there are more profitable challenges for their most creative catalyst researchers, many catalyst companies will not take the risk of entering an aggressive research program in automotive catalysts.

This panel believes that the nation will benefit from devising an incentive program to divert more creative catalyst researchers into automotive catalysis. There is a precedent in Germany, where industrial research in automotive catalysts is funded by the federal government. A possible plan in the United States would be government insurance against unrecovered research costs above some set minimum figure.

2. PRESENT CATALYSTS AND REACTORS

The active ingredients used in the catalysts which have been tested for the control of exhaust emissions may be classified into three main categories: noble metals, base metals, and metal alloys (Table 2). These components are generally dispersed as small crystallites on a thermally stable, chemically inactive support such as alumina or a ceramic. In addition, a metallic support has been used for metal alloy catalysts. The supports have been used in the form of spheroids, cylinders and monolithic honeycombs, or, in the case of metallic supports, as metallic mesh or saddles.

ACTIVE CATALYST INGREDIENTS

Noble Metals

Among the noble metals[*] of the platinum family, platinum occupies a prominent position as an oxidation catalyst of hydrocarbons (aliphatic, olefinic, and aromatic), of partially oxygenated organic compounds (such as alcohols and ketones), and of carbon monoxide as encountered in typical auto exhaust gas. Except for methane, many organic compounds are readily oxidized (1) in the presence of platinum at temperatures below 500°C. Carbon monoxide, which is strongly bonded to Pt at room temperature, is rapidly oxidized at elevated temperatures in an oxidizing atmosphere. Under reducing conditions, Pt can convert significant amounts of NO to N_2 or NH_3. Within a narrow range of the oxidant/reductant ratio (near stoichiometry, slightly reducing), Pt catalyzes simultaneously the reduction of NO and the oxidation of CO and hydrocarbons. More recently palladium has been examined as a catalyst for HC and CO oxidation (2).

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[*] The term "noble metals" refers to silver, gold, and the platinum family (rows 5 and 6 of Group VIII of the Periodic Table), ruthenium, rhodium, palladium, osmium, iridium, platinum.

Table 2 Active Ingredients in Auto Exhaust Catalyst Systems

Type	Elements
Noble metal[a]	Platinum, palladium, ruthenium
Base metal	Copper, chrome, nickel, manganese, cobalt, vanadium, iron, copper chromite, rare earth metal oxides
Alloys and mixed metals	Monel, nickel/copper, palladium/chromium, platinum/nickel

[a] The noble metals of interest belong to the "platinum family."

The other elements of the platinum family are either in short supply (iridium, rhodium) or form volatile toxic oxides (osmium, ruthenium) (see Chapter 5). Ruthenium has the unusual property of producing low NH_3 concentrations as a byproduct of the NO_x reduction compared with other catalysts (3). It has shown ability to catalyze methane formation from carbon monoxide and hydrogen (4); in the presence of water and some oxygen, NO_x removal is primarily via the water - gas shift reaction in reducing exhaust atmospheres (3).

Base Metals

Considerable effort has been devoted to the development of non-noble-metal catalysts for auto exhaust control because of the current relatively high cost and lack of supply of precious metals such as platinum and palladium (Chapter 5). Since the early work of Taylor as well as Roth and Doerr (5a,5b), the copper chromites (mixtures of the oxides of copper and chromium) have received special attention. These materials are generally employed as metal oxides deposited on an insulator support. The Cu/Cr oxides can exist in a number of crystalline modifications and valence states ranging from inverse spinels $Cu^{+2}_{0.9}\ Cr^{+3}_{0.1}\left[Cr^{+3}_{1.9}\ Cu^{+2}_{0.1}\right]O_4$ (where the square bracket denotes octahedral site occupation by the cations, and the remainder ions at tetrahedral sites) to a mixed oxide $Cu_2O \cdot Cr_2O_3$ with copper in 1^+ oxidation state. Of special significance is the activity of such mixed oxides both for the oxidation of HC and CO and for the reduction of NO_x in the presence of CO. Because of the highly competitive reaction of CO and oxygen, the reduction of NO_x to N_2 requires low levels of oxygen. As a result the reduction of NO_x on base metal oxides has to be carried out in a catalytic reactor separated from the oxidizing environment of HC and CO oxidation, although both reactors may employ the same type of metal oxide catalyst. In an attempt to develop a dual function catalyst, some manufacturers have combined the active ingredients of noble-metal and base-metal on the same substrate, a composition commonly referred to as "cocktail catalyst" (2,3).

Rare earth oxides have been investigated for CO oxidation (1,13). Results so far indicate that the activity is too low: considerable effort would be required before an active and rugged catalyst could be developed.

Alloys and Mixed Metals

To enhance the rate of catalyst warmup to the light-off temperature and to improve the rate of heat dissipation during catalytic reaction, the development of all-metal catalytic systems has been undertaken (8,9). Such systems may employ stainless steel 310 as a substrate clad with monel metal alloy (typical composition of monel alloy: 60-70 Ni, 25-35 Cu) (10); the material used is in the form of open metallic mesh or saddles (0.03 inches in diameter) located inside a converter of suitable design. A Ni/Cu alloy catalyst of higher attrition resistence is reported to have been developed by Gould (10) ("GEM"). Surface activation of the monel catalyst is achieved by heating in moist air for several hours (11).

This class of alloy catalyst appears to have particular application for NO_x without the problem of ammonia appearance in the gas phase (in the presence of low concentrations of oxygen and at temperatures above 1300°F). Such alloy catalysts have been produced on metallic monolith (10) and pebble (3) supports. Also the monel catalyst may function as an oxidizing catalyst for HC and CO removal (for example, during warm-up with secondary air injection into the exhaust manifold).

SUPPORT MATERIALS

Although the geometric forms of the substrate may differ, the basic material employed in its manufacture is alumina and related materials such as cordierite $[Al_3Mg_2(Si_5Al)O_{18}]$. The choice of a substrate is restricted by the demands for high thermal stability, high resistance to attrition, high crush strength, large surface area, and relatively low density and heat capacity. It is of interest that the demand for a substrate suitable for rapid warm-up as demanded by auto exhaust control has led to the development of high surface area materials of much lower density than those previously employed in the chemical industry. Thus the bulk density of some alumina substrates (6a) has been lowered from 0.8 to 0.5 g/cm^3. Unfortunately, the low-density materials exhibit some reduction in crush strength especially at elevated temperatures (6b).

To a large extent, a special group of aluminas have been found particularly useful as catalyst carriers in auto exhaust control. They are described as "transitional aluminas" and are produced by heating of precipitated alumina hydrates or mixtures thereof. The most important phase is gamma alumina; other transitional aluminas are designated delta, eta, theta, iota, kappa, and chi. These nearly anhydrous aluminas are distinguished by different crystal structures and densities. In general, the materials employed for catalyst carriers are partly amorphous and partly crystalline. The conversion of the transition aluminas to α-alumina, at high temperatures, is irreversible and it is generally associated with large reduction in surface area of the alumina, often to only 1 m^2/gm. For use of a support in automobile exhaust control, the surface area of the transitional alumina should be large (in excess of 75 m^2/g).

The geometric configuration of the support is dictated by the operating conditions under which catalysts must function, in particular, at high rates of gas flow with little pressure drop across the catalyst bed. Spherical support pellets (1/16 to 3/8 inch in diameter) generally exhibit a large surface area per unit mass and offer the advantage of simple replacement by refilling the catalytic converter. However some of the pelleted catalysts have been found to have low crush resistance, especially after exposure to temperatures in excess of 1500°F. As a result, a loss of catalyst and support material occurs during the operation of the vehicle.

Continued R&D on pebble supports has recently led to major improvements in the physical properties of such materials. While most pelletized substrates have experienced loss in stability at temperatures exceeding 1500°F, some stabilized alumina supports (6a) have shown little weight loss at temperature exceeding 1800°F. These light-weight pellets possess higher surface areas per unit mass than the monolith and, therefore, lower sensitivity to catalyst deactivation by poisons such as lead, phosphorus, sulfur, and other fuel additives or contaminants.

Ceramic monolithic substrates are materials in the form of cylinders (3 to 6 inches in diameter) containing an internal honeycomb structure extending in a longitudinal direction along the entire length of the cylinder and surrounded by an integral outer skin. The Corning monolith is extruded and then fired; the American Lava product is made with a corrugated paper process machine using a mixture of fiber and ceramic. In typical designs, the honeycomb has hexagonal or square geometry. One monolithic catalyst support (Engelhard) exhibits 8 - 12 corrugations per inch, with a wall thickness ranging from 0.010 to 0.008 inches, an overall volume of about 60 cubic inches (PTX-5 has the cylinder dimensions of 4 inch by 5 inch), and a total surface area of 2.5 to 3.5 $m^2/1000\ cm^3$. Such a design offers the advantages of high-temperature resistance (temperature limit 2100 to 2500°F), low attrition loss, low pressure drop, and quick warm-up because of its low total mass. Also, it appears to exhibit good mechanical strength with high resistance to shock and vibration encountered in automobile vehicle operation. The monolithic supports have found particular application with noble-metal catalysts, the Engelhard PTX series being the best known example. Few data are available on the suitability of such supports for base-metal catalysts.

Open all-metal meshes and saddle shapes have also been used as supports; these supports appear to offer low thermal mass (good light-off characteristics), ease of activation of the active phase, and potential use as oxidizing/reducing beds (9,14). With the Gould catalyst, the active phase and support may or may not be identical; but the Esso monel catalyst is unsupported (14).

A second novel catalyst support of high surface area, low heat capacity, and good thermal resistance is based on coating a filamentary structure of metal wire mesh with alumina ("Leak" catalyst support) (17). This alumina-coated mesh was reported to yield a surface area of about 1 m^2/gm. It was found to be suitable for impregnation with catalytically active ingredients, such as base metals (7).

CONVERTER DESIGN

Individual catalyst beds must house either particulate (extrudate, pellet) or monolith (ceramic, metallic) supported catalysts. The volume of any catalyst bed is determined largely by the available space in the existing car chassis and by the upper limit on allowable space velocity (gas hourly volume flow rate divided by catalyst volume). Typical upper limits for space velocity are 200,000 hr^{-1} (oxidizing monoliths), 50,000 hr^{-1} (oxidizing pellets), 100,000 hr^{-1} (reducing monoliths). The first and last limits primarily reflect the adequate residence time needed to accomplish the desired conversion; the space velocity limit on pelleted or extruded catalysts is due to pressure-drop considerations (higher engine back pressures begin to affect engine performance).

The converter design is dictated in part by whether the 1976 emission system contains a single three-way catalyst (converts CO, HC, and NO_x simultaneously), a dual bed with both catalysts monolithic, or a dual bed with a monolithic NO_x bed and a particulate oxidation bed.

A three-way catalytic converter needs a gas composition monitor such as a solid state oxygen electrode (UOP, Westinghouse, Bosch) downstream from the catalyst bed. Need for the most rapid feedback possible may result in the electrode being placed in the exit or convergent section of the converter housing. The panel has seen no work to date demonstrating achievement of adequate precision in the control of the A/F ratio.

With monolithic catalysts, the converter housing is usually a cylindrical shape (due to monolith manufacture by continuous process) that matches the monolith wall as closely as possible. Dual bed monolith systems may consist of separate NO_x and oxidation beds (e.g., a NO_x monolith converter for each bank of a V-8 and a larger oxidation monolith converter for the combined exhaust) or a single monolith where the gas flows downward through the center for NO_x control and then upward through the periphery for oxidation. Because the steering column is on the left side of the car, the two monoliths for the two sides of a V-8 engine are often asymmetrically spaced, suggesting that one converter is better situated than the other. Since the monolith crossections are larger than exhaust pipe sections, divergent and convergent sections proceed and follow the cylindrical monolith. Replacement may require cutting out the converter and welding on a new converter, unless clamped flanges can be developed that can withstand temperature cycling.

Pelleted bed catalysts seem to permit easier catalyst replacement but may create certain problems. GM prefers a gas downflow through pelleted catalyst beds in order to minimize catalyst attrition and to guarantee uniform flow (15). UOP claims that its lightweight alumina beads yield a uniform bed depth in either horizontal or vertical flow since the flow of exhaust gas is presumably sufficient to distribute the pellets uniformly across a supporting screen (6a). Replacement of spent pellets is accomplished with a vacuum suction device. Both GM and Mobil Oil have attempted mathematical modeling of catalyst bed response (reactor configuration versus conversion of carbon monoxide and hydrocarbons) (15,16).

The optimum reactor design for fresh catalysts has not yet emerged. For instance, GM reported three different catalyst configurations that met the 1976 CO, HC, and NO_x emission standards at approximately zero mileage: NO_x monolith + pellet oxidation bed; NO_x monolith + concentric monolith oxidation bed; and a single three-way catalyst bed (15). The optimum design for lifetime performance has not been systematically investigated.

Another high-temperature system under development by Questor employs an expanded metal screen NO_x catalyst sandwiched between two thermal oxidation reactors and operates under fuel-rich engine operation.

A small amount of preheated air is blended with the exhaust and fed into a rich manifold reactor where the excess HC is selectively burned. Sensible heat from the reaction raises the temperature of an expanded metal screen located in the next compartment to about 1800°F where the NO_x is removed presumably via the reaction

$$2CO + 2NO \longrightarrow N_2 + 2CO_2.$$

Downstream from the screen, excess preheated air is added so that CO oxidation can take place in a lean thermal reactor that follows.
A double-walled exhaust pipe from the rear axle to the engine serves as a preheater for the air.

Although the system is reasonably simple in design and construction, it suffers from relatively poor fuel economy under urban driving conditions (the penalty is in the range of 10 to 25 percent).

The second serious problem is corrosion of the catalyst; this led to failure after about 20,000 miles in the first Questor durability car (Table 3). The problem is not an easy one to solve, since the more thermally stable and corrosion-resistant alloys are also usually less active catalytically. Although the lower activity can be compensated for by using more screens, this solution unfortunately gives the system a higher thermal mass and makes it more expensive to produce. The Questor catalyst that failed was made from an RA-330 alloy. Inconel 601 has a melting point about 150°F above RA-330, and it is much less susceptible to corrosion. Another promising catalyst is a new N-155 alloy by International Nickel which contains cobalt, molybdenum, nickel, chromium, and aluminum. Either of these alloys, while more expensive than RA-330, should be much more durable and stand a much better chance of meeting the 1976 standards.

Table 3 Tests on First Questor Durability Car

Date	Measured by	Mileage	HC	CO	NO_x	MPG
6-26-72	Questor	0	0.08	2.70	0.20	---
9-15-72	EPA	4000	0.15	2.34	0.37	6.9[a]
10-20-72	EPA	8000	0.12[b]	2.27[b]	0.33[b]	6.93[a]
1-10-73[c]	Questor	19000	0.59	3.30	0.38	7.85
1-11-73[d]	Questor	19000	0.21	1.99	0.38	8.03
2-1-73[e]	EPA	23000	0.1	2.3	0.5-0.7	---

[a] Fuel measured using carbon balance; all other fuel measurements based on weight calculations.

[b] Average of two tests.

[c] Test run with defective air pump.

[d] Air pump replaced with new pump.

[e] Failure thought to be caused by a hole in the gauze catalyst.

SUMMARY

A variety of noble-metal or base-metal catalysts (often promoted with noble metals) are known that catalyze the desired reactions of CO, HC, and NO_x. These active components have been supported on porous alumina spheres and extrudate and on relatively nonporous ceramic and metallic monoliths of various kinds. In the past year or so, a number of potential 1976 catalyst-converter configurations have been examined for initial feasibility. Results to date do not yet indicate any single optimum configuration.

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3. OPERATING RANGES AND FAILURE MODES OF CATALYTIC CONVERTERS

The variables determining the performance of any particular catalyst are its past history and the current values of temperature, gas composition, gas flow rate, and concentration of catalyst poisons. In general, the variables are interdependent. For example, the minimum operating temperature of a base metal oxidation catalyst normally depends on the sulfur level in the fuel: The greater the resulting SO_2 level in the exhaust, the higher the temperature needed to avoid metal sulfate formation and deactivation (1,2).

With this point in mind, the desired limits of temperature, gas composition, gas flow and poison level are now discussed. Methods of avoiding excursions from this multidimensional window and the hardware for indicating various catalyst failures are examined in Chapter 4.

TEMPERATURE WINDOW

Variations in catalyst temperature above or below a window appropriate to each catalyst can result in the following malperformances:

Too low:
- insufficient reaction rates to convert CO, HC, and/or NO_x (reversible)
- increased susceptibility to poisoning (reversible in some cases)
- excess formation of ammonia (reversible)

Too high:
- loss of total and active component surface area due to sintering (slow, irreversible)
- reaction of active components with support material (irreversible)
- melting of support material (fast, irreversible)
- volume shrinkage resulting in greater impacts between catalyst and container (slow, irreversible)
- volatilization of active component by reaction

with gas impurities (fast or slow, irreversible)

The catalyst must consistently reach the desired operating window as quickly as possible during each start-up in the vehicle operation. The light-off temperature of the catalyst will largely determine the length of time needed for the system initially to approach efficient temperatures of operation, and is approximately above 400°F for oxidation catalysts, and above 750°F for NO_x reduction catalysts.

The lowest temperature at which a catalyst functions effectively depends on the level of poisons in the exhaust and will be discussed subsequently. Typically, lowest allowable "steady" operating temperature is between 900°F and 1100°F; this range has considerable overlap with the "steady" oxidation catalyst temperatures observed by UOP, Chrysler, and GM (1,2,11).

The upper temperature limit that a catalyst may very briefly sustain depends on the lowest temperature at which melting, phase transitions ($\gamma \rightarrow$ other alumina), solid phase reactions (Ni/alumina $\rightarrow$ nickel aluminate), or volatilization ($Ru \rightarrow RuO_4$ gas) occurs. The upper temperature that any catalyst may sustain for prolonged periods of operation is about 1500°F.

GAS COMPOSITION

For a particular range of concentrations of various exhaust gas components, there are a number of catalysts with sufficient low mileage activity to allow a particular exhaust emission system to meet the 1976 emission standards. The size of these composition ranges or windows depends on two factors: the catalyst role (oxidizing only, reducing only, three-way) and the particular catalyst chemistry involved.

OXIDATION CATALYSTS

With purely oxidizing catalysts, an oxygen level resulting in an air/fuel ratio above stoichiometric (14.7) into the catalyst bed should, in principle, yield satisfactory oxidation performance. In practice, the minimum added or secondary air rate must be such that the air/fuel ratio into the catalyst never falls below stoichiometric during any significant driving mode with allowance made for manufacturing variation, fluctuations in atmospheric pressure and humidity, and reasonable slippage from adjustment of various components. The upper limit may be determined largely by a transient and a long-term factor. Too much secondary air during cold start-up transient may unnecessarily delay the light-off time of the catalyst because of the additional thermal mass of added cool air. The most important long term influence is probably the durability and size of the air pump itself. Probably the air/fuel ratio after added air should be between about 15 and 16. The more exact the carburetion, the closer the system may be set to the stoichiometric ratio.

Reduction Catalysts

The following reactions may occur during reduction of NO_x:

(1) $2NO + 2H_2 = N_2 + 2H_2O$
(2) $2NO + 5H_2 = 2NH_3 + 2H_2O$
(3) $2NO + H_2 = N_2O + H_2O$
(4) $6NO + 4NH_3 = 5N_2 + 6H_2O$
(5) $2N_2O = 2N_2 + O_2$
(6) $N_2O + H_2 = N_2 + H_2O$
(7) $2NH_3 = N_2 + 3H_2$

H_2 can be formed over some catalysts via the water - gas shift reaction:

(8) $H_2O + CO - H_2 + CO_2$.

However, hydrocarbon or CO can probably function as a source of surface hydrogen without the necessity of gas phase H_2 being formed as an intermediate, and reduction of NO_x by CO might proceed directly.

It is indicative of the recent state of understanding of NO_x reduction chemistry that NH_3 formation in auto exhausts was first reported in 1971 (3).

If ammonia is formed and survives removal by reactions 4 and 7, it may be reoxidized on a given oxidation catalyst to NO. The oxidation of NH_3 by O_2 over platinum is a rapid heterogeneously catalyzed reaction (18). The critical performance is the reduction of NO to N_2 (selectively) or that most of the NH_3 produced be subsequently decomposed or oxidized to N_2.

Ammonia formation increases with carbon monoxide level in rich exhaust mixtures. The carbon monoxide influence becomes important above 4 - 5 percent CO on noble metal catalysts (4). High CO levels into the NO_x beds have been correlated with break-through peaks in ammonia from the NO_x bed during the CVS C/H test (11) by Chrysler.

Increased hydrogen concentrations also tend to yield higher ammonia levels. Typically, hydrogen is present in slightly rich exhaust at concentrations of the order of 0.25 times the carbon monoxide surface due to reaction 8, the water - gas shift reaction. This reaction may proceed on both base metal oxide catalysts (6,7) and noble metal catalysts (8). The presence of excess surface hydrogen (due to the sum of inlet exhaust gas hydrogen and that generated by reaction 8 increases ammonia formation probably via reaction 2 above.

Reduction of the ammonia level in the NO_x bed effluent is accomplished by reducing the surface hydrogen available in the NO_x catalyst in the following ways:

1. Use of a manifold reactor to allow further combustion of hydrogen prior to the NO_x bed.

2. Use of additional minor constituents (invariably proprietary) in the base metal oxide catalysts to minimize the rate of water gas shift reaction (17).

On both noble metal and base metal oxide catalysts, ammonia effluent concentration is further reduced by subsequent decomposition of ammonia in the reducing catalyst bed, if sufficient residence time and relatively high temperatures (9,10) are available. Oxidation to N_2 is catalytically feasible but has not been explored.

Since reaction 2 occurs at lower temperatures than reactions 4 and 7, moderate temperature operation may result primarily in conversion of NO to NH_3 without subsequent ammonia decomposition. Water vapor, typically about 10 percent of exhaust gas volume, greatly inhibits NH_3 decomposition over pure alumina and alumina-supported copper chromite, copper, platinum, and palladium, but does not seriously affect the NH_3 decomposition ability of Ni or Ru (9). Inclusion of nickel (in either supported materials such as Cu + Ni on alumina or as a bulk alloy in NO_x catalysts) probably thus functions to decompose NH_3 formed over the same catalyst.

Three-Way Catalysts

A narrow window in gas composition has been discovered, just on the fuel-rich side of stoichiometry (~14.7 air/fuel), within which both oxidation of CO and HC and reduction of NO_x may occur simultaneously on certain catalysts. In principle, precise control of the exhaust oxidant/reductant ratio into the catalyst bed could thus result in high conversion of all three components in a single catalyst bed. The width of the window is small and maintenance of required exhaust composition necessitates a feedback device such as the oxygen sensor under development by UOP (1), GM (2), and Bosch (12). (See also Chapter 5 on exhaust composition excursions due to changes in altitude, humidity, and barometric pressure). Lean-side deviations from this narrow window result in drastic loss of NO_x conversion. Considerable loss in HC and CO oxidation efficiency and increased ammonia formation occurs with rich-side deviations. A typical three-way system might operate satisfactorily with 1.5 percent oxygen and 1.7 to 2.1 percent carbon monoxide. By comparison, during acceleration up a long hill, the carbon monoxide in the cylinder exhaust is 3.7 percent, 0.35 percent, 1.1 percent, and 3.8 percent after 0, 20, 40, 60, and 130 seconds from acceleration start (11a). A workable oxygen sensing system must maintain the oxygen/carbon monoxide ratio within the small window mentioned above by adjusting the inlet air supply in the proper ratio to the fuel supply.

GAS FLOW

Space velocities at which catalysts operate during the EPA cycle vary by a factor of 10 for typical engines. Further, the concentrations of NO_x, HC, and CO exhibit wide deviations. The quantity of catalyst must be adequate to reduce total emissions to less than the EPA level. However, a large amount of catalyst would lead to a long warm-up time. Thus, it is desirable to have a highly active catalyst.

In practice, one would probably choose to permit some breakthrough of NO_x, CO, or HC during the more difficult operating modes. For example, operating modes 2 and 22 of the EPA cycle result in both maximum concentrations of NO_x and maximum space velocities, thereby setting the requirements of a NO_x catalyst.

On the basis of available data, a catalyst will need to operate effectively at space velocities of 50,000 hr^{-1} or more to be of practical value.

DETERIORATION

Deterioration has two aspects: deactivation, or that part of deterioration occurring with contaminant-free fuel and oil, and poisoning, that part resulting from contaminants. Bench tests and engine dynamometer tests have been useful in guiding catalyst development, but only vehicular testing is definite. This poses a very difficult problem. Even in prediction of catalyst behavior in well-established steady-state industrial processes, reliable accelerated aging studies of catalysts are virtually nonexistent.

Repeat tests on the same vehicle under presumably the same conditions exhibit considerable variability as a result of fluctuation in engine performance and analytical errors. The latter become very serious at the low emission levels of 1976 standards. Typical variability appears to be at least 25 percent in any one particular vehicular test system (11b). It is considerably larger if analyses are intercompared on the same system from different laboratories. It is necessary to average nine repeat tests to achieve a ± 10 percent uncertainty on the level of emissions with 80 percent confidence if the variability is 23 percent. This means that securing really reliable deterioration data is costly and time consuming. Gross deterioration may be visible enough, but comparison of two catalysts on the basis of a single test can lead to the wrong choice if differences between the two catalysts are not large. In sum, there are substantial uncertainties in almost all conslusions about any but the gross aspects of deterioration.

Performance data have been obtained that indicate an increase in activity during mileage accumulation (thin metal honeycombs may be in this category). We have not seen sufficient data on deterioration of NO_x catalysts to draw any definitive conclusions about them. There are considerable data on oxidation catalysts, and our discussion is entirely confined to them.

One may recognize two aspects of deterioration even though they may be merely different manifestations of decline in activity. These are increase in the temperature at which the catalyst becomes effective (light-off temperature), and decrease in chemical conversion at normal operating temperatures. In terms of passing the EPA test, both may be important but most workers seem to feel that for most systems the first aspect is the major one. However, Johnson Matthey (13) and UOP (1) feel that their catalysts warm so rapidly that it is the second factor which is major.

Deactivation

All proposed oxidation catalysts start as finely divided crystallites deposited on a particulate or monolithic support. Recrystallization into larger particles is ordinarily thermodynamically favored. Further, new phases may be formed by reaction among the catalytic ingredients or between the ingredients and the support. For example, NiO may react with alumina to give a spinel (4). All of these effects will ordinarily reduce the availability of the active ingredients and, thus, catalytic activity. It is the art of the catalyst manufacturer to minimize the occurence of these undesirable reactions. Such information is almost always proprietary.

At low temperatures, the rate of oxidation is determined by rates of adsorption, desorption, and surface reactions. At high enough temperatures, rates of the surface reactions become fast, and severe concentration gradients develop within the porosity of the catalyst leading to mass transfer controlled reactions. Much of the active ingredients sees little or no reactants and catalytic activity falls substantially below that of an ideal, fully exposed catalyst. Change in texture will affect this phenomenon. The range of transition temperatures between the two modes of operation is probably unknown for many of the oxidation catalysts and NO_x catalysts.

In general, in terms of measured emissions, catalyst deactivation is rather substantial during the first 1,000 to 3,000 miles. An interpretation of the nature of the deterioration is difficult because of the complicated nature of the EPA cycle. In most cases, the increased emissions may result largely from an increase in the light-off temperature, i.e., most of the increase occurs during cold start. However, increasing breakthrough of concentration spikes or a general increase in the emission level may also be substantial.

Following this initial decline, the activity of most catalysts tested may continue to decline at a slower rate. It is doubtful that any general conclusions can be reached at this time.

Poisoning

There is ample evidence that lead can result in poisoning of oxidation catalysts. The variability problem discussed above makes it difficult to set a reliable upper limit on the maximum permissible content in lead. It appears that the effect of 0.01 g per gallon of lead would be of little consequence in comparison with other types of deterioration. It is probable that many catalysts would not be too adversely affected by 0.03 g. The problem is complicated by the fact that lead may be volatilized from some catalysts during driving modes that result in high catalyst temperatures. The UOP Miniverter is reported to recover from occasional exposure to leaded fuel (1). The Gulf NO_x catalyst is claimed to work on leaded fuel and there is some suggestion that the Gould thin metal honeycomb may tolerate lead. However, no prolonged vehicular tests on these catalysts have been reported to us. In the presence of phosphate, some lead is deposited in the relatively innocuous form of lead phosphate (14).

Sulfur is an omnipresent component of gasoline and has been reported to poison oxidation catalysts. Again, however, SO_2 + SO_3 may volatilize from some oxidation catalysts during driving modes giving high catalyst temperatures (1,2). This is apt to be particularly true of noble metal catalysts. Platinum, after all, is a catalyst for the oxidation of SO_2 (18). It is difficult at this stage to set a general upper limit for permissible S content in gasoline. Each catalyst may accept a different level of S (See Chapter 5). Current data indicate that 100 ppm of S can be accepted regardless of whether the oxidation catalyst is noble metal or base metal as long as a temperature of 1350-1400°F is reached periodically.

The minimum average operating temperature of base metal catalysts may be determined by the decomposition temperature of a base metal sulfate; a UOP catalyst exhibits sulfate formation below about 1100°F with a 0.01 weight percent sulfur fuel and below about 1200°F with a 0.1 weight percent sulfur fuel (1). Sulfur poisoning by sulfate formation is largely reversible; a deactivated catalyst may be restored by heating to 1500°F (1), which corresponds to expected gas temperatures at 70 mph (UOP) or 90 mph (Chrysler, GM) (2,11).

Both phosphorus and zinc, common additives to lubricating oil, have been reported to collect on certain catalysts, and it has been reported that phosphorus is a poison (19). However, we have seen no data establishing a clear difference between ashless and conventional lubricating oils in actual vehicular testing.

For noble metal catalysts, the ease of hydrocarbon oxidation increases in the following sequence:

$$\text{methane} < \text{ethane} < \text{other alkanes} < \text{aromatic hydrocarbons} < \text{olefins} < \text{acetylenes}$$

During gradual deterioration, the increase in emissions of HC is not apt to be in olefins and acetylenes but rather in the less reactive types of hydrocarbon. Combustion of methane may be incomplete even on fresh catalyst.

FAILURE MODES

In addition to progressive deterioration, a catalyst may suffer abrupt failure. Catalysts on particulate supports, catalysts on monolithic supports, and thin metal catalysts behave rather differently.

All will melt if the temperature rises too high (alumina pellets, 3700°F; monoliths and Monel metal, about 2400-2500°F, depending on type). Clearly, actual melting of alumina pellets will be difficult. Melting of the other two types has been regularly observed in testing (2, 15, 16). System and catalyst must be mated so that this will not occur under any permissible driving mode and, insofar as possible, under system malfunction. The destruction temperatures of monolithic oxidation catalysts and thin metal catalysts are reached in the presence of excess CO and unburned hydrocarbon at a particular part of the catalyst. Such conditions may be caused by protracted misfires (1), high speeds coasting on long downhill grades (2), and poor catalyst design (16). In at least one case, the melting of a monolist has been reported to be due to maldistribution of the catalyst component, a local high rate of heat generation in a region with low melting points: e.g., w/CuO, mp 975°C versus 1350°C for monolith support.

Thin metal structures that are exposed to substantial excess oxygen when hot (such as when the vehicle runs out of gasoline at 70 mph) can, in essence, burn up. Some sources believe that a catalyst cannot reach melting temperature; other sources believe that a temperature overload valve will be needed.

In addition, temperatures below the melting points may cause rather rapid catalyst deactivation. Pellets may lose area, convert to α-Al_2O_3, or clump and develop excessive back pressures. Some particulate supports of stabilized γ-Al_2O_3 appear to resist 2000°F for short intervals, but continued operation at such temperatures leads to rapid failure. This is partly a matter of the physical properties of the catalyst and partly a matter of containerization. Advances in technology appear to have made attrition failures less common.

Insofar as the support itself is concerned, monoliths are less sensitive to temperatures than are particulate supports, short of melting or sagging temperatures. However, high temperatures may lead to rapid deactivation because of reactions involving the catalytic components. The upper permissible temperature for both particulates and monoliths will depend on the actual catalyst, not just on the support (14).

Monoliths may also crack under thermal cycling and certain forms of monoliths, particularly the spiral wound, may delaminate destructively. The more recently manufactured extruded monoliths seem to have less tendency to such failure (17).

Monel metal catalysts are subject to embrittlement by grain boundary growth and subsequent disintegration (7). Gould claims that its new catalyst preparations are resistant to this effect but we have seen no test data.

Monoliths are subjected to fracture and disintegration caused by vibrations if they are not held snugly in their containers at all operating temperatures (17).

SUMMARY

Operating ranges for NO_x reduction, oxidation, and three-way catalysts are defined by intervals of temperature, gas composition, gas flow rates, and concentration of catalyst poisons.

The limits of such operating windows are relatively well developed for oxidation catalysts; NO_x reduction catalysts are far less understood at present. This position is probably due to the short history of NO_x reduction chemistry compared with that of hydrocarbon and CO oxidation.

Lead, sulfur, and phosphorus are the major poisons in exhaust gases; the infuence of minor constituents is not well established. Variability in test results poses serious problems in the study of the rate of catalyst deactivation and of the effects of poisons.

Catalyst failure modes have been examined in terms of the underlying thermal and chemical behavior of catalyst components. (Methods of avoiding failure are discussed in Chapter 5).

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4. EXCURSION PROTECTIONS AND FAILURE INDICATORS FOR CATALYSTS

The two previous chapters have delineated the varieties of catalysts, reactor configuration, and preferred operating ranges for those variables most influential in determining catalyst performance. This chapter discusses the means of protecting the catalysts from excursions that are harmful to the catalyst or to catalyst performance and the types of indicators that might be used to signal catalyst failures.

Typical 1976 exhaust system components will likely include low thermal capacitance exhaust manifolds or exhaust manifold reactors, programmed secondary air injection in the manifold or between catalyst beds (dual bed system), and exhaust gas recycle. Situations harmful to the catalyst often arise from malfunctions of some other part of the emission control system. The probability of such failures was not considered by this panel; however, the probable results of such failures on catalyst performance are considered in this chapter.

The following sections discuss temperature limits and potential protection modes against such temperature excursions, restrictions on gas flow rates, results of gas composition variations, influences of high poison loads, and means of signaling catalyst failures.

TEMPERATURE EXCURSIONS

Avoidance of excessive low temperature operation is achieved by minimizing the warm-up time of the catalyst and by location of the catalyst bed close enough to the engine to ensure a temperature range of operation above a particular minimum.

The light-off temperature of the oxidizing catalyst is often between 400°F and 550°F with fresh catalysts; the light-off temperature increases on catalyst aging, depending on both catalyst formulation and the poisoning and temperature history of the catalysts. Extended high-temperature excursions (above 1500°F) usually diminish both catalyst activity and favorable light-off characteristics.

Proposed rapid warm-up systems have included electrical preheating of catalyst, by-passing the reducing bed to avoid thermal inertial delay due to NO_x catalyst heating, and a "warm-up" low-mass oxidizer located close to engine used only during warm-up period. Each of these systems raises additional durability problems of considerable difficulty.

Generally, oxidation becomes efficient above 400°F and NO_x reduction above 750°F. For this reason, the first bed of some dual bed systems has been used as an oxidation catalyst until the temperature reaches the order of 750°F, at which time secondary air is switched from the manifold to a between-bed location. The time to switching of secondary air is important: Ford data (2) show that switching secondary air at 120 sec instead of 60 sec results in about 25 percent reduction in CO during the 1975 CVS C/H procedure. Hydrocarbon emission is also reduced about 20 percent and NO_x increases about 20 percent. Clearly an optimum switching time exists that is long compared with projected normal choking times. The thermal mass of the NO_x catalysts is very important in determining the time needed for light-off of the catalyst. Ford-Amoco data (1) show that two 50-in.^{3} NO_x catalyst elements reach operating temperature (400°F) approximately 1 min faster than two 100-in.^{3} pelleted NO_x catalyst beds having the same catalytic promoters.

More rapid warm-up may also be achieved by programmed spark retard (3,6). VW has reported that a 25-sec improvement in reaching a catalyst temperature of 250°C was realized with early spark retard (3). In general, programming of electrical circuitry may be more reliable than programming of mechanical devices such as by-passes. Initial performance of some 1976 systems has been found (by both Ford and GM) to be sufficient to pass the 1976 emission standards at very low or zero mileage; extra control efforts are focused on durability protection including design against catalyst over-temperature.

The minimum bed temperature that permits base metal catalysts to resist sulfur poisoning depends on the percent sulfur in the fuel; typically, sulfate formation occurs below 1100°F with 0.01 weight percent sulfur fuel and below 1200°F with 0.1 weight percent sulfur fuel (5). These temperatures are in the same range as warmed-up oxidizing bed temperatures. The formation of such sulfates may be avoided or diminished by engine tuning to run hotter (leaner) and by location of the base metal bed closer to the engine. Bead type supports, because of their high surface area, are usually poisoned more slowly by particulates than monoliths.

The disadvantages of running an engine hotter to avoid sulfate poisoning include greater NO_x formation in the cylinders. Closer location of the catalyst to the engine also increases the peak temperature experienced by the catalyst. The trade-offs are HC/CO oxidation activity versus catalyst durability and/or need for more active NO_x catalyst.

At high temperatures (above 1500-1600°F), phase transformations are usually rapid if thermodynamically favorable. Thus, base metal reactions to form metal aluminates, substrate failure due to melting, and transformations of γ-aluminas to other aluminas may occur in time periods in the order of seconds. Ford, for example, suggested the need of over-temperature devices with response times in fractions of a second (2).

Over-temperature protection systems usually use thermocouple detectors to activate valves allowing exhaust by-pass of the appropriate catalyst beds. The function of such by-passes is generally to avoid a rapid total deactivation of the catalyst system. The mechanical durability by such by-pass systems appears to be a difficult problem. Some of the recent systems offered as 1976 emission control packages include no over-temperature protection for either catalyst (2,4,6).

An alternative protection for the catalyst would be to have an over-temperature signal cut off the air pump (7). This device is ineffective in the event of a spark plug failure.

Over-temperature systems would need a thermocouple at the catalyst bed exit (insertion into a monolith usually weakens its structure). Durability data on thermocouple systems is not well established in transient exhaust atmospheres; Corning experience suggests about a 3-week lifetime for a shielded thermocouple at continuous engine dynamometer test conditions (8). At 50 mph, this would be roughly

25,000 miles. Toyota's experiences with three thermo sensors (thermal expansion, thermistor, and thermocouple) include sensor failures due to slow response, bad repeatability, corrosion of outer tubes, and snapping and abrasion of outer tubes (4).

An over-temperature protection circuit might be matched to driving speeds. Thus, Chrysler data on a 360 CID engine in a car show that a temperature of the exhaust catalyst exceeds 1550°F only above 90 mph under normal engine running. With one plug shorted, 1550°F is exceeded only above 70 mph (6). A one-plug short at a UOP engine dynamometer stand resulted in the oxidizing catalyst reaching 2000°F within the order of 20 sec (5); with the small volume of the UOP miniverter, such temperatures might not be reached in a car because of the high-velocity air stream cooling the catalyst. GM data under similar conditions yield slightly higher temperatures: 80 mph operation with one plug out gave a temperature of 1750°F (4) versus 1660°F for the Chrysler car (6). With normal running, GM 80 mph catalyst is at 1280°F, Chrysler's monolith is at about 1380°F (4,6).

Mathematical modeling of catalytic converter performance has been studied by GM (4) and Mobil Oil (10,11). Models can predict catalyst temperature versus distance from the exhaust manifold in the Federal CVS C/H test for various system concepts and can be used to establish optimum location.

In summary, over-temperature by-pass appears feasible at zero mileage, but apparently suffers serious mechanical deterioration, especially at the bypass valves and temperature sensors. A strong effort toward improving this situation is needed.

GAS FLOW

The entrance region of the converter should distribute gas fairly uniformly to the inlet edge of pellet or monolith bed in order to minimize local over-heating that could lead to inactivation or cracking of pellet or monolith. Severe temperature nonuniformity can lead to circumferential cracking of the monolith (8). As the pressure drop through monoliths is low, the by-pass opened in such cracking may not seriously affect conversion through the reactor, but it may hasten monolith attrition.

With pellet oxidation beds, a slow internal circulation of beads has been noted by UOP (5). Although such a circulation implies an uneven flow distribution, it also guarantees that all catalyst beads will, over the long run, experience similar levels of temperature and exhaust gas composition.

In NO_x beds, residence time must be sufficient to convert the required amount of NO_x to N_2 or NH_3 and also to decompose enough of the NH_3 formed so that the total (NO_x + NH_3) from the NO_x bed is below the standard of 0.4 g/mile (1976). The upper limit on space velocity for NO_x catalysts (Chapter 3) may be determined by this limitation.

The space velocity over a catalyst will vary by at least a factor of 30 between engine idling and wide-open throttle; the central design objective is to find a catalyst that operates well over most of the high emission portions of the EPA cycle (SV values typical of catalysts during warm-up for oxidizing catalysts, high SV for NO_x converters during accelerations).

GAS COMPOSITION

The conversion of HC, CO, and NO_x is influenced by the balance in concentrations between oxidizers (O_2 and NO_x) and reducers (H_2, CO, HC). Oxidizing requires a stoichiometric to slightly lean mixture, and reducing requires a stoichiometric to slightly rich mixtures, and a three-way catalyst requires a very precise stoichiometry.

Catalyst conversions versus gas composition data have been reported as a function of air to fuel (A/F) ratio, equivalence ratio ($CO + H_2/NO + 2O_2$), carbon monoxide to oxygen ratio, choke angle setting, and ratio of percent secondary air to air/fuel ratio. The appropriate control parameter depends on the catalyst chemistry (whether or not the water-gas shift is catalyzed by the NO_x catalyst, degree of NH_3 formation from H_2, etc.), as seen from previous chapters detailing chemistry and "window" widths.

Oxygen sensing has been examined by GM (4,15), UOP (5) and Bosch (Germany) (12) for feedback control of gas composition. Swithenbank has briefly reported on a platinum combustion filament as a gas composition monitor (13). The types of oxygen sensing systems studied to date include the following:

1. Feedback to secondary air (off-on; modulated) (UOP) (5)
2. Feedback to choke (UOP--large displacement water-cooled engine) (5)
3. Feedback to electronic fuel injection (Bosch, VW, GM) (12,14,15).

A common oxygen sensor is an yttrium oxide-doped zirconium oxide solid state electrode. Westinghouse (16), Bosch (12), and UOP (5) have assembled such electrodes that give a voltage signal that varies logarithmically with the oxygen pressure. UOP, GM, and Bosch all seem to have encountered control stability problems with these devices coupled to engine exhaust systems; the recent emission data from GM (4,15) on the three-way catalyst suggests achievement of control stability and/or development of a considerably wider A/F "window" for their three-way system. Feedback control of fuel injection is generally acknowledged to be more accurate than feedback control of conventional carburetors or secondary air.

The width of the A/F window allowable for three-way catalysts is typically the order of $\triangle(A/F) = 0.1$, or roughly 1 percent variation in the ratio of oxidants to reductants. By way of comparison, on a rainy day, the oxygen concentration is diminished about 3 percent versus dry air; low pressure (29.1 in H_2O) versus high pressure (29.9 in H_2O) yields a similar variation in oxygen concentration. Control of a three-way system under full range of these variables has not yet been demonstrated.

The stability of these sensors in exhaust atmospheres is not yet known. Since the semiconductivity of the electrode is a function of doping level, it is possible that oxide-forming impurities from the gasoline, motor oil, or engine wear may change the net doping level and thus the electrode response.

The precision of control by such sensors may depend on the direction of deviation from the window. UOP data indicate that the signal is insensitive to the oxygen concentration in the rich side of the A/F ratio but that it climbs rapidly on the lean side. Thus, excursions far into the rich region may yield signals not greatly different from those near stoichiometry: the result of poor control in this region is typically loss of CO and HC conversion coupled with higher ammonia formation on noble metal catalysts.

Noble metal catalysts may be used for NO_x, oxidation, or three-way converters since the active component, platinum or palladium, undergoes no harmful chemical changes as the exhaust atmosphere switches from oxidizing to reducing or vice versa. Ruthenium, however, may oxidize to the volatile tetraoxide form.

Base metal reducing catalysts are often deactivated in hot oxidizing atmospheres; this behavior does not appear to preclude their use as oxidizing catalysts during initial warm-up of the engine. Some supported base metal reducing catalysts may be reactivated under a restored reducing atmosphere as is the case for NiO on a monolith (1). All-metal reducing catalysts have been completely destroyed by lean misfires (16). No feedback control on gas composition into the NO_x catalyst has been seen by the panel.

POISONS

The major catalyst poisons are lead, sulfur, and phosphorus. The poisoning of a catalyst by these elements depends primarily on three conditions: the Pb, S, and P levels in the gasoline and motor oil, the average operating temperature of the catalyst bed, and the chemical elements in the active component of the catalyst.

As a basis of discussion, the chart below indicates the total possible emissions of lead, phosphorus, and sulfur over 50,000 miles for a conventional oil (API service "SD" oil) and two fuels (the latter is the proposed EPA fuel specification):

Oil Component (wt %)	G per 50,000 mi
Phosphorus (0.13)	54
Sulfur (0.35)	145
Sulfated ash (1.3)	540
Fuel Component	
A. Phosphorus (0.07 g/gal)	350
Sulfur (0.04 wt %)	5520
Lead (0.07 g/gal)	350
B. (Proposed EPA 1975)	
Phosphorus (0.01 g/gal)	50
Sulfur (?)	--
Lead (0.05 g/gal)	250

Assumptions:

Oil consumption: 1,000 mi/qt
Fuel consumption: 10 mi/gal
Components: as indicated above

Lead

Lead is an efficient poison of noble metal catalysts. The halide scavengers associated with motor mix (tetraethyl lead plus scavengers) are known to deactivate metal oxide oxidation (17) and NO_x (18) catalysts. Thus, reduction of lead and associated scavengers should benefit essentially all catalytic systems. Most of the earlier research on lead poisoning did not include detailed studies at very low lead levels (less than 100 mg/gal) (19). A very tentative evaluation can be based on a recent durability study (20) of the influence of lead on hydrocarbon oxidation by a platinum monolith at 800°F. Catalyst activity declined to a plateau value after about 100-200 hr of aging in engine exhausts (1000 to 1250°F, cycling oxidizing and reducing conditions). Little recovery was evident on replacement of the leaded gasoline by lead-free gasolines. The percentage of initial hydrocarbon oxidation activity at 800°F remaining after 500 hr of aging was about 83 percent, 70 percent, and 62 percent for lead levels of 3, 35, 70 mg Pb/gal respectively. (See Figure 2). A simple extrapolation to 0 mg Pb gal suggests that the catalyst lost 15 percent of initial activity for reasons other than lead. It appears that each mg Pb/gallon will result in loss of 0.5 percent of initial hydrocarbon oxidation activity after 500 hr of aging under typical conditions (1000-1250°F, oxidizing and reducing).

By comparison, previous proposed maximum lead levels in lead-free gasolines for 1975-76 are higher:

20 mg Pb/gal (GM) (21)
50 mg Pb/gal (EPA) (22)
70 mg Pb/gal (ASTM, proposed revision) (23)

The proposed level of lead is probably below what the ASTM and the Army believe will be found as a typical lead contaminant level "which results from contamination when good refinery and distribution practices are followed" (23).

Sulfur

The previous mentioned Ford study (20) also examined the effects of low levels of sulfur (0.02 wt %, 0.07 wt %, 0.12 wt %) on NO_x conversion efficiency for up to 200 hr in the presence of 50 mg Pb/gal, the proposed EPA level. After 100 hr, the NO_x activity diminished to a plateau of about 75, 44, and 36 percent of the initial value. A curve through the three points (plateau NO_x efficiencies versus percent sulfur) passes through 100 percent at zero percent sulfur.

There is no EPA regulation on S at this moment. GM (21) suggested a maximum limit of 0.03 wt % sulfur based on their own oxidation catalyst

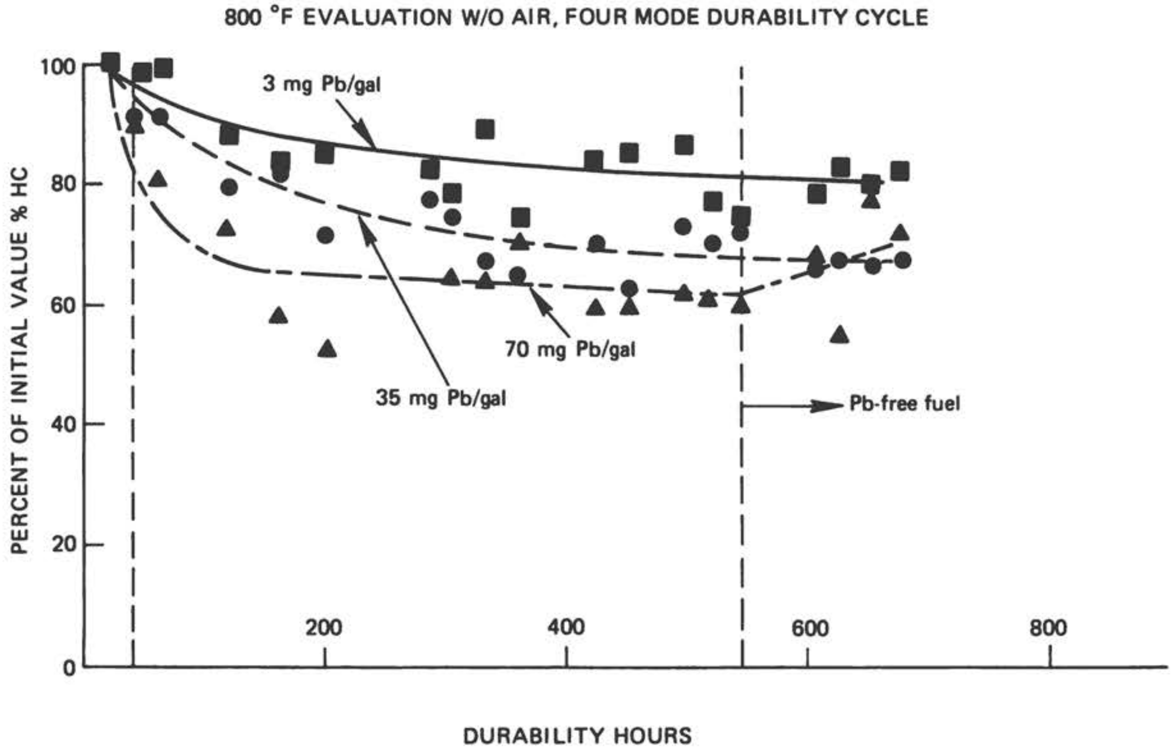

FIGURE 2 Effect of Lead on Oxidation Catalyst Efficiency.

experience.

Phosphorus

Ford data (20) show the effect of 0, 102, and 480 mg phosphorus/gal on percent hydrocarbon removal at 800°F. After 44 hr of alternating oxidizing and reducing atmospheres and temperatures between 1000°F-1250°F, the final hydrocarbon oxidation efficiencies declined 7, 50.6, and 77.3 percent, respectively. Other fuel contaminants were 0.02 wt % sulfur and 3 mg Pb/gal. Ashless motor oil was used. The decrease of 7 percent of initial conversion activity for the 0 mg P/gal fuel is consistent with the expected influence of 0.02 wt % sulfur. On the basis of both Ford (20) and GM (21) data, a very low level of fuel phosphorus is needed. As a point of reference, the Ford data support a very low phosphorus limit of the order of the 0.005 g P/gal as suggested by GM (22). After deactivation, Figure 3 shows significant recovery of activity with P-free fuel.

At these proposed phosphorus levels, the phosphorus from today's motor oil will equal or exceed the contribution from the fuel, as is seen from the consumption estimates in the first part of this section. It appears that a phosphorus specification for motor oils may be needed. UOP has suggested that Shell X-100 motor oil contains no components harmful to their noble or base metal catalysts (5).

Other Contaminants

Zinc has been shown to have a negligible influence on hydrocarbon oxidation activity over a platinum catalyst after 110 hr of composition and temperature cycling. Zinc levels of 0, 160, and 650 mg/gal produced no appreciable differences (20). The influence of very low levels of manganese, boron, magnesium, calcium, or barium is probably not important.

Other exhaust system metals such as copper, nickel, chromium, and iron are deposited in the catalyst bed as oxidation products of EGR system wear and as corrosion products from manifold reactions with halide

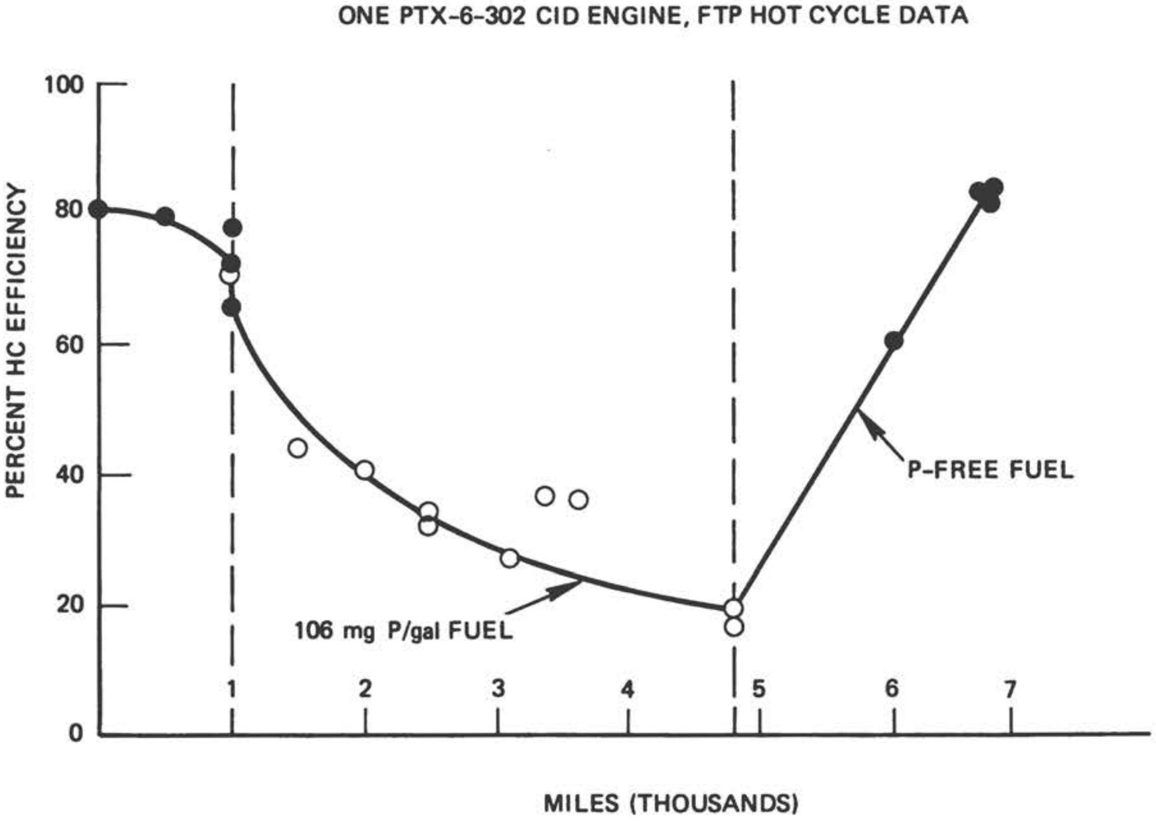

FIGURE 3 Effect of Phosphorus on Oxidation Catalyst Efficiency.

lead scavengers (17) and phosphorus (24). Gagliardi (20) found levels of about 0.3 wt % Fe, 0.07% Cr, 0.24% Cu and 0.037% Ni deposited on a noble metal monolith after 259 hr of engine operation. Roth (17) shows that cycling oxidizing and reducing atmospheres are much more effective than steady oxidizing atmosphere in removing base metal components, perhaps by volatile halide formation. To our knowledge, no work has been done evaluating the rate of metal deposition of manifold metals when a dual bed system is used with programmed manifold air: a situation guaranteeing regular cycling of oxidizing and reducing conditions.

FAILURE INDICATORS

The need for failure indicators is well recognized. While there are some ideas on such devices, there have been no experimental demonstrations. It is particularly difficult to design a short test on an automobile with a warmed-up engine and catalyst to simulate the EPA cold-start test procedure.

Overtemperature

Thermo-sensors are obvious choices, but their durability in exhaust systems is not established. UOP has informally suggested a pyrometric plug in the oxidation reactor wall: Overtemperature would melt the plug, resulting in an audible whistle (5).

Deactivation

UOP suggests a service station test for the oxidation bed: Short one spark plug, measure hydrocarbon emission (idling engine); if HC emission is less than 50 ppm, OK; above 50 ppm, deterioration; above 500 ppm, dead (25). Measurement of the temperature rise through an oxidizing catalyst bed under some standard engine condition has also been suggested as a deactivation test; no data available on feasibility or durability.

SUMMARY

Temperature: Low temperatures are avoided by use of catalysts with short light-off times and by proper location of catalyst bed near engine. High temperature protections might include catalyst by-passing or elimination of secondary air injection; durability on such systems is not established.

Gas composition: Maintenance of desired reducing and oxidizing atmospheres in dual-bed 1976 systems is largely accomplished by engine carburetion settings, percent EGR used, and programmed secondary air addition. A durable composition control for a three-way catalyst by feedback to fuel injection or carburetor has not yet been demonstrated under actual road testing. As with NO_x catalysts themselves, this area of gas composition control is just beginning to receive serious attention.

Gas flow rates: Protection against high or slow flow rates is probably not needed with properly designed catalyst bed. The available test data are inadequate at this time to permit specification of maximum contaminant levels in fuel and lube oil.

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5. RAW MATERIAL SUPPLY AND TOXICOLOGY OF DEBRIS

Most catalysts under serious consideration as candidates for control of automobile emissions involve one or more active catalytic components (see Table 2) deposited on a refractory oxide substrate; exceptions are the all-metal NO_x catalysts being developed by Gould (10), Humble (11), and Chrysler (12). The availability and cost of some of these raw materials will undoubtedly have a significant impact on which is actually chosen for use in the exhaust systems. Another important factor is the toxicity of the materials and compounds that may form by reaction with the exhaust gases, since the demanding thermal and mechanical stresses may cause them to escape from the exhaust system and into the atmosphere. The availability and relative toxicity of some of the materials is dealt with in this section.

SUPPLY AND DEMAND

Substrate Materials

Refractory oxide support materials are usually a mixture containing one or more of the following: SiO_2, Al_2O_3, MgO, Li_2O, and ZrO. They may also contain small amounts of promoters such as iron oxides, calcium oxide, or fluorine. Assuming a maximum total weight of 10 lb/car, it is estimated that no more than 50,000 to 75,000 tons of base materials will be required annually to satisfy requirements of the United States automobile industry beginning in 1975.

The raw materials for these substrates are readily available. However, the ease with which they can be converted into the actual substrate depends on the form of the final product. If pellets or extrudates are used, the manufacturing processes are well known and have been used for decades by the catalyst companies. Catalyst hardness (attrition resistance), low density, and high thermally-stable surface areas are some of the desirable requirements. No insurmountable problems are anticipated in scaling up existing processes to meet these demands, although a lead time of the order of one year will be required to build the plants.

It is more probable that monolithic structures will be used, and the problems here are somewhat more difficult to assess. The old process for making monoliths involves use of a "paper machine" to form flexible corrugated material that can be spiraled or layered and then calcined into the final ceramic product (8). A newer process employs an extrusion technique that can form monoliths of almost any desired shape (13). Either of these processes can be easily scaled up, and one company (American Lava) claims it can have in operation within one year a plant capable of producing 20 million units/year (14). For over 10 years that company has been manufacturing a limited number of these monoliths for use in fork lift trucks and vehicles that operate in confined quarters.

Most monolithic substrates have relatively low specific surface areas and require a thin "wash coat" of γ-alumina on which the active catalyst is impregnated. Relatively small amounts (less than 5,000 tons) of alumina will be required for this purpose, and supply is no problem. Work is currently under way in several companies to develop high area monolithic supports that will eliminate the need for a wash coat. Prototypes have been made, but it is doubtful that these techniques will be perfected by 1975.

Base Metal Catalytic Materials

As stated previously, the possible active catalytic materials may be divided into noble and base metals. None of the candidates is available in unlimited quantities, and most are on the list of strategic and critical materials compiled by the Office of Emergency Preparedness (Table 4) (15). However, the total amount of these materials that would be required is relatively small, ranging from about 0.01 - 0.1 oz/car for noble metals to about 0.1 - 1.0 lb/car for base metals. (This figure may reach as high as 2-5 lb/car for the all-metal catalysts.)

LIST OF STRATEGIC AND CRITICAL MATERIALS

Pursuant to section 2(a) of the Strategic and Critical Materials Stock Piling Act, as amended (Public Law 520, 79th Congress), the Director of OEP is authorized and directed to determine from time to time which materials are strategic and critical under the provisions of this Act. Listed below are the materials that have been determined to be strategic and critical under the provisions of this Act.

1. Aluminum.
2. Aluminum Oxide:
a. Aluminum oxide, fused, crude.
b. Aluminum oxide, abrasive grain.
3. Antimony.
4. Asbestos, Amosite.
5. Asbestos, Chrysotile.
6. Bauxite, metal grade, Jamaica type.
7. Bauxite, metal grade, Surinam type.
8. Bauxite, refractory grade.
9. Beryl:
a. Beryl ore.
b. Beryllium copper master alloy.
c. Beryllium metal.
10. Bismuth.
11. Cadmium.
12. Castor oil:
a. Castor oil.
b. Sebacic acid.
13. Chromite, chemical grade.
14. Chromite, metallurgical grade:
a. Chromite, metallurgical grade.
b. Chromium, ferro, high carbon.
c. Chromium, ferro, low carbon.
d. Chromium, ferro, silicon.
15. Chromite, refractory grade.
16. Chromium, metal.
17. Cobalt.
18. Columbium:
a. Columbium concentrates.
b. Columbium carbide powder.
c. Columbium, ferro.
d. Columbium, metal.
19. Copper:
a. Copper oxygen-free high conductivity.
b. Copper, other.
c. Beryllium copper master alloy.
20. Cordage fibers, Abaca.
21. Cordage fibers, Sisal.
22. Diamond dies, small:
a. Smaller than 0.0004 inch.
b. From 0.0004 to 0.00059 inch.
c. From 0.0006 to 0.00079 inch.
23. Diamond, industrial: crushing bort.
24. Diamond, industrial: stones.
25. Feathers and Down:
a. Down.
b. Feathers.
26. Fluorspar, acid grade.
27. Fluorspar, metallurgical grade.
28. Graphite, natural—Ceylon, Amorphous lump.
29. Graphite, natural—Malagasy, crystalline:
a. Graphite, natural—Malagasy, crystalline fines.
b. Graphite, natural—Malagasy, crystalline flakes.
30. Graphite, natural—other than Ceylon and Malagasy crystalline.
31. Iodine.
32. Jewel bearings.
33. Lead.
34. Manganese, battery grade, natural ore.
35. Manganese, battery grade, synthetic dioxide.
36. Manganese ore, chemical grade, type A.
37. Manganese ore, chemical grade, type B.
38. Manganese ore, metallurgical grade:
a. Manganese ore, metallurgical grade.
b. Manganese, Ferro, high carbon.
c. Manganese, Ferro, low carbon.
d. Manganese, Ferro, medium carbon.
e. Manganese Silicon.
f. Manganese metal, Electrolytic.
39. Mercury.
40. Mica, Muscovite block, stained and better.
41. Mica, Muscovite film, first and second qualities.
42. Mica, Muscovite splittings.
43. Mica, Phlogopite block.
44. Mica, Phlogopite splittings.
45. Molybdenum:
a. Molybdenum disulphide.
b. Molybdenum, ferro.
c. Molybdic oxide.
46. Nickel.
47. Opium:
a. Opium gum.
b. Opium, alkaloids and salts.
48. Platinum group metals, Iridium.
49. Platinum group metals, Palladium.
50. Platinum group metals, Platinum.
51. Pyrethrum.
52. Quartz crystals.
53. Quinidine.
54. Quinine.
55. Rubber.
56. Rutile.
57. Sapphire and ruby.
58. Shellac.
59. Silicon carbide, crude.
60. Silver.
61. Sperm Oil.
62. Talc, Steatite block and lump.
63. Tantalum:
a. Tantalum minerals.
b. Tantalum carbide powder.
c. Tantalum metal.
64. Thorium oxide.
65. Tin.
66. Titanium sponge.
67. Tungsten:
a. Tungsten ores and concentrates.
b. Tungsten carbide powder.
c. Tungsten, ferro.
d. Tungsten metal powder, carbon reduced.
e. Tungsten metal powder, hydrogen reduced.
68. Vanadium:
a. Vanadium, ferro.
b. Vanadium pentoxides.
69. Vegetable Tannin extract, Chestnut.
70. Vegetable Tannin extract, Quebracho.
71. Vegetable Tannin extract, Wattle.
72. Zinc.

Dated: February 18 1972.

G. A. LINCOLN,
Director,
Office of Emergency Preparedness.

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(Federal Register, Vol. 37, No. 39 - Saturday, February 26, 1972)

For base metals, the total amount of material required should be less than 10,000 tons/year. For comparison, Table 5 shows the estimated United States consumption in 1971 (5,9) of some base metals that are candidates for use in exhaust catalysts. Excepting cobalt, vanadium, and the rare earths, the projected new use in this area is only a small fraction of the total consumption of these materials in other uses. Supply of major base metals thus presents no significant problem.

Noble Metal Catalytic Materials

For noble metals, however, the picture is quite different. If noble metals are the only active components in the catalysts (this is likely to be the case for oxidation), it is estimated that a noble metal loading of about 0.1 oz/car will be required. This would call for at least a million ounces/year to accommodate the needs. For comparison, Figure 4 shows the 1970 supply-demand relationship for one noble metal, platinum. It is apparent that at 0.1 oz/car, the total platinum used by the auto industry in this application alone would be almost double the present total United States consumption (516,000 oz in 1970) and would equal half the present total world production (1,963,000 oz in 1970) of the metal. An even larger fraction of the total world's production of palladium is now used in the United States. Of a total world production of 1,638,000 oz in 1968, the United States demand was 721,000 oz. These results are summarized in Table 6, together with available data for ruthenium and rhodium.

Perhaps the most promising noble metal catalyst for NO_x control is ruthenium. However, the amount of this material available worldwide is less than 10 percent that of platinum and palladium. Table 7 shows the estimated relative amounts of the six noble metals from the three principal sources (1), and it is obvious that only platinum and palladium (and possibly ruthenium) can be considered for extensive use in automobile emission control devices.

Existing mines in South Africa can supply about half the

Table 5 Estimated U.S. Consumption of Selected Base Metals, 1971

Metal	Short Tons/Year
Copper[a]	2,953,000
Nickel	130,000
Chromium[a]	1,150,000
Manganese	2,000,000
Cobalt	5,500
Vanadium	4,500
Tungsten	400,000
Rare earths[b] (as R_2O_3)	5,715

[a] Figures include both scrap and primary; all others represent primary metal use only.

[b] Harris and Hannay, 1970 (reference 9).

Sources:

Mineral Facts - 1971 (reference 5).

Harris and Hannay, 1970 (reference 9).

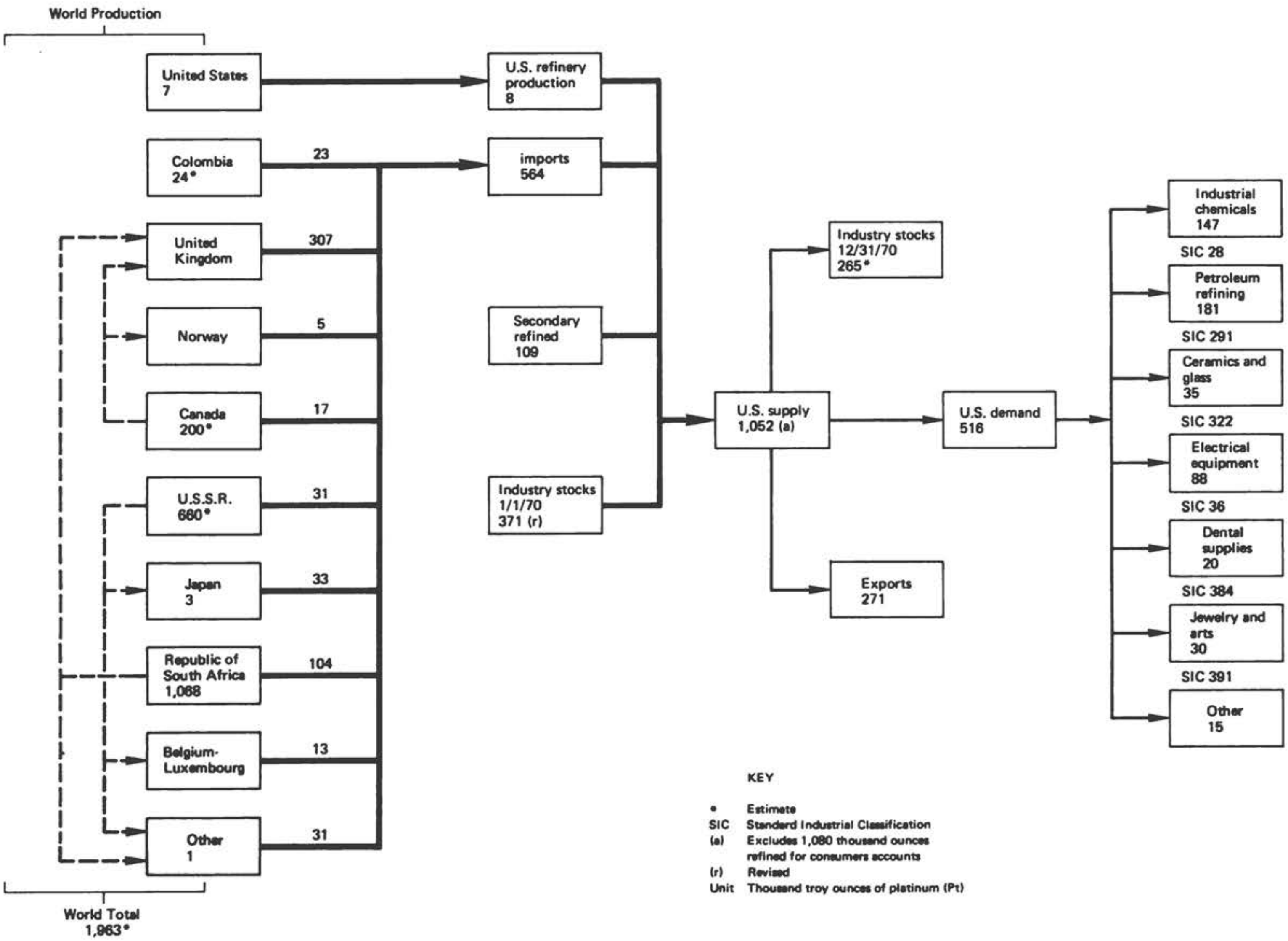

FIGURE 4 Platinum Supply and Demand Relationship -- 1970.

Table 6 Production and Demand for Selected Noble Metals

Metal	Troy Ounces World Production	 U.S. Demand	Year
Platinum	1,963,000	516,000	1970
Platinum	1,465,000	580,000	1968
Palladium	1,632,000	721,000	1968
Rhodium	76,000	45,000	1968
Ruthenium	--	17,194	1968

Source: Ageton and Ryan, 1970 (reference 1).

Table 7 Relative Proportions of Six Co-Product Noble Metals from the Three Most Likely Sources

	Estimated Composition, %		
Metal	Canada	USSR	South Africa
Platinum	43.4	30.0	71.20
Palladium	42.9	60.0	25.10
Iridium	2.2	2.0	0.78
Rhodium	3.0	2.0	2.41
Ruthenium	8.5	6.0	0.50
Osium	--	--	0.01

Source: Ageton and Ryan, 1970 (reference 1).

projected increased demands for platinum, and additional mines can be opened with about one year's lead time if firm long-term commitments for continued use of these materials were secured.

RECYCLE OF CATALYTIC MATERIALS

The low costs and relatively large supplies of substrate materials and base metal catalytic components make it unrealistic to consider reclamation of these materials. However, recovery and recycling of noble metal from used exhaust catalysts can have a significant impact on the annual requirements for new supplies. At levels of 0.1 oz/car, recovery of the noble metal is feasible; it is doubtful if levels below 0.05 oz/car (this corresponds to a value of about $7 of the noble metal at today's prices) could be economically reclaimed. Figure 5 shows the amount of new platinum that would be required each year until 1990 assuming 0, 50, 75, or 90 percent recovery of the noble metal (3). These data assume a platinum loading of 0.1 oz/car and a 50,000-mile durability. If the converters must be recharged in less than 50,000 miles, the noble metal consumption will be even larger than indicated.

TOXICITY OF AUTOMOBILE EXHAUST CATALYSTS

Almost all the materials being considered as components in automobile exhaust catalysts are somewhat toxic. Table 8 lists several of these materials and their relative toxicities. Selected data were taken from Sax's Dangerous Properties of Industrial Materials (6), and in most cases the toxicity values apply to several "representative" compounds that contain each particular metal. Sax defines toxicity as "the ability of a chemical molecule or compound to produce injury once it reaches a susceptible site in or on the body." The two major divisions of Table 8 refer to the length of exposure to the compound, with "acute" meaning of short duration (seconds, minutes, or hours) and

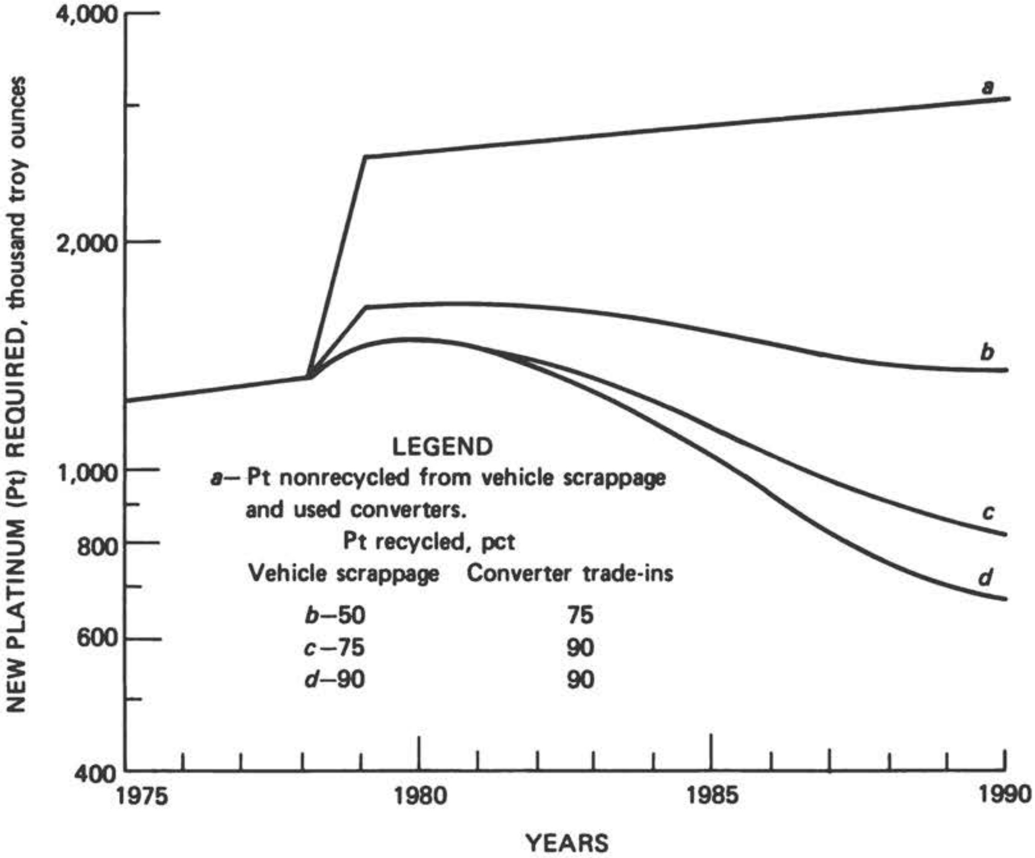

FIGURE 5 Estimated new platinum demand annually at several assumed percentages of platinum recycled from scrapped light-duty vehicle converters and converter trade-ins (assuming a converter life of 50,000 miles).

Table 8 Toxicity of Some Compounds That Might Be Used in Automobile Emission Control Catalysts

Compound	Acute		Chronic		Maximum Allowable Concentration in Air (mg/M^3)
	Local	Systemic	Local	Systemic	
Lead compounds	0	3	0	3	0.15
Chromium compounds	3	U	3	3	0.1
Nickel compounds	1	1	2	2	0.5
Nickel carbonyl	3	3	1	3	
Manganese compounds	U	2	U	3	15.0
Copper compounds	1	2	1	1	
Metal carbonyls	3	3	U	3	
Alumina	1	0	2	0	
Silica	2	0	3	1	
Cobalt compounds	1	1	1	1	0.5
Tungsten compounds	U	1	U	1	
Magnesium compounds	1	2	2	0	15.0
Ruthenium compounds	(Details unknown, but probably toxic)				0.01
Ruthenium tetroxide	2	U	U	U	
Platinum compounds	(Very low toxicity)				
Palladium compounds	(Very low toxicity)				
Mercury					0.1

Source: Sax, 1963 (references 6,7).

Note:
3 very toxic
2 moderately toxic
1 slightly toxic
0 nontoxic
U unknown toxicity

"chronic" meaning long or repeated exposure (days, months, years). The subdivisions refer to the location of the harmful effect, with "local" meaning action limited to the point of contact and "systemic" meaning action occurring at places other than the point of contact. The toxicity values range from nontoxic (0) to severely toxic (3); the symbol U is used when the toxicological effect is unknown.

There are three possible sources of toxicological danger associated with automobile exhaust catalysts: in emissions of the material into the atmosphere during automobile operation, in the manufacture of the catalysts, and in the installation of the catalysts in the automobiles.

Most of the compounds listed in Table 8 are low vapor pressure solids that can only escape from the exhaust system as very fine airborne dust particles formed by catalyst attrition. The predominant mechanism for incorporation into the body would be by inhalation of contaminated air. A few compounds, such as metal carbonyls and ruthenium tetroxide, are liquids under ambient conditions and have boiling points less than $100^{o}C$. While not present in the original catalyst, these compounds might be formed by reaction with the exhaust gases and emitted into the atmosphere in the vapor state (16,17). Fortunately, these compounds decompose at relatively low temperatures, so even if they were formed in the converter, they would probably decompose before they escape. The only time significant emission is likely to occur is during warm-up after a cold start.

In actual practice, tests with monel catalysts (Cu-Ni alloys) have shown no evidence for emissions of significant quantities of $Ni(CO)_4$. Ruthenium is slowly depleted from reduction catalysts, and this is presumed to occur through formation of RuO_4 when the catalyst is used under oxidizing conditions during cold start operation (17). Most companies who favor use of ruthenium are working on ways to avoid RuO_4 formation, and it is hoped that this problem can be adequately solved (17,18).

Regarding actual measurement of particulate emissions from catalysts, GM has reported tests with and without base metal catalysts, using either leaded or unleaded gasoline (17). The results are summarized in Table 9. The primary source of particulate matter is due to the lead in the gasoline, although comparison of the last two rows of the table indicates that some particulate matter may come from the catalyst as well. Assuming the upper limit on particulate matter from the catalyst (0.02 g/mile), this corresponds to about 1 lb/20,000 miles. However, it is thought that monolithic and pelleted catalysts that have been "stabilized" and "pre-attrited" will give particulate emissions far below the values observed in this test. Even at worst the projected catalyst particulate emissions are an order of magnitude less than the present lead emissions, and Table 8 indicates that none of these materials is much more toxic than lead. It is therefore concluded that there will be no significant toxicological hazard from particulate emissions of any of the materials now being seriously considered for use in automobile exhaust catalysts.

For years catalyst companies have been safely manufacturing materials far more toxic than these proposed exhaust catalysts, and it is thought that toxicological dangers associated with production of these materials can easily be avoided. However, installation and replacement of these materials in the cars may pose the greatest danger. It is quite likely that dust particles from the catalysts will be formed during such an operation, particularly in the case of beaded or extruded catalysts. This could create a hazardous environment for the mechanic who may carry out many such operations daily. Chromium compounds are particularly dangerous, as chromate salts have been associated with cancer of the lungs (6,7). Special installation techniques may have to be imposed to protect the mechanics.

SUMMARY

Except for noble metals, which must be imported, there appear to be no problems with raw material supply.

While most of the materials projected for use in automobile

Table 9 Particulate Emissions from Automobiles

Gasoline	Catalyst	Particulate Emissions (gm/mile)
3 gm Pb/gal	none	0.2-0.3
No Pb	none	0.01
No Pb	base metal pellets	0.01-0.03

Source: Klimisch, 1972 (reference 2).

exhaust catalysts have some toxicological activity, it is believed that the dangers to humans from such a use is minimal. Only during manufacture and installation of the catalysts is one likely to contact the materials in concentrations sufficiently high to be potentially harmful, and techniques can be developed to avoid such hazards.

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17. Data presented by GM, June 6, 1972.
18. Data presented by Ford, June 9, 1972.

APPENDIX A

Companies Visited

Date	Company	Visitors
3/29-30	Toyota and Nissan, Japan	Wise
6/5	Universal Oil Products, Des Plains, Illinois	Hightower, Ollis, Wise, Wei
6/6	Volkswagen, Wolfsburg, West Germany	Burwell
6/6	General Motors, Warren, Michigan	Hightower, Ollis, Wise, Wei
6/7	Chrysler, Detroit, Michigan	Hightower, Ollis, Wise, Wei
6/8	American Motors, Detroit, Michigan	Hightower, Ollis, Wei
6/9	Johnson Matthey, London, England	Burwell
6/9	Ford, Dearborn, Michigan	Hightower, Ollis, Wei
6/21	DuPont, Deepwater, New Jersey	Wei
7/4	Johnson Matthey, London, England	Ollis, Wei
7/5	Imperial Chemical Industries Teesside, England	Ollis, Wei
7/6	Degussa, Welfgang, West Germany	Ollis, Wei
7/7	Kali-Chemie, Hannover, West Germany	Ollis, Wei
7/11	Grace, Clarksville, Maryland	Burwell, Hightower, Wei
7/12	Engelhard, Menlo Park, New Jersey	Burwell, Hightower, Wei
7/17	Houdry, Marcus Hook, Pennsylvania	Wei
7/18	Gulf, Hamarville, Pennsylvania	Burwell
7/21	Gould, Cleveland, Ohio	Burwell
7/24	Corning, Corning, New York	Ollis
7/25	American Lava, Chattanooga, Tennessee	Hightower
7/26	Ethyl, Southfield, Michigan	Hightower

7/27	American Cyanamid, Bound Brook, New Jersey	Ollis
7/28	Oxy-Catalyst, West Chester, Pennsylvania	Ollis
8/15	Monsanto, St. Louis, Missouri (correspondence and telephone conversations)	Wise
10/13	Esso Research and Engineering, Linden, New Jersey	Ollis

CATALYST PANEL

QUESTIONNAIRE

May 1972

The topics which the panel would like to discuss are:

1. Catalytic control systems
    - a. The present state of your systems which involve the use of catalysts for controlling CO and HC; for controlling NO_x.
    - b. In the federal emission test (Federal Register, July 2, 1971), the fraction of the emissions during the warm up period for current automobiles and probable 1975 and 1976 automobiles.
    - c. The need for overload protection on the catalyst or catalysts.
    - d. Means of signalling catalyst failure.

2. NO_x catalysts
    - a. The probability that a catalyst for reducing NO_x will be a successful means of controlling NO_x to within federal specifications.
    - b. Formation of NH_3 and thence NO. Catalyst selectivity and influence thereon of water, air/fuel ratio, and any other controlling variables.
    - c. In a dual bed system, the interactions between requirements for one bed upon the performance of the other. For example, the effect of a requirement for a rich mixture in the first bed upon CO and HC contents in the effluent from the second bed.
    - d. Prospects for a three-way catalyst system.

3. Effect of temperature upon catalyst deterioration
    - a. Temperatures reached by catalyst in one and two bed systems in various driving modes, in particular, in severe driving modes, during idling, as a result of misfires.

b. Effect of high temperature upon catalyst activity in laboratory tests, in system tests, and in actual automobile tests.

c. Effect of temperature cycling upon catalyst deterioration.

CURRENT STATE OF KNOWLEDGE ABOUT CATALYST DETERIORATION WITH MILEAGE.

4. Effect of poisons upon catalyst deterioration

   a. Pb, S and other poisons in the fuel.

   b. Fuel (s) used in your driving tests. Analyses of these fuels for possible poisons.

   c. Poisons in lubricating oil.

   d. Upper limits to particular poisons in gasoline and in lubricating oil to be specified.

THE EFFECT OF FREEZING OF WATER CONDENSED IN THE CATALYST UPON CATALYTIC ACTIVITY AND CATALYST TEXTURE.

5. Light-off temperatures for reduction and for oxidation catalysts

   a. Deterioration with mileage, with high temperatures, with severe driving modes and misfires, with poisons.

   b. Division of loss of overall catalyst effectiveness into fractions occurring during and after warm up.

TYPES OF CATALYSTS MOST SUCCESSFUL TO DATE: NOBLE, BASE METAL, MIXED, FOR OXIDATION AND FOR REDUCTION.

6. Support, monolithic versus spheroidal or the like

   a. Relative activities.

   b. Shrinkage during vehicular testing.

   c. Relative resistance to poisons.

   d. Relative resistance to high temperatures and severe driving modes.

   e. Relative deterioration with mileage.

   f. Attrition loss.

TOXICITY. DANGER OF CATALYST ATTRITION LEADING TO EMISSIONS OF POSSIBLY TOXIC DUSTS

7. Testing

   a. Accelerated aging tests which correlate with driving tests.

   b. Data on performance tests which monitor HC, CO and NO_x in and out.

c. Accuracy of HC, CO and NO_x measurements, and problems encountered. Contribution to overall experimental variation.

8. Any other items about which you feel the panel should be informed.

The panel is interested in all matters related to the use of catalysts in the control of motor vehicle emissions but, at the moment, particularly to the control of NO_x. The panel would appreciate receiving any written material which can be provided relating to the matters listed above. The panel realizes that you will have received questions on some of these matters from other panels. Where you have no information beyond that already furnished, please just provide a reference to the information previously given.

COMMITTEE ON MOTOR VEHICLE EMISSIONS

CATALYST PANEL
QUESTIONNAIRE

1. Have you developed catalysts that will successfully remove 90 percent of unburned hydrocarbons and CO, and/or 90 percent of NO_x + ammonia after a simulated endurance of 25,000 miles in laboratory testing? To achieve these results, what are the simultaneous "windows" of operating conditions:

Temperature:	minimum and maximum
Space velocity:	maximum
Gas compositions:	maximum and minimum for oxidation and for reduction of oxygen, hydrogen and CO
Poisons:	maximum of lead, sulfur, phosphorous, ash?

2. Have any of your oxidation and NO_x catalysts been given a vehicle endurance test of 25,000 miles or longer? Was this done by yourself, or by an automobile manufacturer? If the results indicate that the emissions at the end of the test will not pass 1975-76 standards, do you know the external causes of the failure and the resulting damages to the catalysts? Can you specify vehicle hardware or driving changes so that your catalysts will pass the test?

3. Since the vehicle endurance tests discussed in #2, have you developed new catalysts that will overcome these modes of failures, and do you have evidence to show that the new formulations ought to pass the endurance tests? Alternately, what interim standard and replacement frequency can your catalysts satisfy?

4. What is your knowledge of the physical and chemical aging of catalysts with over-temperature and poisons? What is your knowledge of the chemistry of formation of ammonia from NO_x, and the decomposition of ammonia into nitrogen or other oxides of nitrogen?

5. What chemical elements are contained in your catalysts, and what is the maximum quantity required per automobile of 300 cubic inch displacement? What techniques can be used to recycle expensive elements in spent catalysts, and what is your estimate of recycle efficiency? These answers are needed to demonstrate that your catalysts will have adequate raw material supply, and that the catalysts debris will have been acceptable from toxicological considerations.