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THE OXIDATION OF EXHAUST GASES AT ROOM TEMPERATURE

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

ADVANCE RESTRICTED REPORT

THE OXIDATION OF EXHAUST GASES AT ROOM TEMPERATURE

By Harold C. Gerrish, J. Lawrence Meem, Jr.
and Vivian C. Tuck

SUMMARY

An investigation was made to determine the effectiveness of various oxides and oxide mixtures in oxidizing at room temperature the exhaust gases from an internal-combustion engine for the determination of fuel-air ratio. The oxides of silver, copper, manganese, cobalt, nickel, iron, cerium, lead, bismuth, and mercury were tested individually and in various combinations. At a fuel-air ratio of 0.090 and a gas flow of 100 cubic centimeters per minute, it was found that various oxide mixtures would completely oxidize the exhaust gases at room temperature but the useful life of the three best oxide mixtures was only about 60 minutes for the 20-gram sample, which precluded their use for the service intended. The best oxide mixtures were those of silver with Hopcalite, silver with cobalt and nickel, and silver with manganese. Although some oxides had an inhibiting effect on each other, silver oxide had a promoting effect on the life of almost any oxide or oxide mixture tested.

INTRODUCTION

Power, economy, range, and safety of aircraft are dependent upon the fuel-air ratio of the engine mixture. The fuel-air ratio may be determined in flight by the oxidized exhaust-gas method described in reference 1 but the difficulty of maintaining the oxidizer at the required temperature, 600° C to 700° C, and the servicing problem are objectionable.

The purpose of this investigation was to minimize these objections by employing an oxide or a mixture of oxides that would function at room temperature. In order to function satisfactorily, the oxides must oxidize the carbon monoxide, the hydrogen, and the hydrocarbons in the exhaust gases. Figure 1, the data for which was taken from reference 1, shows the amount of these constituents as a

function of the fuel-air ratio. The resulting carbon-dioxide content on a dry basis after the oxidation of the combustibles is shown on the curve labeled CO_2 , oxidized exhaust.

Considerable work has been done on the oxidation of carbon monoxide in air. Hopcalite, a mixture of cupric oxide and manganese dioxide (reference 2), will bring about the oxidation of carbon monoxide in air at temperatures of 0°C or below. Manganese dioxide, nickel oxide, and cobaltic oxide have been prepared in a pure state and have been used to bring about the oxidation of carbon monoxide in air at similar temperatures (reference 3). Little information exists on the catalytic oxidation of hydrogen at low temperatures except by the use of the rare-metal oxides, such as silver, gold, platinum, or palladium.

A total of 48 oxides or oxide mixtures was investigated to determine a practicable means for oxidizing the exhaust gases. This investigation was started in the spring of 1941 at the Langley Memorial Aeronautical Laboratory, Langley Field, Va., and was concluded in the spring of 1943 at the Aircraft Engine Research Laboratory, Cleveland, Ohio.

PREPARATION OF OXIDES

Although the exact chemical composition of some of the oxides to be discussed may be questioned, this report is not concerned with the chemical analysis of the substances prepared and no experimental proof of formulas is presented. The formulas are based on those generally accepted for similar preparations.

Most of the 48 oxides were prepared by the basic precipitation of the metallic oxides from the metallic nitrates. Nitrates were used because of their high solubilities in water and sodium and potassium hydroxides were used as the precipitating bases. After the oxides or the mixtures of oxides had been precipitated, they were repeatedly washed with distilled water until a constant pH was reached. The pH of the various precipitating solutions was determined with a glass-electrode pH meter in all cases involving chlorine and by colorimetric means in all cases involving silver or mercury compounds. About six washings were usually sufficient. After the precipitate was washed, it was filtered, dried to a semimoist condition, and compressed in a hydraulic press. When the resulting cake had been dried for several hours at about 110°C , it was broken up and screened to a particle size of 10 to 20 mesh.

The methods of preparing the various oxides and oxide mixtures are presented in table I in the following order: silver oxide with

Hopcalite, individual oxides, silver oxide with individual oxides, mixtures of two individual oxides, and silver oxide with mixtures of two individual oxides. Future reference to the oxides and the oxide mixtures will be made according to the numbers assigned in the table; for example, MnO_2 (6) will refer to the sixth oxide given in table I.

APPARATUS AND METHOD

The testing apparatus used in the investigation is shown in figure 2. A schematic diagram (fig. 3) shows the gas circuit and the auxiliary apparatus. In all tests the oxide or the oxide mixture was placed between layers of calcium chloride in the test-oxide chamber (a glass tube of 1-in. outside diameter). The sample oxide was activated before each experiment by placing the test chamber in an electric furnace and passing a stream of air at $150^{\circ}C$ through the tube for a period of 1 hour. The chamber was then removed from the furnace and placed in the system, as shown in figure 3.

Normal or unoxidized exhaust gas was obtained from a four-cycle $1/3$ -horsepower single-cylinder engine. The stream of gas coming from the engine was divided into two circuits. In one circuit the exhaust gas flowed into a surge tank and into a stainless-steel tube of 1-inch outside diameter containing cupric oxide maintained at a temperature of $700^{\circ}C$. The resulting oxidized gas then went into a desiccator (containing calcium chloride), into analyzer 2 (consisting of a thermal-conductivity bridge), into a bubbler, and finally into an Orsat gas analyzer. In the other circuit the gas was passed to a surge tank, a constant-flow control tube, a desiccator (containing calcium chloride), an unheated test-oxide chamber, a second desiccator, into analyzer 1 (also consisting of a thermal-conductivity bridge), into a bubbler, and finally into an Orsat gas analyzer. The changes in thermal conductivity of the bridges in the analyzers were indicated with a potentiometer. The bridge potential obtained from analyzer 2 was used as the standard to determine the percentage oxidation of the gas passing through the test oxide and analyzer 1.

The normal exhaust gas was passed first through the complete combustion furnace where all combustibles were oxidized and then through both analyzers to standardize the instruments and obtain observation A, which is the bridge potential of 100 percent oxidized exhaust gas. The normal exhaust gas was then passed through analyzer 1 bypassing the test oxide to obtain observation B, the bridge potential for normal exhaust gas. Observation C, the bridge potential recorded from the test oxide or oxide mixture, was obtained at periodic

intervals while the normal exhaust gas was passing through the test oxide. All observations were recorded in millivolts. During the recording of observations B and C, the completely oxidized exhaust gas flowed continuously through analyzer 2 to insure that the mixture delivered by the engine did not change during the tests. The efficiency of oxidation or the value of each oxide as an oxidant was defined as $\frac{C - B}{A - B} \times 100$, taking into account the proper change in sign when going from a positive to a negative reading, and is indicated on the figures as Oxidation efficiency, percent.

The following conditions were constant for all tests unless otherwise noted:

Fuel-air ratio	0.090
Rate of flow through test oxide, cubic centimeters per minute	100
Quantity of test oxide, grams	20
Particle size of test oxide	10 to 20 mesh
Fuel	100-octane aviation gasoline
Hydrogen-carbon ratio of fuel	0.188

TESTS AND RESULTS

Tests were made on individual oxides, on silver oxide with individual oxides, on mixtures of two individual oxides, and on silver oxide with mixtures of two individual oxides. Results of the tests are shown in figures 4 to 15. In order to prevent confusion, the experimental points are not plotted on the figures. Experimental data tables are available upon request from the NACA at Cleveland, Ohio.

Throughout the following discussion the oxides and the oxide mixtures will be compared with each other in terms of efficiency of oxidation, over-all life of oxidation, and useful life of oxidation. Over-all life is defined as that period of time from the initial indication of oxidation to the end of any indication of oxidation. Useful life is defined as that portion of the over-all life at which the oxide is within 5 percent of its maximum efficiency of oxidation provided that maximum efficiency is within the range of 90 to 100 percent.

Silver Oxide with Hopcalite

Hopcalite was the first material tested for low-temperature oxidation of exhaust gases, inasmuch as a large amount of information is available in the literature concerning the oxidation of carbon monoxide using Hopcalite. The poor oxidation curve of Hopcalite is

shown in figure 4. Because silver oxide can be reduced by hydrogen, it was believed that mixtures of silver oxide and Hopcalite would oxidize both the carbon monoxide and the hydrogen in exhaust gases. The results of a series of tests involving various amounts of silver oxide with Hopcalite are shown in figure 4. The better performance with respect to efficiency and useful life of mixtures of silver oxide and Hopcalite over either one alone is readily apparent. According to the data in this figure, the concentration of silver oxide is not critical in the range of 15 to 50 percent but, because the mixture of 25 percent silver oxide and 75 percent Hopcalite gave the longest useful life (60 min for the 20-gram sample) this concentration was used with subsequent mixtures of other oxides.

Individual Oxides

The results of testing three different preparations of manganese dioxide (oxides (6), (7), and (8) of table I) and three different preparations of cupric oxide (oxides (9), (10), and (11) of table I) are presented in figures 5 and 6, respectively. The figures indicate that MnO_2 (6) is better from a consideration of over-all life and efficiency than MnO_2 (7) or MnO_2 (8), and CuO (9) is better than CuO (10) and CuO (11). All subsequent mixtures involving these oxides will therefore be based on the acid decomposition of potassium permanganate (oxide (6) of table I) in the case of manganese dioxide and on the treatment of cupric nitrate with potassium hydroxide and air (oxide (9) of table I) in the case of cupric oxide unless otherwise stated.

Figure 7 compares the results obtained from all the individual oxides. The oxides of iron, cerium, lead, bismuth, and mercury gave no oxidation. The activity of cobaltic oxide was the most outstanding of the group. In view of the results that will be discussed, it is interesting to note the comparatively poor activity of manganese dioxide and silver oxide.

Silver Oxide with Individual Oxides

As shown in figure 5, manganese dioxide prepared by different methods gave various degrees of oxidation. The question arose as to whether the most active oxide of the individual preparations of manganese dioxide would give the best oxidation and life when mixed with silver oxide. The test results in figure 8 show this to be the case. The great increase in the efficiency and useful life of oxidation brought about by the addition of silver oxide is demonstrated as it was in figure 4 when silver oxide was mixed with Hopcalite. The useful life of the best mixture of silver oxide and manganese dioxide was approximately 60 minutes for the 20-gram sample.

The comparative oxidations obtained from testing all the mixtures of the individual oxides with 25 percent silver oxide is presented in figure 9. The comparison of this figure with figure 7 shows: (1) that silver oxide added to the oxides of iron, cerium, mercury, and cobalt materially assist their oxidizing ability and life; and (2) that the addition of silver oxide does not necessarily assist the activity in the order shown for the single oxides. The best single oxide did not give the best life and oxidizing ability when mixed with silver oxide.

Mixtures of Two Individual Oxides

Because cobaltic oxide gave the best efficiency and useful life of any individual oxide (fig. 7) and manganese dioxide gave the best efficiency and useful life of any oxide promoted with silver oxide (fig. 9), tests were made on two different preparations involving mixtures of these oxides. As can be seen in figure 10, neither of the preparations was very active, which indicates that oxides may act as inhibitors on each other as readily as they may act as promoters.

Figure 11 shows the comparative oxidation given by three mixtures of cupric oxide with manganese dioxide. Neither of the two cupric oxide-manganese dioxide mixtures prepared in this laboratory gave as satisfactory oxidation as Hopcalite. In each preparation the proportions of 40 percent cupric oxide and 60 percent manganese dioxide specified in reference 2 were used. The cupric oxide prepared from sodium carbonate had the greenish appearance of basic cupric carbonate (oxide (11) of table I). When this oxide was mixed with manganese dioxide, however, it showed an activity nearer to that of Hopcalite than the preparation containing cupric oxide made by treating cupric nitrate with potassium hydroxide and air (oxide (9) of table I).

The comparative oxidation of mixtures of two individual oxides is presented in figure 12. Attention is called to the activity shown by cobaltic oxide in combination with nickel oxide.

Silver Oxide with Mixtures of Two Oxides

The effect of adding approximately 25 percent silver oxide to the mixtures of two oxides is shown in figure 13. The silver oxide-Hopcalite and the silver oxide-cobaltic oxide-nickel oxide mixtures have the same life (60 min for the 20-gram sample) at maximum oxidation efficiency. Inasmuch as manganese dioxide is the main constituent of Hopcalite and cobaltic oxide is the most active of

the individual oxides (fig. 7), it would appear that a mixture of silver oxide, manganese dioxide, and cobaltic oxide would give good results. On the contrary, figure 13 shows that this mixture gave the poorest results, again bearing out previous observations that the oxides may act as inhibitors upon each other.

Under the influence of silver oxide, Hopcalite has oxidation characteristics closer to those of manganese dioxide (fig. 5) than to the mixtures of cupric oxide and manganese dioxide (fig. 11). The results of these tests are presented in figure 14. It may be concluded that the mixture of silver oxide and manganese dioxide is about as effective for the oxidation of exhaust gases as that of silver oxide and Hopcalite.

A series of tests was made involving various combinations of the oxides of silver, mercury, and manganese to study the promoting effect of silver and mercuric oxides on manganese dioxide. Figure 15 presents the results of these tests. Although the over-all life of the mixture of mercuric oxide and manganese dioxide approaches that of the mixture of silver oxide and manganese dioxide, the useful life is short. From an analysis of all the figures, it is obvious that silver oxide has a marked promoting effect on almost any oxide or oxide mixture.

The three best preparations shown in the results were silver oxide-Hopcalite, silver oxide-manganese dioxide, and silver oxide-cobaltic oxide-nickel oxide. It should be emphasized that the 25-percent concentration of silver oxide used in the preparations may or may not be the best concentration possible with mixtures other than Hopcalite. Inasmuch as this concentration was used consistently, however, the results should be comparable.

DISCUSSION

In the oxidation of exhaust gases as described in this report, the requirements of the oxide or the oxide mixture in furnishing oxygen to the reaction differed from those of Hopcalite in oxidizing carbon monoxide in air. The oxide or the oxide mixture was required to furnish all the oxygen for the various reactions without the presence of oxygen with which to reoxidize itself. Catalytic oxidation in air may be infinite in life, inasmuch as the oxygen removed from the oxide by the reacting gases may be replaced by the oxygen in air. If air had been available for these room-temperature reactions, much longer lives could have been expected.

The life of the oxide or the oxide mixture was also limited by the amount of oxygen available in the oxide, the quantity of sample,

the amount of unburned combustibles, and the rate of gas flow. There is also reason to believe that the life of the oxide or the oxide mixture was affected by the water of the oxidation process filling up the pores of the oxides. High porosity has been generally considered an important property of oxides of this type (reference 4).

The technique required in the activation of each test oxide was obtained from the best results given in the literature (references 5 to 8). The heated air passing over the test oxide may have had two effects upon it: (1) it may have removed water of hydration or (2) the oxygen present in the heated air may have combined with the oxide to some extent. From observation in the laboratory, the first supposition seems more likely.

It is noted that the average indicated efficiency of oxidation by the best test oxide was slightly lower than 100 percent. When one stream of normal exhaust gas was passed through the test oxide and another stream of normal exhaust gas from the same source was passed through the cupric-oxide furnace, a difference in carbon-dioxide content was noted. The gas oxidized by the test oxide was lower in carbon-dioxide content than that oxidized by the cupric-oxide furnace; however, when the gas, which appeared incompletely oxidized, was passed into the cupric-oxide furnace, no additional amounts of carbon dioxide could be detected. The loss of carbon dioxide was evidently due to some zone of adsorption or absorption in the test oxide and not to incomplete oxidation.

Although the exhaust gas oxidized by these test oxides can be used for determining fuel-air ratio, the life is insufficient for service application.

SUMMARY OF RESULTS

From tests made on the effectiveness of 48 oxides and oxide mixtures in completely oxidizing at room temperature the exhaust gas from an internal-combustion engine operating with 100-octane gasoline at a fuel-air ratio of 0.090 and a gas flow of 100 cubic centimeters per minute, the following results were obtained:

1. Exhaust gas was completely oxidized by various oxide mixtures at room temperature for a short period of time but the maximum useful life of the three best oxide mixtures was approximately 60 minutes for the 20-gram sample, which precludes their use in service installations for the determination of fuel-air ratio.

2. The best oxide mixtures were those of silver oxide with Hopcalite, silver oxide with the oxides of cobalt and nickel, and silver oxide with manganese dioxide.

3. Although some oxides had an inhibiting effect on each other, silver oxide had a promoting effect on the life of almost any oxide or oxide mixture tested.

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TABLE I - PREPARATION OF OXIDES

Oxide	Assumed reaction	Descriptive technique
Silver oxide with Hopcalite		
(1). 5% Ag ₂ O 95% Hopcalite	$2\text{AgNO}_3 + \text{Hopcalite} + 2\text{KOH} \rightarrow \text{Ag}_2\text{O} + \text{Hopcalite} + 2\text{KNO}_3 + \text{H}_2\text{O}$	In (1) through (5) a weighed amount of commercial Hopcalite was added to a solution containing the necessary amount of AgNO ₃ to give the concentrations of Ag ₂ O and Hopcalite specified in the mixtures.
(2). 10% Ag ₂ O 90% Hopcalite	See (1).	See (1).
(3). 15% Ag ₂ O 85% Hopcalite	See (1).	See (1).
(4). 25% Ag ₂ O 75% Hopcalite	See (1).	See (1).
(5). 50% Ag ₂ O 50% Hopcalite	See (1).	See (1).
Individual oxides		
(6). MnO ₂	$4\text{KMnO}_4 + 4\text{HNO}_3 \rightarrow 4\text{MnO}_2 + 4\text{KNO}_3 + 2\text{H}_2\text{O} + 3\text{O}_2$	Care was taken in the reaction to keep the temperature below 60°C so that the resulting product would not sinter and become inactive.
(7). MnO ₂	$\text{Mn}(\text{NO}_3)_2 + 4\text{KOH} + \text{Cl}_2 \rightarrow \text{MnO}_2 + 2\text{KNO}_3 + 2\text{KCl} + 2\text{H}_2\text{O}$	Cl ₂ was bubbled through the solution before and during the addition of KOH.
(8). MnO ₂	$3\text{Mn}(\text{NO}_3)_2 + 2\text{KMnO}_4 + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 2\text{KNO}_3 + 4\text{HNO}_3$	The reaction was accomplished by the oxidation of Mn(NO ₃) ₂ in the presence of concentrated HNO ₃ .
(9). CuO	$\text{Cu}(\text{NO}_3)_2 + 2\text{KOH} \rightarrow \text{CuO} + 2\text{KNO}_3 + \text{H}_2\text{O}$	Air was bubbled through the solution during the entire reaction to insure the presence of sufficient oxygen.
(10). CuO	See (9).	Cl ₂ was employed instead of air. In each case Cl ₂ or O ₂ served to maintain Cu ⁺⁺ at higher valence.

TABLE I - PREPARATION OF OXIDES - Continued

Oxide	Assumed reaction	Descriptive technique
(11). CuO	$\text{Cu}(\text{NO}_3)_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CuO} + 2\text{NaNO}_3 + \text{CO}_2$ or $2\text{Cu}(\text{NO}_3)_2 + 2\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 + 4\text{NaNO}_3 + 2\text{CO}_2$	This reaction attempted to reproduce the CuO reaction given in the Hopcalite patent (reference 2). A green compound resembling $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ resulted.
(12). Ag ₂ O	$2\text{AgNO}_3 + 2\text{KOH} \rightarrow \text{Ag}_2\text{O} + 2\text{KNO}_3 + \text{H}_2\text{O}$	
(13). Ni ₂ O ₃	$2\text{Ni}(\text{NO}_3)_2 + 6\text{KOH} + \text{Cl}_2 \rightarrow \text{Ni}_2\text{O}_3 + 2\text{KCl} + 4\text{KNO}_3 + 3\text{H}_2\text{O}$	See (7).
(14). Co ₂ O ₃	$2\text{Co}(\text{NO}_3)_2 + 6\text{KOH} + \text{Cl}_2 \rightarrow \text{Co}_2\text{O}_3 + 2\text{KCl} + 4\text{KNO}_3 + 3\text{H}_2\text{O}$	See (7).
(15). Fe ₂ O ₃	$2\text{Fe}(\text{NO}_3)_3 + 6\text{KOH} \rightarrow \text{Fe}_2\text{O}_3 + 6\text{KNO}_3 + 3\text{H}_2\text{O}$	See (7).
(16). CeO ₂	$2\text{Ce}(\text{NO}_3)_3 + 8\text{KOH} + \text{Cl}_2 \rightarrow 2\text{CeO}_2 + 2\text{KCl} + 6\text{KNO}_3 + 4\text{H}_2\text{O}$	See (7).
(17). PbO ₂	$\text{Pb}(\text{NO}_3)_2 + 4\text{KOH} + \text{Cl}_2 \rightarrow \text{PbO}_2 + 2\text{KCl} + 2\text{KNO}_3 + 2\text{H}_2\text{O}$	The pH of the solution was watched carefully so that it would not become too basic for example, above 9.0
(18). Bi ₂ O ₃	$2\text{Bi}(\text{NO}_3)_3 + 10\text{KOH} + 2\text{Cl}_2 \rightarrow \text{Bi}_2\text{O}_3 + 6\text{KNO}_3 + 4\text{KCl} + 5\text{H}_2\text{O}$	See (17).
(19). HgO	$\text{Hg}(\text{NO}_3)_2 + 2\text{KOH} \rightarrow \text{HgO} + 2\text{KNO}_3 + \text{H}_2\text{O}$	Care was taken to keep the solution cool. The resulting precipitate was yellow.
Silver oxide with individual oxides		
(20). Ag ₂ O-MnO ₂	MnO ₂ from (6).	In (20) through (30) a weighed amount of x-oxide was added to a solution containing the necessary amount of AgNO ₃ to give a 25% Ag ₂ O-75% x-oxide mixture. Ag ₂ O was precipitated in the presence of the x-oxide by the addition of KOH.
(21). Ag ₂ O-MnO ₂	MnO ₂ from (7).	See (20).
(22). Ag ₂ O-MnO ₂	MnO ₂ from (8).	See (20).
(23). Ag ₂ O-Ni ₂ O ₃		See (20).
(24). Ag ₂ O-Fe ₂ O ₃		See (20).
(25). Ag ₂ O-CeO ₂		See (20).
(26). Ag ₂ O-Co ₂ O ₃		See (20).
(27). Ag ₂ O-CuO	CuO from (9).	See (20).

TABLE I - PREPARATION OF OXIDES - Continued

Oxide	Assumed reaction	Descriptive technique
(28). Ag ₂ O-Bi ₂ O ₅		See (20).
(29). Ag ₂ O-PbO ₂		See (20).
(30). Ag ₂ O-HgO		See (20).
Mixtures of individual oxides		
(31). 40% CuO 60% MnO ₂	$\text{Cu}(\text{NO}_3)_2 + 2\text{KOH} \rightarrow \text{CuO} + 2\text{KNO}_3 + \text{H}_2\text{O}$ MnO ₂ from (6).	MnO ₂ was added to a solution of Cu(NO ₃) ₂ and CuO was precipitated with KOH while air was bubbled through the solution.
(32). 40% CuO 60% MnO ₂	$\text{Cu}(\text{NO}_3)_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CuO} + 2\text{NaNO}_3 + \text{CO}_2$ or $2\text{Cu}(\text{NO}_3)_2 + 2\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{CuCO}_3 + \text{Cu}(\text{OH})_2 + 4\text{NaNO}_3 + 2\text{CO}_2$ MnO ₂ from (6)	Na ₂ CO ₃ was used for the reason given in (11). MnO ₂ was added to the solution while the reaction was taking place.
(33). CuO MnO ₂		This mixture was commercial Hopcalite obtained from the Mine Safety Appliance Company.
(34). 50% Co ₂ O ₃ 50% MnO ₂		These oxides were precipitated separately and mixed in a water solution.
(35). 50% Co ₂ O ₃ 50% MnO ₂	$2\text{Co}(\text{NO}_3)_2 + 6\text{KOH} + \text{Cl}_2 \rightarrow \text{Co}_2\text{O}_3 + 2\text{KCl} + 4\text{KNO}_3 + 3\text{H}_2\text{O}$ $\text{Mn}(\text{NO}_3)_2 + 4\text{KOH} + \text{Cl}_2 \rightarrow \text{MnO}_2 + 2\text{KNO}_3 + 2\text{KCl} + 2\text{H}_2\text{O}$	The oxides were precipitated simultaneously by adding KOH to the Cl ₂ saturated solution of Co(NO ₃) ₂ and Mn(NO ₃) ₂ .
(36). 50% Co ₂ O ₃ 50% CuO	$2\text{Co}(\text{NO}_3)_2 + 6\text{KOH} + \text{Cl}_2 \rightarrow \text{Co}_2\text{O}_3 + 2\text{KCl} + 4\text{KNO}_3 + 3\text{H}_2\text{O}$ $\text{Cu}(\text{NO}_3)_2 + 2\text{KOH} \rightarrow \text{CuO} + 2\text{KNO}_3 + \text{H}_2\text{O}$	See (31).
(37). 50% Ni ₂ O ₃ 50% MnO ₂	$2\text{Ni}(\text{NO}_3)_2 + 6\text{KOH} + \text{Cl}_2 \rightarrow \text{Ni}_2\text{O}_3 + 2\text{KCl} + 4\text{KNO}_3 + 3\text{H}_2\text{O}$ $\text{Mn}(\text{NO}_3)_2 + 4\text{KOH} + \text{Cl}_2 \rightarrow \text{MnO}_2 + 2\text{KNO}_3 + 2\text{KCl} + 2\text{H}_2\text{O}$	See (31).
(38). 50% Ni ₂ O ₃ 50% CuO	$2\text{Ni}(\text{NO}_3)_2 + 6\text{KOH} + \text{Cl}_2 \rightarrow \text{Ni}_2\text{O}_3 + 2\text{KCl} + 4\text{KNO}_3 + 3\text{H}_2\text{O}$ $\text{Cu}(\text{NO}_3)_2 + 2\text{KOH} \rightarrow \text{CuO} + 2\text{KNO}_3 + \text{H}_2\text{O}$	See (31).
(39). 50% Co ₂ O ₃ 50% Ni ₂ O ₃	$2\text{Co}(\text{NO}_3)_2 + 6\text{KOH} + \text{Cl}_2 \rightarrow \text{Co}_2\text{O}_3 + 2\text{KCl} + 4\text{KNO}_3 + 3\text{H}_2\text{O}$ $2\text{Ni}(\text{NO}_3)_2 + 6\text{KOH} + \text{Cl}_2 \rightarrow \text{Ni}_2\text{O}_3 + 2\text{KCl} + 4\text{KNO}_3 + 3\text{H}_2\text{O}$	See (31).
(40). 25% HgO 75% MnO ₂	$\text{Hg}(\text{NO}_3)_2 + 2\text{KOH} \rightarrow \text{HgO} + 2\text{KNO}_3 + \text{H}_2\text{O}$ MnO ₂ from (6).	MnO ₂ was added to a solution of Hg(NO ₃) ₂ and HgO was precipitated with KOH while air was bubbled through the solution.

TABLE I - PREPARATION OF OXIDES - Concluded

Oxide	Assumed reaction	Descriptive technique
Silver oxide with mixtures of individual oxides		
(41). Ag_2O Co_2O_3 Ni_2O_3		In (41) through (45) a weighed amount of x_1 -oxide and x_2 -oxide was added to a solution containing the necessary amount of $AgNO_3$ to give a 25% Ag_2O -37.5% x_1 -oxide-37.5% x_2 -oxide mixture. Ag_2O was precipitated in the presence of the x -oxides by the addition of KOH .
(42). Ag_2O Ni_2O_3 MnO_2	MnO_2 from (6).	See (41).
(43). Ag_2O Co_2O_3 CuO	CuO from (9).	See (41).
(44). Ag_2O Co_2O_3 MnO_2	MnO_2 from (6).	See (41).
(45). Ag_2O Ni_2O_3 CuO	CuO from (9).	See (41).
(46). Ag_2O CuO MnO_2	CuO from (9). MnO_2 from (6).	In (46) and (47) a weighed amount of 40% CuO -60% MnO_2 mixture was added to the necessary amount of $AgNO_3$ to give a 25% Ag_2O -30% CuO -45% MnO_2 mixture. Ag_2O was precipitated in the presence of the CuO - MnO_2 mixture by the addition of KOH .
(47). Ag_2O CuO MnO_2	CuO from (11) MnO_2 from (6).	See (46).
(48). Ag_2O HgO MnO_2	MnO_2 from (6).	A weighed amount of manganese dioxide was added to a solution containing the necessary amounts of $Hg(NO_3)_2$ and $AgNO_3$ to give a 20% Ag_2O -20% HgO -60% MnO_2 mixture. HgO and Ag_2O were precipitated in the presence of MnO_2 by the addition of KOH .

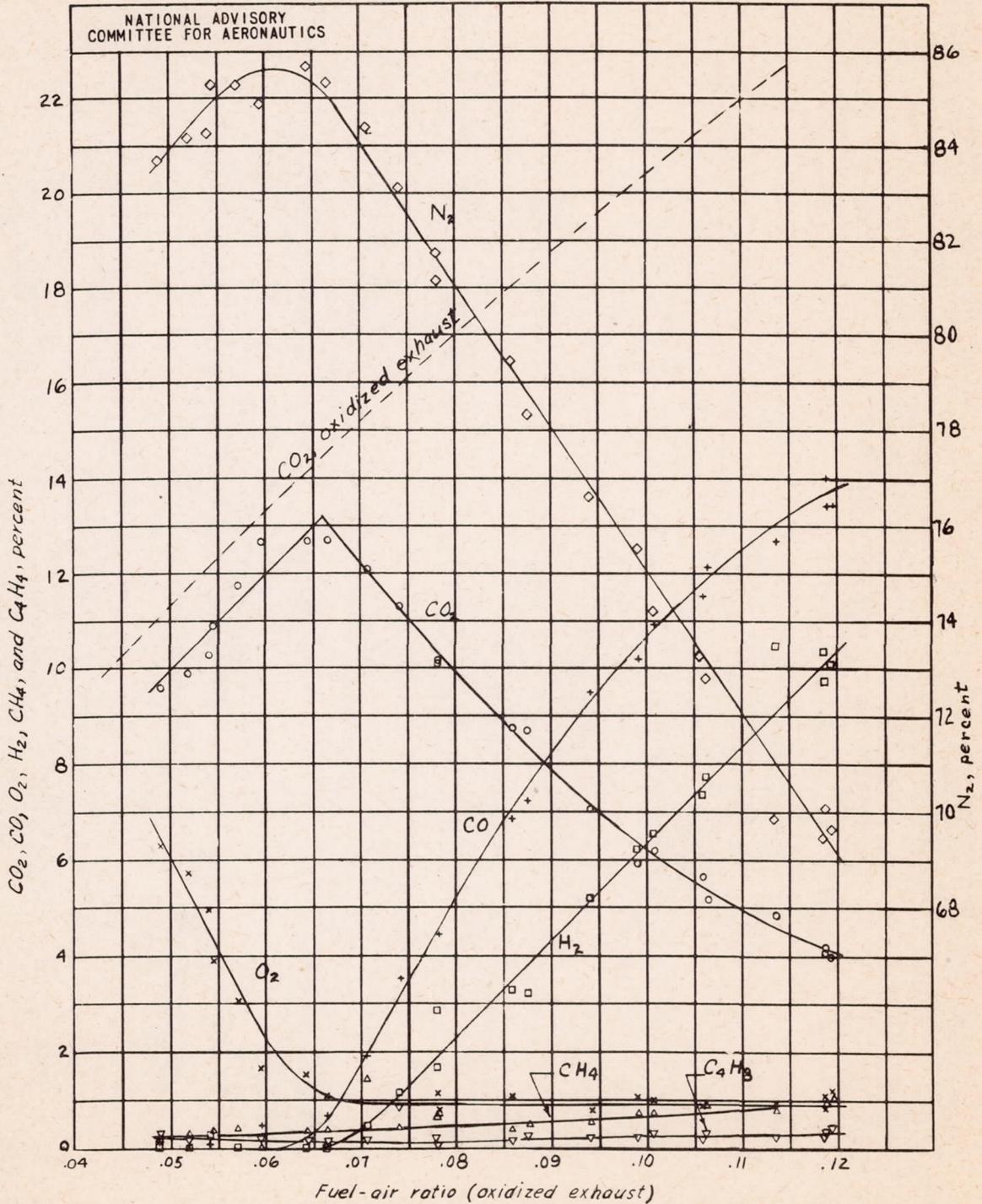


Figure 1. - Relation of constituents in normal exhaust gas to fuel-air ratio. Army 100-octane gasoline; hydrogen-carbon ratio, 0.188, tetraethyl lead, 3 cubic centimeters per gallon. Data from figures 3 and 4 of reference 1.

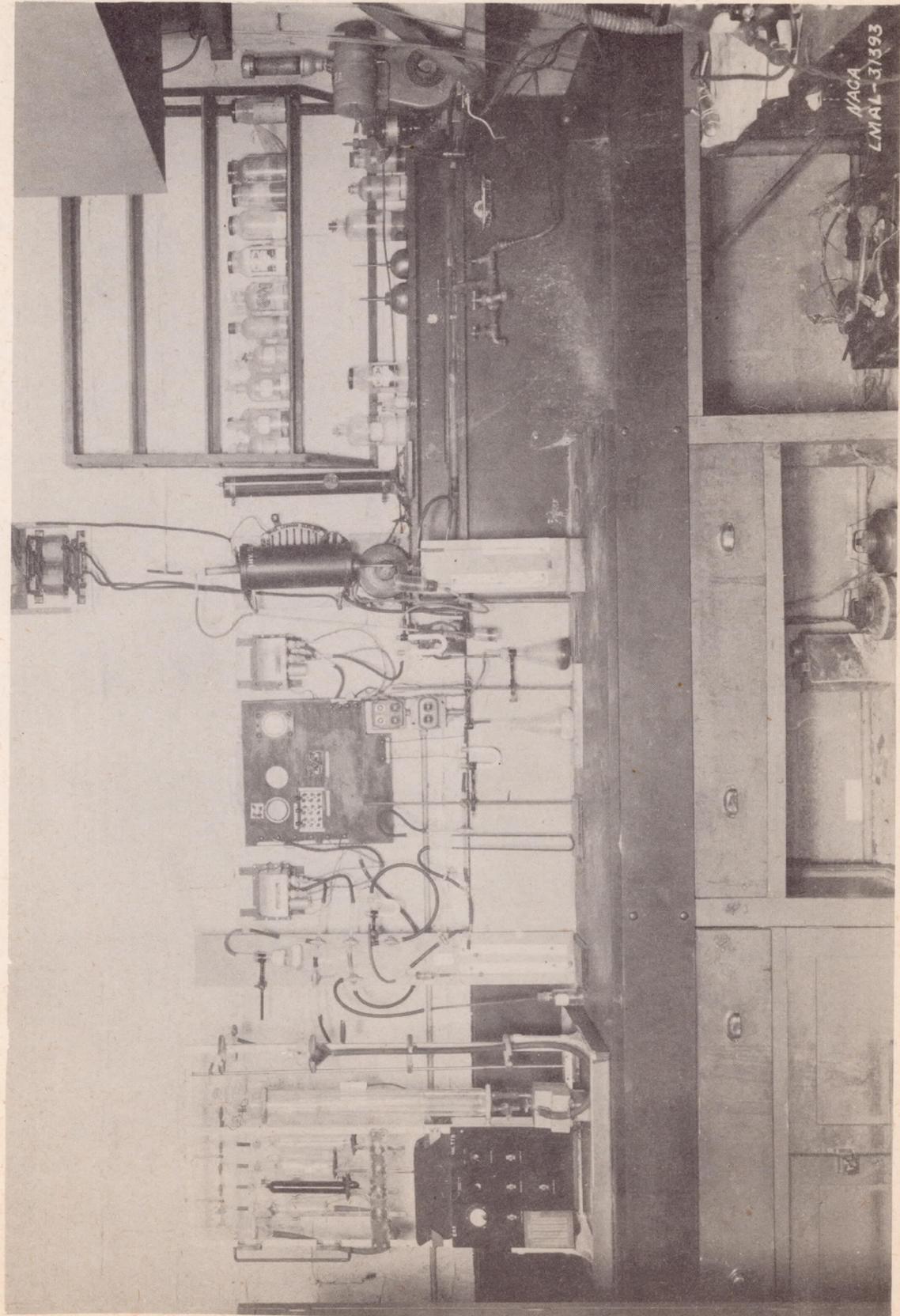
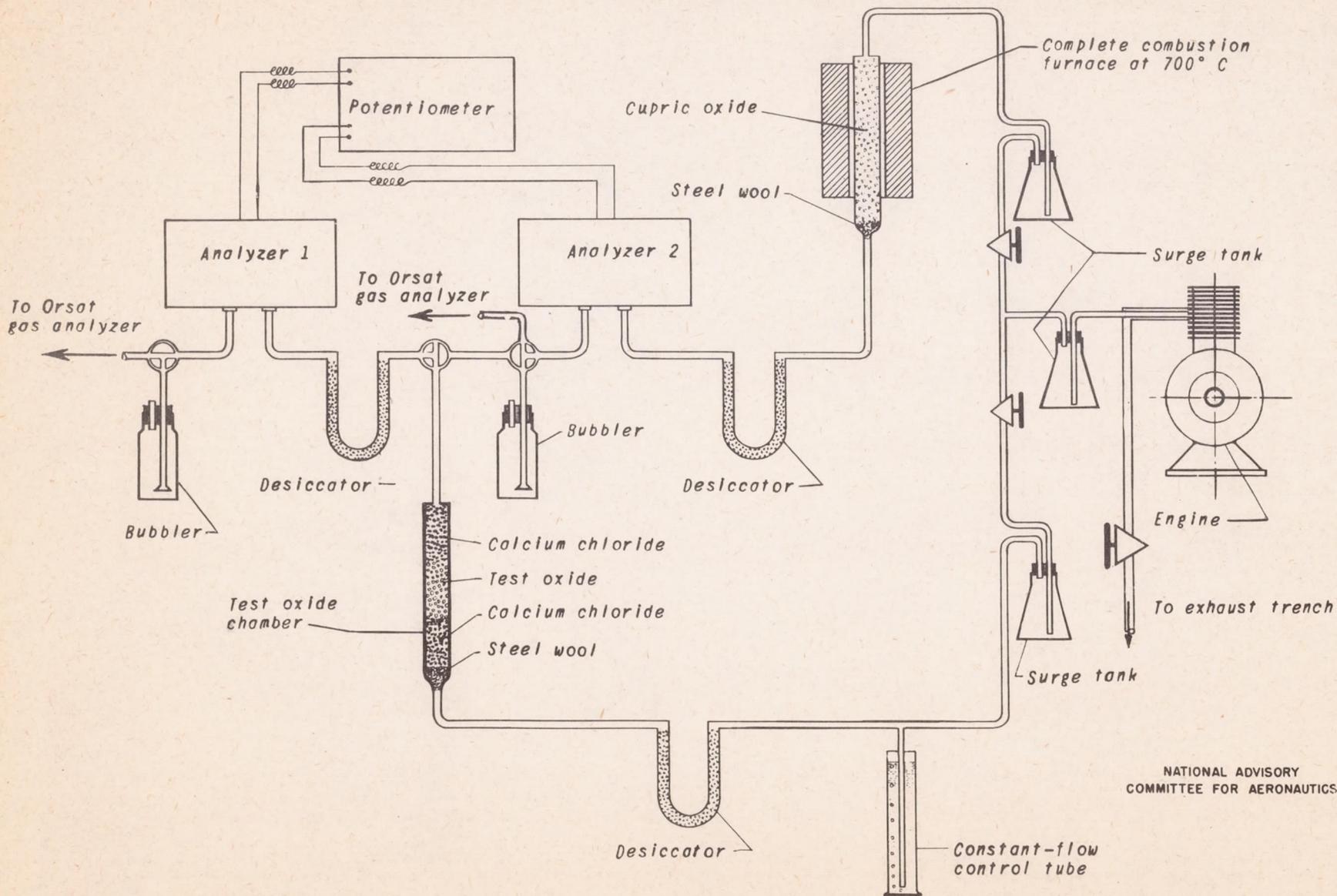


Figure 2. - Apparatus for testing oxides.



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Fig. 3

Figure 3. - Apparatus for room-temperature oxidation of exhaust gases.

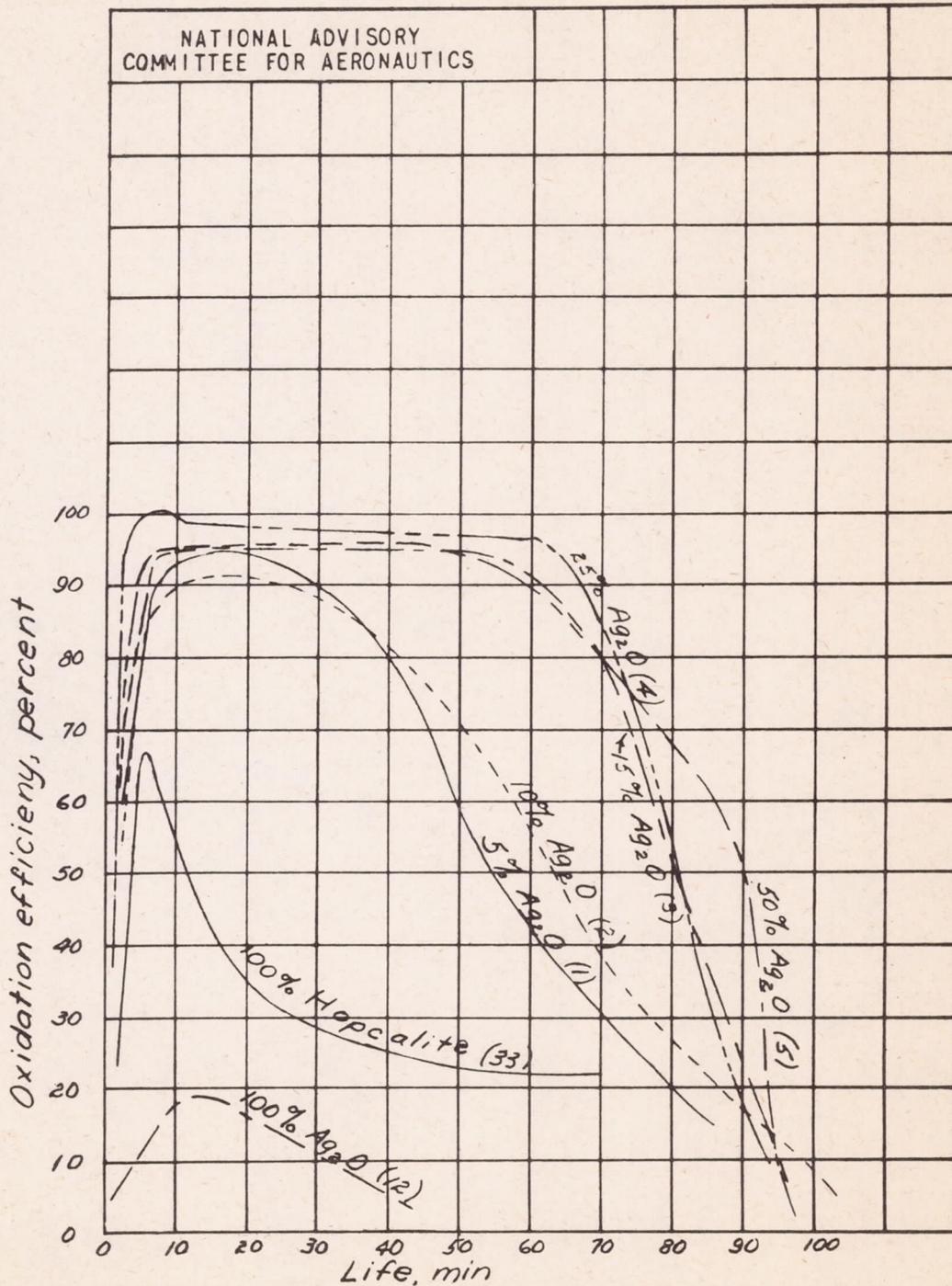


Figure 4. - Comparative oxidation efficiency of commercial Hopcalite with various concentrations of silver oxide. Numbers refer to oxides given in table I.

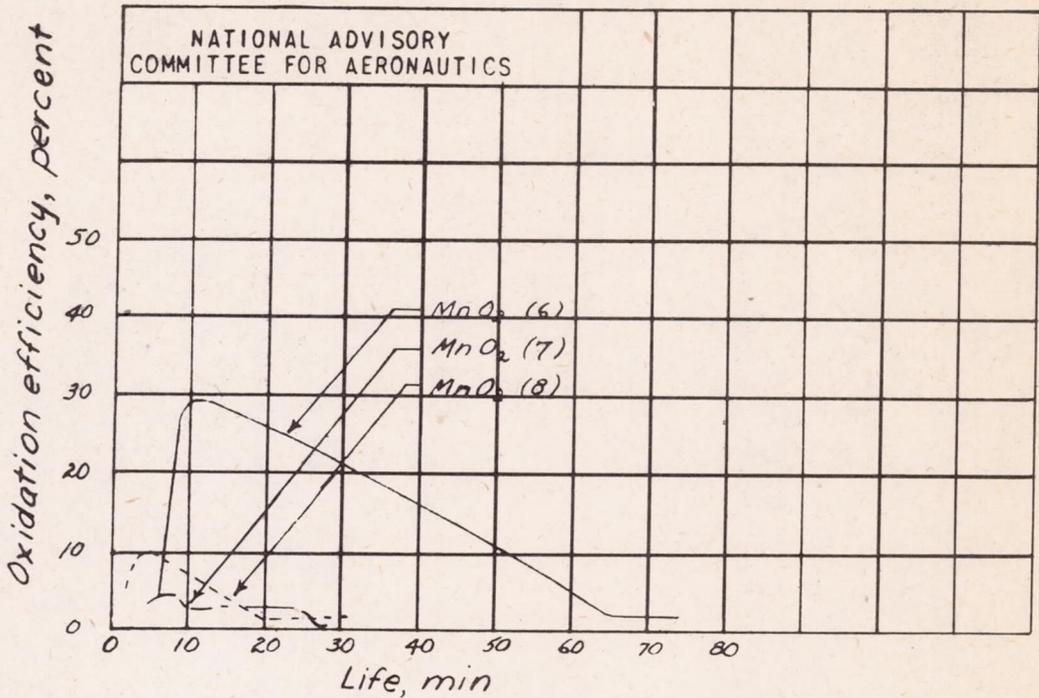


Figure 5. - Comparative oxidation efficiency of manganese dioxide from different preparations. Numbers refer to oxides given in table 1.

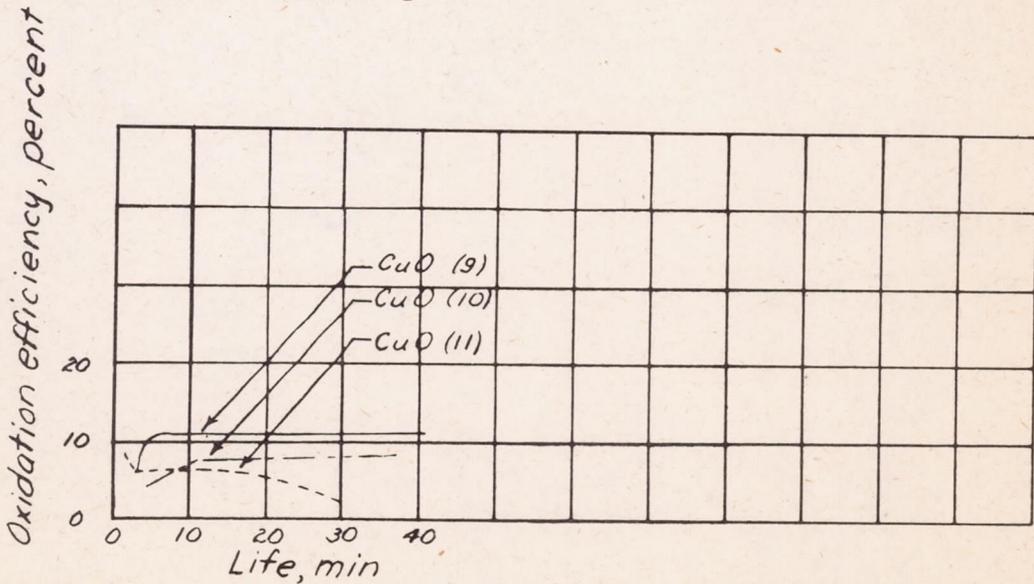


Figure 6. - Comparative oxidation efficiency of cupric oxide from different preparations. Numbers refer to oxides given in table 1.

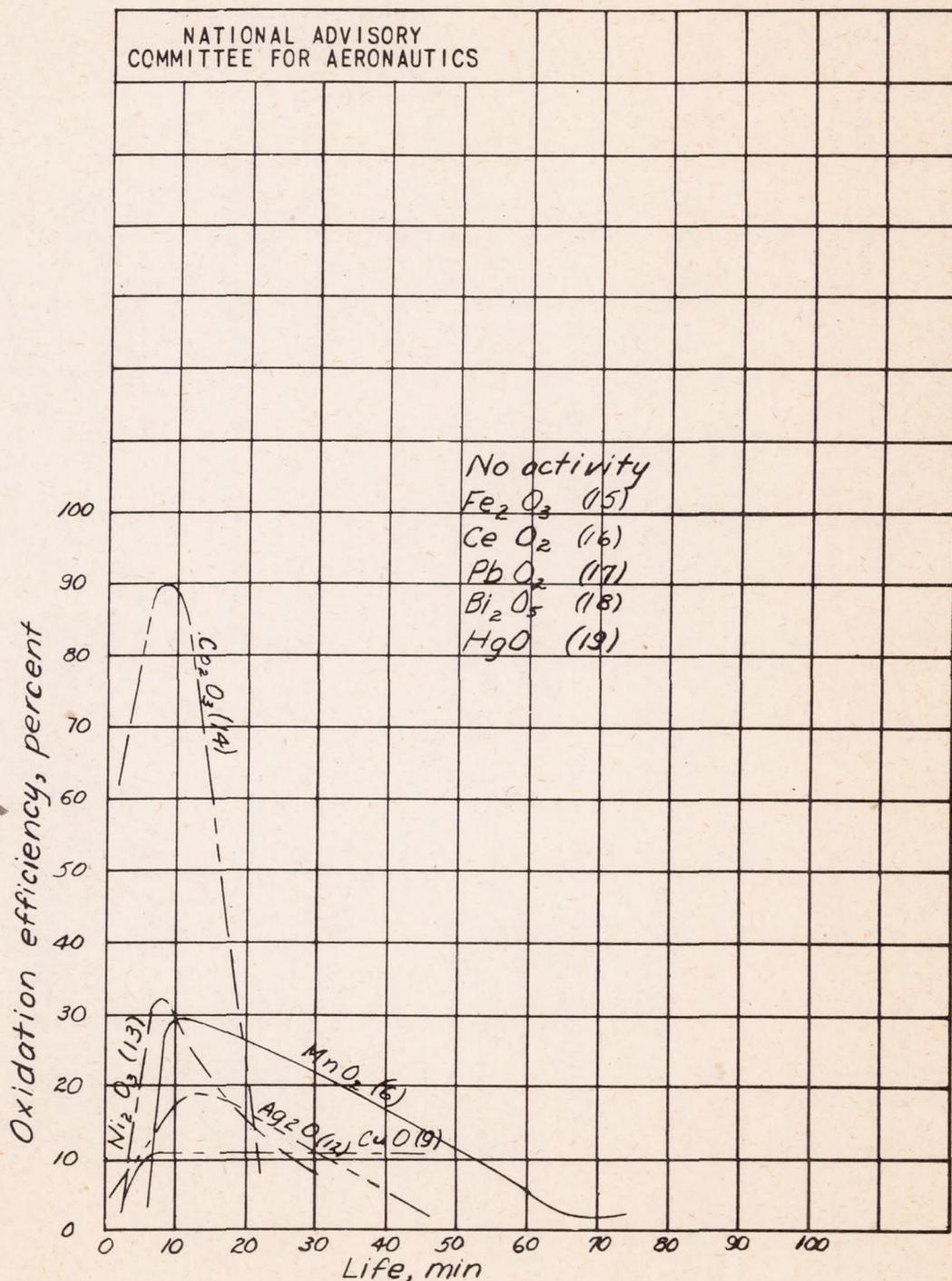


Figure 7. - Comparative oxidation efficiency of individual oxides. Numbers refer to oxides given in table I.

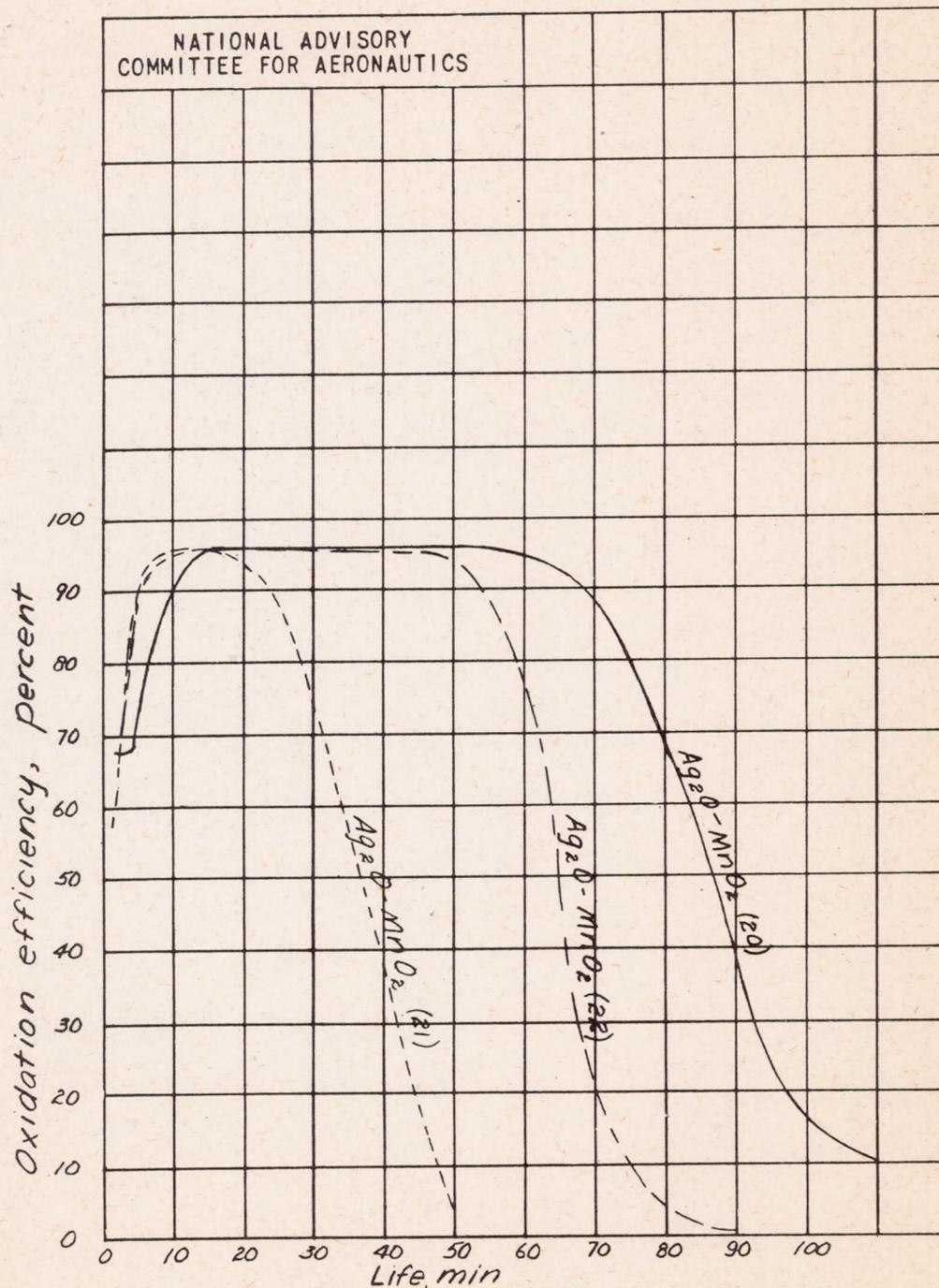


Figure 8. - Comparative oxidation efficiency of 25 percent silver oxide - 75 percent manganese dioxide from different preparations. Numbers refer to oxides given in table I.

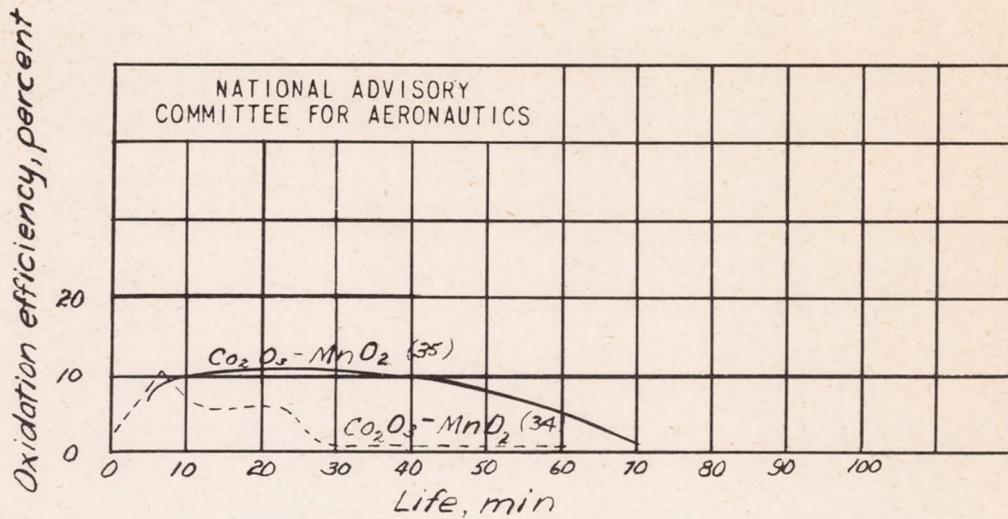


Figure 10. - Comparative oxidation efficiency of 50 percent cobaltic oxide - 50 percent manganese dioxide mixtures from different preparations. Numbers refer to oxides given in table I.

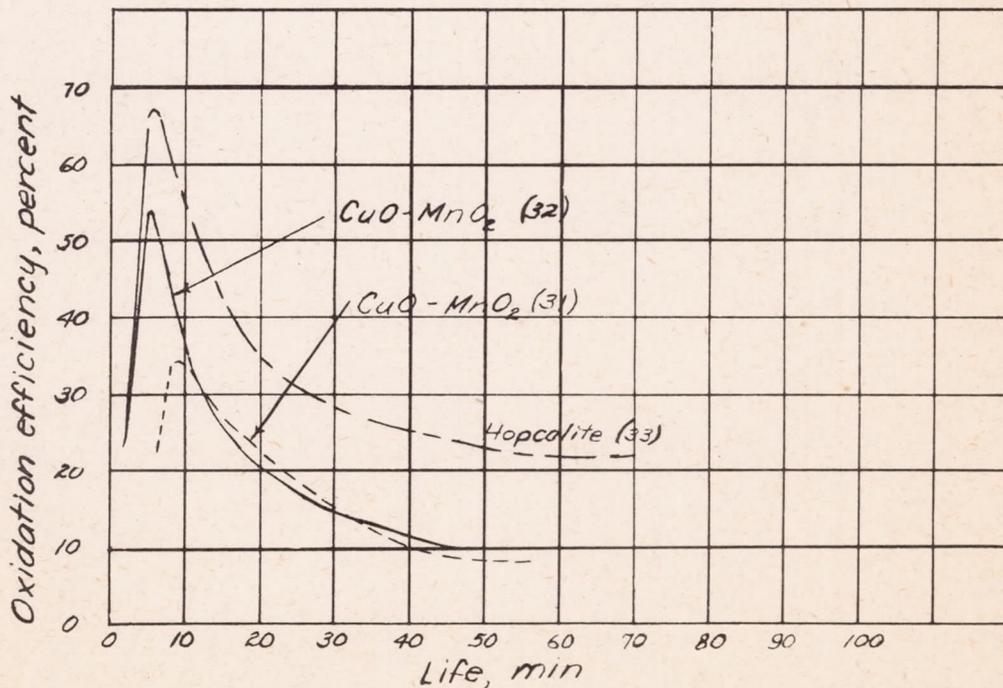


Figure 11. - Comparative oxidation efficiency of commercial Hopcalite and cupric oxide-manganese dioxide mixtures. Numbers refer to oxides given in table I.

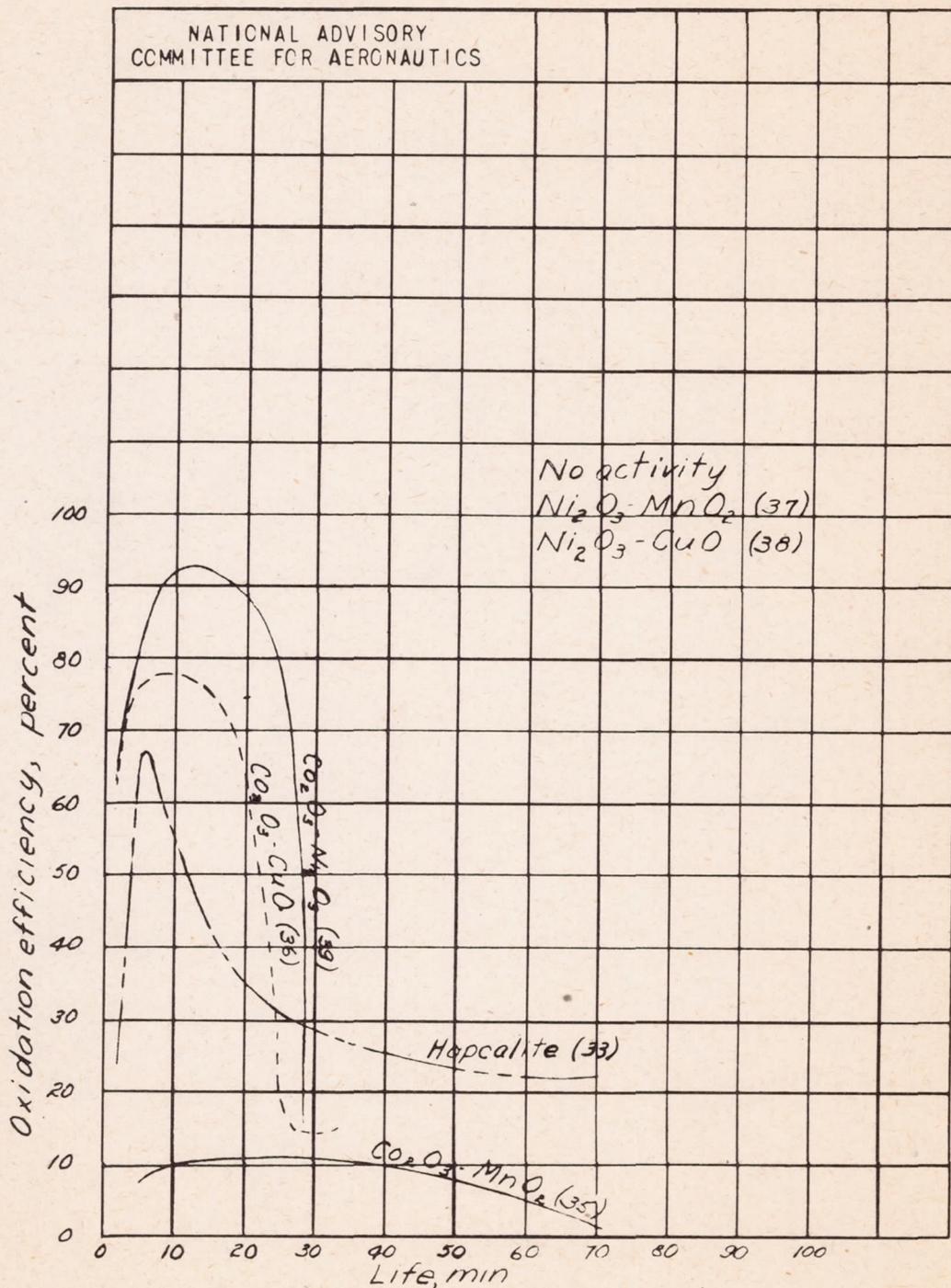


Figure 12. - Comparative oxidation efficiency of mixtures of two individual oxides. Numbers refer to oxides in table I.

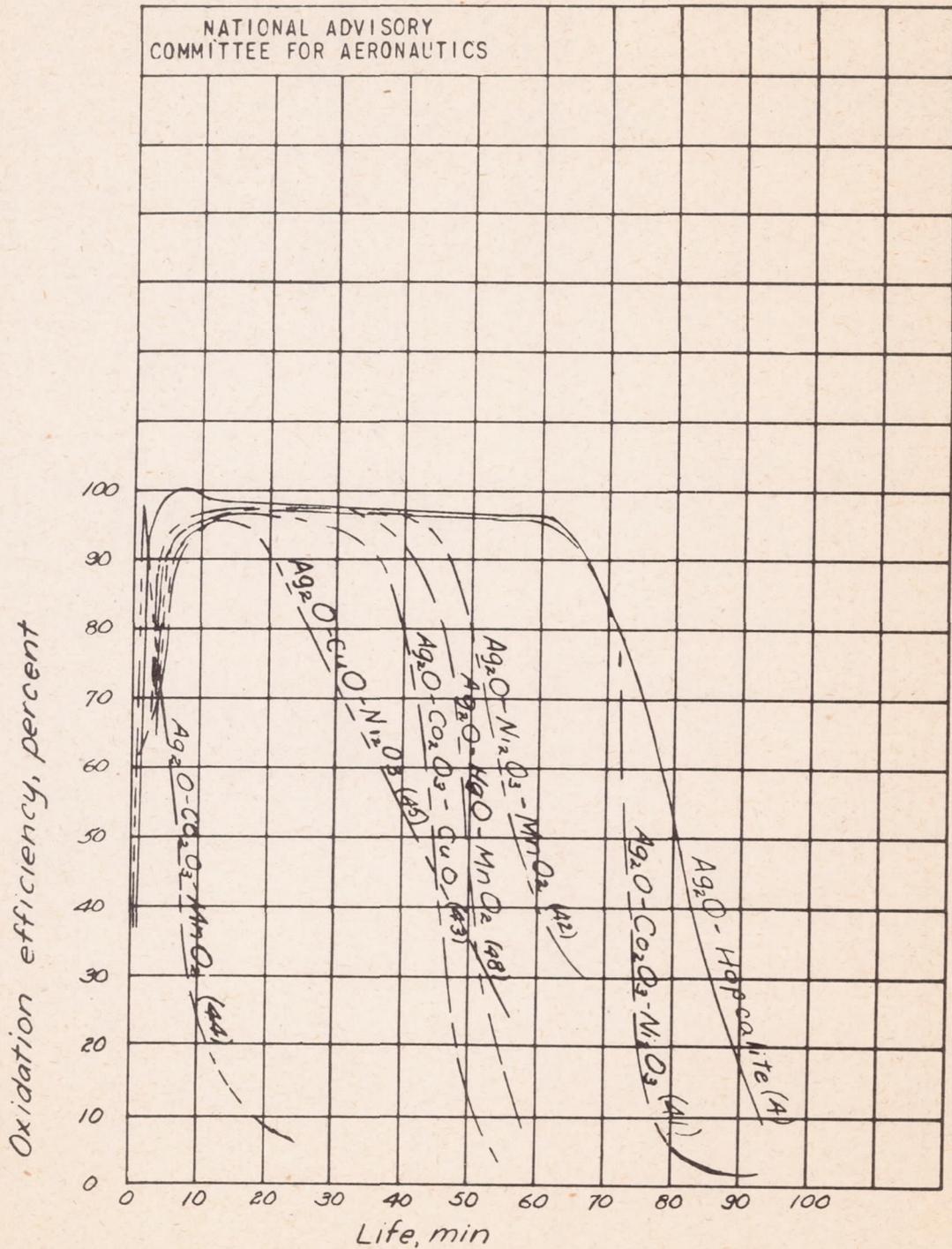


Figure 13. - Comparative oxidation efficiency of two oxide mixtures with 25 percent silver oxide. Numbers refer to oxides given in table I.

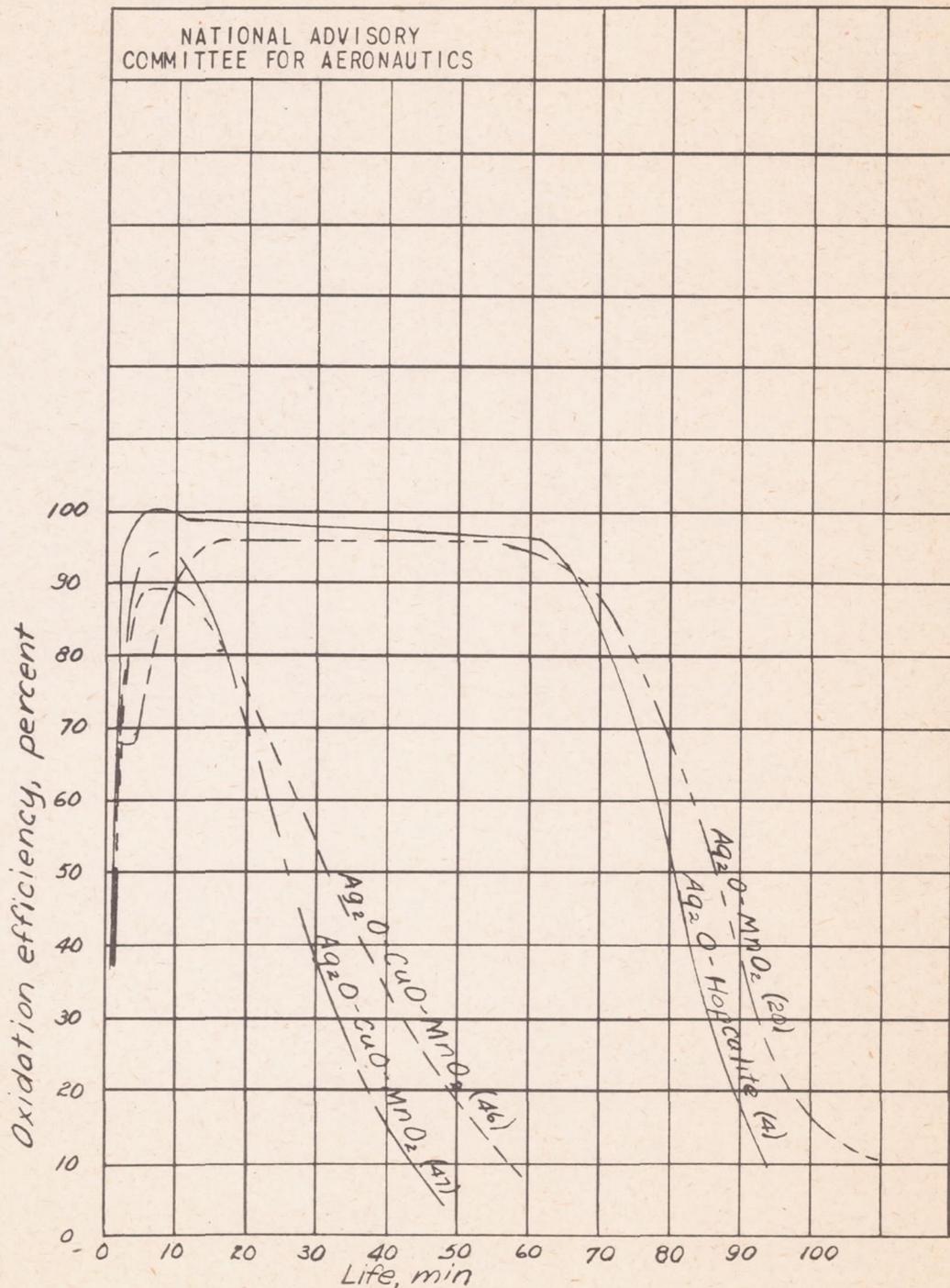


Figure 14. - Comparative oxidation efficiency of 25 percent silver oxide with manganese dioxide, Hopcalite, and cupric oxide-manganese dioxide mixtures. Numbers refer to oxides given in table I.

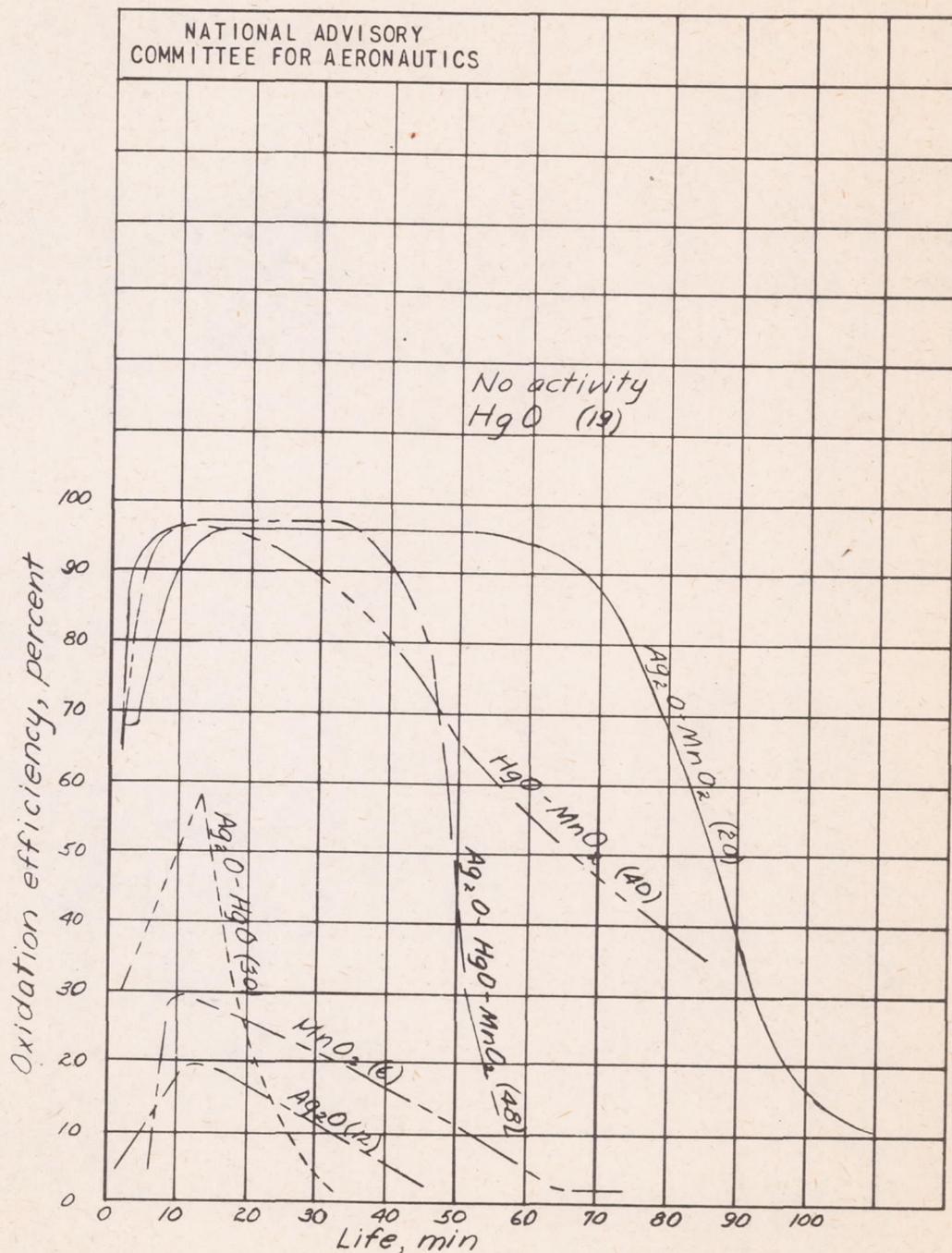


Figure 15. - Comparative oxidation efficiency of all combinations of silver oxide, mercuric oxide, and manganese dioxide. Numbers refer to oxides given in table I.