AFRPL-TR-66-136

486447

HETEROGENEOUS DECOMPOSITION OF HYDROGEN PEROXIDE BY INORGANIC CATALYSTS

A LITERATURE SURVEY

Paul L. Garwig

FMC CORPORATION
Chemical Research and Development Center
Princeton, New Jersey

June 1966

TECHNICAL REPORT AFRPL-TR-66-136
Contract AF 04(611)11208

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals maybe made only with prior approval of AFRPL (RPRR/STINFO), Edwards, California 93523.

AIR FORCE ROCKET PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
EDWARDS AIR FORCE BASE, CALIFORNIA

NOTICES

HETEROGENEOUS DECOMPOSITION OF HYDROGEN PEROXIDE BY INORGANIC CATALYSTS

A LITERATURE SURVEY

Paul L. Garwig

FOREWORD

This technical report was prepared under Contract AF 04(611)11208 (Project 3148) by FMC Corporation, Princeton, New Jersey, for the Air Force Flight Test Center, Air Force Systems Command, Edwards Air Force Base, California. The work reported here was conducted between December 1965 and April 1966. Dr. L. R. Darbee was the Project Director for FMC Corporation, Dr. T. C. F. Munday was the principal investigator in the laboratory part of the program, and Mr. Paul L. Garwig carried out the literature search. The program was conducted by the Inorganic Chemicals Division of FMC Corporation under the general direction of Mr. A. R. Morgan. Lt. Ralph Fargnoli, USAF/RPCL, was program monitor for the Air Force.

This report contains no classified information extracted from classified documents.

Publication of this report does not constitute approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

GEORGE F. BABITS
Lt. Colonel, USAF
Chief, Propellant Division

ABSTRACT

The literature on the heterogeneous decomposition of hydrogen peroxide by inorganic catalysts was surveyed. The aim was to provide background information useful in the development of new catalysts for high-strength hydrogen peroxide in propulsion applications. The survey was prepared as part of a research program on the development of active, stable catalysts for decomposing 98 per cent hydrogen peroxide. Published literature, technical reports, and patents in the period 1945-1965 were included. The survey showed that silver and platinum are the most extensively investigated catalysts. Other major catalysts are palladium, copper, iron, cobalt, manganese, and their compounds. Various methods have bean proposed for increasing catalytic activity by additives that promote the parent activity of elements or compounds. Samarium nitrate-treated silver, cobalt-manganese oxide mixtures, ruthenium and its compounds, and silver-gold alloys are the most active catalysts that have been reported.

TABLE OF CONTENTS

Page

TABLE OF CONTENTS - cont.

TABLE OF CONTENTS - cont.

SECTION I

INTRODUCTION

The development of high-strength hydrogen peroxide and its application to propulsion by Germany in World War II gave impetus to investigations of catalysts useful in torpedoes, rockets, gas generators, and similar devices. Commercial production of 90 per cent hydrogen peroxide in 1945 and 98 per cent hydrogen peroxide about 1948 by the Buffalo Electro-Chemical Company increased the scope and the challenges of successful propulsion systems employing catalytic decomposition.

Many catalysts for the decomposition of hydrogen peroxide have been investigated. Silver has long been known as the best catalyst for rapidly and efficiently decomposing hydrogen peroxide in propulsion applications. However, sustained operations with 90 per cent peroxide and short-term operation with 98 per cent peroxide have shown that the usefulness of silver is limited because of melting and severe erosion at high decomposition temperatures.

Under Air Force Contract AF 04(611)11208, FMC Corporation began a program in December 1965 to develop improved catalysts for decomposing 98 per cent hydrogen peroxide in rocket applications. This literature search was aimed at providing background information from all sources on the development of inorganic catalysts that may be of importance for future development efforts. Published literature, technical reports, and patents issued in the last twenty years were reviewed.

The emphasis of the search was on the development and characterization of catalyst materials. The report is written from a chemical point of view. Engineering aspects of either catalyst design, motor configuration, safety, or testing of propulsion units were included only if they bear directly on the development of new catalysts. Applications of catalysts in specific propulsion devices were not included.

Hydrogen peroxide decomposes at a measurable rate in contact with any substance. The rate depends on both the nature and quantity of trace elements either added to or dissolved from the container. There is a considerable amount of literature devoted to this topic. However, it has little bearing on the choice of catalyst for rapidly decomposing concentrated hydrogen peroxide in bulk unless such impurities either poison the catalyst or promote the decomposition rate without drastically altering the thermal stability of the bulk peroxide. Also, most of those studies relate to homogeneous catalysis. Effects of impurities on the behavior of hydrogen peroxide were included in this survey only if they related directly to heterogeneous catalyst performance.

One of the most active fields of research in hydrogen peroxide decomposition involves complex or coordination-compound catalysts, which are generally considered inorganic. Those complexes containing organic groups were not included here because of their relative instability at the high temperatures of interest in propulsion applications. However, literature dealing with organic promoters of decomposition rate was included.

Strictly speaking, the division of hydrogen peroxide catalysts into heterogeneous and homogeneous may be considered to blur the definition of the parameters involved in heterogeneous catalysis. Certainly a complete study of mechanisms of heterogeneous catalysis must involve detailed considerations of homogeneous catalysis. There are unsettled questions, in fact, as to whether certain reactions are homogeneous only, heterogeneous only, or both homogeneous and heterogeneous. As a practical distinction, catalysts were included in this search only if a solid phase was reported to participate in the reaction. Studies of homogeneous reactions that may relate directly to heterogeneous mechanisms were not included. Studies of the kinetics of thermal decomposition were included because they relate to catalytic decomposition of peroxide at high temperatures.

The text of this report is arranged according to the groups of the elements in the periodic table. References are discussed under the section covering the element contained in the most active catalyst investigated. Thus not all information on a particular element will be found in a single section. An index of cross-references is included at the back of the report to facilitate finding information throughout the report concerning the catalytic behavior of any particular element.

A list of the principal sources used in the literature search is also included. The main source was Chemical Abstracts. Whenever possible, each reference is keyed to its abstract to help in locating further information on those papers difficult to obtain.

SECTION II.

PRIOR LITERATURE SEARCHES AND REVIEWS

During the first few years after World War II a number of reviews appeared covering various aspects of the manufacture of hydrogen peroxide by Germany. The general use of peroxide for propulsion was reviewed by McKee (262).* Various propellants, including 80 per cent hydrogen peroxide and ignition catalysts, were reviewed by Cherney (34). In 1947 Levi (227) reviewed various possibilities for using hydrogen peroxide as a fuel and oxidizer. Later reviews of the use of 90 per cent hydrogen peroxide (25) and "anhydrous" hydrogen peroxide (26) as propellants were published by Bloom and others.

In 1952, Evans and others (57) published a critical review of the energetics of reactions involving hydrogen peroxide, its radicals, and its ions. Hart and McFadyen (98), in a 1954 classified (now declassified) technical report, presented a comprehensive and critical review of the thermal and catalytic decomposition of hydrogen peroxide vapors. The authoritative reviews by Baxendale (15) and by Weiss (362) deal almost entirely with homogeneous catalysis, but because of the emphasis on mechanism, they are frequently cited.

The 1955 monograph by Schumb, Satterfield and Wentworth (309) of M. I. T. remains the most comprehensive source of information on hydrogen peroxide. In their discussion of decomposition by inorganic catalysts the authors pointed out that "progress in predicting the mechanism of the decomposition of hydrogen peroxide by heterogeneous catalysts has been disappointingly slow and lags well behind the understanding of homogeneous catalysis." The same statement applies to the subject today. The more than 15 years of research in the M. I. T. Hydrogen Peroxide Laboratories has generated a considerable number of technical reports, most of which were listed in a final report by Satterfield (255) in 1962.

Tamura (339) published (in Japanese) a 1960 review of the catalytic decomposition of hydrogen peroxide. In the same year Baldwin and others (10) reviewed studies of dissociation of hydrogen peroxide with respect to the role it plays in the reaction of hydrogen and oxygen. Fisher and Zeilberger (58) reviewed in 1960 the state of catalyst development for rocket applications of hydrogen peroxide at concentrations of 90 per cent and higher. A 1962 publication of the Shell Chemical Company (318) contains an annotated bibliography of about 350 references on the production, use, and catalytic decomposition of hydrogen peroxide.

---

*Numbers in parentheses denote references in Section XXI.

A Defense Documentation Center bibliography on hydrogen peroxide (110) prepared for the present search is available through DDC. A general bibliography on rocket propellants published by DDC (297) also contains useful information and leads to the earlier literature.

SECTION III.

ALKALI METALS

The alkali metal compounds normally do not catalyze the decomposition of hydrogen peroxide. However, Krause and co-workers (202) reported that sodium ion can activate the catalysis. Normally inactive $CoCl_2$ in solutions with $pH < 7$ becomes very active in the presence of dilute sodium acetate. Sodium ion also promotes the catalytic activity of a solid mixture of aluminum oxide hydrate and $Co(OH)_2$. Coprecipitation of the hydroxides from a solution containing sodium ion yields a catalyst of greater activity than that of a catalyst of the same composition prepared by mechanical mixing. The activity is ascribed to the formation of a surface polyanion having a free ligand coordination position to cobalt.

SECTION IV.

ALKALINE EARTH METALS

1. BERYLLIUM

Krause and Orlikowska (180) found that the catalytic rate of decomposition of 150 cc of 0.3 per cent H_2O_2 at 87°* by 0.1 gram $Be(OH)_2$ was increased 3-fold by first adding 1.0 cc of a $BaCl_2$ solution containing 10^{-6} gram Ba^{2+} ions. The activation is presumably a result of $Be(OH)_2$-Ba^{2+} complex formation at the surface. These authors (196) later showed that the catalytic activities of Ag(I) and WO_4^{2-} ions are greatly increased when the ions are adsorbed on a $Be(OH)_2$ carrier. Ordinarily the ions are only slightly active. Both ions gave a first-order reaction.

In a comprehensive review of beryllium oxide, Budnikov and Belyaev (32) included a discussion of interactions with hydrogen peroxide.

2. MAGNESIUM

Krause and co-workers (187) compared the homogeneous and heterogeneous catalytic activities of magnesium hydroxide and basic magnesium carbonate in the decomposition of hydrogen peroxide. The heterogeneous systems gave larger conversions.

Krause and others (148) found that the weak activity of $Mg(OH)_2$ in the decomposition of hydrogen peroxide is strongly promoted by adsorption of Cu(II) ions, even at concentrations as low as 10^{-6} gram/liter. Other ions, including Ag(I), Mn(II), Co(II), Ni(II), UO_2^{2+}, Cr(III), and Fe(III) poisoned the catalyst.

The influence of small concentrations of added SnO_2 on the catalytic activity of MgO in the decomposition of hydrogen peroxide was determined by Zhabrova and Fokina (378). SnO_2 contents of 0.01 to 6.4 per cent yielded different results for different methods of preparation. The highest activity resulted with a catalyst containing 0.086 per cent of SnO_2. It was prepared by heating MgO moistened with a chloroform solution of $(C_6H_6)_4Sn$ to 600° for an hour. This catalyst decomposed H_2O_2 4.1 times faster than did MgO alone at 90°. In some instances, low concentrations of SnO_2 could not be detected by x-ray analysis, which suggested that MgO and SnO_2 formed a surface compound.

Krause and Plura (179) found that adsorption of cobalt ions on magnesium carbonate yielded an active catalyst for decomposing hydrogen

---

* All temperatures in this report are degrees centigrade unless noted as °F.

peroxide. Wetting 0.01 gram of $MgCO_3$ by 1 cc of $CoCl_2$ solution decomposed 80 per cent of a 3-per cent H_2O_2 solution in 30 minutes, whereas the $CoCl_2$ solution alone decomposed only 1 per cent in the same time. Mn(II) ions behaved similarly to Co(II), but Zn(II), Cd(II), and Ni(II) ions were ineffective.

Krause and Orlikowska (198) determined the effect of adsorbed ion-pairs on the catalytic activity of $Mg(OH)_2$. The pairs La(III)/Cu(II), Mg(II)/Cu(II), and Al(III)/Cu(II) all promoted the activity but to an extent that depended in each case on the order of adsorption of the ions. This "catalytic mutation" is ascribed to the formation of surface complexes in which the first ion adsorbed becomes the central atom.

Krause and Kukielka (183) reported that Co(II) ions were so active adsorbed on magnesium hydroxide that they yielded observable decomposition rates down to 10^{-6} gram at a dilution of $1:2 \times 10^{8}$. Mn(II) ions were less active; Cu(II) ions were without effect.

3. CALCIUM

Krause and Wolski (141) found that $Ca(CN)_2$ in the presence of Mn(II) ions was an extremely active catalyst for decomposing hydrogen peroxide. Either component alone was inert. The mixture was so active that the decomposition could be used to detect 10^{-6} moles of Mn(II), which experiments indicated to correspond to the decomposition in one second of over 20,000 molecules of H_2O_2 by one gram-atom of Mn(II). The behavior was attributed to the formation of traces of surface complex radicals. Co(II) ions behaved similarly to Mn(II).

Krause (150) later studied the catalytic action of $Ca(CN)_2$ with respect to the decolorization of indigo carmine solution by decomposing hydrogen peroxide. Catalytic activity was promoted by the following ions, in decreasing order: Mn(II), Co(II), Fe(III), Mg(II). In the presence of Ca(II) ions, $Ca(CN)_2$ was inactive.

The use of solid $CaCO_3$, $SrCO_3$ and $BaCO_3$ as carriers for various adsorbed ions in the catalytic decomposition of hydrogen peroxide was investigated by Krause and co-workers (192). Both Co(II) and Ag(I) ions catalyse on any of the three carriers. Mn(II) was similar, but it was more active on $CaCO_3$ or $BaCO_3$ than on $SrCO_3$. Cu(II) and Fe(III) were less active. Ni(II) and Cd(II) were ineffective but small differences between them were consistently observed. $K_4Fe(CN)_6$ gave a positive effect on $CaCO_3$, but a negative one on $SrCO_3$ or $BaCO_3$. The results showed that both active and inactive ions are adsorbed, but evidently only active ions change the crystal lattice defect structure, which allows the surface to assume donor properties and gives the ion/carrier complex a type of n-defect arrangement. On this basis the decomposition can be described as acceptor catalysis.

4. BARIUM

Krause and others (172) reported that although $BaSO_4$ is inactive as a catalyst for decomposing hydrogen peroxide, it can be activated if precipitated at 98° in the presence of a Cu(II)/Co(II) ion mixture. Activation was not observed when the same procedure was used at 20°.

SECTION V.

BORON, ALUMINUM, SCANDIUM, YTTRIUM

1. ALUMINUM

According to Krause and Borzeszkowski (147), various forms of aluminum oxide hydrates can be differentiated by the relative activities of adsorbed Mn(II), Cu(II), and Fe(III) in the decomposition of hydrogen peroxide at 37°. Invariably, adsorbed ions provide lower activity than do either of the ions alone. The relative retardation by the carriers was: amorphous $Al(OH)_3 < \nu$-AlOOH (boehmite) $< \alpha$-$Al(OH)_3$ (hydrargillite) $< \nu$-$Al(OH)_3$ (byerite). The technique can be used as an analytical method for distinguishing the oxides. It was also found that in solutions of mixed ions the activity depended on the order of addition of the ions.

Krause (143) found that although aluminum ions do not decompose hydrogen peroxide at 37° in solution, they do promote or inhibit the activity of other catalysts. Al(III) promotes the decomposition by copper ferro-ferricyanide, but inhibits the decomposition by CuO, mixed gels of $Al(OH)_3$-$Cr(OH)_3$-$Fe(OH)_3$, $Cu(OH)_2$-$Pb(OH)_2$-$Fe(OH)_3$, and $Mg(OH)_2$-$Cu(OH)_2$--$Fe(OH)_3$, and by $Co_2[Fe(CN)_6]$ gel. Complex formation and blocking of active centers are used to explain the results.

Schwab and Greger (311) studied the catalytic decomposition of hydrogen peroxide by semiconductor alloys of aluminum and antimony. At constant surface area the catalytic reaction rate is faster on n-AlSb than on p-AlSb. Also it was first order on n-AlSb and second order on p-AlSb. These facts are said to confirm that the reaction is an acceptor reaction.

In other experiments it was demonstrated that catalyst corrosion is diminished by covering the surface with H_2O_2. Irradiating both catalysts with ultraviolet light resulted in an increase by 20 per cent of the reaction velocity on p-AlSb and a decrease by 20 per cent on n-AlSb.

SECTION VI.

CARBON, SILICON, GERMANIUM, TIN, LEAD

1. CARBON

a. Nature and Mechanism of Carbon Activity

The decomposition of hydrogen peroxide by molded carbons prepared from coal-pitch coke heated above 2200° was investigated by Ichinose (111). Samples of molded carbons heated between 800 and 2800° were used to decompose 87 per cent H_2O_2 (in H_2SO_4) to determine the effect of thermal treatment on activity. The rate was about constant for samples heated up to 1200°, sharply fell off at 1200-1300°, then gradually declined to zero at 2200°, above which no decomposition was detected. The abrupt change at 1200-1300° is ascribed to a major modification of the surface structure.

Brinkmann (28) attempted to relate the activity of activated carbon to the ease with which it decomposes hydrogen peroxide. Sorption of strong acids and alkalies can be used to determine the surface groups that exhibit acid and basic properties, both of which determine the chemical nature of the carbon. By determining the half-time of catalytic activity in the decomposition of hydrogen peroxide it is possible to detect small changes in carbon surfaces.

Brinkmann (29) later published a review of catalysis by activated carbon in which the decomposition of hydrogen peroxide is discussed in detail along with other reactions. The nature of surface-active groups was considered to be important for understanding the behavior of the catalyst in this reaction.

Gants (82) examined qualitatively the products formed in the decomposition of hydrogen peroxide to determine surface properties that affect the mechanism. The reaction was extremely sensitive to the chemical nature of the surface. The mechanism was determined by the relative content of alkaline and acid sites on the surface. It was concluded that surface oxides participate in the reaction, and during decomposition are gradually converted to oxides of carbon, which are given off with oxygen and water.

Additional kinetic evidence from experiments with brick-activated carbon was used to confirm previous theories as to the nature of carbon activity (83). In addition, Gants compared the velocity of H_2O_2 decomposition on anodically and cathodically polarized carbon electrodes. The results indicated that the action of H_2O_2 on active alkali oxides depends on the exchange of OH^- ions on the carbon surface with HO_2^- ions in solution.

Puri and others (295) studied the catalytic activity of charcoal prepared by carbonizing sucrose with sulfuric acid. Three samples were used: (1) as prepared, (2) degassed at 750°, and (3) degassed at 1200°. Sample (1) was the least active and sample (3) the most active. The differences were attributed to changes from acidic to alkaline surfaces as the temperature of thermal treatment increases. Degassed charcoal chemisorbed enough oxygen during the decomposition to form a surface-oxygen complex that makes the surface acid and of diminished activity. A mechanism was suggested:

$$H_2O_2 \rightleftharpoons H^+ + OOH^-$$

$$(C)H^+ : OOH^- \rightleftharpoons (C)H^+ : OH^- + (O)$$

Hydrogen ions are adsorbed, the unstable OOH^- decomposes, and H^+ and OH^- combine.

Isbin and others (246) decomposed hydrogen peroxide at atmospheric pressure by passing solutions through small catalytic tubes of various materials. Porous carbon was the most satisfactory carrier tested. Alundum tubes gave the least reproducible performance. Weight losses were smallest for carbon and irium (cobalt-plated brass) screen catalysts. Equations based upon resistances encountered to the movement of hydrogen peroxide from the main body of the solution to the catalyst liquid interface, and upon the resistance to decomposition at the catalyst liquid interface, accounted for the data according to a first order reaction. The equations indicated that a liquid-film, diffusion resistance was controlling for the silver tubes and irium screen catalysts. The controlling resistances were the sum of the liquid diffusion resistance in pores of the carriers and the resistances to decomposition at the catalyst liquid interface.

Fomenko and co-workers (74) used 0^{18} isotope exchange to study the mechanism of catalytic decomposition of hydrogen peroxide by activated carbon. 0^{18} was included in the surface oxides and in hydrogen peroxide. It was established that in the reaction, oxygen is not exchanged between the basic oxides and H_2O or H_2O_2. When 0^{18} was present in H_2O_2, it was found that in decomposition the 0^{18} content of the basic surface oxides approached that of H_2O_2. On the average the transfer consisted of 25 to 30 per cent of the initial amount in H_2O_2. The results were consistent with the proposal that hydrogen peroxide decomposition on carbon involves the participation of surface oxides, and that a volumetric interaction between basic OH groups on the carbon surface and HO_2^- ions in hydrogen peroxide results in the displacement of the groups by the ions. Since paramagnetic resonance measurements were not successful in detecting free radicals on the carbon surface, a chain mechanism for the decomposition could not be established.

In a later study using the isotope method, Fomenko and others (75) concluded that the liberation of oxygen by activated carbon involved an exchange reaction of surface OH^- by HO_2^-.

b. Effects of Additives and Impurities

The rate of catalytic decomposition of hydrogen peroxide by inorganic reagents adsorbed on activated charcoals was examined by Watanabe and Shiramoto (360). Highest activities were obtained with adsorbed $MnCl_2$, $CoCl_2$, $PdCl_2$, H_2PtCl_4; moderate increased resulted for adsorbed $HClO_4$, HNO_3, NH_4Cl, $(NH_4)_2SO_4$, $MgCl_2$, $FeCl_3$, $Co(NO_3)_2$, and $SnCl_2$. The lowest values were obtained for NaOH, KOH, $KMnO_4$, H_2SO_4, H_3PO_4, and some metallic sulfates.

Magaril and Aksenova (238) determined the effect of sulfur content on the catalytic activity of carbon black. Several methods of thermal treatment were used to induce combined sulfur. It was found that catalytic activity increased with sulfur content and that carbon treated in hydrogen sulfide had autocatalytic activity.

The catalytic activities of coal, coke, lampblack, animal and other charcoals, and graphite were examined by Krause (137). Graphite was inactive. The activities of the other catalysts depended on their iron, calcium, and magnesium contents as well as their absorptive power.

Kobozev and Zubovich (120) reported that the adsorption of micro amounts of mixtures of Fe(III), Cu(II), and Ag(I) inhibited the catalytic decomposition of hydrogen peroxide by sugar charcoal.

Kokado and others reported that persimmon tannin (127) and tannic acid (128) inhibited the decomposition of hydrogen peroxide by active carbon, presumably by blocking active sites at the surface.

c. Behavior of Carbon Electrodes

Ivanyi (113) used the relative rates of hydrogen peroxide decomposition to obtain information concerning the porosity, surface area, and diffusion rate in activated carbons used as dry cell depolarizers. In such depolarizers, bests results are obtained with active carbons having many active and few inactive pores.

Kamiike and others (115) determined the relative activities of carbon electrodes from various manufacturers. Effects of an oxidizing atmosphere and of a waterproof film were also determined. Matsumoto and others (257) reported that the activity of carbon electrodes for wet air cells could not be directly related to activity in the catalytic decomposition of hydrogen peroxide. In a study of carbon electrodes for wet air cells, Makino (242) found that the terminal voltage of wet air cells at constant current discharge, the rate of hydrogen peroxide decomposition, and the electrical conductivity of the carbon electrodes could be related.

2. SILICON

Penner (289) searched for a specific catalytic effect of silica gel. Experiments were designed to compare decomposition rates in the sol before gelation and in the same mixture during and after gelation. Results from the thermal decomposition of hydrogen peroxide in basic silica gels made from sodium silicate and sulfuric acid revealed that gel formation did not affect the stability of the peroxide at room temperature. Both the wall effect, and quantum yields greater than one for the photodecomposition, indicated the existence of reaction chains during the decomposition. In these experiments it was shown that for silica sol and silica gel the first-order reaction rate constants were the same and that the quantum yields were of the same order of magnitude.

3. LEAD

a. Metallic Lead

In 1946-47, the Naval Torpedo Station at Newport, Rhode Island conducted a program to evaluate various catalysts for decomposing 80 per cent hydrogen peroxide in submarine and torpedo applications (277). Lead-plated irium (cobalt-plated brass) catalysts were being produced by the Navy at that time. Techniques for activating catalyst screens were examined. The problem of poor starting characteristics of lead screens was solved by adding silver as an activator. Coating the screens with polyvinyl alcohol was also found to be a possibility for activating the initial reaction. Limited experiments were also conducted to evaluate silver-activated cobalt screens and special irium screens prepared from Inconel, Monel, and stainless steel. No substantial increases in catalyst performance were reported in this program.

Marković (244) studied electrochemically the mechanism of decomposition of hydrogen peroxide on metallic lead. The potentials of cells with Pb/Pt and Pb/Ag electrodes in H_2O_2 were studied as a function of time. For 0.01-0.25 M H_2O_2 at 20°, 40°, and 60°, the decomposition required an induction period, which is not observed for higher concentrations. Neither was an induction period required if the electrode was first immersed for 30 minutes in 0.1 M H_2O_2 at 20°. The decomposition was a zero-order reaction. Catalytic action of H_2O_2 on freshly prepared $Pb(OH)_2$ showed that lead oxides of the formula PbO_n ($n = 2$ to 3) are formed.

Masterson and others (256) obtained a British patent (assigned to Minister of Supply, 1952) covering mixtures with high lead content for decomposing hydrogen peroxide. The catalysts are prepared by igniting mixtures of Pb, PbO, $KMnO_4$, and Se, Te, or S, with asbestos. In a typical formulation, 400 grams of powdered Pb, 100 grams of powdered Se, 200 grams of powdered $KMnO_4$, 100 grams of powdered PbO, and 4 grams of asbestos are pelleted and ignited. The resulting hard, porous pellets have high activity and low erosion in use. The catalyst contains about 4 per cent of free lead.

b. Lead Oxides and Hydroxides

Broughton and others (249) investigated the relative activity of various freshly precipitated metal hydroxides as catalysts for hydrogen peroxide. Lead hydroxide showed high activity. Silver hydroxide had an initially high activity, but it was rapidly poisoned by subsequent additions of the peroxide. Cobalt, osmium, and manganese hydroxides had intermediate activities, averaging from one-fifth to one-tenth that of lead. Iron, copper, nickel, chromium, selenium, cerium, and mercurous hydroxides were considerably less active.

Broughton and co-workers (250) also examined coprecipitated metal hydroxides as catalysts. The hydroxide mixtures were precipitated directly in 48 per cent H_2O_2. When distilled hydrogen peroxide was used, only the following combinations showed an activity higher than that of lead hydroxide alone (the most active single hydroxide tested): silver plus any of the following: 20-40 per cent nickel, 20 per cent cadmium, 40 per cent magnesium, 20 per cent copper, 20 per cent manganese, or 20-40 per cent calcium. As successive portions of H_2O_2 were added, the activity of these systems dropped more rapidly than that of lead hydroxide so that, at high cumulative values of peroxide added, lead was again more active than any of these combinations. In the case of catalysts evaluated with Navol C-3 peroxide, the only combinations having activities above that of lead were silver with 20 per cent of magnesium or calcium. The activities of these systems also dropped below that of lead at moderate cumulative values of H_2O_2 added. Activity promotion was observed for other mixed catalysts but all such activities were below that of lead.

Kulitskii (209) attempted to relate photoconductivity relaxation times of semiconducting PbO to catalytic activity in the decomposition of hydrogen peroxide. Different samples of catalysts gave one or two relaxation times, one of which could be directly related to catalytic activity. For the second relaxation time, there was no apparent relation. In a succeeding study Kulitskii (210) found a qualitative relationship between catalytic activity and the stationary photoconductivity of PbO.

Broughton and others (248) conducted experiments that provided strong evidence that the catalytic action of lead salts in the decomposition of hydrogen peroxide is due to a cyclic oxidation-reduction of lead. In the catalysis by metallic lead, the active agent is a coating of Pb_3O_4 formed on the metal. This coating appears to be formed by the initial dissolving of lead, in divalent form, in the H_2O_2, followed by oxidation and redeposition as Pb_3O_4 on the metal surface. The evidence did not indicate that Pb_3O_4

forms by direct reaction of lead and H_2O_2.

A 1949 U. S. patent by Wernlund (364) assigned to Du Pont, covers a lead oxide-containing catalyst especially useful for decomposing hydrogen peroxide. In the preparation, lead is first electrodeposited on a porous iron support. This is then briefly electrolyzed first in an alkali metal cyanide solution, then in an alkali metal carbonate solution. The catalyst thus produced has a very large surface area.

On the basis of O^{18} distribution in the hydrogen peroxide decomposition reaction, Fomenko and co-workers (75) concluded that in the presence of PbO_2 the decomposition is explained by an electron transfer from PbO_2 to H_2O_2, with rupture of the O-O bond.

Krause and Magas (149) studied the effects of adsorbed ions on the catalytic decomposition of hydrogen peroxide by lead hydroxide $Pb(OH)_2$ at 37°. Cu(II) and Mn(II) ions promote the activity, whereas Ag(I), Hg(II), Mg(II), Zn(II), Fe(III), and Pb(III) ions have no effect. Activity is inhibited by Ni(II), Co(II), and UO_2^{2+}. Cu(II) was said to be adsorbed on $Pb(OH)_2$ as CuO, which participated in a cyclic reaction:

$$(1) \quad 2CuO + H_2O_2 \rightarrow Cu_2O + H_2O + O_2$$

$$(2) \quad Cu_2O + H_2O_2 \rightarrow 2CuO + H_2O$$

The results indicated that the reaction was first order with an activation energy of about 18 kcal/mole in all cases.

The "superadditive" activity of mixtures of several amphoteric metal hydroxides in the decomposition of hydrogen peroxide was studied by Krause (151). Mixtures of 100 mg $Ni(OH)_2$ with 1 mg of either CuO, ortho $Fe(OH)_3$, or $Co(OH)_2$, were inactive as catalysts at 37°. However, mixtures of 100 mg $Ni(OH)_2$ with 1 mg of $Mg(OH)_2$ or $Mn(OH)_2$ were very active. Also, a mixture of $PbO \cdot \frac{1}{2} H_2O$ with CuO and $Mn(OH)_2$ was inactive, but a mixture of $PbO \cdot \frac{1}{2} H_2O$ and $Mg(OH)_2$ was extremely active. Direct mechanical mixing of $Fe(OH)_3$ with $Mg(OH)_2$ gave an inactive catalyst in peroxidative HCOOH oxidation, but the same mixture was active when the two hydroxides were melted together.

SECTION VII.

NITROGEN, PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH

1. PHOSPHORUS

Krause (153) examined insoluble phosphates as carriers of adsorbed ions for the catalytic decomposition of 200 cc of 0.3 per cent hydrogen peroxide. $Mg_2P_2O_7$ (0.1 gram) reduced the activities of most ions, including the ordinarily active Fe(II) and $Fe(CN)_6^{4-}$. Cu(II) ions at greater than 10^{-4} gram remained active. $MgNH_4PO_4 \cdot 6H_2O$ inhibited the activity of Co(II) ions below 10^{-6} gram. The following ion mixtures gave active catalysts: Cu(II) + Mn(II), Cu(II) + Co(II), and Fe(II) + Al(III) + $Fe(CN)_6^{4-}$.

2. ANTIMONY

Clopp and Parravano (35) attempted to correlate the kinetics of catalytic hydrogen peroxide decomposition with changes in the electronic structures of antimony alloys containing gallium and indium. Measurements of electrical properties and calculated activation energies supported the theory that electron availability for bond formation between the adsorbate and the conducting surface depends on the electronic properties of the surface.

3. BISMUTH

Krause and Urbanowicz (191) found that a hydrous oxide of bismuth gave various catalytic decomposition rates for the hydrogen peroxide, even though the test samples of catalyst had been prepared by ostensibly identical procedures. All the catalysts were shown to have the same composition, $Bi_2O_3 \cdot H_2O$, by x-ray measurements. The most effective catalysts were found to have malformed lattice planes in the crystalline structure.

Yadava and Ghosh (372) compared the catalytic activities of hydrous bismuth oxides prepared by adding (1) 10 per cent excess, (2) equivalent, or (3) 10 per cent deficient, amounts of sodium hydroxide to acid $Bi(NO_3)_3$ solutions. The order of activity was (1) > (2) > (3), with (3) practically inactive. The reactions were first order except in concentrated H_2O_2, for which the rate constant first decreased before it leveled off. The mechanism is described as the formation of a $Bi(OH)_3 \cdot H_2O$ adsorption complex, which decomposes to OH radicals and then induces cyclic decomposition of H_2O_2. Bismuth oxidizes from Bi(III) to unstable Bi(IV) in the process.

Shushunov and Fedyakova (323) examined the kinetics of hydrogen peroxide decomposition by various metals and alloys. The technique involved immersion of a cylinder of the catalyst in 5 to 25 per cent H_2O_2 solutions. The activation energy proved to be independent of the H_2O_2

concentration, and the large magnitude of the energy indicated that true chemical rates, not diffusion rates, were measured. Over the range 30 to 60°, activation energies were 15,600 cal/mole for bismuth, 9000 for tin, 9200 for cadmium, and 8200 for antimony. In bismuth-tin alloys the activation energy varied with concentration, and had no one single value. In cadmium-bismuth alloys a minimum activation energy of about 6000 cal/mole was obtained for the composition CdSb. It was concluded that eutectics cannot, but compounds can, be detected by the catalytic activity of an alloy.

SECTION VIII.

TITANIUM, ZIRCONIUM, HAFNIUM

1. TITANIUM

Torkar (342) developed a relationship between adsorption measurements, gas permeability, and catalytic activity towards H_2O_2 decomposition of powdered titanium dioxide (rutile).

SECTION IX.

VANADIUM, NIOBIUM, TANTALUM

For information on vanadium in hydrogen peroxide decomposition, see Section XXIII.

SECTION X.

CHROMIUM, MOLYBDENUM, TUNGSTEN

1. CHROMIUM

The chemical, electrical, and catalytic properties of calcined chromic oxide gels were investigated by Deren and others (49). The results showed that an amorphous monohydrate forms at 280-360°. Oxidation occurs with dehydration and increases with annealing temperature. The O/Cr ratio is a maximum of 2 at 350°, and sexivalent chromium ions produce an excess charge at the surface. Cr_2O_3 crystallized at 400° and there was no further oxidation with temperature increases. Adding magnesium increased the excess charge in Cr_2O_3. The oxide decomposed H_2O_2 by a first-order reaction, and by a manner which indicates that the rate constant and frequency factor may correlate with surface concentrations of sexivalent chromium.

In a later paper Deren and Haber (50) investigated the thermal behavior of Cr_2O_3 oxide gels containing magnesium and titanium hydroxides as doping agents. Magnesium increased the surface concentration of Cr(VI) ions in the thermal treatment, but titanium decreased it. The specific rate constants in hydrogen peroxide decomposition could be closely correlated with the surface concentrations of Cr(VI) ions. The activity of Cr(VI) active centers was found not to depend on the type or amount of doping agent, but the activity did decrease slightly at higher annealing temperatures.

Alekseevskaya and others (4) found that the catalytic decomposition of hydrogen peroxide by $Cr(OH)_3$ and its dehydration products depended markedly on the conditions of thermal treatment. Heating $Cr(OH)_3$ liberates water up to 170°. At 320°, the compound changes from amorphous to crystalline. The specific surface increases with temperature to 200°, where it is a maximum, and declines at higher temperatures. The rate at which H_2O_2 is decomposed declines with higher temperatures of thermal treatment, with the exception that the highest activity results when $Cr(OH)_3$ is heated to 300°, evidently because of crystallization.

Matsunaga (258) studied the effect of chromium oxide treated in an oxidizing atmosphere on the decomposition of hydrogen peroxide. The oxygen content of Cr_2O_3 was increased above the stoichiometric amount by heating the oxide in oxygen at 250°, 350°, and 450°. The products had 0.34 to 2.83 meq O_2/gram catalyst, which gives a mean oxidation number for chromium of 3.12 to 5.65. Results from decompositions of 30 per cent H_2O_2 at 25° indicated that rates were constant for a constant oxygen content of the catalyst, regardless of chromium oxidation number. Activity was ascribed principally to chromic anhydride, which forms on the catalyst surface under the conditions of these experiments

California Research Corp. (33) obtained a British patent in 1963 covering a process for rejuvenating a spent, chromia-on-alumina catalyst that can be used to decompose hydrogen peroxide. The treatment involves heating the catalyst at 150-1500°F in air (or oxygen) for 4 to 40 hours. The catalyst contains 3 to 40 per cent of chromia and may also contain up to 3 per cent of alkali metal oxides.

Voltz and Weller (356) found that the catalytic activity of oxidized (500°) chromia and chromia-alumina catalysts are related to the quantity of excess surface oxygen, which in turn can be related to pH and titratable acidity. The same investigators (357) also found that the presence of potassium increases the surface oxidation of chromia and stabilizes it against reduction. The activity in hydrogen peroxide is also enhanced. The formation of potassium chromates is suggested as an explanation for the results.

The effect of nuclear radiation on oxygen chemisorption by Cr_2O_3, Cr_2O_3-Al_2O_3, and Cr_2O_3-SnO_2 catalysts, and the effect of the treatment on the rate of hydrogen peroxide decomposition were studied by Nachman and others (274). Radiation promoted chemisorption, even at temperatures where it is not normally observed. Both chemisorption and activity increased with the degree of dispersion of Cr_2O_3 in the mixed catalyst. For this reason, radio-chemisorption is said to result from the action of x-rays and fast neutrons on the gas.

2. MOLYBDENUM

Nikolaev and Askadskii (285) studied the effect of low-frequency ultrasonic waves on the catalytic activities of $(NH_4)_2MoO_4$, $P_2O_5 24MoO_3 \cdot xH_2O$, and SiO_2 gel in hydrogen peroxide. Ultrasonic promotion occurred in all cases. Control experiments showed that the rate increased was not a result of increased surface area or increased temperatures during the treatment. The activity increase is presumed to result from mechanical comminution.

3. TUNGSTEN

Kreimer and others (204) measured the rate of catalytic decomposition of hydrogen peroxide at 25° by samples of tungsten and tungsten carbide prepared under various conditions of reduction and thermal treatment. In both cases, the initial activity fell off rapidly. For tungsten it fell nearly to zero in 25 minutes, and for the carbide it fell to a constant level in 10 to 15 minutes. Tungsten samples liberated from 7 to 59 ml of oxygen/gram/min and tungsten carbide samples liberated from 0.57 to 2.7 ml of oxygen/gram/min during the periods of highest activity. One tungsten sample gave a low activation energy of 3811 calories between 20 and 35°.

SECTION XI.

MANGANESE, TECHNETIUM, RHENIUM

1. MANGANESE

Fisher and Zeilberger (58) described the development of special catalysts that overcome the problem of mechanical disintegration observed with once widely used manganese dioxide pellets.

Composite catalysts of the oxides of manganese, iron, copper, and silver are compacted to pellets and sintered at high temperature to form hard and porous lumps. Catalytic activity can be improved by impregnating the catalysts with various solutions, such as potassium permanganate. A similar type of catalyst is prepared by impregnating lumps of porous silicon carbide with calcium permanganate, then firing them to convert the permanganate to calcium and manganese oxides.

It is stated that pellet-type catalysts are suitable for H_2O_2 concentrations up to about 80 per cent. Above that, more active catalysts are needed.

Several materials are useful as base screens for silver catalysts. Below a hydrogen peroxide concentration of 90 per cent, cartridge brass (70 Cu, 30 Zn) can be used. The copper-silver eutectic that can form in this catalyst melts at 1435°F. Iron screens can be used, but plated metals are seldom adherent, and porosity leads to rusting. Stainless steel eliminates corrosion, but it requires special procedures to plate well.

It was also reported that Rocketdyne developed a new catalyst that remains strong and stable above 1800°F, and can therefore be used for decomposing hydrogen peroxide of the highest strength. It is described as "a stainless steel screen type with an active ingredient other than silver embedded in a ceramic coating." It is cheaper to produce than silver screens and it has the following operational characteristics: (1) stable to 1800°F, (2) retains activity after repeated exposures, (3) has a specific decomposition rate equal to or greater than that of silver, (4) operates smoothly without pressure drop increases, and (5) starts efficiently under full-flow conditions at low temperatures.

Hart and others (102) carried out a systematic study of a series of oxides as catalysts for decomposing hydrogen peroxide vapor in order to determine relative activities and reactivity in relation to electronic structures. A nitrogen-gas flow system, H_2O_2 up to 1 mm Hg pressure, and temperatures of 38-184° were studied. The oxides were supported on vacuum-flashed metal films and Specpure metal slips, or the bulk oxides were used as compressed slips. The relative activities of the bulk oxides were: $Mn_2O_3 > PbO > CoO/Co_2O_3 > CuO > Fe_2O_3 > CdO > ZnO = MgO > \alpha\text{-}Al_2O_3 >$ glass.

The order corresponds to a classification by defect type. Positions of favored electron exchange were suggested as the active catalyst sites. Such positions could correspond to (1) trapped excess surface electrons, and (2) electron deficiencies (or p-holes) held either at a surface cation vacany, at an impurity or excess surface anion, or at an impurity of a metal having lower valency. The reaction depends on a cyclic exchange of electrons between the oxide surface and hydrogen peroxide.

Hart and Ross (100) evaluated equimolar mixtures of Mn_2O_3 with PbO, ZnO, and NiO as decomposition catalysts for hydrogen peroxide vapor. $PbO \cdot Mn_2O_3$ formed the most active mixture. The rate was also found to increase with sintering temperatures up to a maximum at 600°. NiO-Mn_2O_3 mixtures were inhomogeneous below a sintering temperature of 600°, but underwent a structural change at 760°, probably forming a solid solution.

Broughton and Wentworth (30) reported that hydrogen peroxide is not decomposed by solutions of potassium permanganate or manganous sulfate until base is added. Upon the addition of base, a known colloid forms and initiates the decomposition of H_2O_2. Quantitative studies on the amount of base needed to start the reaction and data from tracer studies indicated that the decomposition is catalyzed by an alternate oxidation and reduction of manganese. Oxidation does not occur until the solution is saturated with $Mn(OH)_2$.

In view of the fact that solid MnO_2 was known to decompose hydrogen peroxide even though the bulk solution contains no manganous ions, Broughton and Wentworth (31) examined the behavior of MnO_2 electrodes to determine whether the reaction proceeded by the same mechanism as that suggested above. Potential measurements with MnO_2 electrodes at various H_2O_2 and Mn(II) ion concentrations gave results consistent with the following half-cell reactions as controlling the potential: $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$. The solution adjacent to the electrode was saturated with $Mn(OH)_2$, even though the bulk solution was not, as evidenced by measurements of manganese concentrations in H_2O_2 solutions decomposing in contact with MnO_2.

A U. S. patent assigned to Du Pont (363) covers a manganese dioxide catalyst for decomposing hydrogen peroxide. The two-stage process used to prepare the catalyst is fairly complicated:

(1) Manganese metal is cathodically electrodeposited on an iron support, using graphite electrodes and a plating solution of basic manganous acetate;

(2) Manganese dioxide is cathodically electrodeposited on the manganese surface, using steel anodes in an electrolyte solution of potassium carbonate and potassium permanganate.

Many variations in the electrolysis conditions and the composition of electrolytes are used to prepare suitable catalysts and to optimize the catalyst for maximum rate of decomposition of hydrogen peroxide.

Broughton and others (245) used radioactive manganese as a tracer to study the catalytic decomposition of hydrogen peroxide by MnO_2. The results indicated that the reaction was an alternate reduction and oxidation. Experiments to determine the relative amounts of KOH and manganese salt needed to initiate the decomposition indicated that reoxidation of manganous ion does not occur until the solution is saturated with $Mn(OH)_2$. Free energy calculations indicated that the oxidation is favorable even at very low Mn(II) concentrations.

The same investigators further studied the mechanism of the catalytic decomposition of hydrogen peroxide by manganese dioxide (247). The electrode potential of MnO_2-coated manganese rods in distilled hydrogen peroxide solutions was measured as a function of the concentrations of H_2O_2, H^+, and Mn(II), and of the speed of rotation of the rod. Another series of tests was made to measure the change in manganese concentration in distilled H_2O_2 solutions, and the decomposition in contact with MnO_2 surfaces. It was found that under certain conditions manganese leaves the solution and deposits on the MnO_2 surface. Attempts to measure the rate of decomposition of distilled H_2O_2 on stationary and rotating MnO_2 surfaces gave non-reproducible results.

Mooi and Selwood (267) studied the catalytic decomposition of hydrogen peroxide by manganese oxides supported on powdered γ-Al_2O_3. To prepare the catalysts, Al_2O_3 was immersed in $Mn(NO_3)_2$ solution, dried, and ignited at 200°. Each catalyst contained 4.60 mg of manganese. Maximum catalytic activity occurred when 3 to 4 per cent of manganese at an average oxidation state of 3.6 was used. The proposed mechanism requires the presence of both Mn(III) and Mn(IV) ions. H_2O_2 accepts an electron from Mn(III) ion to yield a hydroxide ion and a hydroxyl radical. Hydroxide ion then donates an electron to an Mn(IV) ion, which then transfers it back to the Mn(III) ion that initially carried a +3 charge.

Mooi and Selwood (268) later studied the decomposition of dilute aqueous solutions of hydrogen peroxide on supported manganese oxides. Activity increased regularly with decreasing manganese concentration, but dropped sharply when the manganese concentration was very low. The effects of oxidation state, pH, support phase modification, and temperature were studied also. The suggested mechanism was a cyclic redox reaction involving Mn(III) and Mn(IV).

Wang (359) carried out calculations that showed in catalysis of liquids involving only small molecules or ions, the catalysis rate is not diffusion-controlled. The fact that experiments have shown that the decomposition of hydrogen peroxide by MnO_2 results in O^{18} enrichment of the oxygen gas formed suggests that the rate laws of both heterogeneous and homogeneous decomposition can fit within one formulation. Wang states that in the case of homogeneous catalysis in liquids of only small molecules or ions, stirring would not affect the rate even if the reaction rate were diffusion-controlled.

Wolfram (369) prepared MnO_2 sols from $KMnO_4$ using three reduction methods (1) by oxalic acid, (2) by gelatin, and (3) by H_2O_2. All three gave sols of different catalytic activities. That produced by reduction with H_2O_2 was the most active sol in the decomposition of hydrogen peroxide. None of the reactions was first order. Adding gelatin had no effect on decreased activity of aged catalyst.

Wolfram (370) also reported that the decomposition of hydrogen peroxide on MnO_2 powders did follow first-order kinetics. The rate constants increased with the degree of powder dispersion, but in all cases they were considerably lower than those determined for MnO_2 sol or gels.

Muraki and others (271) used an electrochemical method for decomposing hydrogen peroxide by manganese dioxide as a basis for estimating the quality of the dioxide. The capacity of the catalyst for decomposing hydrogen peroxide could be related to the discharging capacity of the catalyst. Ammonium chloride solutions used in these experiments evidently promoted the catalytic reaction. Zinc chloride acted as an inhibitor.

Nine active and inactive samples of manganese dioxide were studied by Amiel and others (5) in an attempt to correlate catalytic activity with depolarizing properties. It was found in general that increases in activity was accompanied by increases in depolarizing ability and magnetic susceptibility.

Grégus and Grégus (95) examined the effects of ultrasonic vibrations on the catalytic activity of MnO_2 gels and suspensions in the catalytic decomposition of hydrogen peroxide. A frequency of 875 kilocycles increased the initial rate of decomposition, and the degree of dispersion of the catalyst, but there was no effect on the time required for total decomposition of the peroxide.

The effect of nuclear radiation on the catalytic properties of MnO_2 was examined by Otwinowska and others (286). A fast neutron flux, the full neutron flux of a reactor, a Co^{60} γ-ray source, and an accelerated proton flux were all used to irradiate the catalyst. Neutron and proton irradiation doubled the rate of decomposition of hydrogen peroxide by the catalyst. Gamma irradiation was ineffective. X-ray diffraction examination of the catalysts showed that the increased activity was a result of radiation-induced crystal lattice damage. Such lattice changes are similar to those induced by heat treatment.

Krause and others (151) reported that Mn(II) ions adsorbed on $Al(OH)_3$ strongly accelerate the decomposition of aqueous hydrogen peroxide.

SECTION XII.

IRON, RUTHENIUM, OSMIUM

1. IRON

a. Metallic Iron and Iron Alloys

A sensitive method for examining the decomposition of hydrogen peroxide vapor on metal surfaces was devised by Roikh and others (300). The quantity of H_2O_2 adsorbed on a plate suspended over the solution was determined by the gain in weight. The quantity of H_2O_2 desorbed was determined photographically. On magnesium, aluminum, and iron, the amount of H_2O_2 adsorbed increased with the partial pressure of H_2O_2 above the solution. The amount was 1.9 to 2.9 times higher on oxidized surfaces. The amount adsorbed on roughened surfaces with profile heights of 10.3 to 19.3 microns, was independent of the roughness. The amount of H_2O_2 decomposed (adsorbed minus desorbed), on the clean surfaces at an H_2O_2 partial pressure of 0.158 mm Hg, was 91.1, 97.1 and 99.9 per cent for aluminum, mangesium, and iron respectively. The amount decomposed decreased with pressure.

In a 1956 U.S. patent assigned to North American Aviation, Sherwood (320) described a plated steel screen for hydrogen peroxide decomposition. The steel screen is cleaned with NaOH and H_2SO_4 then coated electrolytically with copper, followed by a thin coat of iron. The washed and dried screen is dipped in $AgNO_3$ and HNO_3, drained, and dried. The performance of the screen depends on the reaction products of $AgNO_3$, HNO_3 and the iron coating.

b. Iron Oxides and Hydroxides

Krause and others (170) found that the high activity of a catalyst containing mixed hydroxides of iron, copper, and magnesium in the ratios Fe:Cu:Mg = 1:0.3:0.22 was increased further by adsorbing common ions on the catalyst. It was also found that the content of any particular component is not the main determinant of the activity. The facts led to the conclusion that exchange reactions take place, even between identical atoms, and give rise to active or inactive complexes. The results are used to explain the fact that tungstate ion (WO_4^{2-}) inhibits strongly the oxidation of formic acid by the mixed catalyst, but it does not inhibit hydrogen peroxide decomposition. In contrast Al(III) ions inhibit the decomposition of peroxide but not the oxidation of the acid.

Gupta and Ghosh (96) studied hydrous ferric oxides as catalysts for decomposing hydrogen peroxide. Three modifications of the oxides were prepared by adding basic salts and alkali to $FeCl_3$ solutions: (1) Fe_2O_3

(yellow), by slow precipitation from excess $FeCl_3$ by K_2SO_4 and a small amount of alkali; (2) $Fe(OH)_3$ (red), by precipitation from $FeCl_3$ by equivalent amounts of NaOH; and (3) a brown oxide, by precipitation from $FeCl_3$ by K_2SO_4. Red (α-hydrated) Fe_2O_3 was the best catalyst; the brown modification was next. In both cases, activity declined with aging of the catalyst. The yellow oxide was the least active and also least sensitive to aging, which resembles the behavior of γ-Fe_2O_3. Presumably, activity is proportional to both the amount of base used in the precipitation and to the rate of precipitation.

The results suggested the following reaction mechanism:

(1) $Fe^{3+} + H_2O_2 = Fe(OH)^{3+} + OH$ (Fe becomes quadrivalent)

(2) $OH + H_2O_2 = HO_2 + H_2O$

(3) $HO_2 + H_2O_2 = H_2O + OH + O_2$

$$\left.\begin{array}{ll} (4)\ Fe^{3+} + OH & = Fe(OH)^{3+} \\ (5)\ OH + OH & = H_2O_2 \end{array}\right\}$$ chain-breaking reactions.

Since (1) is the rate-determining step, and the concentration of OH is proportional to that of H_2O_2, the rate for the over-all reaction can be expressed as $-dc/dt = k\left[H_2O_2\right]^2$. Aging of the oxides decreases their absorptive capabilities, which reduces the ease with which OH formation can be initiated. Experimental results indicate that the reaction then tends to shift from bimolecular to unimolecular.

Constable and Pekin (41) measured the effect of pH on the catalytic activity of ferric hydroxide in the heterogeneous decomposition of hydrogen peroxide. Rates for colloidal $Fe(OH)_3$ at pH 10.54 through 12.54 are given by: $\log k = 0.649 - 0.270\ (pH)$ and $\log k = 3.456 - 0.560\ (pH)$, at 42° and 31° respectively. The apparent heats of activation for the unimolecular reaction were calculated for various values of pH. It was also found that the same types of measurements could be used to relate concentrations to rate constants for various catalytic poisons at different values of pH (42). Poisons included p-nitrophenol, iodine, bromine, and sodium sulfide.

The decomposition of hydrogen peroxide on ferric hydroxide prepared by precipitation with NaOH from an $FeCl_3$ solution was examined by Ghosh and Ghosh (89). The activities of catalysts precipitated at three concentrations of NaOH were found to have the following order: (1) 5 per cent excess NaOH > (2) equivalent amount of NaOH > (3) 5 per cent deficient amount of NaOH. Evidence indicated that the decomposition follows a unimolecular law at H_2O_2 concentrations above 0.05 N. However, the order increases as H_2O_2 concentration decreases, particularly at high temperatures and at extremely dilute concentrations. A mechanism for the reaction is suggested.

Simon and Guenzler (325) investigated the catalytic decomposition of hydrogen peroxide by γ-Fe_2O_3 prepared by oxidizing a synthetic magnetite (1) in the presence of water and (2) after previous drying. Catalyst (2) had the greater activity. The difference is attributed to changes in Fe_2O_3 in the drying step rather than to any specific effect of the water present during oxidation.

Krause and Binkówna (161) examined the relation between catalytic activity and surface area for the hydrogen peroxide decomposition catalysts $Fe(OH)_3$, γ-$FeO(OH)$ and α-$Fe_2O_3 \cdot H_2O$ (goethite). $Fe(OH)_3$ gave the highest activity, and goethite the lowest, even though the surface areas were in the respective ratios of 5.15:10.6:13.3. The fact that there was no relation between activity and surface area led to the conclusion that activity depends on the number of active centers, or OH groups, which is greatest for $Fe(OH)_3$. Activity can be increased by increasing surface area only if the catalyst has a high density of active centers.

Krause and Olejnik (160) reported that cooling γ-$FeO(OH)$ and amorphous ortho-and isoorthoferric hydroxides to liquid air temperatures reduced the apparent densities and increased their rates of decomposition of hydrogen peroxide at 37°C.

The decomposition of hydrogen peroxide by colloidal iron(III) hydroxide and ferrites was investigated by Krause (176). A hydrogel prepared by peptizing catalytically active, air-dried, amorphous iron(III) hydroxide catalyzed the decomposition. Goethite $(\alpha\text{-}Fe_2O_3 \cdot H_2O)_n$ was inactive as either gel or colloid, but it could be activated when partially dehydrated at 250-300°. A suggested mechanism provides an alternative to that suggested by Schwab and Kraut (312) for ferrites.

Krause and Rychlewska (199) studied the decomposition of hydrogen peroxide by orthohydroxide and polyorthohydroxide sols of iron(III) hydroxide at 27 and 37°. The two hydroxides were prepared from $FeCl_3$ solutions using complicated procedures. The polyorthohydroxide was the better catalyst. It also had a larger particle size and strongly adsorbed H_2O_2. It was concluded that the polyorthohydroxide had more active OH groups for deforming chemisorbed peroxide, leading to HO and HO_2 radicals, which then act as acceptor catalysts that decompose the peroxide by a complex mechanism.

Zaprometov and Shpilevskaya (375) studied the catalytic activity of ferrisilicon gels in hydrogen peroxide decomposition. Gels were formed from mixed sodium silicate and $FeCl_3$, $Fe(NO_3)_3$, and ammonium ferric alum solutions, digested for 3 days, dried (70, 100, 130°), ground, washed, and finally redried (100°). Silica gels alone, and mechanical mixtures of silica gel and $Fe(OH)_3$ were also studied. The differences in catalytic behavior were ascribed to different microstructures. The microstructures in turn depend on the nature of the ions and the concentrations of reactants used to form the gels.

Schwab and Kraut (312) studied the catalytic decompositions of hydrogen peroxide by ferrites with spinel structures. Aqueous suspensions of Fe_3O_4, $ZnFe_2O_4$, $MgFe_2O_4$, and crystalline mixtures were used as catalysts in 0.24 M H_2O_2 at 20-80°. The decomposition was first order at pH below 8 with Fe_3O_4, $ZnFe_2O_4$, Fe_3O_4-$ZnFe_2O_4$ mixed crystals, and Fe_3O_4-$MgFe_2O_4$ mixed crystals containing up to 40 mole per cent of $MgFe_2O_4$. Activation energies were 10 to 18 kcal/mole, and decreased with increasing Fe_2O_3 content. At pH 8 to 10, unbuffered suspensions of MgO, $MgFe_2O_4$, $ZnFe_2O_4$-$MgFe_2O_4$ mixed crystals, and Fe_3O_4-$MgFe_2O_4$ mixed crystals containing greater than 40 mole per cent $MgFe_2O_4$, gave various reaction orders, though all activation energies were about 15 kcal/mole. Suspensions buffered by NH_4Cl-NH_4OH at pH 8 to 9 were first order and more rapid, a fact ascribed to attack of the buffer by H_2O_2. The results are consistent with a reaction in which the rate-determining step is an acceptor reaction by which H_2O_2 takes up an electron from octahedrally surrounded Fe(II) ions in the ferrite, resulting in an OH radical. In the special case of $MgFe_2O_4$, the spinel surface is hydrated and MgO dissolves, and the increasing pH promotes the self-decomposition of H_2O_2, but the catalytic activity of Fe(II) ions at the hydrated surface is reduced. However, the decomposition may be catalyzed by the hydration shell itself. In these spinels, the catalytic results do correlate with structures and specific electrical conductivities.

Trandafelov (347) found that the rate of decomposition of hydrogen peroxide by ferric sulfate in the presence of cupric and hydrogen ions is a function of the concentration of colloidal ferric hydroxide. Hydrolysis of ferric sulfate by long-term storage or by heating (60°) increases its catalytic activity. Heating at 90°, however, caused coagulation and a decrease in activity. The effect was prevented when sulfuric acid was added. Trandafelov concludes that the "ferrisulfate modulus," SO_3/Fe_2O_3, not hydrogen or ferric ions, determines the rate of decomposition. It is pointed out that although cupric ions catalyze the decomposition when adsorbed on colloidal $Fe(OH)_3$, additional cupric ions increase the rate only up to the point of saturation.

Shub and others (322) used Fe_2O_3 as a semiconductor sensitizer in the photodecomposition of hydrogen peroxide. Ultraviolet light and γ-radiation were applied to Fe_2O_3 suspensions in concentrated peroxide. The greatly increased decomposition rate was attributed to the absorption of radiation at the Fe_2O_3 surface, followed by excitation of the active sites and initiation of a chain-reaction decomposition of H_2O_2.

Wawrzyczek (361) measured the influence of ultrasonic vibrations on the catalytic activity of $Fe(OH)_3$ in the decomposition of hydrogen peroxide.

For frequencies from 23 to 1000 kilocycles, catalytic activity toward 1 per cent H_2O_2 was increased. Heating to 100 or 200°C eliminated all catalytic activity.

Krause and others (177) found that infrared irradiation of amorphous $Fe(OH)_3$, $AlO(OH)$, and ZnO increased their catalytic activity in the decomposition of hydrogen peroxide at 20°. The effect was observed for $AlO(OH)$ and ZnO, however, only when small amounts of Co(II) ions were added.

c. Catalytic Activity of Mixtures and Adsorbed Ions

Krause (138) pointed out that as little as 10^{-10} gram of $Fe(OH)_3$ actively catalyzes the decomposition of hydrogen peroxide when the catalyst is adsorbed on a carrier composed of $Cu(OH)_2$ and $Co(OH)_2$. It is suggested that this can be used as a means for detecting traces of iron.

Mixed hydroxides as decomposition catalysts for hydrogen peroxide at 37°C were investigated by Krause and Pawelkiewicz (145). The rate of decomposition by $Fe(OH)_3$-$Mg(OH)_2$ was increased significantly by the addition of $Co(OH)_2$ and to a large extent by the addition of $Cu(OH)_2$. Neither $Mn(OH)_2$ nor $Ce(OH)_4$ affected the rate. Analysis revealed that higher oxides of iron, magnesium, and copper formed at the catalyst surface. They are presumed to be intermediates in the decomposition process.

Krause and Lasiewicz (166) showed that the small catalytic activity of γ-$FeO(OH)$ (18 per cent H_2O) toward the decomposition of hydrogen peroxide is greatly increased by traces of Mn(II) or Mg(II) ions adsorbed on the surface. Neither Cu(II) nor Co(III) gave the effect. It is suggested the promotion involves the formation of metallic ferrite radicals that can initiate a chain reaction.

Krause and Turowska (167) observed that Ag_2O activates a catalyst prepared by coprecipitation of iron and copper hydroxides, even though Ag_2O itself is inactive at 37°. A mixed catalyst containing 1 Fe:$\frac{1}{3}$Cu:$\frac{1}{3}$Ag was more active than one containing 1 Fe:$\frac{1}{3}$Cu. At a higher temperature of 70°, or at higher silver contents, Ag_2O inhibits the catalysis.

Krause and Lezuchowska (173) found that the activity of amorphous $Fe(OH)_3$ in the decomposition of hydrogen peroxide increased with decreased particle size. Addition of Cu(II) ions increased the activity still more. The mechanism of these reactions and their significance for the action of other inorganic catalysts are discussed.

The same authors (188) later studied the effect of adsorbed ions over the catalytic activities of four iron (III) hydroxides prepared in different manners by precipitation from ferric nitrate solutions. It was found that Co(II) and Mn(II) ions in combination promoted the decomposition rate with ortho- and isoorthohydroxides and decreased the rate with two compositions of polyorthohydroxides. Both normal and promoted activities of iron hydroxide catalysts are therefore sensitive to the method of preparation.

The catalytic activity of small quantities of Co(II), Ni(II), and Fe(III) ions adsorbed on carriers was examined by Krause and Wolski (142). Traces of Co(II) and Ni(II) adsorbed on $Ca(CN)_2$ were active catalysts. Concentrations above 10^{-5} gm/liter of Fe(III) ions adsorbed on $Fe(OH)_3$ resulted in active catalysts. No effect is observed below 10^{-9} gm/liter, and at intermediate concentrations, the adsorbed ion acts as a poison. This deactivation is attributed to a blocking of the active centers, and the activation is attributed to the formation of unstable complexes on the carrier.

d. Iron Cyano Compounds

Constable and Pekin (38) measured the effect of the mass of catalytic iron ferrocyanide (Prussian blue) on the catalytic decomposition of neutral hydrogen peroxide. The reaction mixture was prepared as colloidal dispersions of the powder having a surface area of 2.05 m^2/gram. It was found that reaction rate varied directly with catalyst mass for 0.05-0.30 gram of powder suspended in 100 cc of H_2O_2 solution at 20-50°. The heat of activation was 13,380 cal/gram-mole. Practically the same results were found when ferrous ferrocyanide (Turnbull's blue) was used to decompose hydrogen peroxide (39).

Constable and Pekin (40) also determined the effect of dissolved nickel and copper on the heterogeneous catalytic activity of iron ferrocyanide in the decomposition of hydrogen peroxide. Both ions inhibited the reaction in accordance with a linear relation between concentration and the rate constant. The reaction rate constant for the total reaction was found to be the sum of that for the homogeneous reaction and that for the heterogeneous reaction.

Lal (213) investigated the decomposition of hydrogen peroxide by potassium ferrocyanide illuminated by sunlight and by artificial light. This catalyst has the unusual property of increased catalytic activity after short exposures to light. Lal determined the effects of time of exposure and other parameters. The photoformation of $K_4[Fe(CN)_6] \cdot H_2O$ as the reactive species is a reversible reaction. A mechanism based on alternate oxidation and reduction of this species is proposed.

Pinter and Karas (292) found that mercuric ions activated a mixed $K_4[Fe(CN)_6]$ -$K_3[Fe(CN)_6]$ decomposition catalyst for hydrogen peroxide decomposition in a manner similar to the activation caused by exposure of the catalyst to light. The mercuric ion behaves analogously to light in that the decomposition reaction continues after the mercuric ion has been removed by adsorption on casein.

2. RUTHENIUM

In a 1957 British patent to Laporte Chemicals, Banfield and Wood (12) described the use of ruthenium and ruthenium compounds, alone or in mixtures with other active materials or inert materials, as decomposition catalysts for hydrogen peroxide above 50 per cent concentration. It is stated that ruthenium is far more active than any other platinum metal. The reactivity is illustrated by an experiment in which 0.0001 mg per liter of Ru in the form of $(NH_4)_2RuCl_4$ released 2.9 ml oxygen per minute from 25 ml of 85 per cent H_2O_2 at 100°.

SECTION XIII.

COBALT, RHODIUM, IRIDIUM

1. COBALT

a. Metallic Cobalt and Cobalt Alloys

In 1947, Isbin and Thompson (251) issued a report on Navy-sponsored research dealing with the preparation and evaluation of impregnated-type catalysts for hydrogen peroxide decomposition.

The catalysts were prepared by impregnating a number of different kinds of catalyst carriers with solutions of calcium permanganate and the nitrates of manganese, cobalt, lead, chromium, silver, nickel, iron and copper. Following the deposition of the catalysts on the carriers, the materials were evaluated in an atmospheric flow system with a 48 per cent peroxide solution.

The catalyst with the highest activity was a cobalt-lead deposit on a porous carborundum carrier. From the standpoint of high sustained activity (one showing less decline with peroxide throughput), a German carrier impregnated in $Ca(MnO_4)_2$ was the best, even though the similar German catalyst, Katalysatorsteine MP-14, exhibited a rapid decline in activity. One platinum catalyst deposited on porous Aloxite was also found to have a long life at high activity.

Manganese catalysts (form of deposit unspecified) were best prepared from concentrated calcium permanganate solutions, using such carriers as the German porous stone, pumice (bulk) and porous carborundum.

Several promoted catalysts were prepared from mixed nitrate solutions of two metals. Silver catalysts were improved by the presence of copper, chromium, or nickel; manganese by lead or silver; and lead by cobalt or chromium. The most promising combination was cobalt-lead, in which the activation of the cobalt arises from the presence of $Pb(NO_3)_2$. Mechanical mixture of the separately impregnated pellets also produced co-activation, indicating various possibilites for combinations. Several commercial catalysts were also evaluated in the program.

Broughton and others (252) studied the mechanism of catalytic decomposition of hydrogen peroxide by cobalt metal and cobalt compounds. The results indicated that the reaction does not involve an oxidation-reduction cycle between Co(II) and Co(III) ions, but it may involve an oxidation-reduction between Co(III) and a higher oxide stable in the presence of H_2O_2. It was also determined that colloidal $Co(OH)_3$ forms before catalysis takes place, indicating a heterogeneous decomposition reaction. There was also evidence that the reaction involved free radicals.

As part of the Navy sponsored project "Bessie" (Contract Nobs-31494) FMC Corporation (60) developed ceramic or fused-oxide catalysts for the decomposition of 98 per cent hydrogen peroxide and for sustained decomposition of 90 per cent hydrogen peroxide. The well-known catalytic activity of manganese dioxide was used as the basis for formulating new catalysts. Mixtures of cobalt metal and manganese dioxide were found most satisfactory. Three principal formulations were developed:

	Catalyst 50	Catalyst 93	Catalyst 113
MnO_2	41.7%	--	5.9%
Fe_2O_3	25.0	--	3.6
CuO	16.7	--	2.4
$Ca_3(BO_3)_2$	8.3	--	1.2
Na_2CO_3	8.3	--	1.2
Co	--	80.0%	68.6
NaCl	--	20.0	17.1

It was found that additives could be used to overcome the problem of the rapid decline in catalytic activity of MnO_2 on repeated exposures to high-strength hydrogen peroxide. Added cupric oxide gave a constant activity through repeated tests at atmospheric pressure. Further addition of Fe_2O_3 improved both the strength and activity of the catalyst. Sodium carbonate was added to increase the porosity with the liberation of CO_2 gas during sintering. The sodium ion, by destabilization, also improved the starting characteristics of the catalyst. Adding small amounts of calcium borate lowered the normal 3000°F fusion temperature of the mixtures. Catalyst 50 was formulated accordingly.

Cobalt metal in bulk and as a powder decomposed hydrogen peroxide, but with poor starting characteristics at room temperature. Adding sodium chloride (catalyst 93) promoted surface porosity and reduced the fusion temperature from 2700 to 2200°F. Activity also increased but the material was severely oxidized in high pressure tests with peroxide.

Catalyst 113 was then prepared by mixing catalysts 50 (1 part) and 93 (6 parts). This formulation had high activity and a longer active life than the other formulations. It was also mechanically stronger. Perforated discs of this material pressed at 40,000 psi, were tested successfully for 10 hours and 20 cold starts using 98 per cent hydrogen peroxide in a 3-inch reactor bed.

The kinetics of decomposition of hydrogen peroxide on metallic cobalt at 20-25° was investigated by Lopatkin (236). Twenty milligrams of cobalt decomposed 30 cc of 0.2 N H_2O_2 in 11 minutes. Activity declined rapidly after the first 7 minutes. The results fit a relation for autocatalytic reactions, $dx/dt = (k_0 + k_1x)(a-x)$, where $\underline{a}$ is the volume (cc) of oxygen liberated by total decomposition, $\underline{x}$ is the oxygen volume at $\underline{t}$, k_0 is the sintered decomposition rate constant, and k_1 is a constant.

In a 1957 U.S. patent assigned to North American Aviation, Sherwood (321) described a hydrogen peroxide decomposition catalyst consisting of various laminated layers of cobalt that are consumed in the decomposition. The catalyst is comprised of alternate layers of plated, porous, metallic cobalt and an activated cobalt prepared by immersing the screen in a solution of $AgNO_3$, HNO_3, and a soluble cobalt salt.

Wernlund and Bente (365), of Du Pont, obtained a 1958 U.S. patent covering the use of a porous, cobalt-plated steel screen for the decomposition of hydrogen peroxide. To prepare the catalyst, an iron or steel screen is first electroplated with copper, then used in a electroplating bath with cobalt anodes. The bath is a solution of $CoSO_4 \cdot 7H_2O$, $(NH_4)_2SO_4$, and enough NH_4OH to give a pH of 7.5. Electroplating is carried out to give a coating of 0.007 inch of cobalt. The final coating is rough, porous, and fernlike. Its high activity can be increased further by dipping it in hydrogen peroxide and allowing it to dry.

b. Cobalt Oxides and Hydroxides

Ghosh and Ghosh (87) found that the rate of decomposition of hydrogen peroxide in the presence of cobalt(III) oxide was first order, but tended toward second order at low concentrations. The order also increased with temperature. The suggested mechanism, a reduction-oxidation cycle, is similar to that for the reaction on MnO_2 catalyst.

Zvorykin and Perel'man (393) evaluated oxides of cobalt, nickel, and copper, alone and in mixtures, as catalysts for decomposing hydrogen peroxide. For the individual oxide, equimolar quantities of a cobalt oxide, CuO, and Ni_3O_4 gave decomposition rates in the respective ratios 0.013: 1.20:0.029. Various ternary and binary mixtures were studied, but only those with the compositions 80Co:20Ni, or 80Co:15Ni:5Cu were more active than the cobalt oxide alone. Both mixtures gave reaction constants of about 1.40 on the same scale as the ratios mentioned.

The catalytic decomposition of aqueous solutions of hydrogen peroxide at 37° by a mixed-hydroxide catalyst composed of $Cu(OH)_2$, $Mn(OH)_2$, and $Co(OH)_2$ was investigated by Krause and Reysner (174). Catalysts were prepared by simultaneous precipitation using NaOH at 18°. The composition yielding maximum decomposition rate corresponded to the respective ratios 1:5:19. Krause reported that under the conditions of these tests, 1 gram-atom of copper decomposes 12 moles of H_2O_2 per second.

Krause and others (194) studied the catalytic activities of x-ray amorphous $Fe(OH)_3$, $Co(OH)_2$, and CuO in the decomposition of hydrogen peroxide at various temperatures. $Co(OH)_2$ was the most active catalyst. Rates in terms of the volume of 0.1 N $KMnO_4$ consumed in the analysis are given. Respective temperature coefficients were 2.27, 2.27, and 2.67; activation energies were 15.2, 15.3, and 18.2 kcal/mole.

Mitsubishi Edogawa Chemical Company (106) patented solid catalyst formulations of metal oxides useful for decomposing hydrogen peroxide. A representative catalyst is prepared as follows: A mixture of 1.50 parts PbO and 8.50 parts CoO_3 is kneaded with an aqueous (5 per cent) soluble starch solution, then granulated and tableted. The tablets are heated from 500 to 890° for 20 minutes and at 890° for 10 minutes, then cooled. The following oxide mixtures are also suitable in place of PbO and CoO_3 (parts by weight): 1.0 PbO and 9.0 MnO_2; 8.0 MnO_2, 1.0 PbO, and 1.0 Ce_2O_3; and 8.0 MnO_2, 1.0 PbO, and 1.0 CoO_3. The representative catalyst decomposed 90 per cent hydrogen peroxide at a rate of 2 kg/kg catalyst/sec. Constant pressure was reached in less than 0.2 sec.

A 1956 British patent by Peers (287) describes a hydrogen peroxide decomposition catalyst having cobalt or a similarly active oxide (including MnO_2, alkali permanganates, or chromates) as one of the major constituents. The catalyst consists of (1) an active agent, (2) lead oxide, and (3) a refractory cement. The lead oxide serves as a binder before sintering and a filler in the product. In a typical preparation a suspension of 200 grams each of black cobalt oxide and PbO in 120 cc of water, and 100 grams of portland cement in 55 cc of water or in 30 per cent KOH solution, are mixed and allowed to harden. The product is ground and heated to 900° to fuse the lead oxide.

Peers (288) also obtained a 1956 British patent for an "oxidized" cobalt metal catalyst useful for decomposing concentrated hydrogen peroxide. Metallic cobalt is first put into the desired form, such as sheets, wire gauze, or electroplated copper gauze, then oxidized by prolonged immersion in a boiling 30-per cent solution of calcium permanganate. The catalyst is said to be useful in thrust units or engine combustion chambers.

c. Supported Catalysts and Adsorbed Ions

Krause and Wolski (152) studied the catalytic decomposition of aqueous hydrogen peroxide solutions at 25° using Co(II) ions and Ni(II) ions supported on a carrier consisting of a 1:1 mixture of $Co(OH)_2$ and $Ni(OH)_2$. The carriers were prepared either by coprecipitation or by mechanical mixing.

In the case of the coprecipitated carrier, Ni(II) ions were without effect on catalytic activity, but Co(II) ions made the catalyst passive. The mechanically mixed carrier, on the other hand, was made passive by Ni(II) ions, but very greatly activated by Co(II) ions.

The catalytic activity of Co(II) ions supported on various basic carriers in the decomposition of hydrogen peroxide was considered by Krause and Domka (175). Co(II) ions adsorbed on $Zn(OH)_2$ or $Al(OH)_3$ were weakly catalytic, but Co(II) ions adsorbed on $Mg(OH)_2$ was a good catalyst. A catalyst of Co(II) ions adsorbed on $BaCO_3$ was exceptional in that it was strongly active. The phenomenon is believed caused by the formation with $BaCO_3$ of an imperfect complex with the properties of an n-type semiconductor.

Krause and Kukielka (181) pointed out that adsorbed ions can act either homogeneously or heterogeneously in the catalytic decomposition of hydrogen peroxide. Mn(II) ions catalyze the decomposition only heterogeneously when adsorbed on $Mg(HCO_3)_2$ or $Mg(OH)_2$. Co(II) ions are active either heterogeneously only, as on Tl_2O_3, or both homogeneously and heterogeneously, as on $Mg(HCO_3)_2$ or $Mg(OH)_2$. Cu(II) ion on Fe_2O_3 decomposes HCOOH heterogeneously only.

Highly active catalysts for decomposing hydrogen peroxide by using Co(II) ions adsorbed on zinc or cadmium carbonates were developed by Krause and Plura (189). The zinc carbonate carrier is prepared by precipitating a composition of the formula $2ZnCo_3 \cdot 3Zn(OH)_2$ from a mixture of $ZnSO_4$ and Na_2CO_3 solution. The cadmium carbonate carrier was prepared by precipitating $CdCO_3$ (containing about 4 per cent of H_2O) from a mixture of $Cd(NO_3)_2$ and Na_2CO_3 solutions. The catalysts are prepared by moistening the carrier with $CoCl_2$ solution. By extrapolation it was shown that about 10^{-10} gram of Co(II) ions was the limiting amount that provided an active catalyst. At that concentration Co(II) ions on $CdCO_3$ carrier decomposed at least 80,000 molecules of H_2O_2 at 37° according to a first order reaction. Practically the same results were obtained for a zinc carbonate support, and the over-all mechanism behavior is the same as that previously reported (177) for Co(II) ion on $MgCO_3$ carrier. These results demonstrate that inorganic catalysts can be obtained with activities as high as those of biocatalysts.

Krause and others (203) found that the so-called "catalytic mutation" exists for the ion combination of $Al^{3+} + MoO_4^{2-}$ when adsorbed on the mixed carrier $Cd(OH)_2/Co(OH)_2$ and used for the catalytic decomposition of hydrogen peroxide. Catalytic mutation refers to the fact that the catalytic activity depends on the order of adsorption of the ions. In this case, adsorption of Al^{3+}, followed by adsorption of MoO_4^{2-} on a 1:1 CdO:CoO carrier gave a significantly higher reaction rate than did a catalyst made by reversing the order of ion adsorption on the same carrier.

Nikolaev and Kobozev (280) reported that $CoSO_4$ and $NiSO_4$, either in solution or adsorbed on asbestos, Al_2O_3, $BaSO_4$, H_2SnO_3, or charcoal, do not greatly accelerate the decomposition of dilute hydrogen peroxide. Adsorption of the salts (Co(II) and Ni(II) ions) on silica gel did increase the rate of decomposition. As the metal-to-silica cation ratio increased, the activity of Ni(II) passed through one maxima, and the activity of Co(II) passed through two maxima. These data led to the conclusion that the active centers ("ensembles") contain 1 and 6 ions in the case of Ni(II), and 1, 3, and 7 ions in the case of Co(II).

SECTION XIV.

NICKEL, PALLADIUM, PLATINUM

1. NICKEL

a. Metallic Nickel and Nickel Alloys

The catalytic properties of annealed and purified nickel wire in the decomposition of hydrogen peroxide were evaluated by Uhara and others (351). The tests were preceded by further annealing in a hydrogen atmosphere over two temperature ranges to determine the effects of annealing. Decomposition of 30 per cent hydrogen peroxide was carried out at 20°. The rate data indicated that annealing at 300-400°C produced active centers that were point defects at the surface. The point defects existed and vanished with vacancies in the bulk metal. Annealing at 600-700° was said to produce active centers corresponding to terminations of dislocations at the surface. Extended cold-working was found to increase the differences in rate obtained for the two ranges of annealing temperatures.

The structure of active centers in nickel catalyst was investigated (352) as a continuation of the above work. The changes in activity of cold-worked nickel resulting from annealing at various temperatures were in accord with previous conclusions with regard to the effects responsible for the existence of active centers.

In a study designed to elucidate the mechanism of heterogeneous catalytic decomposition of hydrogen peroxide, Schwab (310) determined the activation energies of a series of catalysts. The catalysts included alloys of nickel-copper, gold-iron, nickel-chromium, spinels of zinc and magnesium, metallic nickel and others. Arrhenius activation energies were determined from rate measurements and the equation $d \ln k/dT = E_A/RT^2$. Schwab, in trying to relate activation energies to known electronic structures, concluded that "reactions in which the mechanism of the catalyst action involves a yielding of electrons display a lower energy of activation with catalysts deficient in electrons, whereas the opposite is true for reactions in which the mechanism involves acquisition of electrons."

In 1961 Walter Kidde and Company (358) undertook a laboratory program aimed at a systematic understanding of decomposition catalysts for decomposing hydrogen peroxide at concentrations up to 98 per cent.

As an approach to correlating the general behavior of metals and oxides active in decomposing H_2O_2, atomic diameters were plotted against atomic numbers of metals that are active, of questionable activity, or inactive. A straight line separated the active from the non-active metals.

A second straight line, parallel to the first, connected the points corresponding to known highly active catalysts for H_2O_2 decomposition. The correlations are considered useful in the selection of new catalysts, but only in a general way. Some inconsistencies make experimental evaluation essential.

Nickel and Monel screens were coated with nitrates of lead, silver, manganese, and copper in various formulations, then heated at high temperatures. The purpose of heating was to increase the activity of the screens by increasing the surface area. It was found that the incorporation of H_3BO_3 as a bonding agent in the coatings appeared to provide some beneficial effects in catalytic activity and mechanical strength when silver and lead were used together in catalyst coatings also containing Al_2O_3. If the components were present in the proper amounts, a catalyst of good activity, minimum delay time, and relatively high strength at high temperatures was indicated. Continuous exposure of silver-lead formulations to dilute H_2O_2 showed no loss of the metals. Tests were also conducted with 98 per cent H_2O_2.

Further work in this program involved the development of reliable methods for testing and evaluating decomposition catalysts. The program terminated without additional major developments.

b. Nickel Oxides and Hydroxides

Hart and Ross (101) studied the decomposition of hydrogen peroxide by NiO. A flashed film of NiO (95.7 μ thick) gave an activation energy of 11.0 ± 0.5 kcal/mole under the same conditions. It was also found that 0.004 to 2.1 per cent of Li_2O in bulk NiO promoted the catalytic activity. Ga_2O_3 added in the same amounts also promoted, but to a smaller degree.

Maxim and Braun (260) irradiated non-stoichiometric nickel oxide in vacuum in a nuclear reactor, and found that the treatment increased the catalytic activity of the oxide in the decomposition of hydrogen peroxide. Analysis showed that irradiation increased the quantity of surface oxygen, presumably a result of the presence of weakly bound oxygen on the surface. Thermal treatment after irradiation destroyed the increased catalytic activity.

Matsuura and others (259) evaluated zinc oxide and nickel oxide (NiO) containing small amounts of lithium, aluminum, and chromium, as catalysts for the decomposition of hydrogen peroxide. Reaction rate was proportional to H_2O_2 concentration, but the rate constant varied with pH, reaching a maximum at pH 12-13. Low activation energies in NiO were ascribed to higher concentrations of positive holes and in ZnO to lower concentrations of free electrons. The results were discussed in relation to previously proposed mechanisms for catalytic H_2O_2 decomposition.

Zhuravlev and others (382) extended their studies of the work functions of catalysts in an attempt to correlate them with changes in activity caused by aging semiconductor catalysts. Work functions of NiO, Ni_2O_3, CuO, PbO, and Pb_2O were determined immediately after they were annealed and at various times for 12 days after they were first used as H_2O- decomposition catalysts. Both the work function and the activity of NiO and Ni_2O_3 decreased, then leveled out as the aging period increased. Work function and activity changed in opposite directions for CuO, PbO, and Pb_2O. The results are explained by the electron theory of catalysis. Adsorbed reactants remain adsorbed on the catalyst surface after drying. Donor-type reactions occurred on the nickel catalysts and acceptor-type reactions occurred on the others. This conclusion was confirmed by determinations of the signs of the surface changes on the catalysts from work function measurements of the catalysts immersed in hydrogen peroxide solution.

c. Activity of Adsorbed Ions

The effect of traces of adsorbed ions on the catalytic activity of $Ni(OH)_2$ was examined by Krause and others (158). Mn(II) ions were found to be activators. The relative promoting effects of other ions in decreasing order were: Mg(II), Cr(III), MoO_4^{2-}, WO_4^{2-}, and UO_2^{2+}. Ni(II), Zn(II), Fe(III), Pb(II), and $Fe(CN)_6^{3-}$ were without effect. Ba(II) and $Fe(CN)_6^{4-}$ acted as inhibitors. For mixed ions, the combination $Ni(OH)_2$-$Fe(CN)_6^{4-}$--Cu(II) gave the most active catalyst.

Krause and Domka (201) found that both Fe(III) and Cu(II) ions increased the normally feeble activity of $Ni(OH)_2$ as a catalyst in the decomposition of hydrogen peroxide. Fe(III) increases the rate slightly, and Cu(II) more strongly, but the greatest increase results from the ions in combination. The order of addition is also important: $Ni(OH)_2$ + Cu(II) + Fe(III) yields markedly greater activity than $Ni(OH)_2$ + Fe(III) + Cu(II). In all cases the reaction was first order. The mechanism suggested was adsorption of ions at the $Ni(OH)_2$ surface, resulting in complexes that facilitate electron transfer.

These same investigators (182) found that nickel (II) ions at low concentrations markedly affect the rate of catalytic decomposition of hydrogen peroxide when adsorbed on cobalt carbonate carrier. The decomposition rate of 0.3 per cent H_2O_2 at 37° was determined for additions of Ni(II) ions to 1.0 mg $CoCO_3 \cdot Co(OH)_2 \cdot 3.5H_2O$. The rate increased to a maximum at 10^{-6} gram Ni(II), dropped to a minimum at 10^{-9} gram, and at 10^{-12} gram rose back to the rate due to the cobalt carbonate alone.

It was also found (184) that Ag(I) and Mn(II) ions, which are normally inactive in hydrogen peroxide decomposition at 37°, can accelerate the reaction if they are adsorbed on $2NiCO_3 \cdot Ni(OH)_2 \cdot 7H_2O$ carrier. Each ion adsorbed alone promotes decomposition. However, in combination they are less active, and the degree of activity depends on the order of adsorption (catalytic mutation). The results are obtained for concentrations of 1 mg of ion per 0.1 gram of carrier. If the ion concentration is doubled, the effects are not observed.

Tomassi and Jankowska (341) used a potentiometric technique to study the catalytic decomposition of hydrogen peroxide by nickel ions adsorbed on silica gel. It was found that the gel would actively catalyze the decomposition when the potential difference between a $NiSO_4$-silica gel and a calomel electrode was between 55 and 160 millivolts. A gel with 2 per cent of $NiSO_4$ gave the highest activity. In the cell, potential increased if the concentration was higher, and dropped if it was lower.

2. PALLADIUM

The catalytic action of palladium foils at 37°, 50°, and 70° in the decomposition of hydrogen peroxide was examined by Krause and Hermann (170). It was found that the reaction was first order and that palladium lowered the activation energy by 1-2 kcal/mole. Etching the foils increased the activity.

Sal'nikov and others (303) regenerated spent palladium dust catalyst by exposure to an ultrasonic field. Best results for a catalyst used to decompose hydrogen peroxide were obtained using about a 40 per cent mixture of the dust in Decalin, irradiated in a field of greater than 3.5 watts/sq cm intensity for 5 to 10 minutes. Before treatment the dust should be washed with boiling alcohol and hot water; after treatment, it should be washed with benzene, then dried.

The relation between crystal structure and catalytic activity of thermally treated palladium films was studied by Umeda and others (353). Electron microscope and x-ray diffraction analysis indicated that the lowering of activity was caused by a decrease of lattice interplanar distances, by growth of crystallites, and by a decrease of distortion and disorder in the lattice. Umeda and others (354) used differential thermal analysis to determine the relative catalytic activities of evaporated metal films. Reaction rate was proportional to the quantity of metal. Increasing the pH decreased the activation energy. The order of activity for various metals was Pd> Pt> Fe> Au> Ni> Ag> Cr> Cu> Al.

Umeda and others (355) also observed that the electrical resistance of a palladium film increased during the catalytic decomposition of hydrogen peroxide. Applying a negative potential increased the catalytic activity. Measurements also showed that at the pH yielding the highest activity, the electrical capacity of the double layer at the surface was large. Electron transfer from the surface to H_2O_2 molecules was said to be the rate-determining step of the reaction.

Kokado and Okubo (125) measured the effect of hydrogen peroxide and palladium sol concentrations on the rate constant for the catalytic decomposition of hydrogen peroxide. Below a peroxide concentration of 0.05 M the first-order rate constant was independent of concentration. At high concentrations of peroxide the rate constant was proportional to the concentration of the palladium sol.

Tverdovskii and Karpova (348) studied the catalytic properties of palladium-nickel alloys in the decomposition of hydrogen peroxide. Rate constants were determined as a function of nickel content and at 40°C. The rate passed through a maximum at 25-30 per cent nickel, dropped gradually to a plateau at 40-60 per cent dropped abruptly to a second plateau at 65-83 per cent, and finally declined to zero at 100 per cent nickel. In all cases the reaction was first order; Arrhenius equation activation energy and frequency factor reached maxima at 20-25 per cent nickel.

The decomposition of hydrogen peroxide by palladium-gold alloys in normal H_2SO_4 at 18 and 35° C was investigated by Mosevich and others (270). The first-order reaction rate constant was unchanged for gold concentrations from 0.0 to 60-65 per cent. At higher concentrations the rate constant decreased to zero as gold concentration increased to 100 per cent. The activation energy was unchanged up to 55 per cent of gold, increased sharply before leveling off at 60-70 per cent of gold, then declined in the region of 70-100 per cent of gold. No explanation of the results was given.

Pospelova and Kobozev (294) studied the rate of decomposition of 30 per cent hydrogen peroxide by silica-supported palladium in the presence of HCN, HCl, and H_2SO_4. In sulfuric acid the reaction was first order and practically independent of the acid concentration. Hydrochloric acid also gave a first order reaction, but a decline in activity with increased concentration. In HCN, the reaction increasingly deviated from a first order reaction and the catalytic activity continuously declined as concentration was increased. The degree of coverage of the silica support by the palladium catalyst markedly affected both the over-all and the specific activity. Activity increased slowly in the range of 0.3 to 1.0 per cent and rapidly above 1.0 per cent of palladium. It was concluded that the mechanism involved cleavage of a hydrogen atom rather than cleavage of an oxygen atom.

Hayashi (104) reported that lead ion accelerates the decomposition of H_2O_2 by palladium. Lead inhibits platinum, however, as a result of a Gibbs-type adsorption on the catalyst surface.

Ishizaki (112) reported that saponin inhibited the decomposition of hydrogen peroxide by palladium.

3. PLATINUM

a. Untreated Platinum as a Catalyst

Tovbin and co-workers conducted a series of studies on the non-stationary catalytic decomposition of hydrogen peroxide with platinum.

It was found that the activity of a fresh platinum surface increased with time of contact with hydrogen peroxide (343). The results showed that oxygen compounds produced on the surface cause the highest activity. It was demonstrated that the decomposition reaction continues in the substrate for a time after the catalyst is removed.

Tovbin and Lyashev (344) decomposed hydrogen peroxide solutions flowing through a tube coated internally with bands of platinum catalyst. The amount of peroxide decomposed was found to increase with the length of the non-coated portions of the tube up to a point where the peroxide remained out of contact with platinum for ten seconds. The total length of the portions with platinum bands was held constant. These experiments were said to demonstrate that the decomposition is a chain reaction, initiated at the platinum surface, and propagated within the liquid itself.

It was pointed out in a later paper (345) that the tube experiments do not conclusively prove that the decomposition reaction proceeds in the homogeneous phase after initiation by a platinum surface. It was argued that if the rate were diffusion-controlled, the flow past the tube wall containing no platinum would allow diffusion of fresh material for contacting a subsequent catalyst band, with the net result that the effect of the same length of platinum is increased. Later experiments used a rotating platinum catalyst that gave an increasing decomposition rate up to 450 rpm, beyond which the rate leveled off. Further evidence of the diffusion effect is that samples ejected from a narrow platinum tube into a permanganate solution for analysis, consistently gave lower results than if the samples were held 1 to 2 minutes in the tube before analysis. It was also shown that hydrogen peroxide put in contact with platinum bleached methylene blue more rapidly than peroxide that had not been in contact with platinum. These results showed that although the reaction is diffusion-controlled, it is to some extent propagated by reaction in the body of the liquid after contact with the catalyst.

Earlier experiments (344) indicated that oxygen compounds were the real catalysts for the decomposition. Activity of the platinum was observed to increase with use. Surface treatments also affected activity. The best catalyst resulted from treatment of platinum with hot chromic acid, followed by air drying. Treatment by heating in a stream of hydrogen gave a considerably poorer catalyst.

It was found that the catalytic activity of platinum declined with exposure to successive samples of hydrogen peroxide (345). Treatment with chromic acid between exposures, however, sustained the high activity. In experiments where hydrogen peroxide was passed through a fresh platinum tube, the first-order reaction rate constant was determined to be 8.9×10^{-3}/min. Sustained flow experiments gave a reaction order of 1.73.

Satterfield and Yeung (306) studied the decomposition of hydrogen peroxide vapor on platinum and stainless steel in a tubular reactor. Temperature ranged from 130-460° and H_2O_2 concentrations up to 2.1 mole per cent. Both mass transfer and surface reaction were found important in the overall process. It was unexpectedly found that the true surface rate went through a maximum as temperature increased. Surface rate constants for both catalysts were determined.

Krause and Hermann (165) reported that scratching the surface of platinum or palladium increased considerably the activity as a catalyst in decomposing hydrogen peroxide. Scratching did not affect the activity of gold. The effect is attributed to increased ease of radical formation.

Franklin and others (80, 81) found that the decomposition of hydrogen peroxide by platinum in 2 N H_2SO_4 was a first-order reaction. From measurements of the absorption by hydrogen of the platinum surface, it was determined that hydrogen peroxide decomposed at certain sites only, whereas quinone could be hydrogenated using the entire platinum surface.

The problem of "active centers" in catalysts such as platinum used for the decomposition of hydrogen peroxide was considered by Erbacher (54). Various investigators have attributed high catalytic activity to edge effects of the particles, edges of crystallites, or mechanical discontinuities. Erbacher argues that since all heavy metals except platinum have straight-line logarithmic adsorption isotherms, and since the absolute surfaces found by monatomic electrochemical exchange and from ion adsorption are the same, only metal atoms are the active centers for most metals. The fact that roughened platinum is more active than smooth platinum in the decomposition of hydrogen peroxide is attributed to the greater number of adjacent discontinuities.

The effects of various surface treatments on the rate at which platinum catalytically decomposed hydrogen peroxide were compared by Garton and Turkevich (85). Polished foils, heat-treated foils, and foil etched by catalyzing the oxidation of ammonia were compared. The foils were examined by an electron microscope. Etched platinum exhibited a million-fold increase in the number of surface peaks, and predominance of the (100) faces. Rate data from the decomposition of peroxide indicated that activity is proportional to surface area, although some crystal faces may have greater activity.

Keating and others (117) found that the decomposition of hydrogen peroxide on annealed and cold-worked platinum foils was first order. The reaction rate constant increased with the degree of cold work. The catalytic activity could be correlated directly with the deformation of platinum. Increased activity is attributed to deformation because any effects of preferred orientation or increased surface area were proved negligible.

The fraction of active centers on platinum black in the decomposition of hydrogen peroxide at 25° C was determined by Gorokhova and others (94). Adsorption of lead acetate, which poisons platinum, was used to control the extent of blocking of active sites. Adsorption isotherms increased rapidly up to an equilibrium value of 150 mg Pb/liter. The relation between the number of active centers and the probability of poisoning could be expressed mathematically. The fact that poisoning reduced platinum catalytic activity 65 per cent was attributed to mutual repulsion of adsorbed lead ions. Active surface constituted 1/5 of the total according to adsorption measurement and 1/3 of the total according to poisoning of the catalyst.

Maxted and Ismail (261) investigated the activation of platinum by various oxides. Small quantities of ThO_2, ZrO_2, Cr_2O_3, CeO, MgO, TiO_2, V_2O_5, La_2O_3, Pr_6O_{11}, Tl_2O_3, and Sm_2O_3 strongly promoted the decomposition of hydrogen peroxide by platinum particles at 20°. In general there is a maximum in the decomposition rate for increasing concentrations of the oxides. The order of promoting ability for the oxides is as follows: $ThO_2 > ZrO_2 > Cr_2O_3 > CeO > MgO > TiO_2 > V_2O_5 < La_2O_3 > Pr_6O_{11} > Tl_2O_3 > Sm_2O_3$. Activation in many cases is considerable; ThO_2 and ZrO_2 increase it 9 times the value of that for platinum alone.

Dole and others (51) evaluated the fractionation of isotopes in the decomposition of hydrogen peroxide by metallic platinum. It was established that some of the liberated oxygen comes from the substrate water when the peroxide is decomposed. The enhancement of the O^{18} percentage is not explained.

Myuller and Nekrasov (272) obtained electrochemical evidence indicating that a platinum oxide forms by a chemical process as an intermediate in the catalytic decomposition of hydrogen peroxide by platinum. Oxygen reduction in 0.125 N KOH was studied as a function of various platinum electrode treatments. Treatment for 5 minutes at -0.25 v gave a more positive half-wave potential for the reduction of oxygen to H_2O_2 than did a similar electrode treated for 1 minute at 1.30 v. This fact indicated that the first stage of the reaction was electrochemical and did not involve participation of the surface oxide. In another experiment, it was shown that in a ring-dish electrode, all the evolved oxygen could be attributed to H_2O_2 decomposition. This result supported the conclusion that the catalytic decomposition involved a layer of PtO formed on the surface. The first stage of the reaction up to a maximum potential corresponded to the reaction $H_2O_2 + PtO \rightarrow Pt + H_2O + O_2$. A decrease of the cathodic current in the region where the diffusion potential was less than the maximum was attributed to platinum reduction at the surface.

Hickling and Wilson (105) found that platinum, platinized platinum, nickel, gold, and graphite, anodically decomposed hydrogen peroxide at all but very high current densities. The reaction postulated for alkaline solutions, $HO_2^- = H^+ + O_2 + 2e^-$, is rapid. It is also diffusion-controlled and independent of the electrode material. Potentials about 10 times higher are required for decomposition, and the reactions that do proceed require potentials equal to that for the same reaction in an electrolyte not containing hydrogen peroxide. These facts suggest that an OH radical participates as follows:

$$OH^- = OH + e^-$$

$$OH + H_2O_2 = H_2O + HO_2$$

$$OH + HO_2 = H_2O + O_2$$

The behavior of platinum and platinum electrodes in acids and neutral solution indicates that platinum oxides are reaction intermediates in these processes.

Gerischer and Gerischer (86) examined electrochemically the decomposition of hydrogen peroxide by platinum. A reaction mechanism is proposed to account for the results. Reaction is initiated by electron transfer from the metal to H_2O_2. The radicals OH and HO_2 produced remain adsorbed on the surface. In acids the radicals react to form OH^- and O_2, principally by electrochemical reactions. A parallel chain reaction speeds up the decomposition, particularly in neutral or alkaline solution.

Bianchi and others (18) investigated the catalytic decomposition of dilute solutions of hydrogen peroxide by platinum, iridium, palladium, and gold. In sulfuric acid, gold was the only inactive catalyst. None of the metals was active in hydrochloric acid solutions. The decomposition reactions were first order. Polarization, decay, and charging curves for the metals as electrodes showed that the catalyst surfaces become coated by practically a monolayer of metal oxide during the reaction. Activity is lost if the metal cannot be covered by an adsorbed oxide layer, as when direct complexation by the solution prevents oxide formation. This explains the behavior of platinum and iridium in HCl solutions, and of gold in H_2SO_4 solutions. It is also apparent that the rate of H_2O_2 decomposition is determined by the differences in the rate of formation of oxides and by the rates at which the oxides decompose the peroxide.

Polarization curves for the reduction of oxygen on platinum electrodes in the presence and absence of hydrogen peroxide were obtained by Berenblit and Lantratova (16). The results were applied to a chain reaction mechanism for decomposition of hydrogen peroxide. All electrochemical evidence indicated that decomposition at platinum electrode should proceed at equal rates in acid and alkaline solution. The fact that the acid reaction is faster is explained by the higher probability of chain reaction in alkaline solutions. The results also indicated that electrochemical processes play an important part in the catalytic decomposition of hydrogen peroxide by metals.

Forker (76) studied the catalytic decomposition of hydrogen peroxide on platinum sheets immersed in buffers of various pH at constant ionic strength. Decomposition rate varies with pH and reached a maximum at pH 12.1. Potential measurements on the immersed sheets showed characteristic alterations to the platinum surfaces. Reaction velocity constants and a mechanism for a first-order reaction were presented.

As part of a general analysis of catalytic reactions aimed at a better understanding of biochemical catalysts, Kobozev (123) compared various catalysts in which it was attempted to determine the effect of the support and linkage with otherwise inactive groups on the active catalysts. The relative activities of various H_2O_2 decomposition catalysts were determined. Relative to a value of 1.0 for Fe(III) ions in solution, the activities were: MoO_4^{2-}, 0.1; CrO_4^{2-}, 0.1; WO_4^{2-}, 0.1; $CrWO_7^{2-}$, 10 (all in solution); Fe(III) ions on carbon, 100; hemin (in solution) 100, hemin on carbon, 1000; Fe_2O_3, 10,000; MnO_2, 10,000, platinum, 500,000; hemin on albumin, 500,000,000. Other examples of biochemical catalytic reactions are used to illustrate the effects of using different supports.

The catalytic decomposition of 3 per cent hydrogen peroxide by platinum electrodes was used by Flis (59) as the basis for potentiometric titration. The electrode potential is proportional to the pH of the solution. Hypochlorites, hydroxides, carbonates and other anions can be determined.

b. Effects of Thermal Treatment

Nikolaev and Shlygin used electrochemical methods to study the sintering of platinized platinum and the effect on the catalytic decomposition of hydrogen peroxide.

The effects of thermal treatment of platinum in hydrogen atmospheres on the polarization curves and the reaction rate constant for the decomposition of hydrogen peroxide was determined (282). The polarization curve of platinum immersed in 0.1 N H_2SO_4 was used as a standard, and all measurements were taken at 70°. Polarization curves and rate constants were then determined for the same electrode heated for one hour each at 40, 60, 80, 100, 120, 150, 200 and 250°. Invariably the potential required to reach a fixed value relative to a hydrogen electrode in 0.1 N

H_2SO_4 decreased for higher heating temperatures. The decrease was about 10 per cent for the lower temperatures and about 96 per cent at 300°. The rate constant decreased to about 75 per cent after heating to 60°, increased to 40 per cent after 80°, then gradually declined to 3 per cent after 300°. It was concluded that below 80°, only lattice faults, which are catalytically active, disappear. Platinum starts to recrystallize at 80°, but adsorbed hydrogen evidently distorts the lattice, causing increased catalytic activity. It is further concluded that hydrogen accelerates sintering instead of stabilizing the surface by adsorption.

These studies were extended (283) to include heat treatment in air. Platinized platinum heated at 0°, 100°, 300°, and 400° gave values for the relative reaction rates of 100, 34, 127, and 105 respectively. Increased values of the rate constant were attributed to deformation of the platinum lattice by the oxygen adsorbed.

The same method was used to determine the effects of thermal treatment in a nitrogen atmosphere (284). Platinum was sintered in nitrogen at 20, 100, 200, 300, 400, and 500°C. Measurements of catalytic activity showed that adsorption capacity decreased with increasing temperature, a fact attributed to a decrease in the true surface area. Sintering at 300° and above markedly increased the activity, presumably because of activated adsorption. A general observation was that recrystallization rates at the surface were much less in a nitrogen atmosphere than in a hydrogen, but greater than in an oxygen atmosphere.

Strel'nikova and others (328) investigated the thermal activation and deactivation of platinum black over the range 100 to 700°. In the curve of catalytic activity in H_2O_2 decomposition plotted against calcination temperature, maxima resulted at 160, 220, 250 and 500°. These experiments confirmed earlier ones (326) that indicated a drop in activity when platinum black is calcined between 250 and 500°.

The effect of thermal treatment on the catalytic activity of platinum was investigated by Lopatkin and others (234). Over the range 100-700°C, a curve of activity against temperature disclosed reactivity maxima at 100, 220, and 250°. Activity declined steadily from 260 to 500°, at which point it increased slightly, then continued a steady decrease.

Strel'nikova and others (326) studied the thermal activation and deactivation of platinum adsorbed on silica gel in the decomposition of hydrogen peroxide. Samples were prepared with different degrees of filling of the support by the catalyst, and ignited at 300-700°C. Curves of activity against treatment temperature gave regions of activation and of deactivation, as well as prominent maxima. The carrier tended to stabilize the catalytic platinum centers against temperature effects, particularly as the effects become more pronounced at high platinum content. Activity maxima shifted to high temperatures with more dilute catalysts, an effect that was compared with extinction of luminescence and magnetic effects.

Strel'nikova and others (330) also studied the effect of sintering temperature on catalytic decomposition by platinum supported on silica. Activity isotherms for the decomposition reaction as a function of duration of sintering (400-700°) passed from the type having several maxima to the type in which activity fell off initially, then leveled. The pattern was ascribed to changes in the number of active catalyst centers on the adsorbed platinum. Both trends in activity and calculated apparent activation energies supported the conclusion.

Strel'nikova and Lebedev (327) studied the effect of sintering temperature and degree of coverage on the activity of platinum catalysts, supported on carbon, silica, and cadmia. Catalytic activity was determined from activation energies and the number of active centers, which is in proportion to the exponential coefficient, k_0, in the Arrhenius equation. The authors distinguish nine theoretically possible types of catalyst behavior, as determined by relative variations in the activation energy (E) and the exponential coefficient. The two most common types are an increase in k_0 compensated by an increase in E, and a decrease in k_0 compensated by a decrease in E. Experimental examples of the various types are cited. Changes in activation energy with the degree of carrier coverage by the catalyst were attributed to the formation of different valent-activity structures.

Tyurin and Shlygin (349) used charging curves as a basis for a method to determine the effects of sintering on the catalytic decomposition of hydrogen peroxide by platinum. The aim was to determine the relation between catalytic activity, specific surface, and adsorbing capacity for hydrogen and oxygen. Charging curves were determined by suspending the catalyst powder in a basket immersed in an electrolyte, and measuring the quantity of electricity passed as a function of potential. Surface areas could be obtained from such measurements. The results showed that sintering had no effect on the bond energies of adsorbed gases or the catalyst surface except in the case of oxygen, where the increased bond strength was attributed to penetration of the gas into the platinum crystal lattice during the recrystallization caused by thermal treatment. Oxygen adsorption markedly activated platinum in the catalytic decomposition of hydrogen peroxide.

Tyurin and Feoktistov (350) studied further the effect of sintering on the activity of platinum black catalyst at 20°C. The effect of adsorbed oxygen was determined by sintering the catalyst at 100-600°C in an oxygen atmosphere. Surface properties were determined by the charging curve method. The specific catalytic activity declined severely to a minimum for sintering temperatures up to about 180°. At higher sintering temperatures, activity increased to a maximum at 500°C. It was concluded that the initial decline in activity is due to the blocking of active centers by adsorbed oxygen. Activity increases at the higher temperatures were attributed to the formation of platinum oxides.

The effects of long-term storage on the catalytic activity of a silica-supported platinum catalyst were measured by Strel'nikova and Lebedev (331). Catalytic activity was first measured 3 days after the catalyst was prepared, after which it was stored in a desiccator for 2 years. Regardless of platinum content of the catalyst, storage decreased the first order reaction rates by a factor of 10. Storage did not change the relative activities of catalysts having different amounts of platinum. The ratio of active centers in catalysts of various platinum contents was also unchanged.

Lopatkin and others (235) correlated magnetic susceptibilities with thermal treatment for three compositions of platinum-on-silica catalysts (surface fractions covered = 0.0054, 0.0178, and 0.035). For the two catalysts with the highest fraction of platinum, variations in susceptibilities with treatment temperature were identical. For the remaining catalyst it was found that the paramagnetism increased with any increased activity towards hydrogen peroxide decomposition produced by thermal treatment. This was true for the first two catalysts below 550° only.

c. Effect of Irradiation and Ultrasonics

The effect of the electronic properties of carriers on the photosensitivity of platinum catalysts in the decomposition of hydrogen peroxide was studied by Krylova and others (207). Irradiation reduced activity in all cases. Charcoal, germanium, and bismuth were the carriers used. The source of irradiation was a mercury quartz lamp. A catalyst of 1.5 per cent of platinum on charcoal was irradiated at a pressure of 0.5 mm Hg. Two catalysts, 0.5 per cent of platinum on germanium, and 0.5 per cent of platinum on bismuth were irradiated at 1 atmosphere pressure. Activity declined 50 per cent after exposures of 20, 5, and 10 hours respectively for the three catalysts. The magnitude of the changes in activity were related to the ease of electron exchange between the carrier and the adsorbed metal. In passing from dielectrics to semiconductor to metals the zone of forbidden electron energies narrows, thus increasing the possibility of electron exchange. Carrier paramagnetism increased as catalytic activity decreased.

Krylova and others (207) evaluated the reduction in catalytic activity by irradiation of silver, platinum, and palladium catalysts in the decomposition of hydrogen peroxide. Irradiation of platinum and palladium with a mercury arc lamp reduced the activities by 70 per cent. Losses were even higher for the metals adsorbed on silica or alumina. The deactivations were ascribed to formation of inactive ions (loss of valence electrons) instead of formation of active adsorbed ions of the metals.

Kobosev and Krylova (124) measured the effect of ultraviolet irradiation of platinum, palladium, and silver, on the catalytic activity toward the decomposition of hydrogen peroxide. Platinum free and adsorbed on silica gel, carbon, germanium, and bismuth were the catalysts examined in detail in various atmospheres over a range of pressures. In all cases, irradiation decreased the activity. Decline was least in a hydrogen atmosphere and greatest in an argon atmosphere. Activity could be restored by heating the catalysts for 2 hours in vacuum at 180°. The changes in activity are attributed to ionization of platinum and consequent trapping of the electrons at stable levels of the carrier.

Krylova and others (208) studied the effect of ultraviolet radiation on reaction order, activation energy, and rate of catalytic decomposition by platinum supported on silica gel. All these variables were found to depend in a complex manner on the amount of irradiation, the atmosphere in which the experiments were conducted, and the degree and kind of annealing treatment given the catalyst. Activation energy varied from 5700 to 10,800 cal/mole. The results indicate that photo-oxidation of platinum cannot explain the deactivation by irradiation.

The effect of γ-radiation on the catalytic activity of platinized aluminosilicate was determined by Minachev and others (264). Reduced platinic acid gave a catalyst of 0.5 per cent platinum, with a surface area of 252.2 sq m/gm. Radiation of $(0.27\text{-}10) \times 10^{-19}$ electron volts increased the catalytic activity in accordance to the dose. The increase due to irradiation was lost in six months.

Minachev and Khodakov (265) studied the effect of γ-radiation on alumina-supported platinum black catalysts having various platinum concentrations, and treated under different thermal conditions. In one case, irradiation had no effect; a deactivation was reported for the other cases.

Li and co-workers (228-231) conducted a series of investigations on the effect of ultra-sound on the catalytic activity of platinum and other catalysts in the decomposition of hydrogen peroxide.

The activity of a platinum-black catalyst could be increased or decreased, depending on the ultrasonic frequency, the atmosphere (air, nitrogen, hydrogen) and peroxide concentration (228). Highest activity was observed for high frequencies, a nitrogen atmosphere, and platinum prepared from diluted H_2PtCl_6 solutions (230).

Platinum black and palladium black were prepared by the reduction of the chlorides by 40-45 per cent formaldehyde, placed for 3 hours in an ultrasonic field of frequency 20-3000 kc, and in nitrogen, air, or hydrogen atmosphere. The greatest activity resulted from platinum prepared in a nitrogen atmosphere at 3000 kc. The treatment more than doubled the catalytic activity. The treatment also increased the magnetic susceptibility from 0.866×10^{-6} to 1.70×10^{-6}, the specific surface from 11.7 to 19.0 m^2/g, and the linear dimension of the crystals from 85 to 106A. Palladium increased in activity as the ultrasonic frequency was decreased to 20 kc (229).

Li and others (231) also determined the effect of ultrasonic treatment on the activity of catalysts prepared by adsorbing platinum ammoniate or H_2PtCl_4 on silica or alumina, followed by reduction with hydrogen (300°). Exposure to an ultrasonic field before the reduction step did not affect catalyst activity.

d. Supported Platinum

A 1964 U.S. patent by Andersen and Romeo (6) assigned to Englehard Industries, covers the use of platinum, ruthenium and palladium supported on carbon as a catalyst for decomposing organic peroxy acids and H_2O_2 in solution. A typical catalyst contains 5 per cent each of platinum, palladium, and ruthenium on carbon.

Kobozev and Reshetovskaya (122) investigated active "ensembles" on catalyst surfaces used in hydrogenation and the decomposition of hydrogen peroxide. Carbon and alumina were used as supports for platinum. The number of platinum atoms in the active "ensemble" and the area of the "migration cell" were calculated from the catalytic activity and the fraction of surface coverage. In the decomposition of hydrogen peroxide the number of platinum atoms in the active ensemble was 1 for carbon and 4 to 6 for alumina. The "migration" cell was on the order of 10^{-13} sq cm, with a specific value for each support.

Studies of catalyst poisoning by decomposition products of hydrogen peroxide and other reactions led to an analysis by Lebedev and Strel'nikova (224, 225) of active centers in the decomposition of peroxide. Experimental data for platinum supported on carbon, silica, alumina, cadmium oxide and cadmium were summarized and examined. It was deduced that active centers in catalysis are formed only by odd numbers of platinum atoms, e.g., Pt, Pt_3, Pt_5 and Pt_7. An interpretation based on kinetic data was attempted. A rate equation could be developed by assuming an intermediate compound of the type $\underbrace{Pt\cdot O\cdot O}$ in the reaction. An explanation of the odd number of atoms in active center could then be obtained by a graphical analysis of the experimental data applied to the rate equation.

To determine whether decomposition of hydrogen peroxide does take place at active centers of odd numbers of platinum atoms, Lebedev and Trosman (226) examined the reaction using platinum on cadmium (semiconductor), carbon, and silica gel. The results corroborated the theory that active centers contain odd numbers of platinum atoms. The data for cadmium showed that the composition of the active center is determined only by the reaction taking place, and not by the physical nature of the support. The relative specific activities for the three supports were $C < Cd = SiO_2$.

Lebedev (223) determined the Arrhenius equation parameters for platinum catalysts on silica gel and carbon applied to the decomposition of hydrogen peroxide. Decomposition was carried out at 20-30° using catalysts reduced in a stream of hydrogen at 300° for 12 hours. Packings on silica gel carriers were 0.00005-0.05 and 0.0005-0.03 monatomic platinum layer. Values of parameters in the Arrhenius equation $z = ae^{E/h}$, were, respectively for the two catalysts, $E = 2000\text{-}12,000$ cal/mole and $E = 4000$ to 21,000 cal/mole; $\log z = 1.5$ to 6.5 and $\log z = 3$ to 14.3. The temperature used for thermal treatment of the catalyst is essentially the same as the experimental range of the catalytic activity. Platinum at packing fractions of 0.01, 0.02, and 0.04 was calcined in vacuum at 350-700° at 20° intervals for 3 hours. At each temperature, E in the Arrhenius equation ranged from 2700 to 21,000 cal/mole, log z from 0 to 15, and a from 0.0 to 0.1. Calculation of the heat treatment temperature from $\log k_0 = f(E)$ approximated the experimental temperature used to determine catalytic activity.

Lopatkin and others (233) investigated platinum on silica in the decomposition of hydrogen peroxide at 25°. Pt-to-SiO_2 weight ratios of 0.0015 to 0.05 were included. The reaction was second order. Activity increased with "available" surface of the carrier, but it was a complex function of the weight ratio of Pt to SiO_2. Relative maximum activities were 16, 27, and 28 for weight ratios of 0.013, 0.027, and 0.042. Relative minimum activities were 12.5 and 20 for ratios of 0.02 and 0.035. This behavior was attributed to the existence of active centers with definite compositions and to energy heterogeneities at the carrier surface.

Strel'nikova and others (329) determined the catalytic activity of platinum supported on cadmium oxide (CdO). Over-all activity was determined by plotting moles H_2O_2 decomposed/sec/gm catalyst as a function of the number of atoms on the surface of the catalyst. The curves passed through three maxima corresponding to active centers of odd-number platinum atom groupings $(Pt)_1$, $(Pt)_3$, and $(Pt)_5$. The kinetics of the reaction were formulated on the basis that PtO_2 dissociated reversibly.

Shashkov and others (313) attempted to correlate electron emission with catalytic activity of platinum supported on $BaSO_4$ in the decomposition of hydrogen peroxide at 20°. X-radiation was used to induce emission. At a concentration of 2×10^{-5} gm Pt/gm $BaSO_4$, the emission intensity was double that of $BaSO_4$ alone. As the platinum concentration increased the intensity decreased. At $(2\text{-}4) \times 10^{-4}$ gm Pt/gm $BaSO_4$, the intensity was constant and about the value of that of the carrier alone. At 4×10^{-3} gm Pt/gm $BaSO_4$, the intensity decreased to 1/2. Plotting catalytic activity against the logarithm of concentration gave S-shaped curves. Plotting emission intensity against temperature gave peaks at 110 and 160°, whereas the same plot for $BaSO_4$ alone gave a single peak at 140°. Changes in emission intensity with time could be mathematically correlated. Magnetic measurements showed that for concentrations of 0.0018-0.0036 gm Pt/gm $BaSO_4$, the catalyst is diamagnetic, and for concentrations of

0.00001-0.000036, it was paramagnetic. At low concentrations, catalytic activity is associated with electron emission extinction and reflective capacity.

The catalytic activity of platinum on silica as a function of its method of preparation was determined by Adamenkova and Poltorak (1). Silica was prepared by hydrolyzing $SiCl_4$. H_2PtCl_6 was treated with ammonia and the platinum compound adsorbed on the silica. Reduced platinum was obtained by passing hydrogen through the heated silica granules. Catalytic activity towards H_2O_2 decomposition was higher when the granules were made smaller. Optimum temperature for the hydrogen treatment was 300°. Specific activity increased with platinum content and it was affected by the nature of the H_2PtCl_6 used.

The same investigators (2) later attempted to define the parameters affecting the performance of platinum supported by silica in the decomposition of hydrogen peroxide. Recommended techniques for measuring activity are stated. The activity depends on the starting platinum compound selected, the method of application to the silica, drying conditions, and reduction conditions.

Kersonov (128) compared the catalytic activites of ionic ytterbium on sugar charcoal with that of an ytterbium-platinum mixture on the same support. A constant 0.05 per cent platinum and a variable quantity of ytterbium salt were used. The salt alone had very low catalytic activity that increased only slightly with concentration. The mixed catalyst was more active than platinum catalyst alone, as indicated by a decrease in the activation energy from 12.7 kcal/mole for platinum to 9.9 kcal/mole for the mixed catalyst. Increased concentrations of ytterbium in the mixed catalyst led ultimately to a decline in activity. At a Pt/Yb ratio of 2:1, activity was lower than that of platinum alone.

Enright and others (290) studied the effect of adsorbed metal ions on the decomposition of hydrogen peroxide. Experiments demonstrated that heavy metal ions such as Hg(II), Pb(II), or Ag(I) have little or no effect on the decomposition of hydrogen peroxide in aqueous solution unless they are adsorbed on a rigid carrier. An explanation of the profound influence of the nature of the carrier on the catalytic behavior of these ions is presented on the basis of K. Fajans' theory of the polarization of ions.

e. Platinum Alloys

Zubovich (384-390) carried out a series of studies on binary, noble-metal catalysts deposited on alkaline earth carbonates or sulfates. These studies were in part an attempt to relate catalyst activities to electronic structures and magnetic properties.

An interaction was found between the components of Pt-Ag, Pt-Au, Pd-Ag, Pd-Au, and Pt-Pd mixed catalysts adsorbed on alkaline earth sulfates (384). Behavior could be related to the position of the elements in the periodic table and to effects of the carrier. Maximum activity resulted when the elements were in the stoichiometric proportions of 1:1 or 1:2. Silver exhibited a poisoning effect on platinum and palladium. Poisoning was a maximum at a silver concentration of 0.0275-0.055 per cent on the carrier, which corresponds to a proportion of Ag to Pt or Pd of about 1:1. The decline of catalyst activity in H_2O_2 reduction was accompanied by a considerable increase in activation energy, from 6.6 to 22 kcal/mole for a 0.1 per cent Pt-on-$BaSO_4$ catalyst when the Ag:Pt ratio was 1:1. Addition of gold to palladium or platinum catalysts resulted in a different behavior. Gold slightly reduced the activity of platinum, but it increased the activity of palladium up to a maximum for a Pd:Au ratio of 1:2.

Zubovich (385) showed that experimental data for the decomposition of hydrogen peroxide by Pt-Ag and Pd-Ag mixed catalysts supported on alkaline earth sulfates agreed with the theory of catalytically active ensembles. According to the theory, the catalyst activity is related to the amount of catalyst present by the expression

$$A = A_0 e \exp(-g/z^*)$$

where A is the original catalyst activity, g is the concentration, and z^* is the number of catalyst migration regions on the surface. For other binary alloys, it was found that, unlike silver, palladium activates platinum in Pt-Pd mixtures. Gold activates palladium, but does not affect platinum activity. Additional experiments confirmed the previous result (384) that in those mixtures the strongest activation occurs for a Pd:Au ratio of 1:2.

Zubovich (386) also studied thin layers of Pt-Ag, Pt-Au, Pd-Cu, Pd-Ag, Pd-Au, and Pt-Pd catalysts supported on alkaline earth carbonates and of Pt-Cu catalysts on $SrSO_4$. Catalytic behavior was related to the electronic structure of the metal ions, to the existence of unpaired electrons, and to carrier properties. In agreement with previous results, highest activities resulted with catalysts having the simplest stoichiometric ratios of active metals on the carrier. Minimum activity yielded maximum activation energy. Catalytic activity was also related to changes in magnetic susceptibility.

The poisoning of platinum by silver as mixed catalysts supported on lead sulfate was also investigated (387). The behavior was identical to that obtained earlier (384) for the same catalyst supported on barium sulfate and minimum activity resulted when the Ag:Pt atomic ratio was 1:1. Zubovich suggests, therefore, that the behavior of the mixed catalyst depends on the nature of the components, and not on the properties of the carrier.

In a further study of the poisoning of platinum by silver, Zubovich (388) used anatase and rutile (two crystalline forms of TiO_2) as supports.

In this case it was found that minimum catalytic activity corresponded to a 1:1 Pt:Ag ratio on rutile, but to a 1:2 Pt:Ag ratio on anatase. It was pointed out that the general behavior is the same for semiconducting rutile as it was for alkaline earth sulfates (384, 385, 387) and carbonates (386), which are not semiconductors.

Zubovich also observed a correlation between changes in catalytic activity and magnetic susceptibility of palladium-silver catalysts supported on polymorphic TiO_2 (389) and of platinum-silver catalysts supported on sugar charcoal, carbon black, and graphite (390).

Bogdanovskii and Shlygin (27) reported that the addition of palladium to a platinum catalyst does not noticeably promote the rate of decomposition of hydrogen peroxide. However, palladium does prevent self-poisoning of the catalyst, particularly when added in amounts of 10 per cent and higher.

Lopatukhina and Shlygin (232) found that an electrochemically prepared palladium-platinum catalyst prepared from $PdCl_2$-$PtCl_4$ solution was 100 times more active than palladium alone in decomposing hydrogen peroxide. Greater hydrogen and oxygen adsorption showed that the mixed catalyst had a more highly "developed" surface; however it was concluded that the catalyst did not consist of mixed crystals; it was probably a solid solution.

f. Platinum Colloids

Blesa (20) studied the effect of micellar surfaces on the catalytic decomposition of hydrogen peroxide by platinum sols prepared by the electrolytic Bredig method. In the first study, the effect of KCN on the rate of decomposition was determined. Platinum sols with particles in the range 75-95 millimicrons were prepared electrolytically. Small concentrations of KCN decrease the rate of decomposition of hydrogen peroxide, but larger amounts increase the rate. The concentration of KCN that yields the minimum rate increases roughly with the total surface area of the sol particles. A nearly constant value of 0.65 mg per sq cm was obtained for all sols studied. Substitution of iodine in place of KCN gave similar results, but in this case the dose required for minimum rate was nearly a constant 0.095 mg per sq cm of sol surface.

In a second study by Blesa (19) the relation between the particle size of the sol and the amount of poison necessary to produce a minimum in the rate of decomposition of hydrogen peroxide was investigated. Each salt was found to have a specific value. Substances studied included KCN, thiosulfates, iodine, and iodides.

Hasegawa (103) measured the decomposition rate of hydrogen peroxide by platinum sol over the range 30 to 50°C. An initial decrease in reaction rate was followed by a main stage in which the reaction was first order with an apparent activation energy of 11.6 kcal/mole. The initial retardation was attributed to the accumulation at the surface of reaction products which blocked active sites.

Kokado (126) reported that tannic acids inhibits the catalytic decomposition of hydrogen peroxide by platinum sols. The logarithms of the first-order rate constant and tannic acid concentration followed a linear reaction.

The effect of deuterium oxide on the decomposition of hydrogen peroxide by solutions of colloidal platinum was determined by Deleo and others (47, 48). A regular relationship between the concentration of deuterium oxide and the inhibition of the decomposition reaction rate was established. A series of exchange reactions is postulated to explain replacement reactions that took place. All results were for 0.05 N hydrogen peroxide at 25°.

Kobozev (121) derived kinetic data for the catalytic decomposition of hydrogen peroxide on several catalysts by analyzing experimental results based on three reactions:

$$(1) \quad \mathrm{Cat} + \mathrm{H_2O_2} = \mathrm{Cat{\cdot}O} + \mathrm{H_2O}, \qquad K_1$$

$$(2) \quad \mathrm{Cat} + 2\mathrm{H_2O_2} = \mathrm{Cat}{:}^{\mathrm{O}}_{\mathrm{O}} + 2\mathrm{H_2O}, \qquad K_2$$

$$(3) \quad \mathrm{Cat}{:}^{\mathrm{O}}_{\mathrm{O}} = \mathrm{Cat} + \mathrm{O_2} \qquad k_r$$

where "Cat" is the catalyst. Reactions (1) and (2) were considered rapid reactions that could be treated as steady-state equilibria. Reaction (3) was the rate determining step. Experimental rate data were plotted in a manner that yielded values for the constants K_1, K_2 and k_r. The relative "time activities per active center" for various catalysts at 0°C were as follows: MoO_4^-, CrO_4^-, WO_4^-, and iodine, 0.1; Fe^{3+}, 1.0; $Cr_2O_7^{2-}$, 11.0; Fe^{3+} on charcoal, 100; hemin, 50 to 650; hemin on charcoal, 800; catalase, 5×10^6; Fe_3O_4 and MnO_2, 10^4; and Pt-black sol, 10^6. Since the value of k_o in the expression $k_r = k_o E^{-q/RT}$ (q_o = activation energy) was approximately 10^{10} for all catalysts, the increased activity of the mixed catalysts was attributed to a lowering of the activation energy only. A plot of log k_r against the difference in free energies of reaction (1) and (2) gave two straight lines, one for homogeneous catalysts and the other for heterogeneous catalysts. Enhanced catalytic activity for either series was attributed to decreasing repulsion between the oxygen atoms of the intermediate couples, $\mathrm{Cat}{:}^{\mathrm{O}}_{\mathrm{O}}$. A thermodynamic analysis permitted a model in which the repulsion decreased proportionally to an increase in the total amount of supporting material to which active centers are attached.

g. Effects of Accelerators, Poisons, and other Agents

Horiba (109) studied the effect of methyl, ethyl, and propyl alcohols on the decomposition of hydrogen peroxide by a platinum-palladium mixed sol and activated carbon powder. Methyl or ethyl alcohol in small amounts accelerated the reaction, but equivalent amounts of propyl alcohol depressed the rate. All three alcohols depressed the rate at high concentration. In most cases it was possible to establish a linear relation between the reaction rate constant and the dielectric constant of the alcohol.

In further studies of catalytic poisons Köppen (134) reported that thiophosphate esters retarded the catalytic decomposition of hydrogen peroxide by acidic, platinum-coated silica gel. In this case, however, the retardation could be eliminated by adding what was found to be the optimum amount of saponin to the reacting mixture. Foam was produced in proportion to the amount of oxygen evolved in the reaction. Foam height was more sensitive than foam amount as a measure of the decomposition rate.

Strel'nikova and Lebedev (332) studied the poisoning of catalytic platinum in various forms by hydrochloric acid. Colloidal platinum, platinated, dehydrated SiO_2 and platinum black were examined in the decomposition of hydrogen peroxide. The poisoning is related in a complex manner to the partial dissolution of surface atoms (usually up to 1 per cent, but up to 33 per cent for platinum black) as a result of simultaneous reaction of H_2O_2 and HCl. The bivalent surface atoms are assumed to represent active centers, which can form intermediate compounds that dissolve in HCl. The fact that activity towards the hydrogenation of cyclohexane was also observed for this catalyst is taken as evidence of supporting the assumption.

The same investigators (334) studied the effect of HNO_3, H_2SO_4, and HCl on platinum-on-silica catalysts in the decomposition of hydrogen peroxide in order to determine the anomalous behaviour of HCl. Platinum was soaked in the various acids for 5 hours, after which 2 N H_2O_2 was added. Nitric acid deactivated the catalyst least, followed by sulfuric acid. Hydrochloric acid was several tens of times more effective in deactivation, a magnitude too great to be attributed to pH. A distinction is that HCl can dissolve adsorbed platinum, which is taken as an explanation for the action of this acid. It is pointed out as very significant that no more than one per cent of the surface atoms is responsible for the catalytic activity.

In a study of the poisoning effect of mercuric chloride on platinum catalyst supported by cadmium oxide in the decomposition of hydrogen peroxide, Strel'nikova and others (333) found that platinized CdO adsorbed more $HgCl_2$ than CdO alone, regardless of $HgCl_2$ concentration. Catalytic activities of platinized CdO treated with various concentrations of $HgCl_2$ were then determined, as was the activity of an untreated platinized CdO catalyst. The log of the ratios of the activities plotted against the amount of $HgCl_2$ adsorbed gave two intersecting straight lines. The results could be expressed by a mathematical relationship involving the relative activities of poisoned and unpoisoned catalyst, the probability of poisoning an active center, the number of regions of poison migration, and the quantity of adsorbed poison. The activation energy was independent of the quantity of poison adsorbed, and varied irregularly with the amount of platinum employed.

Zykova and others (394) studied in detail the poisoning of platinum black by large amounts of mercuric chloride. In the presence of hydrogen peroxide, $HgCl_2$ is reduced to Hg_2Cl_2, which is then adsorbed by platinum. Hg_2Cl_2 is not adsorbed by platinum in the absence of hydrogen peroxide. Since crystals of Hg_2Cl_2 were observed on the catalyst surface, the amount of $HgCl_2$ reduced considerably exceeded that amount needed to form a monolayer. Absorption isotherms possessed three distinct regions, but eventually leveled off as the surface became saturated. No alteration in activation energy was observed for various surface coverages, which was taken as confirmation that the active centers are energetically uniform on the catalyst surface.

Suito (335) studied the effect of various poisons of platinum sols toward the decomposition of hydrogen peroxide. Poisons included $HgCl_2$, $Hg(CN)_2$, KCN, and KCl. Activity declined in proportion to the logarithm of the concentrations of $HgCl_2$ and $Hg(CN)_2$; in the case of KCl, a linear relation was found between the logarithms of activity and poison concentration; the behavior of KCN was more complex. The relative degrees of poisoning were $Hg(CN)_2 > HgCl_2 > KCN >> KCl$. The relative quantities required to reduce catalytic activity by 90 per cent were 0.008, 0.02, 0.03, and 250, respectively. Complete poisoning corresponded to a unimolecular layer of the poison on the catalyst surface. Kinetic evidence showed two types of behavior. Poisoning by mercuric and chloride ions did not involve reaction with hydrogen peroxide; but in the case of cyanide ion, poisoning did involve reaction with the peroxide.

Mizuwatari (266) used a fundamental pyrolysis equation to derive first-and second-order equations applicable to the decomposition of hydrogen peroxide by platinum sol. Experiments were conducted in order to determine the poisoning effects of CO, $HgCl_2$, $Hg(CN)_2$, KCN, and KCl. Various explanations are advanced to rationalize the inhibiting effects.

Gonzalez-Salazar and Blesa (93) observed that potassium iodide inhibits the catalytic decomposition of hydrogen peroxide by colloidal platinum. Reaction rate is a minimum at a concentration of 0.146 mg KI per square centimeter of platinum sol surface area.

SECTION XV.

COPPER, SILVER, GOLD

1. COPPER

a. Metallic Copper and Copper Alloys

Markovic (243) found that dilute hydrogen peroxide was decomposed by copper at 20° by a zero-order reaction. A reaction mechanism was proposed on the basis of adsorption potentials for oxygen, water, and hydrogen peroxide. The double layer on copper electrodes in hydrogen peroxide solution was studied by measuring the growth rate of polarization potentials. It was found that only high peroxide concentrations affect the size of the hydrogen double layer and that the charge on the double layer in a nitrogen atmosphere was about the same as that of all polycrystalline metals.

Kotkowski (135) determined the kinetics of decomposition of dilute solutions of hydrogen peroxide by powdered copper. Solutions containing 0.3, 0.6, and 0.9 per cent H_2O_2 at 27, 37, and 47° were examined. Electrolytic copper and copper reduced in hydrogen gave different kinetic equations that permitted distinguishing the two processes. In the case of electrolytic copper, chemisorption of atomic oxygen ($H_2O_2 = H_2O + O$) was followed by desoprtion ($O + H_2O_2 = H_2O + O_2$), at measurable rates. For hydrogen-reduced copper, the chemisorption step is so fast that only the desorption rate is measurable. It was found that the rate depended more on the degree of dispersion of the catalyst than it did on the catalyst concentration.

Ross (301) examined the activities of abraded copper-copper oxide foils in the catalytic decomposition of hydrogen peroxide. The foils were prepared by depositing films of Cu_2O on smooth and abraded copper sheets. The reaction was studied in a flow reactor at 40 to 100°C. Abraded foils were more active than smooth ones, particularly at low temperatures. Smooth foils gave an activation energy of 18.4 kcal/mole; abraded foils gave 9.2 kcal/mole. Since no significant differences in surface area could be detected, increased activity with abraded foils were attributed to changes in the dislocation site density caused by abrasion.

On the basis of the hypothesis that reactions controlled by the rate of transfer of an electron from metal to substrate should decrease in rate as the 3d band begins to empty, Dowden and Reynolds (52) conducted experiments using nickel-copper alloy foils to decompose hydrogen peroxide. Rate determinations as a function of the atomic fraction of the alloy components provided general confirmation of the hypothesis. Activation energies and frequency factors for the various alloys were also determined.

Krause and Kotkowski (178) compared the activity of fresh and used catalysts of copper-iron alloys in the decomposition of hydrogen peroxide.

The criteria for activity was the rate at which the catalyst decolorized indigo carmine. Mn(II), Cu(II), and Fe(II) ions were adsorbed on fresh and used catalysts and the activation or inhibition towards further catalytic activity observed. Mn(II) inhibited the fresh catalyst but activated the used catalyst. Cu(II) and Fe(III), either alone or in combination, activated both catalysts.

b. Copper Oxides and Hydroxides

Shashkov and Krylova (314) studied the activity and magnetic susceptibility changes in Cu, Cu_2O, CuO, and CuOOH during repeated use as decomposition catalysts for hydrogen peroxide. In some instances it was observed that the changes of activity in one catalyst ingredient were compensated roughly by opposite changes in another ingredient. A mixture of Cu, Cu_2O, CuO, and CuOOH in the respective ratios by weight of 50:62.5:57:75 gave constant activity through repeated H_2O_2 decomposition processes. The following mechanism was postulated to account for the results:

$$2CuO + H_2O_2 \rightarrow Cu_2O + H_2O + O_2$$

$$Cu_2O + H_2O_2 \rightarrow 2CuO + H_2O.$$

Cu(II) ions were said to constitute the active centers in the catalysts.

Zhuravlev and Kolosova (383) examined the relation between the distribution of thermal emf over the surface of cupric oxide and the catalytic activity of the oxide. Cupric oxide plates were prepared by compressing the powder at 400 kg/cm^2, followed by sintering at 580°. Measurements of thermal emf potentials over the surface were distributed as a normal Gaussian type in every case, though average deviations from the normal varied. Increased deviation from the normal corresponded to an increase in the catalytic activity towards the decomposition of hydrogen peroxide. Thus the activity was higher for samples with a flat distribution curve than for those with pointed distributions. It is concluded that since the probability of the development of a high-potential field between adjacent points of the surface must be greater for catalysts with flat emf distributions, the activity in those cases must be higher.

Zhuravlev and Kruzhelyuk (379) measured the emf of a cell containing hydrogen peroxide in which one electrode was a catalyst and the other electrode a non-catalytic conductor. When copper oxide (CuO) was used as one electrode over the range of 20 to 90°C, the emf passed through a maximum at 40°, and a minimum at 60°, beyond which it increased. The decrease in emf in the temperature region of 40 to 60° was accompanied by a small increase in decomposition rate, which indicates that there is some connection between the emf and the reaction taking place in the cell. The same results were obtained using zinc oxide on copper as the active electrode.

Hart and Weir (99) used thermistors to study rapid changes of catalytic behavior in the decomposition of 1 to 4 N H_2O_2 by copper oxide (Cu_2O). Temperature changes were measured by thermistors at the upstream and downstream surfaces of the catalyst in a flow apparatus. The temperature differences were extremely sensitive to changes in activity and provided a continuous measure of catalyst efficiency. Effects unobservable in a static system can be studied with this technique.

D'Ans and Mattner (45) reported that $Cu(OH)_2$ catalyzed the decomposition of alkaline hydrogen peroxide according to a first-order reaction. Based on the fact that magnesium hydroxide adsorbs traces of copper from solution, a series of experiments was carried out to determine the fixation by $Mg(OH)_2$ of copper dissolved in sodium hydroxide and the catalytic action of copper on hydrogen peroxide in 1 N NaOH solution.

Hart and Ross (100) studied the decomposition of hydrogen peroxide vapors by catalysts containing equimolar binary mixtures of CuO with Fe_2O_3, α-Al_2O_3, and Co_2O_3. Catalysts were heated to 600° as part of the preparation. A mixture of CuO and Fe_2O_3 was more active than either oxide separately. CuO - α-Al_2O_3 mixture was no more active than CuO alone. The high activity of Co_2O_3 prevented distinguishing effects due to CuO in CuO-Co_2O_3 mixtures.

The effect of various ions on the activation of CuO, sintered at 600°, in the decomposition of hydrogen peroxide was investigated by Krause and Wolski (154). Iron(III) was the best activator. Thorium(IV), manganese(II), zirconium(IV), cobalt(II), lead(II), lanthanum(III), and mercury(II) also activated CuO. Aluminum(III) was the poorest activator. Chromium(III) ions destroyed the catalytic activity of CuO completely. Combinations of the above ions with CuO were also investigated as catalysts. Cations of the first- and second-group elements were activators.

Krause and Wosinska (144) studied the activation and inhibition of copper hydroxide in the catalytic decomposition of hydrogen peroxide. Calcium, magnesium, and cobalt(III) hydroxides activated the catalysts when precipitated with $Cu(OH)_2$. Precipitation with beryllium, lead(II), and nickel(II) had no effect on the catalysts. Cadmium and zinc hydroxides were inhibitors. Calcium and magnesium ion do not appear to affect the catalysis, but cobalt(II) ion inhibits it.

Krause and others (163) studied the effect of various ions on the catalytic activity of Cu_2O in the decomposition of hydrogen peroxide at 37°C. In the case of single ion species on Cu_2O as a carrier, catalytic activity was increased by $[Fe(CN)_6]^{4-}$, WO_4^{2-}, Mn(II), Fe(III), and Cu(II). Catalytic activity was decreased by Al(III), Ni(II), Na^+ and NH_4^+. It was found that the activity of catalysts containing mixtures of the above ions depended on the order of addition of the ions (an effect known as catalytic mutation). Mutation was most pronounced for orders of addition Cu_2O-[$Fe(CN)_6$]$^{4-}$-Fe(III) and Cu_2O-Fe(III)-[$Fe(CN)_6$]$^{4-}$, and the six possible arrangements of Cu_2O, [$Fe(CN)_6$]$^{4-}$, Fe(III) and Cu(II). Catalytic mutation is observable when 0.01 gram of carrier is mixed with 1.0 mg of the given ions. Krause and Smoczkiewiczowa (155) evaluated the relative activities of 14 iron and copper minerals in the decomposition of hydrogen peroxide. Minerals included chalcocite, covelite I and II, chalcopyrite, bornite I and II, cuprite I and II, malachite, pyrites I and II, marcasite, hematite, and FeS. The action of the various metals in the minerals was selective and specific.

Köppen (132, 133) invented a means for determining waste waters from the poisoning effects of biological materials in the catalytic decomposition of hydrogen peroxide. Potassium cyanide shows marked effects and therefore illustrates the process. The rate of decomposition of 30 per cent H_2O_2 decreased by half in the presence of 0.000002 molar KCN. The effects of hardness, pH, and dissolved salts can be buffered by adding about 0.5 per cent of glycine to the solution. The method is general for any inhibitor by comparing the rates for a test substance and that of a blank. Köppen reported that low concentration of KCN accelerates rather than retards the decomposition rate for hydrogen peroxide by CuO, mineral MnO_2, and precipitated ferric oxyhydrate.

c. Other Copper Compounds

The effect of pyrolyzed tetraethyl lead on the catalytic activity of a copper chromite catalyst for decomposing hydrogen peroxide was determined by Zhabrova and others (376). The catalyst material was prepared by heating $CuCrO_4$, then removing excess CuO to yield a material corresponding closely to $CuCr_2O_4$. The friable, porous, crystalline catalyst was treated with tetraethyl lead in solution or as a vapor. The mixture was treated thermally or photochemically to decompose the lead compound. About 1/8 of the lead was taken up by the catalyst. Rate measurements for the decomposition of peroxide (1.7 molar) showed that the rate reached a maximum for a catalyst containing 3 per cent of PbO_2. The reaction was first-order. Although the rate was higher, there was practically no difference in activation energy (20 kcal/mole) between the promoted and unpromoted catalyst.

Wolfram (368) measured the effect of added silica gel on the catalytic activity of $FeCl_3$ (0.1 M) and $CuCl_2$ (0.05 M) solutions. Silica gel of 3.2 m^2/gram and 60-100 micron particle size was used. Adding gel doubled the activity of $CuCl_2$, but slightly decreased the activity of $FeCl_3$. Wolfram suggested that in the case of $CuCl_2$ very active intermediates such as H_2Cu_2O are formed. In the case of $FeCl_3$, active micelles that form are adsorbed and deactivated on silica gel.

Constable and Ohanian (36) studied the variation in activation energy for the decomposition of hydrogen peroxide on copper ferrocyanide. For 0.1 mg/cc of $Cu_2Fe(CN)_6$ and temperatures of 2-48.4°, the reaction followed the relation $\log k = 7.31 - (3788/T) + (121.3\ pH/T)$, where T is the absolute temperature. The apparent activation energy depended on pH according to $E_a = 4.57\ [3758 - 121.3\ pH]$ and varied from 17,080 cal at pH 1 to 11,540 cal at pH 10.

Constable (37) determined the catalytic activities of (1) copper ferrocyanide ($Cu_2[Fe(CN)_6]$, (2) Prussian blue, $Fe_4[Fe(CN)_6]_3$, and (3) Turnbull's blue, $Fe_3[Fe(CN)_6]_2$. In all three cases the reactions followed the relation $\log k = \log m + A - B/T + C(pH)/T$, where k is the unimolecular rate constant (time in minutes), m is the catalyst weight (mg), T is the absolute temperature and A, B, and C are constants, with these values for the above catalysts respectively (1) 5.612, 3738, 121.31 (2) 4.809, 3243, 98.6; and (3) 5.108, 3275, 53.6.

Erkut (55) reported that colloidal $Cu_2[Fe(CN)_6]$ is an excellent catalyst for decomposing hydrogen peroxide. Catalytic activity was depressed in the presence of salts of cobalt, nickel, cadmium, lead, mercury, and manganese, Copper salts had practically no effect. Ferric chloride and alkaline sulfide solutions increased the activity. Erkut also reported that $Fe_2[Fe(CN)_6]$ did not significantly catalyze peroxide decomposition, and that the ferrocyanides of nickel, cobalt, manganese, cadmium, lead and silver were inactive.

The effect of hydrogen-ion concentration on the catalytic activity of copper ferrocyanide for the decomposition of hydrogen peroxide was studied by Kandare and Constable (116). Finely divided $Cu_2[Fe(CN)_6]$ was investigated at 2-48°C and pH 2-10. Phosphate buffers were used above pH 5. The reaction was unimolecular, with a reaction rate constant related to pH and absolute temperature as follows: $\log k = a - (b/T) + c(pH)$, where a, b, and c are constants. For 0.1 mg/ml of $Cu_2[Fe(CN)_6]$, $a = 3.987$, $b = 2746$, and $c = 0.4039$.

Krause (143) reported that although Al(III) ions do not catalyze the decomposition of hydrogen peroxide, they do promote the decomposition by copper-iron ferrocyanide gels. Al(III) ions inhibit the catalytic activities of CuO, $Al(OH)_3$-$Cr(OH)_3$-$Fe(OH)_3$, $Cu(OH)_2$-$Pb(OH)_2$-$Fe(OH)_3$, $Mg(OH)_2$--$Cu(OH)_2$-$Fe(OH)_3$, and $Co_2[Fe(CN)_6]$ gels.

2. SILVER

a. Metallic Silver

Davis and McCormick (46) presented an analysis of design parameters in the use of samarium oxide-coated silver catalyst for decomposing high-strength hydrogen peroxide to oxygen and superheated steam. Various applications were discussed.

Shell Development Company (316) conducted a comprehensive program in 1957-58 to study decomposition catalysts for 90 per cent hydrogen peroxide. The effects of impurities, the mechanism of the reaction, effects of promoters, silver loss rates, and new catalysts were included.

Silver was the catalyst of principal concern. Detailed analysis of the kinetics of decomposition in catalyst beds of silver screens supported by stainless steel screens led to the conclusion that there are four reaction zones, each dominant for a range of bulk solution temperatures.

In the low temperature zone, the rate is probably chemically controlled. Rate varies with surface parameters, heat transfer (convection) to the solution is rapid, and the catalyst is only slightly above the temperature of the solution. On the basis of experiments, two plausible reaction mechanisms are proposed for the reaction in this zone.

In the nucleate boiling zone, liquid contacts the surface and therefore the catalyst temperature does not exceed the boiling point of the liquid.

At higher temperature the nucleate boiling zone changes to the film boiling zone. Liquid contact no longer transfers all the heat from the surface, a vapor zone forms, the rate of decomposition declines, and the catalyst surface temperature exceeds the boiling temperature of the liquid.

In the high temperature reaction zone, hydrogen peroxide decomposes rapidly without need for a catalyst. Homogeneous decomposition is rapid in both liquid and vapor, and relatively inert materials become active heterogeneous catalysts.

The effects of impurities in hydrogen peroxide on the decomposition by silver were studied in detail. This work was aimed at gaining a more complete understanding of how impurities modify the decomposition mechanism. It was concluded that quantitative correlation of the results was not possible because of the various results obtained under different conditions, and because of the complex behavior of mixed impurities. The large numbers of inorganic and organic impurities were classified as poisons, innocuous compounds, or promoters. Ammonium perfluorocaprylate was found to greatly promote the decomposition by silver in the low temperature reaction zone. The rate is accelerated by a factor of 50 at the concentration (0.075 gram/liter H_2O_2) of maximum activity. Process carbon concentrate behaved similarly, but to a lesser extent.

Among the other catalysts investigated, an alloy of 1 per cent gold and 99 per cent silver was found to be far superior to silver catalyst alone. Decomposition rates were higher and catalyst loss rates were lower. In practice this could mean faster start-ups at low temperatures and fewer clogging difficulties caused by catalyst deposition downstream. Other gold-silver alloys with up to 20 per cent of gold had activites comparable to that of silver. At higher gold contents, activity was much lower.

The behavior of a 1 per cent palladium-in-silver alloy relative to silver alone depended on the decomposition temperature. At low temperatures, the activity was about the same as that of silver. Activity declined at intermediate temperatures then increased markedly at 212°F. Very high rates of silver loss were apparent in this alloy. Increasing the palladium content to 10 per cent reduced the silver loss, but the activity was also much less.

Experiments with silver-platinum, silver-copper, and silver-copper-iridium alloys indicated that activities were not high enough for practical applications in propulsion. The fact that copper alloys accelerated the decomposition rate led to the suggestion that copper ion in solution could provide higher decomposition rates by homogeneous decomposition at high temperatures.

A report on the state of the art of catalyst packs for use in rocket applications of 98 per cent hydrogen peroxide discussed some of the work carried out by FMC Corporation before 1962 (73). Some of the problems of improving catalyst performance and design were also covered.

A program carried out in 1958 by FMC Corporation (73) was designed specifically to develop a satisfactory catalyst for rocket applications of 98 per cent hydrogen peroxide. An improved approach was to put a few silver screens above a section of Monel screens in the catalyst pack. Presumably the silver screens would start the decomposition but escape the high temperatures produced by complete decomposition. Monel screens would then complete the decomposition. The partial success of the system led to the development of a gas generator employing it. The average starting transient of 1/2 second (room temperature feed) was considered a drawback for some of the other applications of interest. Adding fine-mesh plated silver screens above the pure silver screens already in the catalyst pack reduced starting transients, but erosion was severe enough to remove the plating within three starts.

A second approach was to use platinum-plated steel screens alternated with Monel screens in the lower part of the catalyst pack. Starting transients were still not small enough and the Monel screens were severely oxidized.

Another approach was to replace the Monel screens with nickel screens. This system operated satisfactorily for long periods but starting transients were impractically long.

A further approach was to use cobalt-plated iron or nickel screens in place of the Monel screen. In decomposition trials using packs containing

16 silver screens at the inlet end, cobalt was completely eroded from the iron screens. Starting transients were short, but increased with successive starts. Cobalt-plated nickel screens were interspersed with oxidized nickel screens in order to test the possibility that electrochemical interaction would increase the stability. No silver screens were used in initial tests. Good performance and small starting transients resulted, but again the transients increased with successive starts. When the 16 silver screens were used at the inlet section of this catalyst pack, starting transients changed very little in successive starts.

In 1957 FMC Corporation (73) conducted a program on the development of a gas generator. As part of that program a number of different catalysts, including copper-plated nickel, nickel, Monel, silver, and silver-plated brass, were evaluated for decomposing 90 per cent hydrogen peroxide. With the exception of silver alone, the silver-plated brass catalyst was the most active. Repeated tests, however, caused the plating to flake off and the activity to decline. It was suggested that improved plating techniques would improve catalyst performance.

Under a Navy contract in 1953, FMC Corporation (61) investigated various catalysts in an attempt to prepare an effective and long-lived catalyst for application in the Alton cycle power plant. Of the formulations studied, including pellet-type catalysts, fine silver was found to be the best. It could be further activated by treatment with a 2 per cent solution of samarium nitrate, followed by heating at 840°F to give a coating of the oxide. Corregated silver spirals were found to be the best forms of the catalyst in the application.

Laboratory and large scale tests of activities of several different argent ($KMnO_4$-coated silver) and irium (cobalt-plated brass) screens supplied by the Naval Underwater Ordnance Station were carried out by FMC Corporation in 1956-57 (67). Laboratory tests indicated that irium screens with rough surfaces were the most active catalysts. Smooth argent was closer in activity to rough irium screens than were smooth irium screens. Full-scale tests using large quantities of catalyst did not give the same results as did the laboratory data.

Under a NASA program, Runckel and others (275) at the Langley Research Center investigated the effect of variation in screen composition and arrangement on the performance of a 90- and 98-per cent concentration hydrogen peroxide catalyst beds for rocket propulsion. Conventioncal catalyst beds with certain modifications were found to be suitable for use with a 98 per cent concentration hydrogen peroxide. Up to 25 silver screens were used without excessive melting of silver provided they were located at the upstream end of the bed. The use of 40-mesh silver screens afforded better starting response characteristics than 20-mesh screens. The use of 2 per cent concentration samarium nitrate, in lieu of 10 per cent, was found to be adequate for treatment of silver screens under certain conditions.

Bed life was sufficient for reaction-control-rocket missions. The tests covered environmental temperatures from 350°F to 820°F and a chamber pressure range from 100 to 315 pounds per square inch absolute.

Runckel and others (302) investigated silver catalyst beds for use with 98 per cent hydrogen peroxide in reaction-control type rocket motors. Seven types of catalyst beds of lengths from 1.38 to 1.50 inches, containing 14 to 75 active silver screens, packed at a pressure of 1000-1500 lb/sq in. were investigated at 35-85°F. Catalyst beds for 98 per cent hydrogen peroxide with performance about the same as for 90 per cent peroxide were obtained. Melting was not serious when 25 silver screens were used. The 40-mesh screens were better than 20-mesh screens. Treatment of the silver screens with 2-per cent $Sm(NO_3)_2$ solutions gave better performance than treatment with concentration of 10 per cent. The best results were obtained with the screens arranged as follows: 2 pieces of 20-mesh, 0.014 inch, stainless-steel screen, 1 antichannel baffle, 25 pieces of 40-mesh 0.010-inch silver screens treated with 2 per cent $Sm(NO_3)_2$, 1 antichannel baffle, and 60 pieces of 20-mesh 0.015-inch nickel screen at a packing pressure of 4000 lb/sq in.

Cooper and others (3) conducted an investigation of various catalyst materials that might be useful for full-scale propulsion units in the decomposition of concentrated hydrogen peroxide. Silver plated on copper gauze was found to be the outstanding catalyst. A manganese alloy prepared in the form of scrolled strips showed some promise, but a cobalt-plated gauze and copper-lead mixture were not effective catalysts.

In chamber tests using silver-plated copper screens it was found that an optimum thickness of 0.004 inch of silver deposited on 16-to 20-mesh screens gave good results. Quick starts were achieved by putting some anodized screens in the top of the bed. Good starts resulted at a flow rate of 60 pounds per square inch. Catalyst life was 3 to 4 hours, after which silver was stripped from the support screen.

This investigation included an analysis of an involved concept of ebullition temperature in the decomposition of H_2O_2 vapor by silver screens.

A 1959 U.S. patent to De Havilland Engine Co. (97) relates to metal-catalyst packs employing silver catalyst for use in rocket motors. Several layers of transversely corrugated thin strips containing a catalyst, at least on the surface, are separated by thin strips of the same material. The strips are arranged edge-on to the fluid flow.

Jacob (114) obtained an East German patent on the use of fuel-air-hydrogen peroxide mixtures ignited by silver or platinum wire as a means for starting gas turbines. Hydrogen peroxide concentrations above 70 per cent are used.

Saunders (308) obtained a U.S. patent in 1949 on a silver-plated activator for decomposing hydrogen peroxide in underwater propulsion systems. A steel screen is first electroplated with silver by a process that yields a porous surface. The screen is then coated with a metal permanganate solution and dried in an oven at 100-110°.

A 1957 U.S. patent assigned to D. Napier and Sons (44) relates to a catalyst suitable for decomposing high-strength hydrogen peroxide in rocket motors. A thin layer of molten catalytic metal is sprayed on a perforated support. For rocket motors silver supported by a copper gauze is preferred. Start-up times are shortened by anodizing in a bath of sodium carbonate.

In a 1964 patent assigned to Bell Aerospace Corp., Sill (324) described a thrust chamber catalyst structure useful for propulsion units employing decomposition of 90 per cent hydrogen peroxide. The catalytic bed itself consists of porous nickel plated with a 99:1 silver-gold alloy having open surfaces. The alloy is plated in wrinkled surface form.

Baumgartner and others (13) carried out extensive quantitative studies on the decomposition of 90 per cent hydrogen peroxide on silver surfaces at both low and high temperatures. They determined rates of hydrogen peroxide decomposition and silver mass loss as a function of bulk solution temperature, hydrogen peroxide concentration, and pressure. Two distinct regions exist, corresponding to an abrupt change in mechanism. In the low temperature region, the rate is chemically controlled; in the high temperature region, the rate is limited by heat transfer.

At low temperatures, hydrogen peroxide decomposes at a rate proportional to catalyst surface area and peroxide concentration. The rate of silver mass loss is proportional to the catalyst area and the square of the peroxide concentration. Silver (I) ions and hydroxide ions present in hydrogen peroxide solution inhibit the rate of silver loss. In this region, reaction rate is chemically controlled: experimental evidence indicates a chain mechanism. The abrupt transition from a lower to a higher rate is strongly influenced by the rate of decomposition at low temperature.

At high temperatures, the decomposition rate is limited by heat transfer. Evidence for this is that at constant temperature of the bulk solution, both the catalyst surface temperature and the decomposition rate increase with increasing pressure in a way expected for a heat-transfer-limited process. Increasing the bulk solution temperature at constant pressure increases slowly the catalyst surface temperature, but decreases slowly the decomposition rate and the silver loss rate.

Sutton (298) reported that the rate of decomposition of hydrogen peroxide on a smooth silver surface at 0°C rises linearly with concentration of peroxide up to about 50-60 percent w/w and then becomes independent of concentration up to about 70-80 per cent w/w. At still higher concentrations the rate rises again. It is tentatively concluded that decomposition occurs by a strictly heterogeneous mechanism at the metal/liquid interface in concentrations up to about 70-80 per cent, but that a free-radical chain mechanism is superimposed above this concentration.

According to Hazlett and Pilato (276) the decomposition of liquid H_2O_2 on a silver catalyst is complicated by the existence of a vapor barrier at high peroxide concentrations. The barrier arises because localized decomposition at the catalyst surface raises the temperature of the silver far above the boiling point of the peroxide, and liquid approaching it is vaporized. Passing water through the catalyst can lower its temperature and suppress the vapor barrier. Under these conditions the decomposition is changed and approaches the expected behavior. The film barrier is also diminished by increasing the pressure. This affords a greatly altered decomposition curve and supports the thesis that the vapor barrier masks the chemical kinetics of the decomposition. Results with the pressure system indicated that the film barrier is not important in a rocket motor. As the pressure in the reaction chamber is increased, the silver loss is decreased.

In a program conducted by FMC Corporation (68), silver metal was reacted with both dilute and concentrated H_2O_2 semi-adiabatically and at atmospheric pressure. A method was developed for preparing silver surfaces which were reproducible in their reactivity toward both dilute and concentrated H_2O_2, as evidenced by the rates of oxygen evolution measured in the static-type reaction systems. The pure metal was found to be more reactive to H_2O_2 than metal which had been either tarnished by exposure to the atmosphere or given $Sm(NO_3)_3$ treatment. In the case of tarnishing, the initial reaction rate is believed to be controlled by the diffusion of H_2O_2 through a layer of combined oxygen on the silver surface.

The $Sm(NO_3)_3$-treated metal afforded a "catalyst" which was not reproducible in activity towards H_2O_2. The nature of the coating produced by such treatment is discussed. The phenomenon of $Sm(NO_3)_3$ "activation" of pure silver surfaces in the decomposition of concentrated H_2O_2 was attributed to a decrease in the degree of vapor binding at the metal surface. A detailed mechanism for this reduced vapor binding was offered. The merits of a heterogeneous surface, composed of active and inactive centers, are discussed with respect to increased efficiency of decomposition of concentrated hydrogen peroxide.

Results indicated that, at room temperature and atmospheric pressure, the rate limiting process in the decomposition of concentrated H_2O_2 is the migration of O_2 and water vapor bubbles from the "catalyst" surface. For dilute H_2O_2 of high purity, the primary rate controlling process was considered to be oxidation of silver metal.

The reaction between pure silver and 5 per cent H_2O_2 followed first order kinetics very closely; $Sm(NO_3)_3$-treated silver, however, reacted with the same H_2O_2 to give very nearly a zero order reaction. The latter reaction therefore appeared to be controlled by the rate of diffusion through the coating formed on the metal surface as a result of the treatment.

The isothermal reaction between silver metal and 90 per cent H_2O_2 at 20°C and atmospheric pressure was examined in detail by FMC Corporation (69). The reaction was followed by measuring the rate of O_2 evolution and the rate of dissolution of silver. Calculations were made in such a way as to be independent of the silver surface area. The primary reaction was considered to be oxidation of the silver; results were consistent with the idea that this process is followed by free radical chain reactions, which are responsible for the major portion of the H_2O_2 decomposition, the mole ratio of O_2 evolved to silver dissolved was found to be in the order of 10^2 in the decomposition of 90 per cent H_2O_2. Vapor phase decomposition, and thermal decomposition of peroxide vapors, played a negligible role in the reaction. The simultaneous rate controlling factors were considered to be the oxidation of silver and the concentration of adsorbed free radicals, with the possible rate limiting process being the migration of O_2 bubbles from the reaction surface.

In order to study the effect of trace impurities upon the reaction, the following compounds were added singly to 90 per cent H_2O_2 (unhydrated formulas given): Na_2SO_4, Na_3PO_4, Na_2SnO_3, Na_2SiO_3, NaCl, KF, NaCN, $NaNO_3$, $CuSO_4$, $Al_2(SO_4)_3$, $(NH_4)_2SO_4$, KOH, H_2SO_4, and $AgNO_3$. In no case was there a promotion of the decomposition. The main depressants, Na_3PO_4, Na_2SnO_3, $Al_2(SO_4)_3$ and $AgNO_3$, all had the same general effect upon the decomposition, i.e., the rate dropped sharply and then leveled off as the impurity concentration increased. In no case were impurities visually observed to build up on the silver surface. This fact, coupled with measurements of the ratio O_2/Ag, led to the conclusion that trace impurities that lower the decomposition rate under the experimental conditions do so either by capturing free radicals or by affecting the adsorption of free radicals at the reaction surface.

It is concluded that if the above conclusions are correct, silver metal cannot be considered a true catalyst in the H_2O_2 decomposition. General requirements for a solid reagent for H_2O_2 decomposition, based upon the silver mechanism study, are discussed.

Bagg (7) measured the effect of pH and concentration on the rate of decomposition of H_2O_2 by a single crystal of silver. Reaction order varied with concentration for various concentrations of up to 1.8 molar H_2O_2 and 1.0 normal NaOH. Ag_2O was identified on silver crystals after catalytic decomposition of H_2O_2 and silver(I) ions were found in the solution. The first order reaction at 0.16 molar H_2O_2 and 1.0 normal NaOH was postulated to proceed as follows:

$$(1)\quad 2Ag + HO_2^- \rightarrow Ag_2O + OH^-$$

$$(2)\quad Ag_2O + HO_2^- \rightarrow 2Ag + OH^- + O_2$$

The kinetics indicated that at a concentration of 1.8 M H_2O_2 the silver surface is saturated with reacting species.

Maggs and Sutton (239, 240) studied the rate of silver dissolution and the resultant pH changes in concentrated hydrogen peroxide.

The solubility of silver in 15 to 80-per cent hydrogen peroxide was determined by direct means and by evaluating the $[Ag^+]\,[HO_2^-]$ ionic product needed to start rapid catalysis (239). Solubility was constant from -11 to 25°C. Dissolution rate of silver in hydrogen peroxide at strengths over 50 per cent were diffusion controlled. In solutions of H_2O_2 containing Ag(I) ion, rapid catalysis was initiated when the solubility product of AgO_2H was reached. If NaCl was present, AgCl precipitated in the diffusion layer. Both the diffusion of Ag(I) ion from the silver surface and of chloride ion to the silver surface were considered in the study of concentration gradients.

It was established that Ag^+ and HO_2^- formed when silver dissolved in 20 to 80 per cent hydrogen peroxide (240). Electronic conductivity measurements revealed that pH increased proportionally with the amount of silver dissolved, giving higher values at the two extremes of concentration than at intermediate concentrations. The acceleration of decomposition rate in H_2O_2 saturated with silver ions was attributed to the continuous precipitation of silver particles. As further decomposition decreased the H_2O_2 concentration, Ag^+ and HO_2^- were removed from solution in accordance with the limiting ionic product.

Wentworth (253) found that in the decomposition of hydrogen peroxide by silver and silver salts, no catalysis occurs until the solubility product of $Ag(OH)_2$ is exceeded in the solution. When the solubility product is exceeded, divalent silver can be reduced. At a hydroxyl concentration sufficient to initiate catalysis, the silver is present in the colloidal state, the decomposition is homogeneous, and the reaction is first order. When the silver metal is precipitated the reaction is zero order. The evidence indicated that the catalysis proceeds through an oxidation-reduction mechanism consistent with the following reactions:

$$Ag + H_2O_2 + 2H^+ \rightarrow Ag^{2+} + 2H_2O$$

$$Ag^{2+} + H_2O \rightarrow AgO + 2H^+$$

$$AgO + H_2O_2 \rightarrow Ag + H_2O + O_2 .$$

Bliznakov and Peshev (21, 23) measured the effect of heating silver catalysts on the decomposition of hydrogen peroxide. Polished 99.95 per cent silver plates heated in air for various times and temperatures up to 920°C provided various decomposition rates. Heating at 750° for up to two minutes gave very high catalytic activity. Continued heating decreased the activity sharply; a minimum was reached at five hours, after which the activity increased slowly to a constant value after ten hours. Changes in activity were attributed to silver oxide formation on the catalyst surface. Heating the catalyst at varied temperatures gave a maximum activity at about 500°.

Heating silver in vacuum at 180° gave a maximum first-order rate plot for a heating period of nine hours. Bliznakov (23) concluded that chemisorbed oxygen is necessary for the decomposition.

Krause and Hermannówna (168) noted that the catalytic activity of silver increases if the catalyst is immersed in fresh hydrogen peroxide at 37°. The result is attributed to formation of colloidal silver through intermediates such as Ag_2O or silver peroxide.

Cota and others (43) found that among 14 catalysts used to decompose H_2O_2 in solutions containing K_2CO_3 and KOH, silver gave the highest decomposition rate. Silver was more active than Pt black, Pd black, or $Co_{1.1}Fe_{0.9}O_4$, which were the other most active catalysts.

Sviridov and others (336, 337, 338) investigated the catalytic effects of Ag-$Ag_2C_2O_4$ mixtures prepared by thermal and photochemical decomposition of $Ag_2C_2O_4$. Activity depended in a complex manner on the quantity of silver in the mixture, the degree of crystallinity, and the crystal structure. Thermally decomposed $Ag_2C_2O_4$ gave maximum activity for silver content of 35 per cent. Activity increases with time of exposure when pure $Ag_2C_2O_4$ was irradiated with ultraviolet light. Irradiation with gamma rays had little effect on activity.

The relative catalytic activities of "atomic" silver and crystalline silver were determined by Krylova and Kobozev (205). "Atomic" silver was in the form of a dispersion produced by the chemical reduction of silver salts. Crystalline silver was prepared by photoreduction of silver halides. The crystalline material was inactive whereas the dispersion was very active.

Kulskiy and others (211) studied the effect of silver on the oxidation of indigo carmine by hydrogen peroxide.

b. Silver Alloys

Mixtures of metals with silver as catalysts for decomposing 87.2 per cent hydrogen peroxide were investigated in detail by FMC Corporation (73).

The objective of this work was to relate the enhancement of silver catalyst activity by additives to the thermal conductivity and the mode of heat transfer during the reaction. Additives included platinum, gold, silicon carbide, and stainless steel.

Silver-gold and silver-platinum alloys were found to have a higher activity than silver metal, samarium nitrate-treated silver, or silver-silica cermets.

Silver surface area changes could not account for the increased activity. In fact, a negative correlation was found. One possibility based on the heat transfer theory is that "the inactive material furnishes a pathway through which reaction heat can be transferred to the liquid H_2O_2, thus cooling the silver. This cooling, to a point, could increase the reaction rate due to a reduction in vapor binding over the silver site."

The enhancement of silver catalytic activity by gold is offset by the tendency of gold to alloy with silver. The use of smaller proportions of gold makes it possible to prepare a catalyst having a continuous phase of silver flocked with Ag-Au alloy. A mixture containing 10.7 per cent of gold was pressed into a pellet and examined under a microscope. Distinct areas of two different materials were observed. Heating to 1000°C did not alter the structure. Catalytic activity toward 87 per cent H_2O_2 was high and remained high. Higher concentration of gold tended to form continuous phase alloys with lower activity.

A silver-platinum catalyst gave extremely high activity, which, however, dropped markedly after heating the catalyst to 1000°C. Considerable shrinkage occurred at 970°C. Flocked catalysts similar to those observed for gold and silver are suggested as possible with silver-platinum mixtures, which apparently do not alloy below 970°C.

Silicon carbide additive gave the highest start-up activity. This fact appears to be attributable to the low heat conductivity, but this cannot be concluded unequivocally.

Stainless steel additive gave a higher specific activity than did silicon carbide

As part of a program conducted by FMC Corporation (72) under U.S. Navy Contract NOas 58-689-c, catalytic decomposition of hydrogen peroxide vapor, and vapor binding in mixed catalysts were studied.

Hydrogen peroxide vapors were decomposed at about 200°C over various catalyst materials with the following order of activities: silver > Monel > platinum > stainless steel (316) > Pyrex > Teflon. The exceptional activity of Monel in the series is explained by a proposed electrochemical effect. At the high temperature of decomposition, the copper-nickel alloys are presumed to exhibit a cell effect at the alloy interfaces, yielding increased electron densities and exceptional activity at those points.

A second phase of this program involved a study of mixed catalysts designed to further test a theory of vapor binding. According to the theory, rapid decomposition of hydrogen peroxide at a silver surface at high temperatures results in a vapor barrier that limits the rate at which fresh peroxide can migrate to the surface. Catalyst activity of silver coated with samarium oxide or other materials that modify the thermal conductivity at the surface is enhanced because the effect of the vapor barrier is diminished. Temperature build-up at reactive silver sites is curtailed by heat withdrawal to the inert additive. Previously it had been shown that the behavior of silver-silica, silver-silicon carbide, silver-copper, and silver-gold mixed catalysts was apparently in accord with the theory.

To further examine the theory, mixed catalysts of silver and gold pellets were used to decompose hydrogen peroxide (90 per cent, and diluted). In general, the experimental results confirmed the hypothesis, at least for some cases. Activity varied with gold content in an irregular manner, and peak activities were greater than could be accounted for by changes in surface area. These data constitute additional evidence that the theory is correct but they are inconclusive because of the problems encountered in trying to achieve reproducible catalyst surface areas.

Brief experiments were conducted as an attempt to confirm the existence of a "catalysis point" for silver in the decomposition of 90 per cent hydrogen peroxide. Maggs and Sutton proposed that silver decomposes peroxide by conversion to a silver compound (such as AgOOH). This initial slow decomposition proceeds until the solubility product of the dissolved compound is exceeded, at which point the unstable compound precipitates and decomposes, releasing silver particles. Contact with the particles then greatly accelerates the decomposition. This is known as the "catalysis point."

Experiments to test the theory involved placing a silver rod in 90 per cent H_2O_2 at 16°C, preventing the temperature from rising above 20°C until the reaction became very vigorous (catalysis point). In repeated tests of duration up to three hours, at various silver losses and H_2O_2 concentration decreases to 9 per cent, the rate immediately declined when the silver rod was removed from the reaction mixture. Had a catalysis point been reached, the reaction would be expected to be sustained, at least for brief periods, after removal of the rods. Thus no catalysis point was observed.

In 1963, Walter Kidde and Company (358) studied the anomalous behavior of silver and silver-nickel alloys as catalysts in the decomposition of dilute and concentrated H_2O_2. In dilute H_2O_2, decomposition rate was found to increase with silver content of a silver-nickel alloy catalyst, reaching a maximum at 100 per cent silver. In concentrated H_2O_2, the behavior was reversed: the highest decomposition rate was obtained for a catalyst of low silver content. A "gas envelope" hypothesis is developed to explain the anomalous behavior, and extended to show how mixed compositions could be used to sustain peak decomposition rates during repeated exposures to H_2O_2, and how to achieve sustained activity.

Catalytic activity was also shown to depend upon the sintering steps in preparing silver-nickel catalysts from $AgNO_3$ and $Ni(NO_3)_2$ mixtures. Slow heating is essential for reducing scatter in decomposition data. Rapid heating leads to surface eruptions and data scatter.

c. Silver and Metal-Oxide Mixed Catalysts

In a program conducted by FMC Corporation (70), cermet catalysts, which are composed of inert materials dispersed in a continuous phase of silver metal, showed significantly higher activity in the decomposition of concentrated hydrogen peroxide than that of silver metal alone.

The effect of discrete particles of catalytically inactive material, uniformly dispersed in a continuous phase of silver metal, upon the phenomenon of vapor binding at silver surfaces in contact with concentrated hydrogen peroxide, was investigated. A method for producing the desired surface was developed to yield a cermet, in which inactive material is uniformly distributed throughout the body of the "catalyst." The behavior of such cermets toward concentrated hydrogen peroxide was followed by measuring oxygen evolution rates of the semi-adiabatic, atmospheric pressure reactions.

The cermets, prepared in pellet form, contained silica, silicon carbide, or copper oxide as the inert material. The available silver areas of cermet surfaces and the roughness factors were estimated by reaction with dilute hydrogen peroxide. The start-up activity of all cermets with concentrated H_2O_2 was higher than that of pure silver, and markedly higher than that shown by $Sm(NO_3)_3$ treated silver surfaces.

The apparent specific activities (reactivity with concentrated H_2O_2 per unit geometric area of surface) attained with cermets was as high as 25 per cent of the value found for consolidated silver metal. Reactivity with concentrated peroxide per unit apparent silver surface area was as high as twenty times that of consolidated silver.

In the silica series, the specific activity of the 9.1 per cent SiO_2 cermet was higher than those containing 7.4 or 11.5 per cent SiO_2, which indicated a maximum somewhere in the interval. The 9.1 per cent SiO_2 cermets combined the merits of high activity and constancy of activity with repeated reaction.

The behavior of the surfaces with repeated reaction, the effect of high temperatures upon reactive surfaces, and the effect of roughness, are discussed. Silicon carbide and silica cermets maintained their shape, except for local silver flow, at 1000°C, under no stress. The CuO pellets, however, melted at 960°C (melting point of silver) or below.

The density of the 9.1 per cent SiO_2 cermet, found to be 5.05 gm/cc (less than half that of silver metal), shows the porous nature of the material. Compression of cermets resulted (with one exception) in a decrease in specific activity.

A $Sm(NO_3)_3$ treated silver pellet was studied for comparison. Some similarities in the behavior of the latter with that of cermets tend to confirm that $Sm(NO_3)_3$ activation is a physical and not a chemical phenomenon.

Between 1957 and 1961, a series of patents on hydrogen peroxide decomposition catalysts employing silver as the active material was assigned to D. Napier and Son, Ltd., England.

Lane and Ramsden (214) obtained a British patent for a catalytic bed employing a silver-copper catalyst suitable for rocket propulsion and similar devices. The main decomposition chamber is filled with pellets consisting of, or coated with, silver mixed with small amounts of copper. A catalyst of the same composition is stacked in gauze form at the outlet where hydrogen peroxide is decomposed into steam and oxygen. Decomposition begins in the low-flow-rate region of the main chamber and is completed at the high-flow-rate region of the outlet.

Lane and Strickland (215) obtained a British patent covering a catalyst for instantaneous decomposition of hydrogen peroxide, thus eliminating the delay of start-up. Copper gauze is abraded with crushed grit, then degreased. Silver is hot sprayed on the gauze, and this is followed by anodizing in an alkaline carbonate solution. The gauze is washed, placed in 10-per cent NH_4OH for 24 hours, and finally washed with distilled water and dried. Lane and others (217) also patented a process for preparing a metallic silver catalyst in a form suitable for use in the catalyst bed chamber described in the earlier patent (215).

Lane (216) obtained a German patent on sintered compositions containing powdered silver and copper oxide useful for decomposing hydrogen peroxide. The preferred catalyst contained 87 per cent by weight of silver.

Laxton (219) obtained a U.S. patent covering a catalyst made by sintering 80 to 90 per cent of silver with 5 to 20 per cent of copper oxide. No eutectic forms in the sintering step, in contrast to the case where metallic copper is used. The pellets can be heat treated nearly to the melting point of silver.

Laxton patented in Britain (220) and Germany (218) a catalyst, based on silver, that can be prepared readily in tablet form. Active silver is mixed with inert ingredients, such as Al_2O_3, SiO_2, or SiC (all of which are stable up to the melting point of silver), then pelleted. A suitable catalyst contains 75 per cent of silver and 25 per cent of inert material.

Beginning in 1958, Rocketdyne (299) carried out an extensive Navy-sponsored program on the properties and applications of hydrogen peroxide. One task of the program comprised the development of catalysts for sustained decomposition of 90 per cent peroxide and for use with 98 per cent peroxide.

A basic catalyst formulation consisted of a mixture of silver, manganese dioxide, and aluminum oxide. As a suspension of the powders in oil and slow drying lacquers, the catalyst mixture was applied as a coating on stainless steel screens. This catalyst was thoroughly tested to compare the activities of modified formulations.

It was found that adding gold to the basic catalyst promoted the activity up to a maximum for a gold concentration of about 2.5 per cent. Adding glass to the formulation increased the adherence of the coating.

Catalyst activity declined with increasing sintering temperatures in the preparation. However, even for a sintering temperature of 1950°F the catalyst gave a decomposition rate 33 per cent higher than that of conventional silver-plated screen catalysts.

Particle size of 38 to 74 microns had no effect on catalytic activity, but particle size below 38 microns increased the decomposition rate as much as 48 per cent.

Sintering the catalyst at various temperatures after samarium oxide activation had no discernible effect. Also, substituting samarium oxide for part of the aluminum oxide in the basic formulation eliminated the need for final activation. Using 40 to 60 per cent of samarium oxide in place of aluminum oxide improved activity and the adherence of the coating.

The catalyst formulations developed under this program were demonstrated to maintain their activity in repeated tests with 90 and 98 per cent hydrogen peroxide.

d. Promoters, Adsorbed-ion Catalysts, and Poisons

FMC Corporation (73) investigated in 1958-59 the effect of added wetting agents on the catalytic decomposition of 90 per cent hydrogen peroxide at 0°C. FC-126, Triton X-100, and Deceresol OT agents produced a 25-fold increase in the rate of decomposition by silver. The lowest concentration of agent at which promotion occurred was 30 to 40 mg/liter. Optimum concentration was about 50 mg/liter; at this concentration there was no appreciable difference in behavior among the wetting agents. Major emphasis in this program was given to determination of impact sensitivities and compatability and storage stability using concentrations of wetting agents up to 270 mg/liter of H_2O_2.

Shell Internationale Research Maatschappij N. V. (319) patented the use of alcohol oxidation products as promoters for the decomposition of hydrogen peroxide by silver. The products are usually obtained as residues from the distillation of the partially oxidized alcoholic mixture. In a typical case, hydrogen peroxide (60°) containing 400 mg residue/liter is decomposed in a reactor at a flow rate of 45 grams/minute on a silver catalyst to give oxygen at a rate of 4.15 liter/min/sq cm catalyst, compared to 2.62 liter/min/sq cm under the same condition without the promoter.

A 1964 patent to Shell Oil Co. (296) relates to the use of ammonium parfluorocaprylate as a promoter for decomposing concentrated hydrogen peroxide with silver. At 0°C a silver catalyst decomposed 90 per cent peroxide containing 0.075 gram of promoter per liter at a rate 50 times faster than in the absence of the promoter.

In a 1964 patent assigned to Shell Oil Co., Baumgartner and Roberts (14) described the use of certain promoters that increase the rate of catalytic decomposition of 30 to 100 per cent hydrogen peroxide. Promoters, such as the residue containing organic peroxides resulting from the manufacture of hydrogen peroxide, particularly C_{3-5} alcohols, aldehydes, and ketones, are added in concentration of 100 to 750 mg/liter of H_2O_2. The promoters allow start-up temperatures as low as the freezing point of the hydrogen peroxide and they reduce catalyst loss as much as 50 per cent.

A 1963 Shell Oil Co. British patent (53) covers the use of organic peroxide or hydroperoxide residues as promoters for the silver-catalyzed decomposition of hydrogen peroxide. The residues are the bottom product obtained during the purification by distillation of hydrogen peroxide manufactured by the use of aldehydes and ketones, such as alkylanthraquinone or primary and secondary alcohols. Residues can be added to purified or electrolytic hydrogen peroxide. Preferred concentrations range from 100 to 750 mg of carbon in the residue per liter of hydrogen peroxide.

Ordinarily, silver phosphate does not catalyze the decomposition of hydrogen peroxide. Krause and Zielinski (162) found, however, that Cu(I), Cr(III), Mn(II), and Co(II) ions activated the catalyst at 37°. $Fe(CN)_6^{4-}$ in the presence of Ag_3PO_4 acted as a stabilizer for hydrogen peroxide. The highest activity was shown by Ag_3PO_4 with Al(III), Cu(II), and $Fe(CN)_6^{4-}$, added in that order to the hydrogen peroxide solution in contact with Ag_3PO_4.

Krause and Domka (200) reported that the activity of Ag(I) ions was greatly increased when adsorbed on a mixture of $Al(OH)_3$ and $Co(OH)_2$. An effect was observed at concentrations as low as 10^{-10} gram Ag at a dilution of 1:6 x 10^{-11}. Ag(I) ions were also catalytically active when adsorbed on alkaline earth carbonates.

Nikolaev (281) found that ions of silver, cobalt, and nickel adsorbed on barium sulfate and metastannic acid led to inactivation of the ions towards the decomposition of hydrogen peroxide.

Kolarov (129) examined the effect of a series of salts dissolved in hydrogen peroxide on the catalytic activities of MnO_2, charcoal, and silver powder. Salts included NaOAc, Na_2SO_4, $NaNO_3$, NaCl, NaBr. KOAc, K_2SO_4, KNO_3, KCl, KBr, and sodium and potassium tartrates. In general the effects of the anions corresponded to the Hoffmeister series (i.e., in decreasing order of their salting-out effect on hydrophilic solutions or in the lowering of gelation temperature: e.g., $SCN^- > I^- > Br^- > NO_3^- > ClO_3^- > Cl^- > > C_2H_3O_2^- > SO_4^=$). Acetate ion on charcoal was an exception because of strong adsorption. Silver powder lost its activity in the presence of Cl^- and Br^-. Acetate caused a marked decline. Ultraviolet irradiation of the silver and MnO_2 reduced activity in a manner similar to rapid aging. Irradiation increased the activity of charcoal, evidently as a result of superficial oxidation by O_3, ozone is produced in the ultraviolet and can give rise to active centers.

In a succeeding study, Kolarov (130) related the decline in activity of silver and MnO_2 to the solubility products of AgCl, AgCNS, and AgBr, and to limiting anion concentrations, beyond which decomposition ceases. The effect of cations was also investigated. The order of retarding action in the case of silver was $K < Ba < Ca < Mg$ for 0.16 and 0.32 per cent hydrogen peroxide. The rate increased markedly at pH 4-5 and reached a maximum at pH 11.7. The corresponding cation order for MnO_2 was $K < Mg < Ba = Ca$; activity reached a maximum at pH 0.5, a minimum at 4.2, and finally increased up to pH 10 and beyond.

Lazarov and others (221) studied the effect of chloride ion on decomposition of hydrogen peroxide by silver powder. In the process, Cl^- replaces OH^- formed at the silver surface during decomposition. The rate of chemisorption of Cl^- increases with H_2O_2 concentration up to 0.38 N without effect on the final equilibrium. Adsorption of Cl^- increases at high temperature, and lower pH, but total adsorption is independent of temperature and is 1.41×10^{-4} gram-ions per gram of adsorbent in the case of 0.38 N H_2O_2 and 0.013 N KCl solution. Calculation showed that Cl^- does not form a monolayer, but penetrates the adsorbent.

Similar results were obtained with bromide, iodide, and sulfate ions (222). The process is in accord with specific adsorption. During decomposition, the ions block active sites of the catalyst. This leads to an increase in pH and consequent acceleration of the rate of decomposition of peroxide. A curve of activity against ion concentration passes through a characteristic maximum.

Bliznakov and Lazarov (22) measured the effect of KCl dissolved in a 0.5 per cent solution of H_2O_2 on the rate of catalytic decomposition of H_2O_2 by silver. Small concentrations of KCl markedly promoted the reaction rate, but high concentrations decreased the rate to a small value. At high pH the effect of the chloride is to poison the catalyst. Bliznakov concludes that the concentration of chloride affects the pH of tne medium and therefore the adsorption processes on the silver surface. A kinetic expression relating chloride concentration to the hydrogen peroxide decomposition rate constant is derived and a consistent mechanism proposed.

Krause and Olejnik (139) found that the decomposition of hydrogen peroxide by Ag_2O at 37° was retarded by H_2CO_3, HCl, H_2SO_4, Na_2SO_4, H_3PO_4 and CH_3COOH, presumably as a result of complex formation with the catalyst.

3. GOLD

The catalytic properties and poisoning of gold in the decomposition of hydrogen peroxide were examined by Krause and Hermann (171). Two gold foils, containing 0.1 and 1.5 per cent of Cu + Ag, had low activities. The foil containing 0.1 per cent additives always gave a higher activity. Both increased in activity with temperature. Relative first order rate constants were 0.9 and 1.35. As_2O_3 and H_2S strongly poisoned both catalysts, whereas NaCN activated both.

Tamura and others (340) studied the catalytic decomposition of hydrogen peroxide by gold sols prepared with different reducing agents. Sols prepared in H_2O_2 itself gave first-order reactions with respect to H_2O_2 concentration and catalyst surface area; it was 1/2 order with respect to base concentration. About 20 kcal/mole was calculated for the activation energy. Higher pH increased the rate and yielded a linear relation between log k and log g (zeta potential). A thinner electrical double layer and the greater charge density of the sol particles yields higher activity. Transfer of electrons from gold to H_2O_2 was concluded to be the rate-determining step.

SECTION XVI.

ZINC, CADMIUM, MERCURY

1. ZINC

Krause and Miedzinski (169) studied the influences of traces of metals on the catalytic activity of zinc hydroxide. Although $Zn(OH)_2$ has low activity, at 37°, adsorption of Ag(I) and Mn(II) ions greatly increases the activity at certain concentrations. Below 2×10^{-7} grams Mn(II) per 0.1 gram $Zn(OH)_2$, the ions inhibit the decomposition. The most active ternary catalyst consisted of 0.1 gram $Zn(OH)_2$ + 2×10^{-6} gram Co(II) + 2×10^{-4} gram Mn(II).

Krause (159) pointed out the importance of lattice imperfections ("active centers") in investigations of contact catalysis. A method involving the decomposition of hydrogen peroxide was proposed as a means for determining imperfections. It consists of activation of a catalytically inactive solid by adsorption ions. For example, inactive ZnO (heat-treated at 1000°) was activated by adsorption of Cu(II), Co(II), and Na(I) ions. Fe_2O_3 containing adsorbed Co(II) was active if heated to 700°, but inactive if heated to 800°. Similar experiments were used to confirm the transformation of γ-Al_2O_3 into α-Al_2O_3 at 1000°.

Nergararian and Markaham (278) found that both cyanides and amides inhibit the decomposition of hydrogen peroxide at infrared-irradiated zinc oxide surfaces. Analysis showed that cyanates are formed at the surface. The process is described as a competition between the inhibiting ion and H_2O_2 for donating electrons to the photoactivated catalyst.

2. CADMIUM

Krause and Winowski (193) used cadmium oxide as a carrier to illustrate "catalytic ion antagonisms" in the decomposition of hydrogen peroxide. It was demonstrated in two cases that the catalytic activity of one ion on the carrier depressed by the adsorption of the second ion even if the added ion, when alone on the carrier, catalyzes the reaction. It was found that CdO alone or the ions Mn(II), La(III), and Cr(III) alone are very weak catalysts. Co(II) ions have little more activity, and the ion pairs Co(II) ions have little more activity, and the ion pairs Co(II) + La(III) and Mn(II) + Cr(III) slightly accelerate the reaction. In experiments with ions adsorbed on CdO, Mn(II) and Co(II) were very active, Cr(II) was little more active than the weakly active La(III). The reaction was slower for the combination Co(II) + La(III) than with Co(II) alone, and slower for Mn(II) + Cr(III) than with Mn(II) alone. The antagonism was related to the formation of complexes and the blocking by a stronger complex of decomposition by an active complex.

Krause and others (195) studied the kinetics of catalytic hydrogen peroxide decomposition by various ions adsorbed on solid carriers. Catalysts included Co(II) on $CaCO_3$, Co(II) on CdO, Mn(II) on CdO, and Ag(I) on CdO. All the reactions were first order and had activation energies smaller than the non-catalyzed reaction.

3. MERCURY

The rhythmic catalysis of hydrogen peroxide decomposition by metallic mercury was studied by Ernst (56). Hydrogen peroxide in contact with mercury did not begin to decompose immediately, but passed through a latent period, then became periodic. The latency period decreased as pH increased and it vanished completely at very high pH, where the reaction reached a constant maximum rate. Lower peroxide concentrations or higher temperatures had the same effect as pH. The transition from periodic to continuous catalysis was ascribed to diminishing peroxide concentration and higher pH. Irregular pulsations in activity were observed in the various transition regions.

Bethe (17) studied the rhythmic catalysis of hydrogen peroxide by a mercury surface. Catalysis by mercury is greatly affected by pH. At high pH the reaction is continuous, at intermediate values it varies, and at low pH it is negligible. An active surface changes to a passive one at a pH that depends on the content of foreign ions; usually the pH is higher for higher ion contents. For active mercury, cathodic polarization promotes catalysis and increases the pH, whereas anodic polarization gives opposite results. For passive mercury, the effects of polarization are reversed, which is ascribed to a change at the phase boundary from mercury to an oxide film. Depending on pH and other conditions, agitation can promote or inhibit the catalysis. For active mercury, the potential between it and a platinum electrode in the H_2O_2 solution increased with activity. The potential decreased if the mercury was passive.

Bagotskii and Yablokova (8) carried out electrochemical experiments aimed at determining the mechanism of catalytic decomposition of hydrogen peroxide on metallic mercury. Decomposition of 0.09-0.3 N H_2O_2 at pH 12-13 by a mercury electrode, corrected for non-catalyzed decomposition, was studied. Both the potential measurements of the mercury electrode during decomposition and the rate of the reaction gave values that had been predicted from previously determined polarization curves obtained by cathodic and anodic polarization of a mercury dropping electrode. The results support a theory that the reaction involves a mechanism of simultaneous reduction and oxidation of H_2O_2 at different points of the surface.

Gardiner (84) used electrochemical methods to investigate the periodic catalysis of hydrogen peroxide decomposition by metallic mercury. The phenomenon was of interest because of possible analogy to physiological irritation mechanisms in living organisms.

Krause (157) carried out a short series of experiments to determine the catalytic effect of ions supported on various solid compounds of mercury. Both cations (Co(III), Al(III), Mn(II), Fe(III)), and anions (AcO$^-$, Br$^-$, [Fe(CN)$_6$]$^{4-}$, [Fe(CN)$_6$]$^{3-}$) were supported on HgI$_2$, HgS, Hg$_2$O, and HgO.

SECTION XVII.

GALLIUM, INDIUM, THALLIUM

Krause and Blawacka (190) found that the rate of catalytic decomposition of 3 per cent hydrogen peroxide by Tl_2O_3 at 37° is a first-order reaction having a minimum reaction rate at a concentration of 5 mg/150 ml and a maximum rate at 1.5 mg/150 ml. The behavior of this catalyst is described as "latent activity."

Tl_2O_3 was used as a carrier to determine the catalytic activities of a series of metal ions in the decomposition of hydrogen peroxide at 37° (185). Co(II) ions especially promoted the reaction. Other promoters, according to decreasing activity, were Ag(I), Mn(II), Cu(II), Al(III), and Pb(II). Ions that were ineffective include Na^+, K^+, Cs^+, Be^{2+}, Mg^{2+}, Ni(II), UO_2^{2+}, La(III), Cl^-, NO_3^-, SO_4^{2-}, $Fe(CN)_6^{3-}$, and $Fe(CN)_6^{4-}$. A mixed ion promoter of Co(II) - Ag(I) - Cu(II) was very active.

It was later reported that adsorbing ion pairs such as Co(II)-Mn(II) and Co(II)-Zn(II) on Tl_2O_3 carrier could produce the so-called "ion antagonism" (186). This refers to the lower catalytic activity obtained by adding the ions simultaneously from a mixture, as compared to the higher activity obtained by adding each in separately.

SECTION XVIII.

LANTHANIDES AND ACTINIDES

Khodakov and Minachev (119) studied the kinetics of peroxide decomposition by lanthanum hydroxides. Experimental data for γ-irradiated and nonirradiated $La(OH)_3$ were obtained to confirm a complex set of equations derived from a postulated mechanism. The mechanism involved the formation of an intermediate complex of the type $[La(OH)_3 \cdot H_2O_2] \cdot H_2O_2$. The energy of activation for decomposition of the complex was determined to be 24 kcal/mole.

Krause and Posswinski (156) studied the catalytic activities of a series of uranium oxides in the decomposition of hydrogen peroxide at 37°. UO_2, UO_3, U_3O_8, and hydrated UO_4 were included. The highest activity was obtained with U_3O_8 thermally treated at 800 and 1000°. UO_2 was less active; UO_4 and UO_3 were least active, and both had very small activities.

Nabe and Gyani (273) studied the kinetics of hydrogen peroxide (0.350-0.022 M) catalytic decomposition by hydrated CeO_2 at 25-40°. The first-order rate constant was initially unchanged, but it declined in value as the reaction proceeded. The activation energy of 1200 cal/mole was considered low. Dehydration of the oxide was accompanied by a decline in activity up to 730°, where all activity vanished.

Maxted and Ismail (261) used platinum catalysts activated by rare earth and other oxides for the decomposition of hydrogen peroxide at 20°. The order of reactivities for various promoters was found to be $ThO_2 > ZrO_2 > Cr_2O_3 > CeO > MgO > TiO_2 > VO_8 < La_2O_3 > Pr_6O_{11} > Tl_2O_3 > Sm_2O_3$. The catalyst activity increased to a maximum with promoter content and then declined as the oxide-to-platinum ratio increased. The activity increases were large. ThO_2 and ZrO_2 yielded nearly 9 times the value of unpromoted platinum at the peak.

Zubovich (391) investigated the activities of mixed adsorption catalysts adsorbed on sugar charcoal. Catalyst mixtures included (1) Pd-Ag, (2) Pd-Au, (3) Pt-ZnO-Mn(II) ions, and (4) Fe(III) ions-Ln(III) ions (where Ln = Lu, Pr, Nd, Sm, or Yb). Different results were obtained for each catalyst when activity was plotted against the atomic ratios of the active components. Catalyst (1) yielded a minimum and catalyst (2) yielded a maximum, regardless of the method of preparation. Catalyst (3) yielded a sharp minimum when very small amounts of additives were used. Catalyst (4) yielded a monotonic increase in activity with increased amounts of additives. The chemical and magnetic properties of the elements are used to explain the correlations obtained between catalytic activities and magnetic susceptibilities.

The effect of adsorbed lanthanide ions on the catalytic activities of platinum and palladium catalysts supported on barium sulfate and sugar charcoal were also investigated by Zubovich (392). Lanthanides were adsorbed as the chlorides of trivalent lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, and lutetium. It was found in all cases that small doses of the lanthanides activated both platinum and palladium, and yielded maximum activities at ratios of Pt (or Pd) to Ln(III) of less than 25 to 1. There was no evidence of homogeneous decomposition by dissolved ions, nor of heterogeneous decomposition by lanthanides adsorbed on barium sulfate. Some activity of the ions adsorbed on sugar charcoal was observed.

The behavior of the lanthanides was contrasted with that of the d-transition elements. Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) reduce in decreasing order the catalytic activity of palladium, silver, and platinum. Unlike the f-transition elements, the d-transition elements markedly decrease activity of the lowest concentrations. The differences in catalytic behavior led to the suggestion that the 100-fold difference in crystal field splitting energies accounts qualitatively for the catalytic action of the trivalent ions of the lanthanides in dilute adsorption layers.

Wolski (371) determined the catalytic activities of lanthanum, praseodymium, and especially samarium hydroxides in decomposing hydrogen peroxide at 37°. $Sm(OH)_3$ was an ineffective catalyst, and it could be activated only by adsorbing Cu(II) ions. The activation is presumed due to the formation of copper samarate, which can initiate the chain decomposition. Adding Group II ions further increased the activity of the mixed catalyst, presumably by promoting the activity of copper samarate.

Krause and Slawek (197) used the effect on catalytic decomposition of hydrogen peroxide as a means for differentiating rare oxides. The oxides La_2O_3, CeO_2, Nd_2O_3, and Pr_6O_{11} strongly inhibit the catalysis by mixtures of Mn(II)/Cu(II) and Mn(II)/Co(II) ion pairs. The fact that the decomposition rate increases according to $La_2O_3 < Pr_6O_{11} < Nd_2O_3 < CeO_2$ can be used to determine the different rare earths.

SECTION XIX.

THERMAL DECOMPOSITION

Shell Development Company (315, 317) conducted a two-year program (1956-58) of research on the thermal stability of 90 per cent hydrogen peroxide. The principal concern was the safety hazards associated with the use of hydrogen peroxide in rocket applications. The explosion limits of the vapor were determined as a function of composition, temperature, and pressure up to 100 psia. Heat transfer and drop-weight test data were also determined. A large part of the experimental work was devoted to a study of the effects of impurities, such as those encountered with typical peroxide containers, on the kinetics of decomposition.

Whittaker and Drew (366) investigated the thermal decomposition of concentrated hydrogen peroxide in quartz, dust-free vessels. The results indicated that the reaction was zero-order, but they were not precise enough to eliminate the possibility of a half-order reaction. Between 59.3 and 86.3° the activation energy was 14.4 kcal/mole and the collision factor was about 10^4 mole/liter.

Williams and others (367) published a paper on the calculation of adiabatic decomposition temperatures of aqueous hydrogen peroxide solutions. The temperature and states attained on the fractional adiabatic decomposition of peroxide solutions were calculated using the best available thermodynamic data. The technique of calculation is described and graphical presentations are given of the temperature, and liquid and vapor compositions as a function of the fraction of hydrogen peroxide decomposed for several initial solution concentrations and at several pressures.

Giguère (90) investigated the thermal decomposition of hydrogen peroxide vapor at low partial pressures (1 to 6 mm) of water in the range to 50 420°C. The objective was to determine the effect of the nature and treatment of the active surfaces on the reaction. Soft glass, Pyrex, quartz, and metalized surfaces were used. In most cases the decomposition was mainly first order but the rates varied markedly from one vessel to another, even with vessels made of the same kind of glass. On a quartz surface the decomposition was preceded by an induction period at low temperatures. Fusing the glass vessels slowed the reaction considerably and increased its apparent activation energy; this effect was destroyed by acid washing. Attempts to poison the surface with hydrocyanic acid gave no noticeable result. The marked importance of surface effects at all temperatures was considered an indication that the reaction was predominately heterogeneous. Apparent activation energies ranged from 8 to 20 kcal. It was concluded that the decomposition of H_2O_2 vapor is not very specific as far as the nature of the catalyst is concerned.

Giguère and Liu (91, 92) used a static method to determine the kinetics of thermal decomposition of hydrogen peroxide at 0.2 to 20 mm Hg pressure and from 300 to 600°. The reactions were first order with respect to time. Water and oxygen were the products. Up to 400° the surface reaction was predominate, but above that the phase reaction was faster. The activation energy of 48 kcal/mole for the over-all reaction corresponds to the 0-0 bond dissociation energy. The suggested mechanism is:

(1) $H_2O_2 \rightarrow 2OH$ (rate determining)

(2) $OH + H_2O_2 = H_2O + HO_2$

(3) $HO_2 + HO_2 = H_2O_2 + O_2$

(4) $HO_2 + OH = H_2O + O_2$.

Yatsimirskii (374) studied in detail the energy characteristics of the particles produced by the dissociation of hydrogen peroxide vapors and of hydrogen peroxide in solution. Electron affinities, proton affinities, and heats of hydration and formation in aqueous solution were determined for H^+, O^+, OH^+, O_2H^+, H, O, OH, O_2, O_2H, O_2H_2, H^-, O^-, OH^-, O_2^-, O_2H^-, and O_2^{2-}. The heat effects of H_2O_2 dissociation in the vapor phase and in solution are related to the number and types of particles produced.

The thermal decomposition of hydrogen peroxide vapor in glass vessels was considered by Baker and Ouellet (9). A first-order heterogeneous reaction was observed up to 140°. At higher temperatures the kinetics were more complicated. The rate was unaffected by air, carbon dioxide, or water vapor, but did depend on the shape of the vessel. The reaction was very much faster on soda glass than on Pyrex glass. No explosion occurred in experiments up to 335° and 18 cm Hg pressure. Activation energies ranged from 13.5 to 18.5 kg-cal/mole.

Forst (78) found that the thermal decomposition of hydrogen peroxide followed second-order unimolecular kinetics. Experiments were conducted using H_2O, O_2, and He as diluent gases at 431°, and helium at 431-468°. Pressures were below 100 mm Hg. Below 10 mm and at 431.5°, the reaction was 65 per cent homogeneous. Foreign gases inhibited the heterogeneous reaction, and helium above 431.5° completely inhibited it. The activation energy was 45 kcal/mole. The critical energy of 48 kcal/mole corresponds to the 0-0 bond strength.

Baldwin and others (11) studied the kinetics of the thermal decomposition of hydrogen peroxide in the presence of hydrogen. The studies were based on a mechanism proposed originally by Baldwin and Brattan (10) and later by Forst (79):

(1) $H_2O_2 + X (= H_2, N_2) = 2OH + X$

(2) $OH + H_2 = H_2O + H$

(3) $H + H_2O_2 = H_2O + OH$

(4) $H + H_2O_2 = H_2 + HO_2$

(5) $OH + H_2O_2 = H_2O + HO_2$

(6) $2HO_2 = H_2O_2 + O_2$

(7) $H + O_2 + X = HO_2 + X$

If it is assumed that the relative coefficients of H_2 and N_2 in reactions (1) and (7) are identical, and because for (7), $k_{N_2}/k_{H_2} = 0.43$ and for (1), $k_p/k_{N_2} = 6\text{-}7$, the calculated value for (1) is $k_{H_2}/k_p = 0.33\text{-}0.38$, where $p = H_2O_2$. A plot of experimental data gave a ratio of 0.30, which indicates that no additional reactions have to be postulated to explain the reaction.

Hoare and others (107, 108) used a flow system to study the thermal decomposition of hydrogen peroxide vapor from 241 to 659°. Above 420° the predominate reaction was a second-order homogeneous decomposition with the following proposed mechanism:

(1) $H_2O_2 + M \rightarrow 2OH + M$ (rate determining)

(2) $OH + H_2O_2 \rightarrow H_2O + HO_2$

(3) $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

The calculated activation energy of 48 kcal/mole corresponds to that expected as the minimum energy to break the 0-0 bond.

The decomposition of hydrogen peroxide vapor at pressures below 1 mm Hg in silica vessels from 15 to 140° was investigated by Mackensie and Ritchie (237). In general the reaction was bimolecular, but the order depended on the vessel used for the reaction. Most diluents retarded the reaction (none accelerated it), but water vapor at above 10 mm pressure caused a periodicity in the rate. Approximate heats of activation were 4200 calories from 15 to 70° and 8400 cal from 80 to 140°. For 1 mm pressure of peroxide at 50°, the velocity of decomposition was calculated to be

0.70×10^{13} mole/cm^{-2}/sec^{-1} using absolute reaction rate theory and the assumption that the lower value of heat of activation corresponds to a surface reaction. The calculated velocity agreed with the experimental value of 0.76×10^{13} mole/cm^{-2}/sec^{-1}. Above 140°, the reaction was too rapid to measure rates.

Satterfield and Stein (305) used a flow reactor of Pyrex glass to study the homogeneous decomposition of hydrogen peroxide vapor. The reaction changed from heterogeneous to homogeneous at 400-450° and a partial pressure of 0.02 atm. The homogeneous reaction was 3/2-order and had an activation energy of 55,000 cal/mole. The rate at 460° and 0.02 atm yielded a calculated value of 1.9×10^{17} molecules decomposing per cc per second. About 1.8×10^{10} collisions per second had energy greather than the activation energy. The large difference in the two calculated numbers indicated that long chains are involved.

McLane (263) used a flow system to study the thermal decomposition of hydrogen peroxide at partial pressures of 1-2 mm Hg in the presence of nitrogen or oxygen at atmospheric pressure. The reaction was first order and had an activation energy of 40 kcal/mole at about 520°. The reaction is partially homogeneous at 470-540° in boric-acid treated vessels.

Nikitin (279) calculated the rate constant for thermal bimolecular decomposition of H_2O_2, taking into account the breakdown in the Boltzmann distribution for the vibrational states.

Kondrateva and Kondratev (131) investigated the thermal decomposition of hydrogen peroxide vapor in a molybdenum glass tube. The decomposition was carried out in moist air containing 0.01 to 0.4 mm Hg of H_2O_2. The reaction was second order with an activation energy of 8.5 kcal/mole.

The explosive characteristics of hydrogen peroxide vapor were examined by Satterfield and others (304). Explosion limits were determined for hot wires, heated surfaces, and catalytic surfaces under various pressures. At atmospheric pressure vapors with 26.0 mole per cent or more could be exploded. Either a noncatalytic surface at 150° or a catalytic surface at room temperature exploded the vapors. Vapor-liquid equilibria diagrams were prepared to show the temperatures at which various aqueous peroxide solutions have explosive vapors over them. A minimum H_2O_2 concentration of 74 per cent was determined necessary to yield explosive vapor. The explosion reaction was believed to be thermal, involving straight chains only.

SECTION XX.

GENERAL AND APPARATUS

FMC Corporation (62-66) conducted a two-year program (1956-1958) under U.S. Navy contract to study the parameters involved in the catalytic decomposition of hydrogen peroxide. This work included techniques for determining the surface areas of catalysts, analysis of the effects of impurities on the catalytic activity of silver and platinum, analysis of the mechanism of heterogeneous and thermal decomposition, and analysis of catalyst screen design and configuration. Static and dynamic tests and laboratory and large-scale tests were conducted. Brief literature surveys on catalysts for decomposing hydrogen peroxide and thermal decomposition of hydrogen peroxide were also included.

In a general analysis of the catalytic activities of the chemical elements, Krause (140) cited a number of examples to illustrate that there is no way to predict a priori the activity of mixed catalysts. Sometimes it is not even permissible to generalize on whether a particular element is active, indifferent, or inhibiting in mixed systems because behavior may depend on the particular combination of elements on the material used as a carrier. For example, Mn(II) ions alone do not catalyze the decomposition of H_2O_2 at 37°, but it is extremely active adsorbed on $Mg(OH)_2$. Group I and II metal ions are not active on $Zn(OH)_2$, and aluminum ion can inhibit the reaction. However, these same ions activate the catalysis when Cu(II) or Co(II) ions are also present. The behavior of sodium ion on $Bi(OH)_3$ illustrates that the catalytic activity is not always proportional to the ion concentration. The behavior of activating salts of sodium adsorbed on magnetite in the presence of Co(II) and Cu(II) ions depends on the anions that are present. These components affect the catalysis by forming a variety of complex and undefinable radicals. The radicals can start and interrupt chain reactions, depending on the presence of poisons. In some instances, substances that are ordinarily poisons promote the reaction. Sodium fluoride normally poisons the peroxidic oxidation of formic acid catalyzed by γ-FeOOH and CuO, but at small concentrations, it is an accelerator.

Block (24) reviewed the work of other investigators in the field of heterogeneous catalysis in an attempt to correlate activity with the electronic defects of semiconducting properties of catalysts. It was found that a relation does exist, and that it can be used as a basis for catalyst selection. In an analysis of a wide variety of catalytic reactions, including the decomposition of hydrogen peroxide, two general reaction types were distinguished. Donor reactions which produce cations of the reactants at measurable rates, are effectively catalyzed by p-conducting agents. Acceptor reactions, which have anion formation as the rate-determining step, are effectively catalyzed by n-conductors. Defects are consistently without effect if molecular rearrangements are rate-determining since such reactions do not involve electron transfer with the catalyst. Semiconducting properties can also be used to relate catalytic activity and properties of contact sites for some reactions. These relations are only qualitative; exact relations require knowledge of the surface activated complexes in the catalytic reactions.

Poltorak (293) attempted to relate the active centers in heterogeneous catalysts to lattice defects of crystals. An analysis of previous theories and of the thermodynamics of real crystals led to a mathematical expression relating an increase in the chemical potential of a bounded finite crystal to that of an "infinitely large" crystal. The differences in chemical potentials can be determined approximately from heats of sublimation.

The theory was applied to metallic and semiconductor catalysts. The energy required to form crystal defects in metals was related mathematically to the heat of sublimation. The results could be used to relate changes in catalytic properties to the type or the mode of preparation of the crystals.

The general theory may serve as a basis for explaining the effects of sintering on the catalytic activity of metals. Four modes of behavior have been observed experimentally: (1) activity is independent of either preparation method or sintering temperature; (2) activity decreases with sintering temperature; (3) activity increases to a maximum with sintering temperature, and (4) activity passes through maximum and minimum with increasing sintering temperature. Case (4) can occur when the surface at the initial temperature has an amorphous phase that crystallizes with nonequilibrium boundaries when heated. This was demonstrated for the decomposition of hydrogen peroxide by silver. Two groups of silver catalysts were prepared by reducing silver nitrate at -4°. One group was sintered at 100-500° in hydrogen. The activity was in accordance with case (4). The second group was initially heated to 150°. Extended sintering at 150-400° gave only a gradual change in activity. It was concluded that active catalytic centers reach equilibrium more often than has been thought, and that non-equilibrium in the crystal lattice is the main cause of non-equilibrium of catalysts.

Poltorak also discussed experiments which demonstrated that the fraction of active centers on semiconductors, in contrast to metals, does not depend on the dispersity or mosaic nature of the crystals. Activity depends on "metallic ensembles" on the surface.

Krause (136) discussed the theory of catalytic decomposition of hydrogen peroxide on the basis of electrochemical behavior. Electrolytic dissociation of H_2O_2 into H^+ and HO_2^- by a catalyst leads to decomposition because the HO_2^- ion is unstable. Krause assumes that solutions of H_2O_2 contain two isomers in definite equilibrium that can be altered by various chemical environments. $\mathrm{H}-\underset{\mathrm{O}}{\mathrm{O}}-\mathrm{H}$, which acts as an oxidizing agent, is catalyzed by metals because this molecule is the final acceptor. HOOH, which acts as a reducing agent, is also catalyzed by metals by dehydrogenation, which gives oxygen and water as the products. In this reaction, HO and HO_2 radicals are produced and they can initiate an uninterrupted chain reaction involving electronic resonance. Efficient resonance allows observation of only a contact catalyst, which is active even in the smallest quantities.

Kushelyuk (212) attempted to correlate emf measurements with the activities of semiconductor catalysts in the decomposition of hydrogen peroxide solutions. Changes in emf and catalytic activity over the range 29-90° were measured for p-type catalysts (CuO and Ni_2O_3) and n-type catalysts (ZnO, Fe_2O_3, MnO_2, PbO, and Al_2O_3). In the case of Ni_2O_3, emf increased to a maximum, decreased to a minimum at 65°, then increased. Catalytic activity increased continuously over the temperature range, but it accelerated between 52 and 65°. Both p- and n-type catalysts showed the same behavior. Al_2O_3, which does not catalyze H_2O_2 decomposition, was the only exception. In this case the emf decreased continuously with increasing temperature.

Pierron (291) studied the rate of hydrogen peroxide decomposition by a series of metal oxides in alkaline solutions. At all base concentrations, oxides of the following metals increased the rate: nickel, cobalt, iron, copper, lead, manganese, silver, and mercury. ZnO, CdO, and Al_2O_3 inhibited the reaction over a narrow range of alkalinity. MgO, CaO, and BaO decreased the rates over a wider range of alkalinities. $Sn(OH)_4$ decreased the rate in all cases. It was concluded that the most stable oxides decrease the rate, and the least stable oxides increase the rate. The effects are more pronounced at higher temperatures and H_2O_2 concentrations.

The catalytic activities of several groups of metal oxides and salts in the decomposition of hydrogen peroxide were investigated by Zhabrova and others (377). The compounds were selected on the basis of chemical properties and color: (1) non-transition, insoluble salts ($PbSO_4$, $BaSO_4$, $BaCO_3$, aluminum silicate); (2) acidic and amphoteric colorless oxides (SnO_2, SiO_2, ZnO, Al_2O_3, and colorless transition metal oxides); (3) colorless alkaline earth oxides (BaO, CaO, MgO); and (4) ionic semiconductors (Cr_2O_3, MnO_2, NiO, Fe_2O_3, CuO, and others). It was found that in certain cases, such as V_2O_5, Cr_2O_3, and Fe_2O_3, the homogeneous reaction caused by dissolved catalyst plays an important part in the over-all decomposition. In general, catalytic behavior does depend on the position of the elements in the periodic table and on the chemical properties of the solids. Catalysts that are both colored and contain transition elements are the most active. The activity of colorless basic oxides is substantially higher than that of colorless acidic oxides and increases with alkalinity. The fact that activity can be correlated with electronic properties indicates that there is a direct exchange of electrons in the decomposition reaction.

Zhuravlev and Kuzhelyuk (380) used an electrochemical procedure to measure changes of activity with time for hydrogen peroxide decomposition catalysts. Changes in activity with time of electron and hole semiconductors were correlated with emf changes. One cell electrode consisted of the catalyst and the other was a conductor (carbon) that did not affect the rate. Hydrogen peroxide was the electrolyte. Emf was measured every ten minutes for ten days. The following groups of catalysts were distinguished: p-NiO, n-MnO_2, and n-CdO; p-Ni_2O_3, and p-Co_2O_3; p-CuO, n-ZnO, and n-PbO; and n-Fe_2O_3. A second degree equation for relating activity and emf best fitted the data.

Zhuravlev and others (381) attempted to correlate the work functions of various oxides with catalytic behavior in the decomposition of hydrogen peroxide. The method of contact potential difference was used to measure the work functions of Co_2O_3, CdO, NiO, PbO, ZnO, and Pb_2O. A correlation with work function was possible only in some cases, a result explained by simultaneous adsorption of H_2O_2 and H_2O molecules on the catalyst surface. In the case of semiconductor catalysts the work function in the adsorption of various gases correlated with activity. Higher activity corresponded to larger changes in work function. However, it was not possible to distinguish acceptor and donor gases and vapors since the characteristics depended on the adsorbent used.

Satterfield and Audibert (307) studied the apparently analogous behavior between phenomena observed in catalytic decomposition of concentrated hydrogen peroxide on a solid catalyst and the behvaior of non-reacting fluids in nucleate and film-boiling heat transfer. Decomposition rates as a function of H_2O_2 concentration, surface temperature, surface curvature, and corresponding heat fluxes were measured for comparing the two phenomena.

In a study of heat and mass transfer in the catalytic decomposition of hydrogen peroxide, Satterfield and others (254) reported that the rate of decomposition of H_2O_2 vapor is controlled by the rate of mass transport to the catalyst surface.

Yamada and Nishioka (373) proposed methods for evaluating the decomposition rate of concentrated hydrogen peroxide. Rates were given by the ratio of exhaust gas flow rate to liquid inflow rate using a catalyst pack. Low feed rates gave high decomposition rates, and a maximum rate was reached for a hydrogen peroxide concentration of 70 per cent.

A simple tester for comparing catalyst activities was developed. Small samples of catalyst yielded results consistent with full-scale tests.

Formwalt (77) obtained a 1953 U. S. patent covering an apparatus used to measure catalytic activity. The apparatus continuously measures pressure with a cylinder containing hydrogen peroxide and catalyst.

Temperature-compensated resistance-wires strain gages connected to an oscillograph are used for the measurements

Maglio and Poole (241), of General Electric Company, obtained a 1962 U.S. patent covering a catalytic chamber useful for decomposing hydrogen peroxide in various types of propulsion units.

In a 1962 U.S. patent assigned to General Mills, Moore and others (269) described a catalytic chemical heater that employs hydrogen peroxide.

SECTION XXI.

REFERENCES

1. Adamenkova, M. D., and O. M. Poltorak, Vestn. Mosk. Univ., Ser. II, Khim., 18(5), 12-16 (1963). (CA 60, 47f)

2. Adamenkova, M. D., and O. M. Poltorak, Vestn. Mosk. Univ., Ser. II, Khim., 19(3), 9-13 (1964). (CA 61, 8937e)

3. Admiralty Metals Laboratory, England. "Silver Metal as an H_2O_2 Decomposition Catalyst. I. Decomposer Chamber Design Factors. II. Some Observations with a Bearing on the Mechanism." By C. Cooper, A. B. Hart, and A. E. Wetwyn, 3 June 1945; see also "Testing of Various Decomposition Screens for Use with H. T. P. Solutions," by C. Cooper, 3 June 1948.

4. Alekseevskaya, N. V., V. B. Grigor'ev, and A. V. El'tsov, Sbornik Stud. Rabot. Leningrad. Tekhnol. Inst. im. Lensoveta (Leningrad), 1956, 18-21; Referat. Zhur., Khim., 1957. (CA 53, 9875b)

5. Amiel, Jean, Georges Rodier, and Jean Brenet, Compt. rend., 227, 1356-8 (1948). (CA 43, 7313d)

6. Anderson, Holder C., and Philip L. Romeo, Sr. (to Engelhard Industries, Inc.), U. S. Patent 3,146,243, August 25, 1964. (CA 61, 11376e)

7. Bagg, J., Australian J. Chem., 15, 201-10 (1962). (CA 57, 9265g)

8. Bagotskii, V. S., and I. E. Yablokova, Doklady Akad. Nauk S. S. S. R., 95, 1219-21 (1954). (CA 49, 10029f)

9. Baker, Bruce E., and C. Ouellet, Can. J. Research, 23B, 167-82 (1945). (CA 40, 1722^7)

10. Baldwin, R. R., P. Doran, and L. Mayor, Symp. Combust., 8th, Pasadena, Calif., 1960, 103-9 (1962). (CA 58, 47f)

11. Baldwin, R. R., D. Booth, and D. Brattan, Can. J. Chem., 39, 2130-3 (1961); see also "Role of Hydrogen Peroxide. 2. The Dissociation of Hydrogen Peroxide and its Role in the Hydrogen-Oxygen Reaction," by R. R. Baldwin, P. Doran, and L. Mayor (University of Hull, England) 1962. (AD 611 357).

12. Banfield, Reginald H., and Wm. S. Wood (to Laporte Chemicals Ltd.), British Patent 783,590, September 25, 1957. (CA 52, 4068f)

13. Baumgartner, H. J., G. C. Hood, J. M. Monger, R. M. Roberts, and C. E. Sanborn, J. Catalysis, 2(5), 405-14 (1963). (CA 60, 1152d, e)

14. Baumgartner, H. J., and R. M. Roberts (to Shell Oil Co.), U.S. Patent 3,156,089, November 10, 1964. (CA 62, 1506h)

15. Baxendale, J. H., "Decomposition of Hydrogen Peroxide by Catalysts in Homogeneous Aqueous Solution," Advances in Catalysis, 4, 31-86 (1952). (132 references)

16. Berenblit, M., and N. Ya. Lantratova. Trudy Gosudarst. Inst. Priklad. Khim., 44, 65-76 (1960). (CA 55, 25540d)

17. Bethe, A., Z. Naturforsch., 3b, 69-77 (1948). (CA 43, 927a)

18. Bianchi, G., F. Mazza, and T. Mussini, Electrochim. Acta, 7, 457-73 (1962). (CA 57, 14464i)

19. Blesa, A. A., Rev. univ. ind. Santander, 2, No. 1, 25-35 (1960). (CA 54, 21937a)

20. Blesa, A. A., Rev. acad. cienc. exactas, fis.-quim. y nat. Zaragoza 2A, 3, No. 2, 39-64 (1948); Anales real. soc. espan. fis. y quim., 45B, 561-76 (1949). (CA 44, 6712b)

21. Bliznakov, G., and O. Peshev, Godishnik Sofiiskiya Univ., Fiz.-Mat., 54, No. 3, 165-78 (1959/60). (CA 56, 5436h)

22. Bliznakov, G., and D. Lazarov, Kinetika i Kataliz, 2, 929-30 (1961). (CA 56, 9463e)

23. Bliznakov, G., and O. Peschev, Naturwissenschaften, 48, 551 (1961). (CA 56, 2919e)

24. Block, J., Werkstoffe u. Korrosion, 7, 127-37 (1956). (CA 50, 17255g)

25. Bloom, R., N. S. Davis, and S. D. Levine, "Hydrogen Peroxide as a Propellant," J. Amer. Rocket Soc., 80, 3-17, March 1950.

26. Bloom, R. Jr., and N. J. Brunsvold, "Anhydrous Hydrogen Peroxide as a Propellant," Chem. Eng. Progr., 53, 541 (1957).

27. Bogdanovskii, G. A., and A. I. Shlygin, Vestnik Moskov. Univ., Ser. Mat., Mekh., Astron., Fiz., Khim., 14, No. 1, 155-63 (1959). (CA 54, 2070d)

28. Brinkmann, G., Angew. Chem., 61, 378-83 (1949). (CA 44, 418i)

29. Brinkmann, G., Kolloid-Z., 123, 116-29 (1951). (CA 46, 8787i)

30. Broughton, D. B., and R. L. Wentworth, J. Am. Chem. Soc., 69, 741-4 (1947); cf. F. Fouinat, Compt. rend., 226, 1619-21 (1948); ibid., 228, 1593-5 (1949).

31. Broughton, D. B., and R. L. Wentworth, J. Am. Chem. Soc., 69, 744-7 (1947). (CA 41, 4364i)

32. Budnikov, P. P., and R. A. Belyaev, Zhur. Priklad. Khim., 33, 1921-40 (1960).

33. California Research Corp., British Patent 915,809, January 16, 1963. (CA 58, 7415a)

34. Cherney, P., U.S. Government Research Report, PB 6669 (1945).

35. Clopp, P. P., and G. Parravano, J. Phys. Chem., 62, 1055-9 (1958). (CA 53, 835f)

36. Constable, F. H., and V. Ohanian, Rev. fac. sci. Univ. Istanbul, 20C, 123-8 (1955). (CA 50, 659g)

37. Constable, F. H., J. Colloid Sci., 11, 647-52 (1956). (CA 51, 3343h)

38. Constable, F. H., and B. Pekin, Rev. fac. sci. univ. Istanbul, 21C, 64-71 (1956). (CA 51, 57f)

39. Constable, F. H., and B. Pekin, Rev. fac. sci. univ. Istanbul, 22C, 47-53 (1957). (CA 51, 11829e)

40. Constable, F. H., and B. Pekin, Rev. fac. sci. univ. Istanbul, 22C, 353-70 (1957). (CA 53, 14662a)

41. Constable, F. H., and B. Pekin, Istanbul Univ. Fen Fak. Mecmuasi, 26C, No. 1, 53-63 (1961). (CA 56, 2914i)

42. Constable, F. H., and B. Pekin, Istanbul Univ. Fen Fak. Mecmuasi, 26C, No. 1, 72-82 (1961). (CA 56, 2914i)

43. Cota, H. M., T. Katan, M. Chin, and F. J. Schoenweis. Nature, 203, (4951), 1281 (1964). (CA 61, 13924a)

44. Crum, J. P. (to D. Napier & Sons Ltd.), U.S. Patent 2,808,940, October 15, 1957. (CA 52, 3205c)

45. D' Ans, J., and J. Mattner, Angew. Chem., 64, 448-52 (1952). (CA 46, 9959f)

46. Davis. N. S., Jr., and J. C. McCormick, Prog. in Astronaut. Rocketry, 2, 589-616 (1960). (CA 56, 4131i)

47. Deleo, E., R. Indovina, and A. Parlato, Gazz. Chim. ital., 79, 451-3 (1949). (CA 43, 8829a)

48. Deleo, E., R. Indovina, and A. Parlato, Ann. chim. (Rome) 40, 251-6 (1950). (CA 45, 10019)

49. Deren, J., J. Haber, A. Podgorecka, and J. Burzyk, J. Catalysis, 2(3), 161-75 (1963). (CA 60, 1319c)

50. Deren, J., and J. Haber, J. Catalysis, 4(1), 22-33 (1965). (CA 62, 4659h)

51. Dole, M., D.P. Rudd., G.R. Muchow, and C. Comte, J. Chem. Phys., 20, 961-8 (1952). (CA 47, 2025c)

52. Dowden, D.A., and P.W. Reynolds, Discussions Faraday Soc., No. 8, 184-8 (1950). (CA 45, 9988d)

53. Downes, H.I. (to Shell Oil Co.), British Patent 945,370, December 23, 1963. (CA 60, 15675g)

54. Erbacher, O., Z. Elektrochem., 53, 54-67 (1949). (CA 43, 6028e)

55. Erkut, H., Rev. fac. sci. univ. Istanbul, 19C, 1-14 (1954). (CA 48, 12529i)

56. Ernst, K.H., Pflügers Arch. ges. Physiol., 254, 79-97 (1951). (CA 47, 10978i)

57. Evans, M.G., N.S. Hush, and N. Uri, "The Energetics of Reactions Involving Hydrogen Peroxide, its Radicals, and its Ions," Quart. Revs., 6, 186 (1952). (CA 46, 8305f)

58. Fisher, J.G., and F.J. Zeilberger, "Catalyst Design Keeps Up With H_2O_2 Progress," Space/Aeronautics, 84-7, May 1961.

59. Flis, I.E., Zhur. Anal. Khim., 10, 38-43 (1955). (CA 49, 8044d)

60. FMC Corporation, Special Projects Laboratory, Buffalo, New York. "Grade Peroxide Decomposition by Catalytic Means," Technical Report No. G-5, by R. Bloom and D.K. Squires, U.S. Navy Contract Nobs-31494 (Project Bessie), 30 June 1950. (See also Technical Report G-3, 15 November 1948.)

61. FMC Corporation, Special Projects Laboratory, Buffalo, New York. "Development of a Catalyst for Alton Cycle Power Plant." Final Report, by N.S. Davis and N.L. Amend, U.S. Navy Contract Nobs-31494 and Nobs-47983; also Technical Report DC-1, "Development of Direct Combustion Chambers for Alton Submarine Propulsion Plant," by J.C. McCormick, L. Wisniewski, E. Weinberg and R. Bloom, U.S. Navy Contract Nobs-54089, December 1953.

62. FMC Corporation, Special Projects Laboratory, Buffalo, New York. "A Study of Catalysis for the Decomposition of Hydrogen Peroxide," First Quarterly Progress Report 213-4, U.S. Navy Contract NOas 56-921-d, 15 September 1956. (AD 113 878)

63. FMC Corporation, Special Projects Laboratory, Buffalo, New York, "A Study of Catalysis for the Decomposition of Hydrogen Peroxide," Second Quarterly Progress Report 213-8, U.S. Navy Contract NOas 56-921-d, 15 December 1956. (AD 122 649)

64. FMC Corporation, Special Projects Laboratory, Buffalo, New York. "A Study of Catalysis for the Decomposition of Hydrogen Peroxide," Third Quarterly Progress Report 213-12, U.S. Navy Contract NOas 56-921-d, 15 March 1957.

65. FMC Corporation, Special Projects Laboratory, Buffalo, New York. "A Study of Catalysis for the Decomposition of Hydrogen Peroxide," Fourth Quarterly Progress Report 213-16, U.S. Navy Contract NOas 56-921-d, 15 June 1957.

66. FMC Corporation, Special Projects Laboratory, Buffalo, New York. "A Study of Catalysis for the Decomposition of Hydrogen Peroxide," Fifth Quarterly Progress Report 213-20, U.S. Navy Contract NOas 56-921-d, 15 September 1957.

67. FMC Corporation, Becco Chemical Division, Buffalo, New York. "Application of Concentrated Hydrogen Peroxide to Torpedo Propulsion Systems," Final Report 210-6, U.S. Navy Contract NOrd-16536, 1 April 1957.

68. FMC Corporation, Central Research Laboratory, Princeton, New Jersey. "Decomposition of Hydrogen Peroxide. Semi-adiabatic Reaction between H_2O_2 and Silver Metal," Technical Report 213-2, by A. B. Gancy, 6 August 1958. U.S. Navy Contract NOas 56-921-d.

69. FMC Corporation, Central Research Laboratory, Princeton, New Jersey. "Isothermal Reaction of 90 Per Cent Hydrogen Peroxide with Silver at 20°C. Reaction Mechanism and Effects of Impurities," Technical Report 213-3, by A. B. Gancy, 11 September 1958. U.S. Navy Contract NOas 56-921-d.

70. FMC Corporation, Central Research Laboratory, Princeton, New Jersey. "Reaction of Concentrated Hydrogen Peroxide with Silver Metal - The Behavior of Cermet Surfaces with Respect to Vapor Binding," Technical Report 224-1, by A. B. Gancy, 12 November 1958. U.S. Navy Contract NOas 58-689-c.

71. FMC Corporation, Central Research Laboratory, Princeton, New Jersey. "Metal Mixtures as Catalysts for the Decomposition of hydrogen Peroxide," Technical Report 224-2, by A. B. Gancy et al., 30 June 1959. U.S. Navy Contract NOas 59-689-c.

72. FMC Corporation, Special Projects Laboratory, Buffalo, New York. "Hydrogen Peroxide: Catalytic Decomposition, Compatible Materials at High Temperature, and Surveillance Devices," Final Technical Report 224-17, U.S. Navy Contract NOas 58-689-c, July 1959. QPR 224-1 (1 June 1958, AD 301 202); 224-5 (1 September 1958, AD 303 748); 224-13 (1 March 1959, AD 308 999).

73. FMC Corporation, unpublished data.

74. Fomenko, A. S., I. L. Gankina, and T. M. Abramova, Kinetika i Kataliz, 2, 732-6 (1961). (CA 56, 10975f)

75. Fomenko, A. S., I. M. Abramova, and I. L. Gankina, Khim. Perekisnykh. Soedin., Akad. Nauk S.S.S.R., Inst. Obshch. i Neorgan. Khim., 56-62 (1963). (CA 61, 5189b)

76. Forker, W., Z. physik. Chem. (Leipzig), 205, 351-9 (1956). (CA 50, 16315d)

77. Formwalt, J. M., U.S. Patent 2,658,819, November 10, 1953. (CA 48, 1606g)

78. Forst, W., Can. J. Chem., 36, 1308-19 (1958). (CA 53, 1900c)

79. Forst, W., Can. J. Chem., 37, 1616-19 (1959). (CA 54, 17013g)

80. Franklin, T. C., and D. H. McClelland, J. Phys. Chem., 67(11), 2436-9 (1963). (CA 59, 14621g)

81. Franklin, T. C., D. McClelland, and N. F. Franklin, "Catalytic Processes on Platinized Platinum Electrodes," U.S. Dept. Com., Office Tech. Serv., 1963. (AD 410 477).

82. Gants, V. I., Trudy Leningrad. Tekhnol. Inst. im. Lensoveta, 37, 69-78 (1957). (CA 52, 11542h)

83. Gants, V. I., Trudy Leningrad. Tekhnol. Inst. im. Lensoveta, 61, 126-31 (1960). (CA 55, 23012i)

84. Gardiner, W. C., Z. physik. Chem. (Frankfurt), 15, 75-92 (1958). (CA 52, 11629a)

85. Garton, G., and J. Turkevich, J. chim. phys., 51, 516-19 (1954). (CA 49, 5094f)

86. Gerischer, R., and H. Gerischer, Z. physik. Chem (Frankfurt), (N.F.), 6, 178-200 (1956). (CA 50, 6163f)

87. Ghosh. J., and S. Ghosh, Proc. Natl. Acad. Sci., India, A32(2), 171-4 (1962). (CA 59, 65f)

88. Ghosh. J., and S. Ghosh, Proc. Natl. Acad. Sci., India, A32(2), 166-70 (1962). (CA 59, 65e)

89. Ghosh, J., and S. Ghosh. Proc. Natl. Acad. Sci., India, A33(1), 67-72 (1963). (CA 59, 3354g)

90. Giguère, P.A., Can. J. Research, 25B, 135 (1947). (CA 41, 4364g)

91. Giguère, P.A., Can. J. Research, 28B, 17 (1950). (CA 44, 3753d)

92. Giguère, P.A., and I.D. Liu, Can. J. Chem., 35, 283-94 (1957). (CA 51, 11824f)

93. Gonzalez-Salazar, G.G., and A.A. Blesa, Rev. acad. cienc. exact. fis.-quim. y nat. Zargoza, 10(2), 49-59 (1955). (CA 52, 13390e)

94. Gorokhova, T.I., A.N. Mal'tsev, and N.I. Kobozev, Zh. Fiz. Khim., 39(5), 1206-10 (1965). (CA 63, 6365a)

95. Grégusa, A., and P. Grégues, Akust. Zhur., 6, 441-5 (1960). (CA 55, 16094f)

96. Gupta, S.R., and S. Ghosh, Z. physik. Chem., 204, 6-15 (1955); Proc. Natl. Acad. Sci., India, A23(6), 55-62 (1954). (CA 53, 3859e)

97. Halford, F.B., A.V. Cleaver, and G.E. Preece (to De Havilland Engine Co. Ltd.), U.S. Patent 2,887,456, May 19, 1959. (CA 53, 20629d)

98. Hart, A.B., and J. McFadyen, "The Decomposition of Hydrogen Peroxide in the Vapor Phase," Paper presented at the HTP (High Test Peroxide) Symposium, RAE/RPD, Westcott, England, March 1954.

99. Hart, A.B., and D.S. Weir, Chem. & Ind. (London), 563-4 (1957). (CA 51, 14393h)

100. Hart, A.B., and R.A. Ross, Nature, 193, 1175-7 (1962). (CA 57, 1604a)

101. Hart, A. B., and R. A. Ross, J. Catalysis, 2, 251-3 (1963). (CA 60, 1148d)

102. Hart, A. B., J. McFadyen, and R. A. Ross, Trans. Faraday Soc., 59, 1458-69 (1963). (CA 59, 9369f)

103. Hasegawa, S., Rev. Phys. Chem. Japan, Shinkichi Horiba Commen. Vol. 1946, 21-30. (CA 44, 4319e)

104. Hayashi, K., Kyoto Furitsu Ikadaigaku Zasshi, 64, 923-52 (1958). (CA 54, 24969d)

105. Hickling, A., and W. H. Wilson, J. Electrochem. Soc., 98, 425-33 (1951). (CA 46, 43g)

106. Hiratsuka, K., E. Yonemitsu, and J. Kanno (to Mitsubishi Edogawa Chemical Co., Ltd.) Japanese Patent 1887(63), March 8, 1963. (CA 60, 14705h)

107. Hoare, D. E., J. B. Protheroe, and A. D. Walsh, Nature, 182, 654 (1958). (CA 53, 3851d)

108. Hoare, D. E., J. B. Protheroe, and A. D. Walsh, Trans. Faraday Soc., 55, 548-57 (1959). (CA 54, 2905d)

109. Horiba, M., Minami Osaka Byoin Igaku Zasshi, 8, 320-38 (1960). (CA 57, 5333d)

110. "Hydrogen Peroxide," A Report Bibliography, Defense Documentation Center, Alexandria, Va., November 1965. (ARB No. 041869). (30 references)

111. Ichinose, G., Tanso (Carbons), 1, 7-9 (1949). (CA 49, 13555a)

112. Ishizaki, S., Minami Osaka Byoin Igaku Zasshi, 10, 132-4 (1962). (CA 58, 963d)

113. Iványi, G., Nehézvegyipari Kutató Intézet Közleményei, 2, 107-16 (1960). (CA 55, 13711c)

114. Jacob, P., (East) German Patent 21,128, applied August 13, 1959. (CA 56, 7621d)

115. Kamiike, O., E. Naruko, and I. Sawada, J. Electrochem. Soc. Japan, 22, 608-11 (1954). (CA 49, 9402i)

116. Kandare, S., and F. H. Constable, Rev. fac. sci. univ. Istanbul, 19C, 238-61 (1954). (CA 49, 7347h)

117. Keating, K.B., A.G. Rozner, and J.L. Youngblood, J. Catalysis, 4, 608 (1965).

118. Kersonov, V.I., Uch. Zap. Yaroslavsk. Tekhnol. Inst., 8, 213-17 (1962). (CA 61, 13921c)

119. Khodakov, Yu. S., and Kh. M. Minachev, Zh. Fiz. Khim., 37(11), 2445-50 (1963). (CA 60, 3522f)

120. Kobozev, N.I., and I.A. Zubovich, Compt. rend. acad. sci. U.R.S.S., 52, 131-4 (1946). (CA 41, 1540f)

121. Kobozev, N.I., Acta. Physiochim. U.R.S.S., 21, 469-518 (1946). (CA 41, 2309h)

122. Kobozev, N.I., and N.A. Reshetovskaya, Zhur. Fiz. Khim., 23, 388-405 (1949). (CA 43, 6062c)

123. Kobozev, N.I., Uchenye Zapiski, Moskov. Gosudarst. Univ. im. M.V. Lomonosova, 174, 125-54 (1955). (CA 51, 5522d)

124. Kobozev, N.I., and I.V. Krylova, Kataliz v Vysshei Shkole, Min. Vysshego i Srednego Spets. Obrazov. S.S.S.R., Tr. 1-go (Pervogo) Meshvuz. Sovershch. po Katalizu, 1958(1), Pt. 2, 153-8 (1962). (CA 59, 5825g)

125. Kokado, M., and T. Okubo, Kyoto Furitsu Ika Daigaku Zasshi, 59, 1166-8 (1956). (CA 57, 5338d)

126. Kokado, M., and I. Yumori, Kyoto Furitsu Ika Daigaku Zasshi, 59, 1157-65 (1956). (CA 56, 6348a)

127. Kokado, M., M. Nomura, and T. Okubo, Kyoto Furitsu Ika Daigaku Zasshi, 62, 605-9 (1957). (CA 56, 2919f)

128. Kokado, M., T. Shindo, W. Kubokawa, and M. Yamamoto, Kyoto Furitsu Ika Daigaku Zasshi, 67, 1282-4 (1960). (CA 57, 10565a)

129. Kolarov, N., Bulgar. Akad. Nauk., Otdel, Geol.-Geograf. i Khim. Nauki, Izvest. Khim. Inst., 1, 185-203 (1951). (CA 46, 7858f)

130. Kolarov, N., Bulgar. Akad. Nauk Izvest. Khim. Inst., 4, 79-93 (1956). (CA 53, 8908d)

131. Kondrateva, E., and V.N. Kondratev, J. Phys. Chem. (U.S.S.R.), 19, 178 (1945). (CA 39, 5163^3)

132. Köppen, R., Kolloid-Z., 139, 172 (1954). (CA 49, 7162f)

133. Köppen, R., German Patent 1,084,944, applied February 7, 1955. CA 56, 938e)

134. Köppen, R., Gesundh.-Ing., 77, 282-4 (1956). (CA 51, 17563g)

135. Kotkowski, S., Roczniki Chem., 34, 205-20 (1960). (CA 54, 17021d)

136. Krause, A., Poznán. Towarz. Przyjaciól Nauk, Prace Komisji Mat. Przyrodniczej, A5(3), 163-80 (1948). (CA 44, 7131e)

137. Krause, A., Przemysl Chem., 29, 377-83 (1950). (CA 46, 6916e)

138. Krause, A., Roczniki Chem., 26, 3-7 (1952). (CA 46, 11026a)

139. Krause, A., and G. Olejnik, Roczniki Chem., 27, 17-22 (1953). (CA 48, 5624g)

140. Krause, A., Bull. soc. amis sci. et lettres Poznan, B12, 43-57 (1953). (CA 47, 7875g)

141. Krause, A., and W. Wolski, Przemysl Chem., 9, 606-8 (1953). (CA 51, 3255c)

142. Krause, A., and W. Wolski, Roczniki Chem., 27, 321-6 (1953). (CA 48, 6050g)

143. Krause, A., Roczniki Chem., 28, 3-11 (1954). (CA 48, 9168c)

144. Krause, A., and E. Wosinska, Roczniki Chem., 28, 351-8 (1954). (CA 49, 7946)

145. Krause, A., and J. Pawelkiewicz, Roczniki Chem., 28, 317-27 (1954). (CA 49, 7945)

146. Krause, A., S. Granieczny, and W. Wolski, Roczniki Chem., 28, 377-84 (1954). (CA 49, 7947a)

147. Krause, A., and E. Borzeszkowski, Roczniki Chem., 28, 367-76 (1954). (CA 49, 7946i)

148. Krause, A., J. Rosochowicz, and K. Przylecka, Roczniki Chem., 28, 329-36 (1954). (CA 49, 7946a)

149. Krause, A., and S. Magas, Roczniki Chem., 28, 337-59 (1954). (CA 49, 7946b)

150. Krause, A., Roczniki Chem., 29, 300-5 (1955). (CA 49, 15413g)

151. Krause, A., Roczniki Chem., 29, 201-8 (1956); see also Przemysl Chem., 11, 291-94 (1955). (CA 49, 13752a)

152. Krause, A., and W. Wolski, Roczniki Chem., 29, 993-8 (1955). (CA 50, 7556a)

153. Krause, A., Roczniki Chem., 29, 165-72 (1955). (CA 49, 13752b)

154. Krause, A., and W. Wolski, Roczniki Chem., 30, 681-90 (1956). (CA 51, 2369i)

155. Krause, A., and A. Smoczkiewiczowa, Roczniki Chem., 30, 369-84 (1956). (CA 51, 1711a)

156. Krause, A., and P. Poszwiński, Roczniki Chem., 30, 29-38 (1956). (CA 51, 1710d)

157. Krause, A., Roczniki Chem., 30, 39-59 (1956). (CA 51, 1709f)

158. Krause, A., W. Wolski, and H. Wasiak, Roczniki Chem., 30, 723-32 (1956). (CA 51, 2369e)

159. Krause, A., Roczniki Chem., 30, 1047-54 (1956). (CA 51, 7818e)

160. Krause, A., and G. Olejnik, Roczniki Chem., 30, 1095-1102 (1956). (CA 51, 7820g)

161. Krause, A., and A. Binkówna, Roczniki Chem., 31, 801-8 (1957). (CA 52, 5946h)

162. Krause, A., and S. Zielinski, Roczniki Chem., 31, 429-36 (1957). (CA 52, 856f)

163. Krause, A., W. Wolski, and K. Swiatlak, Roczniki Chem., 31, 413-19 (1957). (CA 52, 856c)

164. Krause, A., B. Bethke, and A. Calkówna, Roczniki Chem., 32, 409-11 (1958). (CA 52, 17924c)

165. Krause, A., and A. Hermann, Roczniki Chem., 32, 1025-31 (1958). (CA 53, 19543i)

166. Krause, A., and K. Lasiewicz, Roczniki Chem., 32, 403-4 (1958). (CA 52, 17925a)

167. Krause, A., and A. Turowska, Roczniki Chem., 32, 975-7 (1958). (CA 53, 4612i)

168. Krause, A., and A. Hermannówna, Roczniki Chem., 32, 971-3 (1958). (CA 53, 4061b)

169. Krause, A., and M. Miedzinski, Roczniki Chem., 32, 1199-1201 (1958). (CA 53, 7743f)

170. Krause, A., and A. Hermann, Z. anorg. u. allgem. Chem., 299, 153-7 (1959). (CA 53, 16669i)

171. Krause, A., and A. Hermann, Roczniki Chem., 33, 515-17 (1959). (CA 53, 20624h)

172. Krause, A., W. Wolski, and F. Skrzypczak-Krzyminska, Roczniki Chem., 33, 227-9 (1959). (CA 53, 14384a)

173. Krause, A., and J. Leszuchowska, Z. anorg. u. allgem. Chem., 301, 294-399 (1959). (CA 54, 4230e)

174. Krause, A., and S. Reysner, Roczniki Chem., 33, 811-12 (1959). (CA 54, 2913e)

175. Krause, A., and F. Domka., Roczniki Chem., 34, 1829-32 (1960). (CA 55, 16094d)

176. Krause, A., Z. Anorg. Allgem. Chem., 307, 229-32 (1960). (CA 55, 16248a)

177. Krause, A., F. Domka, and J. Slawek, Z. Anorg. Allgem. Chem., 311, 79-82 (1961). (CA 57, 1778e)

178. Krause, A., and S. Kotkowski, Przemysl Chem., 40, 631-4 (1961). (CA 56, 13598h)

179. Krause, A., and I. Plura, Naturwissenschaften, 48, 693-4 (1961). (CA 56, 9110g)

180. Krause, A., and J. Orlikowska, Naturwissenschaften, 49, 468 (1962). (CA 58, 5073e)

181. Krause, A., and E. Kukielka, Monatsh. Chem., 93, 955-61 (1962). (CA 58, 3943b)

182. Krause, A., and F. Domka, Z. Anorg. Allgem. Chem., 315(1/2), 110-13 (1962). (CA 60, 15189c)

183. Krause, A., and E. Kukielka, Z. Physik. Chem. (Frankfurt), 35, 65-8 (1962). (CA 58, 9659c)

184. Krause, A., and F. Domka, Roczniki Chem., 36, 1123-5 (1962). (CA 58, 8442f)

185. Krause, A., and M. Blawacka, Z. Anorg. Allgem. Chem., 318, 313-17 (1962). (CA 58, 54d)

186. Krause, A., and M. Blawacka, Z. Physik. Chem. (Frankfurt), 33, 369-73 (1962). (CA 58, 55b)

187. Krause, A., E. Kukielka, and L. Plura, Z. Physik. Chem., 35, 289-94 (1962). (CA 59, 10770c)

188. Krause, A., and J. Lezuchowska, Monatsh., 95(1), 203-6 (1963). (CA 61, 8938a)

189. Krause, A., and I. Plura, Naturwissenschaften, 50, 41-2 (1963). (CA 58, 6227f)

190. Krause, A., and M. Blawacka, Z. Anorg. Allgem. Chem., 321, 274-7 (1963). (CA 59, 66g)

191. Krause, A., and M. Urbanowicz, Naturwissenschaften, 50(13), 473 (1963). (CA 59, 7017b)

192. Krause, A., F. Domka, E. Kukielka, and I. Plura, Monatsh., 94(2), 466-9 (1963). (CA 59, 8161d)

193. Krause, A., and Z. Winowski, Monatsh., 94(2), 470-2 (1963). (CA 59, 8158e)

194. Krause, A., F. Domka, E. Kukielka, and J. Orlikowska, Monatsh., 95(1), 231-3 (1963). (CA 61, 8941f)

195. Krause, A., J. Slawek, and Z. Winowski, Z. Physik. Chem. (Frankfurt), 40(3/4), 261-3 (1964). (CA 60, 15190a)

196. Krause, A., and J. Orlikowska, Monatsh., 95(2), 379-81 (1964). (CA 61, 6439h)

197. Krause, A., and J. Slawek, Z. Anorg. Allgem. Chem., 331(5-6), 350-2 (1964). (CA 62, 4655h)

198. Krause, A., and J. Orlikowska, Naturwissenschaften, 51(17), 406-7 (1964). (CA 62, 13894b)

199. Krause, A., and M. Rychlewska, Montash. Chem., 95(4-5), 1332-4 (1964). (CA 62, 7154h)

200. Krause, A., and F. Domka, Naturwissenschaften, 51(6), 136 (1964). (CA 60, 15189h)

201. Krause, A., and F. Domka, Chemiker-Ztg., 88(4), 112-13 (1964). (CA 60, 11412d)

202. Krause, A., F. Domka, and P. Meteniowski, Monatsh., 95(2), 600-2 (1964). (CA 61, 6442g)

203. Krause, A., F. Domka, and W. Sleziak, Experientia, 20(8), 420 (1964). (CA 61, 8936a)

204. Kreimer, G. S., M. R. Vakhovskaya, O. S. Safonova, and E. E. Bogino, Zavodskaya Lab., 15, 159-67 (1949). (CA 44, 1304b)

205. Krylova, I. V., and N. I. Kobozev, Zhur. Fiz. Khim., 30, 2077-84 (1956). (CA 51, 6301c)

206. Krylova, I. V., and N.I. Kobozev, Zhur. Fiz. Khim., 31, 2725-31 (1957). (CA 52, 8741d)

207. Krylova, I. V., V.A. Ogarev, and N.I. Kobozev, Zhur. Fiz. Khim., 34, 2408-13 (1960). (CA 55, 7004e)

208. Krylova, I. V., V.A. Ogarev, and N.I. Kobozev, Zhur. Fiz. Khim., 35, 2311-15 (1961). (CA 56, 4135i)

209. Kulitskii, V. N., Tr. L'vovsk. Med. Inst., 22, 36-42 (1961). (CA 59, 12227e)

210. Kulitskii, V. N., Tr. L'vovsk. Med. Inst., 22, 43-7 (1961). (CA 59, 12227f)

211. Kulskiy, L. A., A. A. Kachan, M. A. Sherstoboyeva, and T. K. Timoshenko, "The Catalytic Activity of Silver Water Upon the Oxidation of Indigocarmine by Hydrogen Peroxide," Ukrain. Khim. Zhur., 29(1), 406-8 (1963). (AD 409 221)

212. Kuzhelyuk, A. A., Zh. Fiz. Khim., 38(5), 1268-9 (1964). (CA 61, 12956h)

213. Lal, B. B., Proc. Indian Acad. Sci., 38A, 522-33 (1953). (CA 48, 7441c)

214. Lane, B. F. A., and P. Ramsden (to D. Napier & Son Ltd.), British Patent 780, 342, July 31, 1957. (CA 52, 2380d)

215. Lane, B. F. A., and G. R. Strickland (to D. Napier & Son Ltd.), British Patent 797, 987, July 9, 1958. (CA 53, 22619c)

216. Lane, B. F. A. (to D. Napier & Son Ltd.), German Patent 1, 091, 093, applied November 6, 1959. (CA 56, 11234g)

217. Lane, B. F. A., P. Ramsden, and G. R. Strickland (to D. Napier & Son Ltd.), British Patent 829, 045, February 24, 1960. (CA 54, 12429b)

218. Laxton, J. W. (to D. Napier & Son Ltd.), German Patent 1, 067, 790, October 29, 1959. (CA 55, 22660f)

219. Laxton, J. W. (to D. Napier & Son Ltd.), U. S. Patent 2, 951, 046, August 30, 1960. (CA 55, 1970g)

220. Laxton, J. W. (to D. Napier & Son Ltd.), British Patent 866, 338, April 26, 1961. (CA 55, 25093e)

221. Lazarov, D., G. Bliznakov, and E. Lazarova, Godishnik Sofiiskiya Univ. Khim. Fak., 56, 37-43 (1961-62). (CA 61, 13909c)

222. Lazarov, D., G. Bliznakov, and E. Popandova, J. Catalysis, 3(3), 201-6 (1964). (CA 61, 3729g)

223. Lebedev, V. P., Problemy Kinetiki i Kataliza, Akad. Nauk S. S. S. R., (10), 204-9 (1960). (CA 55, 12006d)

224. Lebedev, V. P., and Zh. V. Strel'nikova, Nauch. Doklady Vysshei Shkoly, Khim. Tekhnol., (2), 260-3 (1959). (CA 53, 19543e)

225. Lebedev, V. P., and Zh. V. Strel'nikova, Vestnik Moskov. Univ., Ser. II 15, (5), 25-39 (1960). CA 55, 20578a)

226. Lebedev, V. P., and E. A. Trosman, Zhur. Fiz. Khim., 34, 687-90 (1960). (CA 55, 16091g)

227. Levi, R., Chim. et ind. (Paris), 57, 221-7 (1947).

228. Li, W. C., N. I. Kobozev, and A. N. Mal'tsev, Kataliticheskie Reaktsii v Zhidkoi Faze, Akad. Nauk Kaz. SSR, Kazakhsk. Gos. Univ., Kazakhsk. Resp. Pravlenie Mendeleevskogo Obshchestva, Tr. Vses. Konf., Alama-Ata, 1962, 192-6 (1963). CA 60, 12701e)

229. Li, W. C., A. N. Mal'tsev, and N. I. Kobozev, Zh. Fiz. Khim., 38(1), 80-8 (1964). (CA 60, 8680c)

230. Li, W. C., A. N. Mal'tsev, and N. I. Kobozev, Zh. Fiz. Khim., 38(2), 439-41 (1964). (CA 60, 13916e)

231. Li, W. C., A. N. Mal'tsev, and N. I. Kobozev, Vestn. Mosk. Univ., Ser. II, Khim., 19(1), 39-42 (1964). (CA 60, 12702e)

232. Lopatukhina, B. M., and A. I. Shlygin, Izvest. Akad. Nauk Kazakh. S. S. R. No. 101, Ser. Khim. No. 4, 60-4 (1951). (CA 48, 3171a)

233. Lopatkin, A. A., V. I. Shekhobalova, and V. P. Lebedev, Zhur. Fiz. Khim., 28, 2222-31 (1954). (CA 50, 11789b)

234. Lopatkin, A. A., Zh. V. Strel'nikova, and V. P. Lebedev, Vestnik Moskov. Univ. 11, Ser. Mat., Mekh., Astron., Fiz., Khim., (1) 255-9 (1956). (CA 51, 11831c)

235. Lopatkin, A. A., Zh. V. Strel'nikova, and V. P. Lebedev, Zhur. Fiz. Khim., 31, 195-9 (1957). (CA 51, 17283h)

236. Lopatkin, A. A., Zh. Fiz. Khim., 36, 709-13 (1962). (CA 57, 7966a)

237. Mackenzie, R. C., and M. Ritchie, Proc. Roy. Soc. (London), A185, 207-24 (1946). (CA 40, 2377^4)

238. Magaril, R. Z., and E. I. Aksenova, Kauchuk i Rezina, 22(8), 24-7 (1963). (CA 60, 1907a)

239. Maggs, F. T. and D. Sutton, Trans. Faraday Soc., 54, 1861-70 (1958). (CA 53, 16670d)

240. Maggs, F. T. and D. Sutton, Trans. Faraday Soc., 55, 974-80 (1959). (CA 54, 6278f)

241. Maglio, R. A., and W. A. Poole (to General Electric Co.), U. S. Patent 3,056,663, October 2, 1962. (CA 58, 58e)

242. Makino, S., J. Electrochem. Soc. Japan, 22, 615-18 (1954). (CA 49, 9402b)

243. Markovic, T., Werkstoffe u. Korrosion, 5, 285-8 (1954). (CA 49, 5088d)

244. Markovic, T., Werkstoffe u. Korrosion, 6, 136-41 (1955). (CA 49, 12156e)

245. Massachusetts Institute of Technology, Hydrogen Peroxide Laboratories, Cambridge, Mass. "Mechanism of Catalytic Decomposition of H_2O_2 Solutions with Manganese Dioxide." Technical Report No. 1, by D. B. Broughton et al., (91C-6351), U. S. Navy Contract NOrd-9107, 1 November 1945. (PB 136 233)

246. Massachusetts Institute of Technology, Division of Industrial Cooperation, Cambridge, Mass. "Flow Studies of the Catalytic Decomposition of H_2O_2 Solutions." MIT Report No. 5, by H. Isbin et al., 1 March 1946.

247. Massachusetts Institute of Technology, Division of Industrial Cooperation, Cambridge, Mass. "Mechanism of the Catalytic Decomposition of H_2O_2 Solutions by Manganese Dioxide," Report No. 6, by D. B. Broughton et al., U. S. Navy Contract NOrd-9107, February 1946. (PB 133 531)

248. Massachusetts Institute of Technology, Division of Industrial Cooperation, Cambridge, Mass. "Mechanism of Catalytic Decomposition of H_2O_2 by Oxides of Lead." Report No. 12, U. S. Navy Contract NOrd 9107, by D. B. Broughton et al., 1 December 1946. (AD 138 643, PB 137 387)

249. Massachusetts Institute of Technology, Division of Industrial Cooperation, Cambridge, Mass. "Activity of Metal Hydroxides as Catalysts for the Decomposition of H_2O_2," Report No. 7, by D. B. Broughton, D. M. Manke, M. E. Laing *et al.*, U. S. Navy Contract NOrd 9107, February 1946. (PB 130 628).

250. Massachusetts Institute of Technology, Division of Industrial Cooperation, Cambridge, Mass. "Activity of Co-precipitated Metal Hydroxides as Catalysts for the Decomposition of Hydrogen Peroxide," Report No. 9, by D. Broughton *et al.*, 1 August 1946.

251. Massachusetts Institute of Technology, Division of Industrial Cooperation, Cambridge, Mass. "Preparation and Evaluation of Impregnated-Type Catalysts for Hydrogen Peroxide Decomposition," U. S. Navy Contract NOrd 9107-c, Report No. 13, DIC 6351, by H. S. Isbin and D. B. Thompson, 27 January 1947.

252. Massachusetts Institute of Technology, Division of Industrial Cooperation, Cambridge, Mass. "Mechanism of Decomposition of H_2O_2 with Cobalt Compounds." Report No. 16, by D. B. Broughton, R. L. Wentworth, and M. L. Farnsworth, U. S. Navy Contract NOrd 9107-c, May 1947. (PB 130627).

253. Massachusetts Institute of Technology, Division of Industrial Cooperation, Cambridge, Mass. "Mechanism of the Catalytic Decomposition of Hydrogen Peroxide," Report 32, by R. L. Wentworth, U. S. Navy Contract N5ori- 078(19), 1 May 1951.

254. Massachusetts Institute of Technology, Division of Industrial Cooperation, Cambridge, Mass. "Simultaneous Heat and Mass Transfer in the Heterogeneous Decomposition of H_2O_2 Vapor." Reports 33, 34, and 35, by C. N. Satterfield, H. Resnick, and R. L. Wentworth, 2 June 1952; A. R. Winters, Jr., S. M. Thesis, MIT, Cambridge, 1952.

255. Massachusetts Institute of Technology, Hydrogen Peroxide Laboratories, Cambridge, Mass. ["Continuing Studies on Hydrogen Peroxide."] See the following quarterly progress reports under Contracts N5ori-07819 and NOnr-1841(00). September 1952 (PB 116 706); December 1952 (PB 116707); March 1953 (PB 116 708); June 1953 (PB 116709); September 1953 (PB 114 080); December 1953 (PB 115 065); March 1954 (PB 116325); June 1954 (PB 117316); September 1954 (PB 118 313); December 1954 (PB 119 030); March 1955 (PB 120 045); June 1955 (PB 122 156); December 1955 (PB 127 087); March 1956 (PB 124 914); June 1956 (PB 127 167); 30 June 1959 (AD 220 223, PB 146 281); 30 September 1959 (AD 228 153, PB 148 871); 31 December 1959 (AD 231 415, PB 152 095); 31 March 1960 (AD 235 699), PB 153 769); 15 July 1960 (AD 241 230);

15 November 1960 (AD 246 573). For a list of research reports covering studies on the properties and reactions of H_2O_2 carried out at the Massachusetts Institute of Technology during the period 1945-1962, see "Properties and Reactians of Hydrogen Peroxide," Final Report under Contracts NOnr-184111, Proj. NR-092-008 and N5ori-07819, by Charles N. Satterfield, 15 May 1962 (AD 289 270). See also the monograph by Schumb, Satterfield, and Wentworth (309).

256. Masterson, S., C.H. Peers, and R. Willows (to Minister of Supply), British Patent 672,860, May 28, 1952. (CA 46, 10494a)

257. Matsumoto, C., T. Nishi, and S. Okada, J. Electrochem. Soc. Japan, 22, 612-15 (1954). (CA 49, 9402h)

258. Matsunaga, Y., Bull. Chem. Soc. Japan, 30, 984-5 (1957). (CA 52, 14036d)

259. Matsuura, I., Y. Kubokawa, and O. Toyama, Nippon Kagaku Zasshi, 81, 1209-13 (1960). (CA 55, 11039g)

260. Maxim, I., and T. Braun, J. Phys. Chem. Solids, 24, 537-48 (1963). (CA 58, 11921g)

261. Maxted, E.B., and S.M. Ismail, J. Chem. Soc., 1962, 2330-33. (CA 57, 5342e)

262. McKee, L., "Hydrogen Peroxide for Propulsive Power: Production and Use by the Germans during World War II," Mech. Eng., 68, 1045-8 (1946); Engineering, 163, 307-8 (1947); Chem. Age (London), 57, 395-7 (1947); Mech. Eng., 69, 682-4 (1947).

263. McLane, C.K., J. Chem. Phys., 17, 379-85 (1949). (CA 43, 7305h)

264. Minachev, Kh. M., M.A. Markov, and Yu. S. Khodakov, Izv. Akad. Nauk S.S.S.R., Otd. Khim. Nauk, 1227-39 (1961). (CA 58, 3033e)

265. Minachev, Kh. M., and Yu. S. Khodakov, Izv. Akad. Nauk S.S.S.R., Otd. Khim. Nauk, 1430-2 (1961). (CA 58, 3033f)

266. Mizuwatari, E., Repts. Inst. Chem. Research Kyoto Univ., 17, 31-41 (1949). CA 45, 10018b)

267. Mooi, J., and P.W. Selwood, J. Am. Chem. Soc., 72, 4333-4 (1950). (CA 45, 2298c)

268. Mooi, J., and P. W. Selwood, J. Am. Chem. Soc., 74, 1750-4 (1952). (CA 46, 6916)

269. Moore, C. B., T. M. Amundson, and W. K. Dick (to General Mills, Inc.), U.S. Patent 3,064,902, November 20, 1962. (CA 59, 1145d)

270. Mosevich, I. A., I. P. Tverdovskii, and Zh. L. Vert, Trudy Gosudarst. Inst. Priklad. Khim., No. 46, 191-8 (1960). (CA 56, 10964h)

271. Muraki, I., H. Kondo, and K. Shinoda, Kogyo Kagaku Zasshi, 65, 22-6 (1962). (CA 57, 16106g)

272. Myuller, L., and L. N. Nekrasov, Dokl. Akad. Nauk S.S.S.R., 157(2), 416-19 (1964). (CA 61, 12950b)

273. Nabe, D. R., and B. P. Gyani, J. Indian Chem. Soc., 37, 717-21 (1960). (CA 55, 26622c)

274. Nachman, M., I. Maxim, and T. Breun, Acad. rep. populare Romine, Inst. fiz. at. I. F. A. /C. S. /21, (1960). (CA 55, 24201c)

275. National Aeronautics and Space Administration, Langley Research Center, Langley Station, Hampton, Virginia. "Investigation of Catalyst Beds for 98-Per Cent-Concentration Hydrogen Peroxide," by J. F. Runckel, C. M. Willis, and L. P. Salters, Jr. NASA Technical Note D-1808, June 1963. (CA 59, 8537b)

276. Naval Research Laboratory. "Considerations on the Vapor Barrier in the Catalytic Decomposition of 90 Per Cent H_2O_2," NRL Memorandum Report No. 708, by R. N. Hazlett and J. M. Pilato.

277. Naval Torpedo Station, Newport, R. I. "Research and Development on Hydrogen Peroxide and Catalysis and Application to Torpedo Propulsion," Monthly Technical Reports TS No. 86, 89, 95, 105, 124, 145, 148, and 154. Project Re 6a -267, May 1946-July 1947.

278. Nergararian, A., and M. C. Markaham, J. Phys. Chem., 67(12), 2679-82 (1963). (CA 60, 1258h)

279. Nikitin, E. E., Zhur. Fiz. Khim., 33, 1893-4 (1959). (CA 54, 19118f)

280. Nikolaev, L. A., and N. I. Kobozev, J. Phys. Chem. (U.S.S.R.), 20, 145-50 (1946). (CA 40, 5626i)

281. Nikolaev, L. A., Problemy Kinetiki i Kataliza, Akad. Nauk S.S.S.R., Inst. Fiz. Khim. 5, Metody Izucheniya Katalizator, 297-305 (1948). (CA 48, 13384g)

282. Nikolaeva, M.I., and A.I. Shlygin, *Zhur. Fiz. Khim.*, **24**, 427-31 (1950). (CA **44**, 8263e)

283. Nikolaeva, M.I., and A.I. Shlygin, *Zhur. Fiz. Khim.*, **24**, 534-8 (1950). (CA **44**, 8749b)

284. Nikolaeva, M.I., and A.I. Shlygin, *Zhur. Fiz. Khim.*, **30**, 1729-31 (1956). (CA **51**, 7199i)

285. Nikolaev, L.A., and A.A. Askadskii, *Khim. Nauka i Prom.*, **3**, 131-2 (1958). (CA **52**, 11543b)

286. Otwinowska, H., A. Nowacki, and S. Cibrowski, *Roczniki Chem.*, **38**(6), 1007-13 (1964). (CA **62**, 7155e)

287. Peers, C.H., British Patent 749,431, May 23, 1956. (CA **50**, 13336d)

288. Peers, C.H. (to Minister of Supply), British Patent 750,599, June 20, 1956. (CA **50**, 14148g)

289. Penner, S.S., *J. Am. Chem. Soc.*, **74**, 2754-7 (1952). (CA **46**, 9399g)

290. Pennsylvania State College, School of Mineral Industries, State College, Pa. " Influence of the Carrier on the Catalytic Activity of Adsorbed Heavy Metal Ions," Report 1, Contract N6onr 269, by D.P. Enright, E.C. Marboe, and W.A. Weyl, October 1948 (PB 116 212); "Comparison of the Catalytic Activity of Noble and Non-Noble Gas Type Ions on the Decomposition of Hydrogen Peroxide," Report 2, Contract N6onr 269, by D.P. Enright, E.C. Marboe, and W.A. Weyl, January 1949 (PB 132 466); See also "Decomposition of Hydrogen Peroxide by Lead Fluoride," by D.B. Enright, P.A. Marshall, and W. A. Weyl, *in* "New Approach to the Chemistry of Surfaces," Contract N6onr 269, August 1950 (PB 116 215).

291. Pierron, P., *Bull. soc. chim. France 1949*, 754-8. (CA **44**, 2355e)

292. Pinter, T., and V. Karas, *Kolloid-Z.*, **142**, 107-9 (1955). (CA **49**, 15410i)

293. Poltorak, O.M. *Kataliz v Vysshei Shkole, Min. Vysshego i Srednego Spets. Obrazov S.S.S.R., Tr. 1-go [Pervogo] Mezhvuz. Soveshch. po Katalizu,1958*, No. 1(1), 107-23 (1962). (CA **59**, 1133h)

294. Pospelova, T.A., and N.I. Kobozev, *Zh. Fiz. Khim.*, **35**, 1192-7 (1961). (CA **57**, 395i)

295. Puri, B. R., L. R. Sharma, and D. D. Singh, J. Indian Chem. Soc., 35, 765-9 (1958). (CA 53, 16670g)

296. Roberts, R. M. (to Shell Oil Co.), U. S. Patent 3,142,151, July 28, 1964. (CA 61, 10350a)

297. Rocket Propellants - An ASTIA Report Bibliography. Armed Services Technical Information Agency, Arlington, Va., March 1960. (AD 233 500). Supplement No. 1, September 1961. (AD 263 000).

298. Rocket Propulsion Establishment. Westcott, Buckinghamshire. "Some Aspects of the Catalytic Decomposition of Hydrogen Peroxide by Silver. Part VII. "The Rate of Decomposition," R. P. E. Tech. Note 197, by D. Sutton, December 1960.

299. Rocketdyne, Canoga Park, California. "Summary Report, Research Program on Hydrogen Peroxide," Technical Report R-2094, U. S. Navy Contract NOas 56-1052d, 12 July 1960; See also "Applied Research of Hydrogen Peroxide," Contract NOas 56-1052d; Quarterly Reports R-370-1P (23 October 1956, AD 129 594); R-604 (29 August 1957, AD 142 620); 1199-1P (17 November 1958, AD 309 553); R-1199-1 (17 November 1958, AD 305 586); R-1199-2 (21 January 1959, AD 305 018); R-1199-3 (AD 307 106).

300. Roikh, I. L., I. P. Bolotich, V. V. Ordynskaya, S. G. Belitskaya, and L. N. Koltunova, Zh. Fiz. Khim., 38(6), 1588-91 (1964). (CA 61, 8938d)

301. Ross, R. A., J. Catalysis, 3(6), 562-4 (1964). (CA 62, 2279h)

302. Runckel, J. F., C. M. Willis, and L. B. Salters, Jr., "Investigation of Catalyst Beds for 98-Per Cent-Concentration Hydrogen Peroxide," National Aeronautics and Space Administration, Langley Research Center, Langley Station, Va. NASA Technical Note D-1808, June 1963.

303. Sal'nikov, V. V., L. V. Yur'eva, F. N. Makarova, and E. A. Druyan, Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol, 6(3), 416-19 (1963). (CA 59, 13385g)

304. Satterfield, C. N., G. M. Kavanagh, and H. Resnick, Ind. Eng. Chem., 43, 2507-14 (1951). (CA 46, 1767a)

305. Satterfield, C. N., and T. W. Stein, J. Phys. Chem., 61, 537-40 (1957). (CA 51, 13531a)

306. Satterfield, C.N., and R.S.C. Yeung, Ind. Eng. Chem., Fundamentals, 2(4), 257-64 (1963). (CA 59, 12421a)

307. Satterfield, C.N., and F.P. Audibert, Ind. Eng. Chem., Fundamentals, 2(3), 200-2 (1963). (CA 59, 4582f)

308. Saunders, C.E., U.S. Patent 3,019,197, January 30, 1962. (CA 56, 9470h)

309. Schumb, W.C., C.N. Satterfield, and R.L. Wentworth, Hydrogen Peroxide, Reinhold Publishing Corporation, New York, 1955.

310. Schwab, G.M., Chimica e industria (Milan), 35, 810-16 (1953). (CA 48, 4948d)

311. Schwab, G.M., and G. Greger, Z. physik. Chem. (Frankfurt), 13, 248-59 (1957). (CA 52, 2515a)

312. Schwab, G.M., and A. Kraut, Z. Anorg. Allgem. Chem., 295, 36-60 (1958). (CA 52, 17923b)

313. Shushkov, A.S., I.V. Krylova, and N.I. Kobozev, Zh. Fiz. Khim., 37(8), 1851-4 (1963). (CA 59, 14626f)

314. Shashkov, A.S., and I.V. Krylova, Vestn. Mosk. Univ., Ser. II, Khim., 20(5), 37-41 (1965). (CA 64, 5797h)

315. Shell Development Company, Emeryville, California. "Thermal Stability of 90 Per Cent Hydrogen Peroxide," Final Report S-13731, U.S. Navy Contract NOas 56-1023-d, 1 July 1956-30 June 1957. (AD 143 178). See also Quarterly Reports S-13702 (1 July - 30 September 1956, AD 111 740); S-13708 (1 October - 31 December 1956, AD 120 838).

316. Shell Development Company, Emeryville, California. "Study of Hydrogen Peroxide Catalysts and their Performance," by H.J. Baumgartner, G.C. Hood, and R.M. Roberts, Contract NOa(s) 57-795-d. Final Report, May 1957 - July 1958, Report S-13765 (3 vols.): Vol. I., "Fundamentals and Catalyst Development," (AD 304 774), Vol. II., "Decomposer Tests, Correlations," AD 304 775), Vol. III., "Equipment, Methods, Data," (AD 304 776).

317. Shell Development Company, Emeryville, California. "Thermal Stability of 90 Per Cent Hydrogen Peroxide," Final Report S-13756, U.S. Navy Contract NOas 56-1023-d, 1 July 1957 - 30 June 1958, (AD 301 314). See also Quarterly Reports S-13771 (October - December 1958, AD 305 206); S-13777 (January - March 1959, AD 306 878); S-13784 (April - June 1959, AD 309 380);

S-13793 (July - September 1959, AD 313 323). These reports were followed by Quarterl y Reports S-13763 (July - September 1958); S-13771 (October - December 1958, AD 305 206); S-13777 January - March 1959, AD 306 878); S-13784 (April - June 1959, AD 309 380); S-13793 (July - September 1959, AD 313 323).

318. Shell Chemical Company, Industrial Chemicals Division, New York. "Concentrated Hydrogen Peroxide H_2O_2." Second Edition, 1962. Includes a bibliography of 338+ references.

319. Shell Internationale Research Maatschappij N. V., French Patent 1,350,611, January 31, 1964. (CA 61, 6655g)

320. Sherwood, B.J. (to North American Aviation, Inc.), U.S. Patent 2,750,346, June 12, 1956. (CA 50, 13336h)

321. Sherwood, B.J. (to North American Aviation, Inc.) U.S. Patent 2,811,490, October 29, 1957. (CA 52, 14306c)

322. Shub, D.M., G.S. Tyurikov, and V.I. Veselovskii, Zhur. Fiz. Khim., 34, 2245-53 (1960). (CA 55, 21765a)

323. Shushunov, V.A., and K.G. Fedyakova, Zhur. Fiz. Khim., 23, 936-41 (1949). (CA 44, 26g)

324. Sill, M. (to Bell Aerospace Corp.), U.S. Patent 3,135,703, June 2, 1964.

325. Simon, A., and G. Guenzler, J. Prakt. Chem., 19(5-6), 245-51 (1963). (CA 59, 14701f)

326. Strel'nikova, Zh. V., A.A. Lopatkin, and V.P. Lebedev, Zhur. Fiz. Khim., 30, 639-44 (1956). (CA 50, 13581c)

327. Strel'nikova, Zh. V., and V.P. Lebedev, Vestn. Mosk. Univ., Ser. II, Khim., 20(2), 9-15. (CA 63, 3664h)

328. Strel'nikova, A.A. Lopatkin, and V.P. Lebedev, Zhur. Fiz. Khim., 30, 196-201 (1956). (CA 50, 10500b)

329. Strel'nikova, Zh. V., E.A. Trosman, and V.P. Lebedev, Zhur. Fiz. Khim., 35, 1327-30 1961). (CA 56, 8059g)

330. Strel'nikova, Zh. V., L.A. Pribylova, and V.P. Lebedev, Vestn. Mosk. Univ. Ser. II, Khim., 17(3), 46-8 (1962). (CA 51, 10569a)

331. Strel'nikova, Zh. V., and V. P. Lebedev, Vestn. Mosk. Univ., Ser II, Khim., 17(6), 75 (1962). (CA 59, 14626c)

332. Strel'nikova, Zh. V., and V. P. Lebedev, Kataliticheskie Reaktsii v Zhidkoi Faze, Akad. Nauk Kaz. S. S. R., Kazakhsk. Gos. Univ., Kazakhsk. Resp. Pravlenie Mendeleevskogo Obshchestva, Tr. Vses. Konf., Alma-Ata 1962, 304-9 (1963). (CA 60, 13915h)

333. Strel'nikova, Zh. V., E. A. Trosman, and V. P. Lebedev, Zh. Fiz. Khim., 36, 2469-72 (1962). (CA 58, 5075a)

334. Strel'nikova, Zh. V., and V. P. Lebedev, Zh. Fiz. Khim., 37, 920-2 (1963). (CA 59, 2209a)

335. Suito, E., Rev. Phys. Chem. Japan, Shinkichi Horiba Commen. Vol. 1946, 35-41. (CA 44, 4319g)

336. Sviridov, V. V., and G. A. Branitskii, Geterogennye Khim. Rektsii 1961, 146-61. (CA 57, 4089f)

337. Sviridov, V. V., and G. A. Branitskii, Dokl. Akad. Nauk Belorussk. S. S. R., 7(6), 387-90 (1963). (CA 59, 12226h)

338. Sviridov, V. V., G. A. Branitskii, and L. V. Potanina, Izv. Vysshykh Uchebn. Zavedenii, Khim. i Khim. Tekhnol., 7, 577-82 (1964). (NSA 19, 26389)

339. Tamura, K., Shokubai, 1, 112-28 (1959). (CA 55, 2244e)

340. Tamura, K., K. Tarama, and E. Suito, Nippon Kagaku Zasshi, 80, 10-13 (1959). (CA 54, 2912b)

341. Tomassi, W., and H. Jankowska, Ukrain. Khim. Zhur., 24, 162-7 (1958). (CA 52, 15307f)

342. Torkar, K., J. chim. phys., 51, 711-14 (1954). (CA 49, 7349f)

343. Tovbin, M. V., and K. F. Lyashev, Kataliz v Vysshei Shkole, Min. Vysshego i Srednego Spets. Obrazov. S. S. S. R., Tr. 1-go [Pervogo] Mezhvuz. Soveshch., po Katalizu 1958, 1(1), 458-62 (1962). (CA 59, 1130g)

344. Tovbin, M. V., and K. F. Lyashev, Ukrain. Khim. Zhur., 25, 581-6 (1959). (CA 54, 10478h)

345. Tovbin, M. V., I. N. Rozhmanov, and E. V. Savinova, Ukrain. Khim. Zhur., 27, 54-60 (1961). (CA 55, 18254a)

346. Tovbin, M. V., I. N. Rozhmanov, and E. V. Savinova, Ukrain. Khim. Zhur., 27, 60-3 (1961). (CA 55, 18254a)

347. Trandafelov, D., Annuaire univ. Sofia 48, Fac. sci. phys. et math., Livre 3 Pt. 1, 86-90 (1953/54). (CA 49, 12938c)

348. Tverdovskii, I. P., and R. A. Karpova, Tr., Gos. Inst. Prikl. Khim., 49, 224-9 (1962). (CA 60, 1152f)

349. Tyurin, Yu. M., and A. I. Shlygin, Nauch. Doklady Vysshei Shkoly, Khim. i Khim. Tekhnol. 1958(3), 439-42. (CA 53, 2758e)

350. Tyurin, Yu. M., and L. G. Feoktistov, Kinetika i Kataliz, 4(2), 221-9 (1963). (CA 59, 3346a)

351. Uhara, I., T. Hikino, Y. Numata, H. Hamada, and Y. Kageyama, J. Phys. Chem., 66, 1374-5 (1962). (CA 57, 7964f)

352. Uhara, I., S. Kishimoto, T. Hikino, Y. Kageyama, H. Hamada, and Y. Numata, J. Phys. Chem., 67, 996-1001 (1963). (CA 58, 13182c)

353. Umeda, K., K. Tarama, and E. Suito, Nippon Kagaku Zasshi, 84(7), 557-60 (1963). (CA 60, 4844f)

354. Umeda, K., K. Tarama, and E. Suito, Nippon Kagaku Zasshi, 84(6), 464-7 (1963). (CA 59, 14877e)

355. Umeda, K., K. Tarama, and E. Suito, Nippon Kagaku Zasshi, 84(7), 553-7 (1963). (CA 60, 4044e)

356. Voltz, S. E., and S. W. Weller, J. Am. Chem. Soc., 76, 1586-87 (1954). (CA 48, 7410a)

357. Voltz, S. E., and S. W. Weller, J. Phys. Chem., 59, 569-71 (1955). (CA 49, 12939i)

358. Walter Kidde and Company, Belleville, New Jersey, private communication.

359. Wang, J. H., J. Phys. Chem., 59, 1115-6 (1955). (CA 50, 659d)

360. Watanabe, J., and T. Shiramoto, J. Electrochem. Soc. Japan, 19, 274-9 (1951). (CA 46, 1891e)

361. Wawrzyczek, W., A. Jacyk, and A. Przybylski, Kolloid-Z., 195(1), 49-1 (1964). (CA 60, 15190c)

362. Weiss, J., "The Free Radical Mechanism in the Reactions of Hydrogen Peroxide," Advances in Catalysis, 4, 343-365 (1952). (58 references)

363. Wernlund, C. J. (to E. I. du Pont de Nemours & Co.), U.S. Patent 2,465,773, March 29, 1949. (CA 43, 6096d)

364. Wernlund, C. J. (to E. I. du Pont de Nemours & Co.), U.S. Patent 2,432,308, September 20, 1949. (CA 44, 56e)

365. Wernlund, C. J., and P. F. Bente, Jr. (to E. I. du Pont de Nemours & Co.), U.S. Patent 2,842,486, July 8, 1958. (CA 52, 16950i)

366. Whittaker, A. G., and C. M. Drew, J. Phys. Chem., 61, 382-4 (1957). (CA 51, 10205d)

367. Williams, G. C., C. N. Satterfield, and H. S. Islin. J. Am. Rocket Soc., 22, 70-77 (1952).

368. Wolfram, E., Ann. Univ. Sci. Budapest. Rolando Eotvos Nominatae, Sect. Chem., 5, 33-47 (1963). (CA 61, 1307d)

369. Wolfram, E., Ann. Univ. Sci. Budapest. Rolando Eotvos Nominatae, Sect. Chem., 5, 61-6 (1963). (CA 61, 1307d)

370. Wolfram, E., Ann. Univ. Sci. Budapest. Rolando Eotvos Nominatae, Sect. Chem., 5, 67-74 (1963). (CA 61, 1307d)

371. Wolski, W., Roczniki Chem., 30, 733-43 (1956). (CA 51, 2369g)

372. Yadava, R. R., and S. Ghosh, Z. Physik. Chem. (Leipzig), 224(5-6), 289-92 (1963). (CA 60, 11417a)

373. Yamada, K., and K. Nishioka, Mem. Defense Acad., Math. Phys., Chem. Eng., 4(3), 285-303 (1964). (CA 63, 3667f)

374. Yatsimirskii, K. B., Izvest. Vysshikh Ucheb. Zavedenii, Khim. i Khim. Tekhnol., 2, 480-4 (1959). (CA 54, 6289h)

375. Zaprometov, B. G., and I. N. Shpilevskaya. Trudy Sredneaziat. Gosudarst. Univ (Tashkent), 33(4), 3-10 (1952). (CA 50, 14309d)

376. Zhabrova, G. M., S. Z. Roginskii, and E. A. Fokina., Compt. rend. acad. sci. U.R.S.S., 52, 313-16 (1946). (CA 41, 1540a)

377. Zhabrova, G. M., S. Z. Roginskii, and E. A. Fokina. J. Gen. Chem. U.S.S.R., 24, 9-15 (1954). (CA 49, 7348a)

378. Zhabrova, G. M., and E. A. Fokina, Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk 1955, 963-71. (CA 50, 17255d)

379. Zhuravlev, V. A., and A. A. Krushelyuk, Trudy L' vov. Med. Inst., 12, 173-7 (1957). (CA 55, 6200a)

380. Zhuravlev, V. A., and A. A. Kuzhelyuk, Zh. Fiz. Khim., 38(2), 271-6 (1964). (CA 60, 13981b)

381. Zhuravlev, V. A., M. I. Kozak, and A. A. Kuzhelyuk, Tr. L'vovsk. Med. Inst., 22, 5-12 (1961). (CA 60, 48d)

382. Zhuravlev, V. A., M. I. Kozak, and A. A. Kuzhelyuk, Kinetika i Kataliz, 4(2), 312-14 (1963). (CA 59, 3343a)

383. Zhuravlev, V. A., and L. G. Kolosova, Kinetika i Kataliz, 5(2), 293-7 (1964). (CA 61, 3730b)

384. Zubovich, I. A., Zhur. Fiz. Khim., 29, 917-29 (1955). (CA 51, 828c)

385. Zubovich, I. A., Zhur. Fiz. Khim., 29, 1696-1705 (1955). (CA 50, 7558a)

386. Zubovich, I. A., Zhur. Fiz. Khim., 31, 61-71 (1957). (CA 51, 15234d)

387. Zubovich, I. A., Uchenye Zapiski Yaroslav. Tekhnol. Inst. 1959, (3), 117-21. (CA 56, 978c)

388. Zubovich, I. A., and A. V. Kuznetsova, Uchenye Zapiski Yaroslav. Tekhnol. Inst. 1959, (3), 105-13. (CA 56, 978a)

389. Zubovich, I. A., and N. A. Lebedeva, Uchenye Zapiski Yaroslavsk. Tekhnol. Inst., 5, 19-24 (1960). (CA 56, 4137c)

390. Zubovich, I. A., Uchenye Zapiski Yaroslavsk. Tekhnol. Inst., 5, 5-15 (1960). (CA 56, 4137d)

391. Zubovich, I. A., Kataliticheskie Reaktsii v Zvidkoi Faze, Akad. Nauk Kaz. S. S. R., Kazakhsh. Gos. Univ., Kazakhsk. Resp. Pravlenie Mendeleevskogo Obshchestva, Tr. Vses. Konf., Alma-Ata 1962, 38-46 (1963). (CA 60, 13916c)

392. Zubovich, I. A., Uch. Zap. Yaroslavsk. Tekhnol. Inst., 8, 195-206 (1962). (CA 62, 1116b)

393. Zvorykin, A. Ya., and F.M. Perel'man, *J. Phys. Chem.* (U.S.S.R.), **20**, 1095-1101 (1946). (CA **41**, 2973e)

394. Zykova, G.I., Yu. P. Simanov, and V. P. Lebedev, *Kinetika i Kataliz, Akad. Nauk S. S. S. R., Sb. Statei* 1960, 227-38. (CA **57**, 10567h)

SUPPLEMENTARY REFERENCES NOT CITED

1. FMC Corporation, Buffalo, New York. "Decomposition of Grade Peroxide by Means Other than Catalytic." Technical Report G-2, by D. H. Nelson, U. S. Navy Contract NObs-31494, 1 October 1949.
2. Isbin, H. S., "Heterogeneous Decomposition of High Strength Hydrogen Peroxide," Sc. D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1947.
3. Luft, N., "Heterogeneous Catalytic Decomposition of Flowing Concentrated Hydrogen Peroxide," November 1946. (PB 97602)
4. Maggs, F. T., and D. Sutton, "Some Aspects of the Catalytic Decomposition of Hydrogen Peroxide by Silver," Parts I and II, April 1957.
5. Meeken, S. R., "The Role of Diffusional Processes in the Heterogeneous Decomposition of Hydrogen Peroxide Vapors," S. B. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1950.
6. Naval Underwater Ordnance Station. "Hydrogen Peroxide and its Application to Ordnance." NAVORD Report 5215, 8 July 1947.
7. Naval Ordnance Test Station, China Lake, California. "Mechanism of Decomposition of Concentrated Hydrogen Peroxide," by C. M. Drew and A. G. Whittaker, NOTS Memo 1602, 19 January 1954 (AD 30 309)
8. Naval Air Rocket Test Station, Dover, New Jersey. "Mollier Charts for the Decomposition of Hydrogen Peroxide-Water Mixtures," by I. Forsten, Report 43, Project TED-ARTS-S1-505, November 1954. (AD 42 747)
9. Rocket Propulsion Establishment. Westcott, England. "Some Aspects of the Catalytic Decomposition of Concentrated Hydrogen Peroxide by Silver; Part IX, Tests with Decomposers," by F. T. Maggs, D. Sutton, and G. Southern. (AD 346 963).
10. Royal Aircraft Establishment, Westcott, England. "Some Aspects of the Catalytic Decomposition of Hydrogen Peroxide by Silver." by F. T. Maggs and D. Sutton, Parts 1-5, RAE Report RPD 35; Part 6, RAE Tech. Note RPD 153, 1957.

SECTION XXII.

PRINCIPAL SOURCES

1. Chemical Abstracts, Vols. 39-62 (1945-1965).

2. U. S. Government Research and Development Reports [formerly (1) U. S. Government Research Reports, (2) Bibliography of Scientific and Technical Industrial Reports], Vols. 1-40 (1946-1965).

3. Technical Abstracts Bulletin (TAB), 1960-1965.

4. Defense Documentation Center: Computer search system (1945-1965).

5. Scientific and Technical Aerospace Reports (STAR) [formerly (1) Technical Publications Announcements, and (2) Index of NACA Technical Publications], 1945-1965.

6. Nuclear Science Abstracts, Vols. 10-19 (1956-1965).

7. Applied Science and Technology Index [formerly Industrial Arts Index], 1945-1965.

SECTION XXIII.

CROSS-REFERENCE INDEX

This index can be used to locate discussions of catalytic activity of an element when it is not discussed under that element in the body of the report. For example, in this index under silver will be found information on catalysis by silver and silver compounds not included under silver in the text. The notation refers to the page number, followed by the reference number (Section XXI) in parentheses.

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) FMC Corporation Chemical Research and Development Center Princeton, New Jersey	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE
Heterogeneous Decomposition of Hydrogen Peroxide by Inorganic Catalysts. A Literature Survey.

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Special Report

5. AUTHOR(S) (Last name, first name, initial)
Garwig, Paul L.

6. REPORT DATE June 1966	7a. TOTAL NO. OF PAGES 132	7b. NO. OF REFS 405

8a. CONTRACT OR GRANT NO. AF 04(611)-11208 b. PROJECT NO. c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AFRPL-TR-66-136

10. AVAILABILITY/LIMITATION NOTICES Available from DDC. This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of AFRPL (RPRR/STINFO), Edwards, California 93523.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY United States Air Force Rocket Propulsion Laboratory Edwards Air Force Base, California

13. ABSTRACT

The literature on the heterogeneous decomposition of hydrogen peroxide by inorganic catalysts was surveyed. The aim was to provide background information useful in the development of new catalysts for high-strength hydrogen peroxide in propulsion applications. The survey was prepared as part of a research program on the development of active, stable catalysts for decomposing 98 per cent hydrogen peroxide. Published literature, technical reports, and patents in the period 1945-1965 were included. The survey showed that silver and platinum are the most extensively investigated catalysts. Other major catalysts are palladium, copper, iron, cobalt, manganese, and their compounds. Various methods have been proposed for increasing catalytic activity by additives that promote the parent activity of elements or compounds. Samarium nitrate-treated silver, cobalt-manganese oxide mixtures, ruthenium and its compounds, and silver-gold alloys are the most active catalysts that have been reported.

DD FORM 1 JAN 64 1473

UNCLASSIFIED
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Hydrogen peroxide						
Catalyst						
Decomposition, thermal						
Decomposition, catalytic						
Propulsion						
Propellant						
Bibliography						
Literature Search						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. **REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.

8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through
_______________________________________."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through
_______________________________________."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through
_______________________________________."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.