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THE ROLE OF INORGANIC CONTAMINANTS IN THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE

[UNCLASSIFIED TITLE]

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ABSTRACT
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Because of the increasing interest in the use of hydrogen peroxide as a propellant, its decomposition by silver has been studied in the liquid phase. A very high purity peroxide served as the reference point in a program designed to evaluate the role of certain inorganic materials in the decomposition reactions. The rate of decomposition and the catalyst loss were found to be altered by minute amounts of phosphate, stannate, or aluminum ions. The effect of tin was subject to aging, so that its influence was negligible one day after it was added to the peroxide. Aluminum increased the starting activity of the silver catalyst as well as its solution rate. These effects were observed at concentrations of aluminum below 0.5 mg/l but were not increased by raising the aluminum concentration above this value. The increased silver loss due to the presence of aluminum was moderate. When phosphate ion was added to hydrogen peroxide, the activity was increased. With concentrations above 2 mg/l, an inhibiting reaction masked this increase and the decomposition rate became slow. Phosphate sharply magnified the amount of silver that dissolved in the peroxide sample. The catalyst efficiency was cut by a factor of 50 at a phosphate concentration of 4.0 mg/l. Attempts to control the undesirable influence of phosphate showed that addition of tin was partially effective. Addition of aluminum ions or adjustment of the apparent pH to higher values were less satisfactory means of partially counteracting the effects of phosphate. Sulfate and nitrate ions did not alter the catalytic decomposition behavior in these laboratory studies. With respect to the sulfate ion, the results in the laboratory evaluator differ from the results obtained in engine operation, since sulfate salts deposit in the catalyst bed of the rocket chamber, thereby decreasing propellant flow.

PROBLEM STATUS

This is an interim report on this phase of the problem; work on the problem is continuing.

AUTHORIZATION

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CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE
[Unclassified Title]

INTRODUCTION

Because of its versatility, hydrogen peroxide is an attractive source of power for a variety of missile and aircraft applications. Its use in gas generators was pioneered by the Germans in their V-2 rocket program and similar turbine drives have been adapted to American rockets such as the NRL Viking. High strength peroxide may be selected as the fuel for a monopropellant rocket if the requirement of mechanical simplicity counterbalances the need for high performance. Thus the auxiliary power for a Navy helicopter consists of three small hydrogen peroxide rockets situated in the tips of the rotor blades(1). Intermittent thrust can be attained with this compact system since the flow of the liquid propellant can be easily started, stopped and started again.

Large volume uses of high strength peroxide have centered around the development of bipropellant rocket engines for manned aircraft. The requirements of some rocket systems make peroxide preferable to either liquid oxygen or nitric acid as the oxidizer. The World War II experience of the Germans with the Messerschmidt 163A experimental rocket plane proved the feasibility of the peroxide and "C-Stoff"* propellant combination (2). The development of the hybrid "jet-rocket" concept for airplanes has created another demand for rocket fuels. For this new concept in interceptor aircraft, Baxter considered high strength peroxide the most desirable oxidizer because of its good density impulse and moderate combustion temperature (3). This viewpoint has been supported by the Bureau of Aeronautics which plans to utilize 90%† hydrogen peroxide in their "super-performance" aircraft (4).

In monopropellant and gas generator applications of hydrogen peroxide where power is derived solely from decomposition processes, a catalytic means has been required to maintain a high decomposition rate. With the exception of the peroxide and "C-Stoff" combination, catalysts have also been used where combustion of a fuel utilizes the oxygen derived from hydrogen peroxide. In a bipropellant engine, peroxide is decomposed by a catalyst to oxygen and steam with considerable evolution of energy. The resulting hot mixture of steam and oxygen readily ignites a fuel on contact. Thus, in the production of power from hydrogen peroxide, a catalyst is normally employed to effect a high rate of decomposition.

A great number of inorganic substances have been recognized as catalysts for peroxide decomposition (5). Many metals or their salts have been tested in rocket work and have given satisfactory performance. Because of its high decomposition activity and efficiency, its ready fabrication, and its good behavior at elevated temperatures, silver has been the catalyst of choice in most of the newer applications of peroxide. Although this element has generally been an outstanding catalyst, certain difficulties have been associated with its use in some development programs. In practice, the unsatisfactory performance observed

*"C-Stoff" was the German code word for a mixture of 30% hydrazine hydrate, 57% methyl alcohol, and 13% water.

†The choice of 90% rather than some other concentration represents a compromise among such factors as performance, ease of manufacture, and freezing point.

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has been due to a short lifetime for the catalyst bed. The reasons for poor behavior, which may be interdependent, are (a) a build-up of deposits on the screens of the catalyst bed which decreases the flow rate of peroxide and (b) decreased catalyst activity which results in incomplete decomposition.

The silver catalyst used in many engines has been prepared by silver-plating a wire screen fabricated from some baser metal or alloy. The plated material is then subjected to an activation procedure designed to increase its efficiency. The preparation of the catalyst bed involves many variables, particularly in the plating procedure, and rigid control is required to produce a consistently good product. Indeed, irregularities in the silver catalyst have been responsible for the poor performance in some of the engine development work. However, wide variations in behavior have also been encountered when the same catalyst bed has been used with different batches of peroxide. For this as well as other reasons, it was concluded that contaminants in the peroxide have a deleterious effect on engine performance.

The 90% peroxide used in rockets is derived from lower concentrations by a double distillation under vacuum. This processing affords a high quality product which readily meets the older peroxide specification, MIL-H-16005B, 21 February 1952, which was in effect at the time the present work was started.* The principal criterion of impurity level in this specification is the evaporation residue, which measures the sum of the non-volatile material in suspension, in colloidal solution, and in true solution. The maximum allowable residue is 20 milligrams per liter, a value which has not been unduly restrictive. Nevertheless, many peroxide samples with evaporation residues less than this value were not suitable for engine operation. Therefore, efforts were made to correlate the type of impurity with performance. For instance, light scattering studies were tried in order to see if the quantity of colloidal material were causing the poor performance (6), a check for total ionic impurities was made by using conductivity measurements, and the apparent pH was utilized to detect any abnormal acidity or alkalinity in those peroxide samples which gave poor performance (7). When these approaches bore no fruit, a search for specific chemical ions and compounds was begun. Chemical analyses were made for a few inorganic materials whose presence in peroxide was suspected (7). The evaporation residues were examined by electron microscopy and electron diffraction (6). These attempts also failed to produce a worth-while lead to explain differences in peroxide samples.

In view of the seeming inability to correlate motor behavior with some physical or chemical measurement, attempts were then made to develop laboratory scale performance tests which could single out poor peroxide samples and thus eliminate the need for a full scale motor test prior to acceptance of a batch of hydrogen peroxide. A static evaluator was developed at this Laboratory, and the Becco Chemical Division of the Food Machinery and Chemical Corp. developed a flow system, the "Low Pressure Evaluator," which could be used for comparing peroxide samples or catalyst screens. Both evaluators were designed to measure the decomposition rate of hydrogen peroxide and to detect changes in the catalyst. Results obtained through the use of both of these evaluators on production samples did reveal differences in the catalytic decomposition behavior (8,9). Some samples which had been found to be unsatisfactory for engine use were shown to attack the silver catalyst with undue severity, dissolving it at an abnormally high rate.

* A new specification for hydrogen peroxide over 52% concentration, MIL-H-16005C, 10 September 1956, defines maximum impurity limits for several ions, whereas MIL-H-16005B specified only the limits on concentration, evaporation residue, and stability. The limits set for some inorganic materials are not sufficiently stringent to permit purchase of hydrogen peroxide for rocket engines under this recent specification.

The unpredictable occurrence of bad peroxide batches suggested an alternate approach to the problem. This involved the addition of definite amounts of inorganic compounds to a good quality production sample. Tests were then made on this doctored sample in the static evaluator to note any changes in the catalytic decomposition phenomena. Certain additives were found to alter either the decomposition rate, the silver solution rate, or both (10). Phosphate, aluminum, and stannate ions were particularly noteworthy in their effects. Although definite trends were observed in these studies, a given additive did not exhibit identical behavior in all stock samples. This was because these production samples had significant amounts of phosphate or aluminum and unknown amounts of other possible critical ions. Thus, the effect of an additive could not be determined precisely because of its apparent interaction with impurities already present in the sample.

To achieve a more definitive answer it was necessary to obtain truly high purity hydrogen peroxide. Fortunately, such a material became available from the Becco Chemical Division, which produced a peroxide up to 99+% concentration by a partial freezing process (11). This high grade material has been used as the reference point for the contaminant program described in this report. The earlier static evaluator studies were repeated, refined, and expanded. Aging phenomena and interactions between two or more additives were also examined.

The information presented in this report comprises the contribution of this Laboratory to the Bureau of Aeronautics "crash program" on hydrogen peroxide (4). The experimental work of this cooperative effort included rocket engine tests, laboratory performance tests, and analyses for contaminants. It was designed to determine the peroxide quality needed in a motor by actual engine tests and to assess the reliability of laboratory tests for predicting the engine requirements. The ultimate goal was to define a specification for hydrogen peroxide for use in the "super performance" aircraft. Poor batches of peroxide could then be detected by chemical analysis and physical measurements.

EXPERIMENTAL DETAILS

Apparatus

The static evaluator developed at this Laboratory was designed to compare the liquid-phase decomposition rate of peroxide samples on a standard catalyst. Thus it attempts to simulate the decomposition in the initial portion of a catalyst bed of a rocket where the temperature is below the boiling point of the peroxide. It incorporates some of the features of a reactor used by Maggs (12). A small length of silver wire was chosen as the catalyst since changes in its weight could be followed periodically during a run. Pure silver was chosen to eliminate the variables associated with the preparation of a plated and activated catalyst. The diameter and length of the wire were arbitrarily set at 0.020 inch and 2.0 centimeters. As shown in Fig. 1, the catalyst is supported in the peroxide sample by a Teflon holder. The latter fits on a glass rod attached to the cell head.

The sample is stirred by a magnetic stirrer and its temperature is regulated by the flow of water in the surrounding jacket. In most of the experiments a 50.0-ml sample was used and the temperature was maintained at $60 \pm 2^\circ\text{C}$. Since these studies were restricted to temperatures below the boiling point of water, the water formed by peroxide decomposition is retained in the liquid phase. Thus, the peroxide is gradually diluted during a run. The oxygen produced in the decomposition is measured by the wet test meter and this measurement becomes a convenient index of the rate of decomposition and the activity of the catalyst. Complete decomposition of the 50-ml sample of 90% H_2O_2 used affords 20.6 liters of oxygen at STP. However, the low rates of oxygen evolution normally encountered

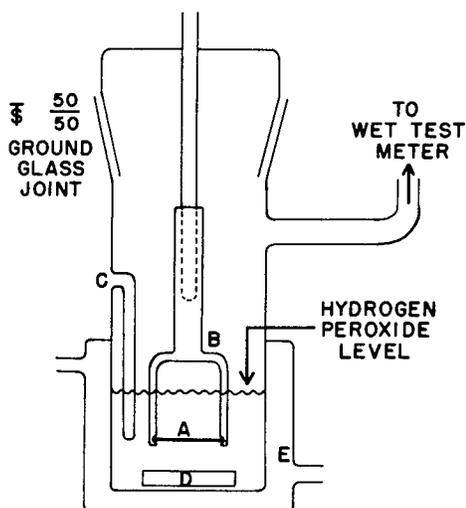


Fig. 1 - Static evaluator for the catalytic decomposition of hydrogen peroxide. A, wire catalyst; B, Teflon wire holder; C, thermocouple well for control of cell temperature; D, Teflon covered magnet for stirring; E, jacket for regulation of cell temperature.

at the lower peroxide concentrations dictated the termination of a run before the sample was completely decomposed.

Two gas washing traps were inserted between the cell and the wet test meter. These served the purposes of removing any droplets of peroxide which might be swept out of the cell and of insuring the saturation of the oxygen with water vapor. Peroxide concentrations throughout a run were calculated from the amounts of oxygen evolved, suitable corrections being made for the water vapor present, and the variations of temperature and pressure from standard conditions.

Materials

A few preliminary studies were conducted with the 99% peroxide made available by the Becco Chemical Division. For tests at 90%, this material was diluted with deionized water furnished for this purpose by Becco. The quality of this super-pure 90% hydrogen peroxide* is indicated in Table 1. The most reliable measurement of its purity is the specific conductance since the precision of the analytical methods for some of the ions at these low concentrations can be questioned. Comparison of the value of $2.2 \times 10^{-6} \text{ ohms}^{-1} \text{ cm}^{-1}$, which is 1/4 to 1/6 that of commercial 90% peroxide, with that of $2.0 \times 10^{-6} \text{ ohms}^{-1}$

cm^{-1} found by Schumb for 90% peroxide highly purified by laboratory methods (13) shows that the SP-90 has at most only minute amounts of ionic impurities. The specific conductance of SP-99 ($0.49 \times 10^{-6} \text{ ohms}^{-1} \text{ cm}^{-1}$) also compares favorably with the lowest value ($0.39 \times 10^{-6} \text{ ohms}^{-1} \text{ cm}^{-1}$) reported for 99.9% hydrogen peroxide (14). Since hydrogen peroxide, like water, is slightly ionized even in the pure state, the absolute values for specific conductance are probably not too different from those given above.

The concentrations found for sulfate and nitrate ions in SP-90 as shown in Table 2 are believed to be too high. The conductivity of SP-90 is influenced markedly by the addition of either sulfate or nitrate salts in small amounts. The specific conductance of SP-90 to which 3.0 mg/l of sulfate had been added was found to be increased by $5.8 \times 10^{-6} \text{ ohms}^{-1} \text{ cm}^{-1}$ while that for SP-90 containing 1.7 mg/l of added nitrate was increased by $2.6 \times 10^{-6} \text{ ohms}^{-1} \text{ cm}^{-1}$. Since both of these values exceed the measured conductance of SP-90 without additives, it seems that the sulfate and nitrate analyses were erroneous. Such a premise would be readily acceptable in the case of the turbidimetric analysis for sulfate. The analytical results for this ion in SP-90 were characterized by extremely poor precision even though some consistency was found for aqueous sulfate standards.†

* Hereafter this material is referred to as SP-90; the undiluted peroxide as SP-99.

† A recently developed analytical method for the determination of sulfate concentration in hydrogen peroxide is considered to be a much more accurate method (15). The sulfate content of a sample of SP-90 (not the one used in this study) was found to be 0.24 mg/l by this method.

TABLE 1
Analyses for SP-90*

Contaminant	Concentration of Ion (mg/l)
Phosphate	0.12
Aluminum	0.05
Sulfate	3.0
Nitrate	1.7
Tin [†]	-
Apparent pH	+0.2
Specific Conductance	2.2×10^{-6} ohms ⁻¹ cm ⁻¹

* See the Appendix for analytical methods

† Tin occurs in peroxide when stannate is added as a stabilizer. SP-90 contained no stabilizer.

It is somewhat more difficult to refute the validity of the nitrate analysis. Its precision was +0.3 mg/l and its accuracy has been verified by determinations in which known amounts of nitrate were added to peroxide. In the face of this dilemma, it is proposed that the analysis was correct but that some of the nitrogen which is detected as nitrate was present in an unionized form prior to the analysis. Although some of the analytical results are questioned, it certainly must be concluded that the quality of the SP-90 is high.

The chemicals chosen for the additive program were all water soluble and were ACS Reagent grade. To effect an addition, a definite amount of a dilute aqueous solution of the compound of interest was added to a known quantity of peroxide. The strength of the aqueous additive solutions were such that the decrease in peroxide concentration would be less than 1% for the highest concentration of any additive used. The salts added and the concentrations used are listed in Table 2. The specific salts used were chosen such that the ions of opposite charge to the ones of interest would not interfere with the decomposition as demonstrated by their inertness when present as the sodium or other salts.

The high purity peroxide was obtained and stored in Pyrex glass and polyethylene bottles to insure that aluminum contamination did not occur during storage. The solutions of additives and the peroxide samples prepared for aging tests were kept in polyethylene bottles.

In the studies of silver erosion the catalyst holder was removed periodically during each run so that the wire could be examined and weighed. The rate of solution of silver could then be determined as a function of the extent of decomposition of the peroxide.

TABLE 2
Compounds Used in Additive Program

Species Studied	Compound	Conc. of Ion in Aqueous Solution (g/l)
PO ₄	disodium phosphate dodecahydrate	0.625
Sn	sodium stannate trihydrate	1.25
Al	aluminum sulfate octadecahydrate	0.625
SO ₄	sodium sulfate	2.50
NO ₃	sodium nitrate	2.50
Li	lithium sulfate monohydrate	0.125
Ca	calcium nitrate tetrahydrate	0.25
Mg	magnesium sulfate heptahydrate	0.25
Ba	barium nitrate	1.25

CATALYTIC DECOMPOSITION BEHAVIOR OF HIGH PURITY HYDROGEN PEROXIDE

The decomposition rate of SP-90 on silver is illustrated along with that for SP-99 in Fig. 2. It should be noted that for a considerable change in concentration the decomposition rates were very low. As will be mentioned again later, they are lower than those observed for any commercial 90% peroxide samples. Also important is the fact that the decomposition rate increased as the concentration of peroxide decreased. This feature is not novel for catalytic decomposition of high strength peroxide on silver, but it is unusual in the light of most chemical kinetic experience. In agreement with the above observations, the starting activity for SP-99 was slightly less than that for SP-90.

The catalyst weight losses for SP-90 and SP-99 were the lowest observed in the static evaluator for any peroxide sample. It is seen in Fig. 3 that for most of the run the silver loss for SP-90 closely follows the oxygen evolution. This behavior, which has been typical of earlier work, was not exhibited by SP-99 for which the loss accelerated during the run. When the peroxide concentration dropped to about 50% (13.6 liters for SP-90 and 18.0 liters for SP-99) the silver solution rate decreased sharply. It is also seen in Fig. 3 that as the runs continued beyond this point the catalyst began to gain weight. Examination of the catalyst showed that this gain was accompanied by the appearance of a rough white coating which resembled a normal matte silver plate. Concurrently with the redeposition of silver on the wire, the peroxide sample itself became turbid. This cloudiness was due to catalytic decomposition occurring on small particles of silver which had formed and were suspended in the solution. Since the solubility of the silver compound formed by reaction with peroxide decreases with a decrease in hydrogen peroxide concentration, the limit of silver solubility was exceeded as the concentration fell. The silver took the two forms referred to above as it left the solution — plating on the catalyst and small particles in the solution. The

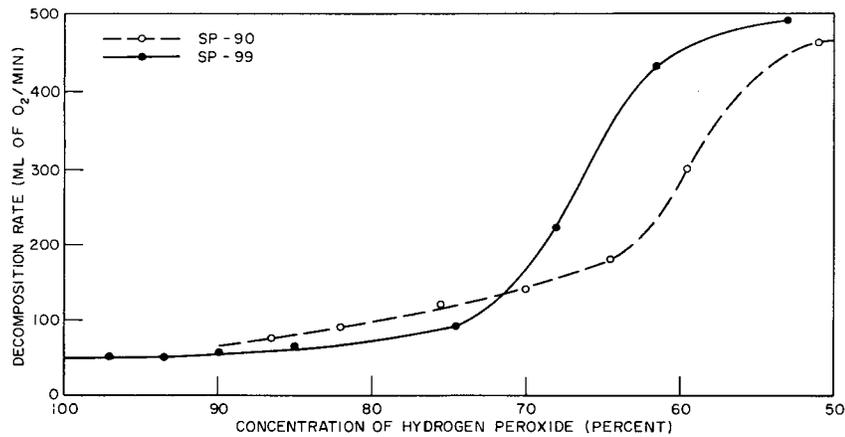


Fig. 2 - Decomposition rate for SP-90 and SP-99 (2.0-cm length of 0.020-inch silver wire catalyst, 50-ml sample at 60°C)

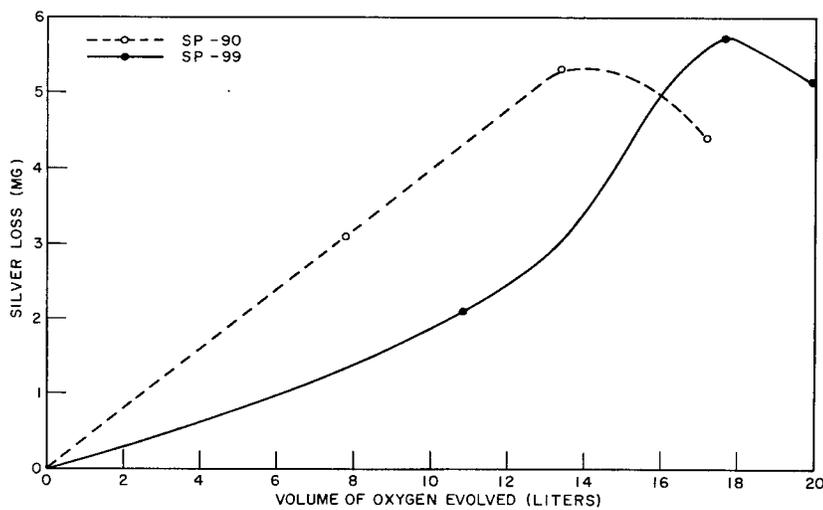


Fig. 3 - Silver loss for SP-90 and SP-99 (2.0-cm length of 0.020-inch silver wire catalyst, 50-ml sample at 60°C)

increased catalyst surface which became available due to the generation of the particles sharply increased the decomposition rate and the runs had to be monitored closely at this point in order to prevent a runaway temperature rise. Normally a run would be stopped prior to this stage since the unknown increase in catalyst area would invalidate the data.

In the catalytic decomposition of SP-90 the silver loss and the starting activity were less than those found for any 90% peroxide produced by normal commercial methods. It was felt that the low values for these properties were due to the absence of certain materials since the SP-90 was a particularly pure peroxide. Hence the conclusion reached earlier on the basis of its conductivity that SP-90 is a high quality product is supported by the catalytic decomposition behavior.

The effect of sample temperature on the catalytic decomposition phenomena was studied. Although a general trend was found for the relationship of temperature to starting activity, the trend was the reverse of that expected. As shown in Fig. 4, the starting rate for SP-90 at 20°C was higher than that at 40°C, with the rates at 60°C and 85°C falling to still lower levels. The maximum rates at the four temperatures were similar; however, these maxima were reached progressively earlier as the temperature was lowered. The silver loss was also dependent upon the temperature of the peroxide. This is illustrated in Fig. 5, where the amount of catalyst lost is plotted against the volume of oxygen produced. The amount of silver dissolved decreased as the temperature was raised.

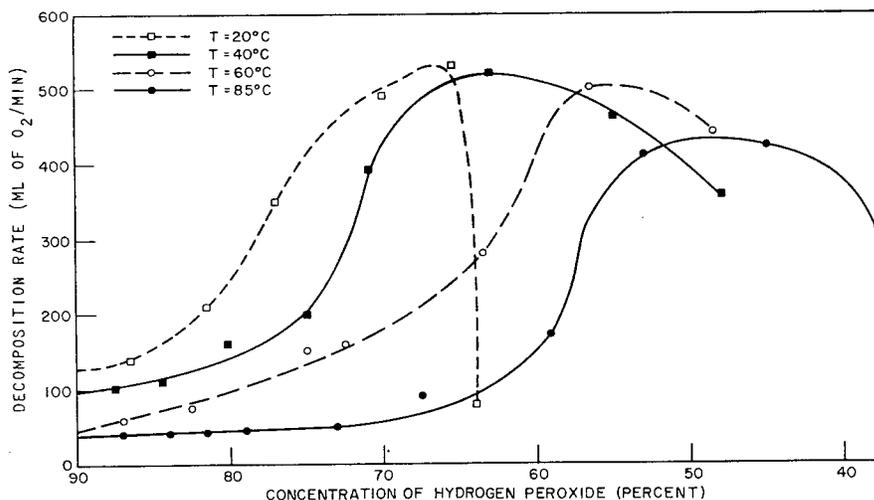


Fig. 4 - Effect of sample temperature on decomposition rate of SP-90 (2.0-cm length of 0.020-inch silver wire catalyst, 50-ml sample)

It has been shown that the liquid phase catalytic decomposition of SP-90 on silver has two unusual aspects, namely, the decrease in starting decomposition rate as the temperature is increased and the increase in activity as the peroxide concentration decreases. The SP-90 peroxide is not unique in these respects, but because of its high quality, this unusual behavior is more pronounced. The explanation advanced by Beard and Smith (16) for these phenomena is that under certain circumstances, a gaseous film encloses the catalyst. Such a film effectively reduces the peroxide-catalyst contact, thus lowering the apparent activity of the catalyst. A more detailed description of this problem will be deferred to the discussion section of this report.

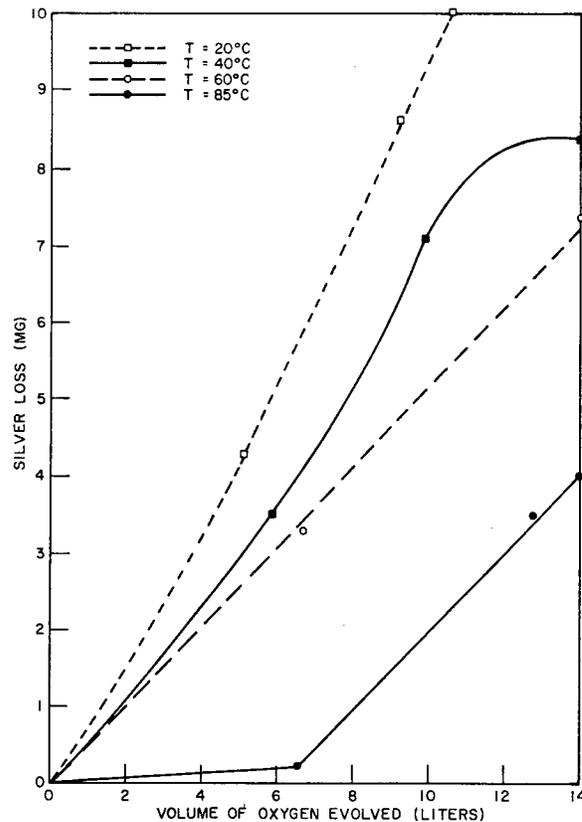


Fig. 5 - Effect of sample temperature on the silver loss in SP-90 (2.0-cm length of 0.020-inch silver wire catalyst, 50-ml sample)

STUDIES ON MATERIALS WHICH ALTER THE CATALYTIC DECOMPOSITION

Because the SP-90 is such a pure material, it can be used as a valid starting point for the evaluation of the effect of additives on the decomposition properties of hydrogen peroxide. It has been reported that the addition of phosphate, aluminum, or tin can alter the decomposition phenomena of production samples (10). Since these three materials are important with regard to the stabilizing and storing of peroxide, their influence on the silver solution rate and the catalytic activity were thoroughly investigated.

Phosphate

The pyrophosphate ion is widely used to inhibit the decomposition rate of hydrogen peroxide in storage. Such a stabilizer, although not necessarily added to the 90% peroxide for rocket use, could be picked up accidentally from pumps, pipe lines, and storage tanks

used for all grades of peroxide. The chemical species which pyrophosphate assumes in 90% peroxide is not known. It is known that equivalent amounts of phosphorus added to peroxide as either pyrophosphate or orthophosphate produce comparable effects on the catalytic decomposition in an engine (17). From this it can be concluded that one of these phosphate ions is converted into the other or that an equilibrium mixture of the two occurs. Since these two are equivalent in this respect, the present study was made with orthophosphate.

In earlier work at this Laboratory, it was observed that phosphate increased the decomposition rate and the amount of silver dissolved (10). An apparent inhibition was also found at phosphate concentrations in the range of 2-4 mg/l. The behavior in different samples was not consistent, however. In particular, the decomposition rate exhibited considerable variation among different stock samples even though their phosphate concentrations were the same. It was thought that this was a result of the presence of other contaminants in some of these samples. The present study using SP-90 has clarified the picture and the role of phosphate can now be detailed accurately.

It can be seen from Fig. 6 that phosphate sharply increased the rate of decomposition of SP-90 in the initial portion of a run. The amount of the increase was dependent upon the concentration of the additive, but the maximum starting rate was attained at a concentration of 2 mg/l and the trend in the activity was reversed at higher concentrations. At the higher phosphate concentrations, it has been found that the activity remains low throughout the run. This is in contrast to the behavior of SP-90, which showed an increasing decomposition rate with a decreasing H_2O_2 concentration. Figure 7 illustrates vividly the effect of phosphate addition on starting activity.

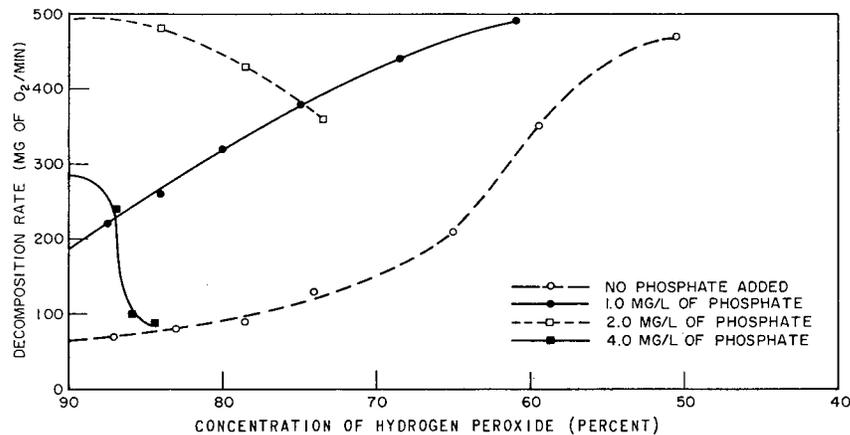


Fig. 6 - Effect of phosphate on the decomposition rate of SP-90 (2.0-cm length of 0.020-inch silver wire catalyst, 50-ml sample at 60°C)

The effect of phosphate added to SP-90 on the loss of silver from the wire catalyst was also spectacular. However, the reversal in rate which was found for the activity did not occur. Figure 8 shows that the silver loss was close to a linear function of the phosphate concentration. The extent of silver solution became extremely high at 4 mg/l.

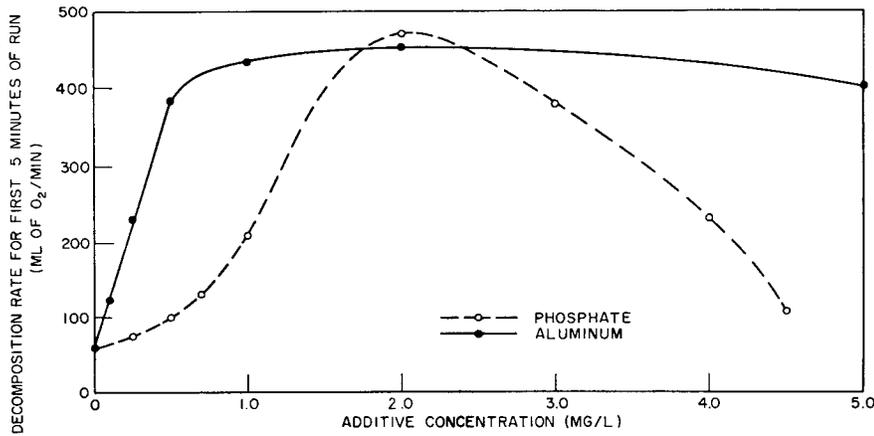


Fig. 7 - Effect of additive concentration of phosphate and of aluminum on the starting activity of SP-90 (2.0-cm length of 0.020-inch silver wire catalyst, 50-ml sample at 60°C)

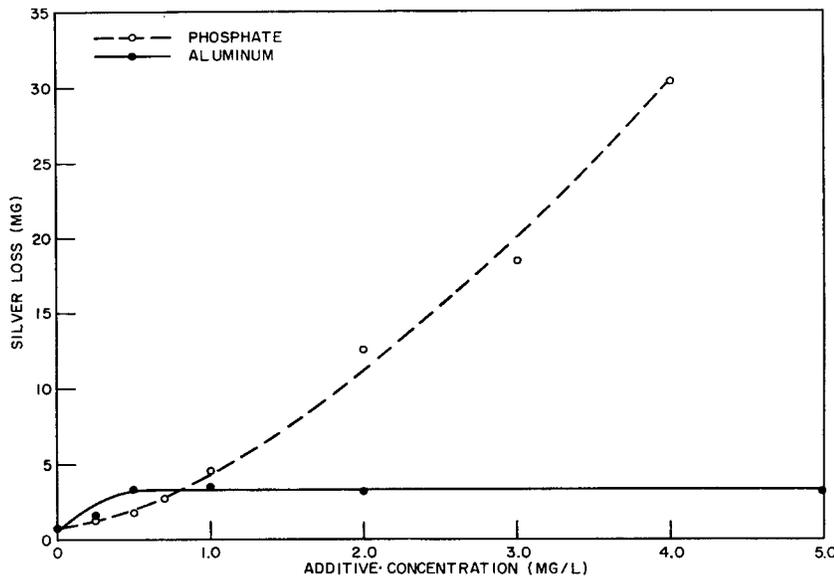


Fig. 8 - Effect of additive concentration of phosphate and of aluminum on the silver loss during decomposition of SP-90 from 90% to 85% (2.0-cm length of 0.020-inch silver wire catalyst, 50-ml sample at 60°C)

Studies at MIT on the silver catalyzed decomposition of hydrogen peroxide showed that the solubility of silver was decreased when the pH was raised (18). On the premise that the addition of alkali might also decrease the ratio of silver solution, runs were made using SP-90 containing varying amounts of sodium hydroxide. It was found that a decrease in

catalyst loss could be achieved even for peroxide samples containing phosphate. The variation in the solution rate as the apparent pH was increased is depicted in Fig. 9. A slight decrease in silver loss was found as the apparent pH was raised to about 2 but above this value the decrease was accelerated. The adjustment of the pH also affects the storage stability of hydrogen peroxide and, unfortunately, the quantity of alkali necessary to reduce the silver loss sufficiently adversely affects the stability. Therefore, this means of nullifying the phosphate influence appears to be of no value for practical application.

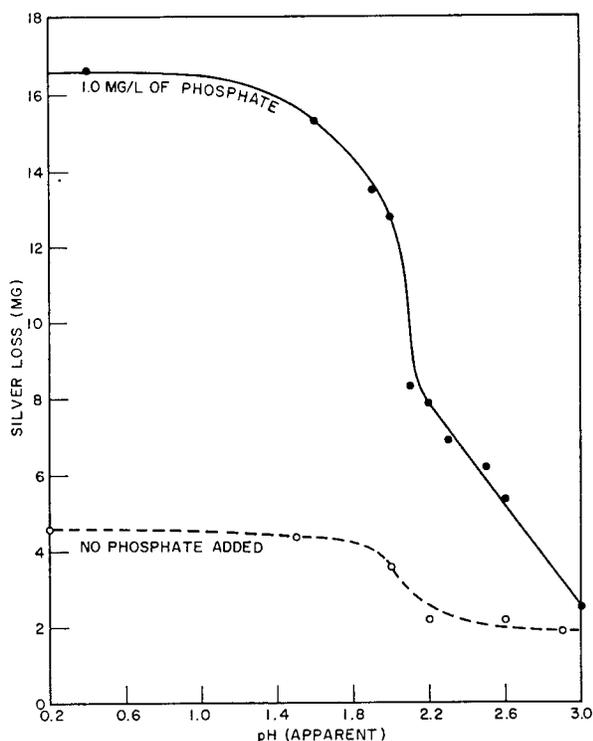


Fig. 9 - Effect of pH on the silver loss during the decomposition of SP-90 from 90% to 62% (2.0-cm length of 0.020-inch silver wire catalyst, 50-ml sample at 60°C)

Aluminum

The importance of aluminum in the present study lies in the fact that most containers for shipping and storing hydrogen peroxide are fabricated from aluminum or its alloys. Although aluminum is highly resistant to peroxide, it is conceivable that small amounts could be picked up from these containers. Earlier studies in which production samples were used had indicated that the presence of aluminum in the peroxide did not alter the catalyst loss but did increase the decomposition rate (10). The present work showed that very small amounts of aluminum increased both the decomposition rate of SP-90 and the solution rate of the silver catalyst. Although these phenomena were observed at aluminum

concentrations up to 0.5 mg/l, no significant change was observed above this value. The data for the starting activity plotted in Fig. 7 and for the silver loss plotted in Fig. 8 show the magnitude of the aluminum effect and the leveling off encountered above 0.5 mg/l. The decomposition rate in the plateau region was about six times that of SP-90 while the maximum silver loss was only four times that of SP-90. A comparison of the influence of aluminum with that of phosphate on the catalytic decomposition phenomena shows that the maximum decomposition rates were about the same but that phosphate was much more detrimental than aluminum with respect to silver loss.

Tin

Low concentrations of stannate are sometimes added to 90% peroxide to increase its stability in storage. Previous work showed that tin might be detrimental to the catalytic decomposition of peroxide since it increased the amount of silver dissolved and seemed to cause some inhibition at low peroxide concentrations (10). This behavior, as well as an increase in starting activity, was verified for SP-90 to which tin was added. However, as a sample of SP-90 containing tin was allowed to age, these phenomena became less pronounced. In fact, 24 hours after addition of as much as 5.0 mg/l of tin, the catalytic decomposition behavior could not be differentiated from that of unadorned SP-90. The change in starting activity with time is depicted in Fig. 10 while the aging rate as measured by the silver loss is shown in Fig. 11. The extent of silver solution decreased slightly faster than the decomposition rate. The apparent pH exerted a slight control over the rate of aging. Thus at a pH of 1.3, the effects of tin were apparent for a longer storage period than at a pH of 0.95. It is seen in Figs. 10 and 11 that the differences were quite small.

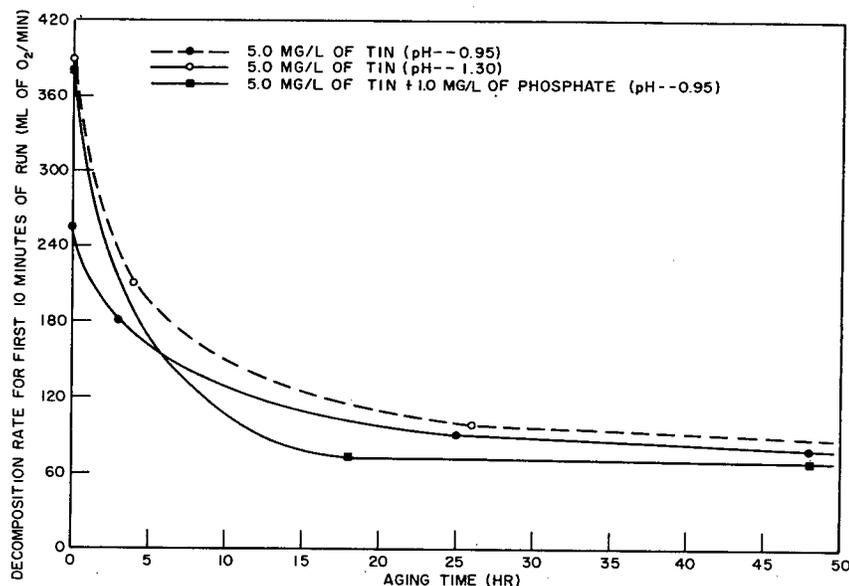


Fig. 10 - Effect of aging time on the starting activity of SP-90 (2.0-cm length of 0.020-inch silver wire catalyst, 50-ml sample at 60°C)

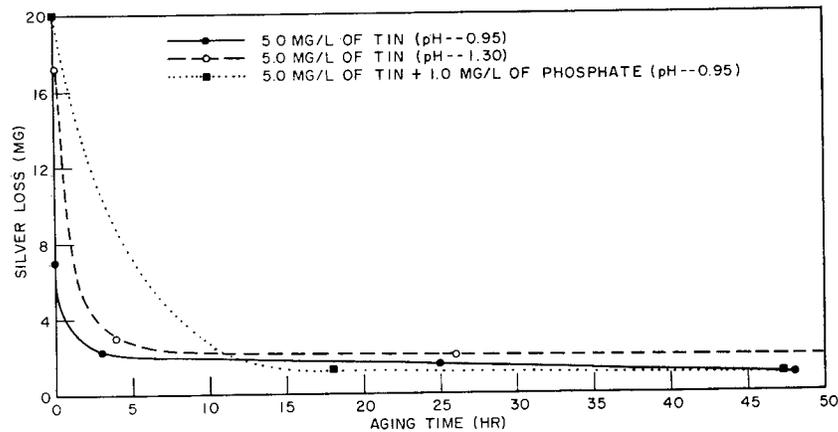


Fig. 11 - Silver loss vs aging time for the catalytic decomposition of SP-90 from 90% to 80% (2.0-cm length of 0.020-inch silver wire catalyst, 50-ml sample at 60°C)

STUDIES ON MATERIALS WHICH DO NOT ALTER THE CATALYTIC DECOMPOSITION

Two common anions, sulfate and nitrate, were included in this study although previous work had indicated that they were not participating in or altering the catalytic decomposition of hydrogen peroxide (10). Sulfuric and nitric acids are widely used chemicals and trace amounts of sulfate or nitrate ions might be picked up during processing, transferring, or storing of peroxide. Either acid might be used to adjust the pH during the manufacturing process and both have been investigated as pickling agents for aluminum storage containers. Sulfate is an integral part of the electrolytic production system. Nitrate could easily be formed by oxidation of any nitrogen-containing material introduced intentionally or accidentally into peroxide. These considerations supported the need for re-defining the role of sulfate and nitrate.

The results of the present work using SP-90 confirm the conclusions of the earlier work. The additions were made to give concentrations of either ion up to 20 mg/l. No anomalies were observed in the catalytic activity or the silver loss at this concentration or at the lower concentrations studied. Thus it was concluded that both ions were entirely innocuous, at least in this study on the liquid phase decomposition.

BEHAVIOR OF PEROXIDE SAMPLES CONTAINING TWO OR MORE ADDITIVES

Since commercial 90% peroxide might be expected to contain more than one contaminant, studies were made with SP-90 containing two or more of the probable impurities. In particular, combinations of stannate, phosphate, and aluminum, each of which affect the silver catalyzed decomposition, were investigated. Also a brief search was made for ions which might nullify the undesirable effects of phosphate.

Phosphate and Tin

A freshly prepared sample of SP-90 containing 1.0 mg/l of phosphate and 5.0 mg/l of tin exhibited high starting activity and high silver loss. Also, in the latter parts of the run inhibition was observed. These effects were slightly more pronounced than those observed for a sample containing 5.0 mg/l of tin alone. A strict comparison of the behavior of the two samples was difficult because of the aging phenomenon exhibited by peroxide samples containing tin. The aging effect was also observed for the tin-phosphate combination. Figures 10 and 11 indicate that the aging rate was fairly rapid. The net effect was that the behavior of SP-90 containing phosphate and tin had returned to that of the stock material within 24 hours after addition of the ions.

Phosphate and Aluminum

When both aluminum and phosphate were added to SP-90, the sample reacted in a way intermediate between that of SP-90 plus aluminum and SP-90 plus phosphate. The concentrations chosen for study were 0.5 mg/l of aluminum since this affords the maximum influence attained by this element and 1.0 mg/l of phosphate because even this low concentration is higher than desirable. It can be seen in Fig. 12 that the effect of 0.5 mg/l of aluminum on the starting decomposition rate of SP-90 was greater than that of 1.0 mg/l of phosphate. The activity of a sample containing both fell in between. The magnitude of their effects on the catalyst loss for SP-90 is shown in Fig. 13. The influence of 1.0 mg/l of phosphate was greater than 0.5 mg/l of aluminum in this case but the combination of the two again fell in the intermediate area. The sample containing aluminum and phosphate continued to give the same decomposition phenomena after four days and it was assumed that no further reaction occurred between these two ions after the initial mixing.

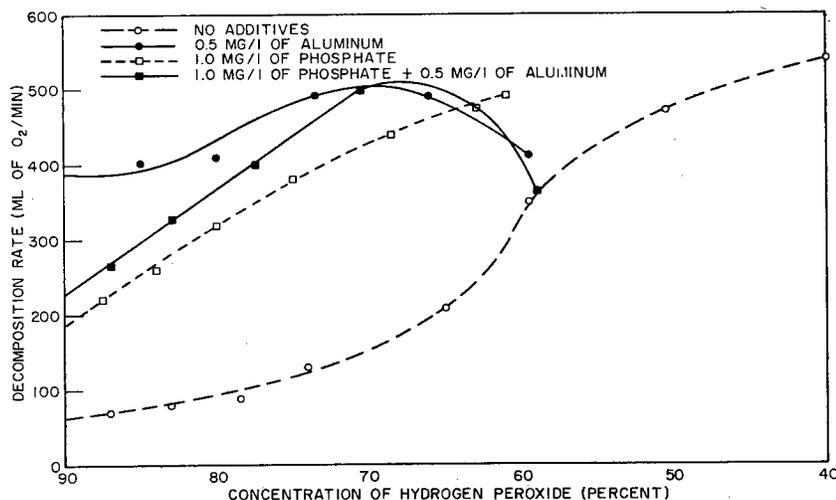


Fig. 12 - Effect of additives on the decomposition rate of SP-90 (2.0-cm length of 0.020-inch silver wire catalyst, 50-ml sample at 60°C)

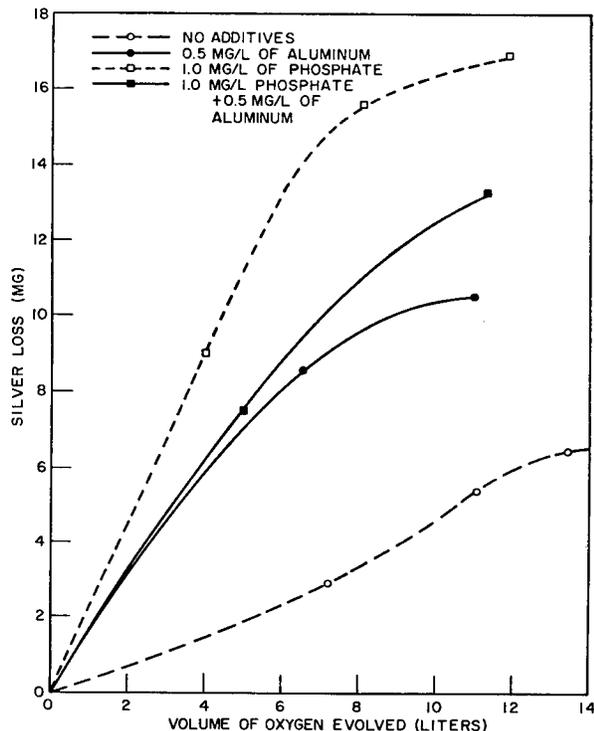


Fig. 13 - Effect of additives on the silver loss of SP-90 (2.0-cm length of 0.020-inch silver wire catalyst, 50-ml sample at 60°C)

Tin and Aluminum

When 5.0 mg/l of tin and 0.5 mg/l of aluminum were added to SP-90, the silver loss and the starting activity were increased relative to that of the stock peroxide. The silver loss was less than that for tin alone but greater than that for 0.5 mg/l of aluminum. The starting activity was considerably less than that of SP-90 containing either element. The aging pattern for this tin-aluminum preparation was inconsistent. When tested after four days, it was found that the silver loss and activity had decreased appreciably and were approaching SP-90 in these respects. A reversal in aging seemed to occur after this initial decrease since the catalyst loss and starting activity after eleven days were greater than those observed for the unaged sample. Little change occurred in an additional six days. Since the overall effect was not startling, the study was not pursued further.

Phosphate, Tin, and Aluminum

When a fresh sample containing 1.0 mg/l of phosphate, 5.0 mg/l of tin, and 0.5 mg/l of aluminum was tested in the static evaluator, a catalyst loss four times that for SP-90 was found. This decreased slowly with time so that after 28 days the catalyst loss was three times that for the unadorned peroxide. The starting activity for a fresh sample was slightly higher than that for SP-90 but this also decreased with age and differed little from

SP-90 after standing for 28 days. The catalytic activity appeared to become somewhat inhibited by this sample when the peroxide concentration dropped to about 75%. Hence the decomposition rate was quite low at concentrations less than this. Aging for 28 days shifted this inhibition point to about 70% concentration.

Other Additives

Some runs were made with a still more complex system. Five mg/l of nitrate and five mg/l of sulfate were included in the additive mixture containing the phosphate, tin, and aluminum. The behavior of the unaged material containing the five contaminants was very close to that of SP-90 with only Al, Sn, and PO_4 added. The sulfate and nitrate did not greatly affect the aging phenomenon either, although the change in starting activity did not show the trend found for the aluminum-tin-phosphate combination.

Search for a Phosphate Neutralizer

The serious consequences of phosphate contamination on the silver catalyzed decomposition of hydrogen peroxide stimulated efforts to find a means of counteracting this ion. Adjustment of the pH to a higher value controlled the influence of phosphate but adversely affected the stability of the peroxide. Addition of stannate seemed to partially nullify the effects of phosphate ion if a short aging period was permitted after the mixing. Aluminum was found to partially block phosphate in that it reduced the silver loss due to this anion. It was hoped that a material might be found which would remove or tie up phosphate yet not participate in or alter the catalytic decomposition. Obviously, a requirement for such a material would be that it must not decrease the stability of peroxide.

The possibility that phosphate would form a salt which was insoluble in 90% hydrogen peroxide seemed to be a promising approach. The ability of aluminum to counteract phosphate might be due to the formation of aluminum phosphate which could have low solubility in peroxide. The solubility of phosphate salts in water was used as the criterion for selection of cations for these experiments. Since most heavy metals and transition metals are good catalysts for peroxide decomposition, their ions were not considered. The neutralizing capabilities of aluminum, the most promising of the Group III elements, were reported above. Thus the choice narrowed down to the alkali and alkaline earth metals. Only lithium of the Group I elements has a slightly soluble phosphate while all the Group II elements form phosphates which have a low solubility in water. On this basis, dilute solutions of lithium, magnesium, calcium, or barium salts were added to SP-90 and tested in the static evaluator. Table 3 shows that these ions were essentially inert as far as the catalytic decomposition behavior of SP-90 was concerned.

When 1.0 mg/l of phosphate was also present along with one of these cations in SP-90, the typical behavior of the phosphate manifested itself as is seen in Table 4. The catalyst efficiency, as expected, was somewhat greater than that for 1.0 mg/l of phosphate alone but still considerably less than that for unadorned SP-90. In these studies the concentration of the cation was present in excess, hence further addition would not be expected to improve this situation significantly unless quite high concentrations of these salts were permissible. It is seen in Table 4 that with the exception of the barium sample the catalyst efficiency for these samples remained the same or decreased with age. The desirable increase exhibited by the barium sample was clouded by the fact that inhibition of the catalyst occurred when the peroxide concentration dropped to about 80%. These cations, which failed to alter the decomposition rate of SP-90 when present alone, combined with phosphate to increase the starting activity. This activity was increased still more when the aged samples were used.

TABLE 3
Catalytic Decomposition Phenomena for
SP-90 Containing Added Cations

Cation Added	Concentration of Cation (mg/l)	Catalyst Efficiency* (cu ft of O ₂ /g of silver lost)	Starting Rate (ml of O ₂ /min)
None		73	64
Lithium	1.0	69	81
Calcium	1.0	56	74
Barium	5.0	50	96
Magnesium	1.0	57	68

* 2.0-cm length of an 0.020-inch silver wire catalyst in 50-ml of 90% hydrogen peroxide at 60°C

TABLE 4
Catalytic Decomposition Phenomena for SP-90
Containing 1.0 mg/l of Phosphate Plus Added Cations

Cation Added	Concentration of Cation (mg/l)	Age (days)	Catalyst Efficiency* (cu ft of O ₂ /g of silver lost)	Starting Rate (ml of O ₂ /min)
None		0	14	195
Lithium	1.0	1	22	195
	1.0	5	14	379
Barium	5.0	0	18	101
	5.0	5	31	383
Calcium	1.0	0	21	429
		3	21	466
Magnesium	1.0	0	21	368
		4	18	485

* 2.0-cm length of an 0.020-inch silver wire catalyst in 50-ml of 90% hydrogen peroxide at 60°C

DISCUSSION

The information presented in the preceding sections shows that the liquid phase decomposition of hydrogen peroxide on silver is a very sensitive phenomenon. The behavior of SP-90 can be altered greatly by the addition of minute amounts of certain inorganic ions, yet it is immune to other ions. The decomposition rate for SP-90 increases as the peroxide concentration decreases and also as the sample temperature is lowered. In order to understand these and other phenomena, a detailed mechanism for the catalytic decomposition of hydrogen peroxide is necessary. Although much is available in the literature concerning the decomposition of peroxide by homogeneous catalyst, studies on the kinetics of heterogeneous catalysis are few in number and limited in scope (19). Any proposed mechanism must thus be composed from conjecture and analogy.

The increase in the decomposition rate of hydrogen peroxide as the concentration decreases has also been observed by Smith and Beard (16). They proposed that this is due to a vapor envelope which surrounds the catalyst at high peroxide concentrations. In their concept, they consider that the heat release for the decomposition of high strength peroxide heats the silver wire to a temperature higher than the boiling point of peroxide. Liquid approaching the hot wire is vaporized. The film resulting functions as a barrier for the transfer of heat from the wire to the bulk of the liquid and for the transfer of peroxide from the liquid to the catalyst. This is analogous to the film boiling phenomena associated with a liquid on a very hot solid (20). Under such conditions the heat transfer rate from the solid to the liquid is low because a film of evaporated liquid forms and insulates the solid. When the liquid-solid temperature differential is less, the film is not continuous and the liquid makes more intimate contact with the solid hence there is a greater transfer of heat.

The effectiveness of the vapor barrier in the peroxide-silver system would depend somewhat on the peroxide concentration. As the concentration drops there would be a greater number of inert water molecules to interfere with the efficiency of the catalyst and more of the heat of reaction would go into the vaporization of the water. Therefore, the wire temperature should fall and the gas film become less restrictive as a run progresses. The increasing contact between the liquid and wire which would result explains the increasing decomposition rate observed. Smith and Beard showed that the catalyst temperature can reach a value above the boiling point of peroxide and that this temperature decreases to the boiling point as the peroxide concentration decreases.

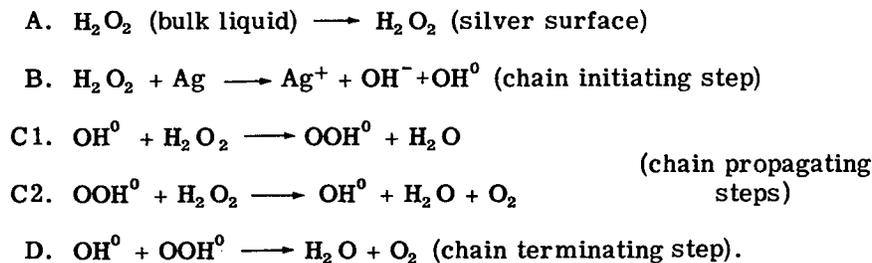
The increase found in the present study for the decomposition rate as the peroxide temperature was lowered is also explained on the basis of the vapor barrier. At the higher sample temperatures, the liquid approaching the silver catalyst would not absorb as much heat in being raised to the boiling point and thus a more extensive gas film would be formed to interfere with the effectiveness of the catalyst.

The silver which is lost by the catalyst during the decomposition of high strength hydrogen peroxide increases the conductivity and the apparent pH of the peroxide (21). This indicates that the catalyst goes into solution as ionic silver and that hydroxyl or perhydroxyl ions are formed. The continuous stripping of silver ions from the surface means that the catalyst itself undergoes a marked change during the peroxide decomposition. Although the catalyst used in these studies loses a significant percentage of its weight, the number of molecules of oxygen produced per atom of silver entering the solution is about 10,000. This ratio remains fairly constant for any particular sample as the peroxide concentration decreases. It is therefore possible that the reaction of silver with hydrogen peroxide is the initiating step of a chain reaction. The picture visualized is one in which a hydroxyl radical is produced in this step, similar to the electron transfer step

suggested by Weiss for peroxide decomposition on a heterogeneous catalyst (22). The chain propagating steps are considered to be those two frequently postulated for peroxide decomposition in which perhydroxyl and hydroxyl radicals are produced (19). A conventional combination of two free radicals is proposed as a possible termination step.

An alternate mechanism to consider is the reversible oxidation-reduction sequence for silver. In such a system, peroxide functions as an oxidizing agent with atomic silver and as a reducing agent with ionic silver. The net effect is an unchanged catalyst and the formation of water and oxygen. Baxendale discusses the participation of ferrous and ferric ions in the homogeneous decomposition of hydrogen peroxide by iron salts (23). He has concluded on the basis of kinetic studies at very low peroxide concentrations that both ions can play important roles in the decomposition of hydrogen peroxide. A mechanism of this type involving atomic and divalent silver has been set forth by Wentworth (18). Such a scheme requires that each silver atom at the surface of the catalyst undergo a complete redox cycle in five microseconds to account for the observed activity in the studies reported here. A mechanism requiring the performance of this complex behavior in such a short time is not as attractive as the chain mechanism presented first.

In an effort to tie the preceding thoughts together, a possible mechanism is presented for the silver catalyzed liquid phase decomposition of hydrogen peroxide:



Step A is a diffusion process which becomes a limiting factor when a vapor barrier surrounds the catalyst. The attack of peroxide on metallic silver produces a free hydroxyl radical in reaction B. This species abstracts a hydrogen from a molecule of peroxide as shown in step C1. It is proposed that the perhydroxyl radical thus formed continues the chain in step C2 by reacting with additional peroxide to produce a new hydroxyl radical. The abundance of peroxide molecules makes the repetition of reactions C1 and C2 very probable. The length of this chain should be long at high peroxide concentrations but could be terminated by the occasional collision of two free radicals. The latter might be a reaction such as that illustrated in step D.

An examination of the role of additives is now in order. It has been seen that tin, phosphate, and aluminum greatly increase the starting activity of SP-90 although they do not increase the maximum rate attained in a run. Smith and Beard observed this phenomena for stannate and aluminum (16). They suggested that these materials, which form colloidal solutions, were functioning to disrupt the vapor barrier thus allowing a higher rate of reaction between peroxide and the catalyst. Their proposal seems to be reasonable and a result of this would be that the rate of step A would be accelerated. The degree of this acceleration should increase with the concentration of additive. This was found to be true experimentally at low concentrations of tin and aluminum, but the starting activity was not further increased by additions above certain amounts. This might be explained if it is assumed that, in the absence of a vapor barrier, the rate for step B of the mechanism is slower than the rate for step A.

Phosphate probably remains in the ionic state in peroxide and its ability to increase the starting activity is considered a result of a mechanism not exhibited by tin or aluminum. Nonetheless, it is thought that phosphate is active at the liquid-solid interface and is capable of disrupting the gas film in its own way.

It should be noted that the film boiling phenomenon referred to earlier is sensitive to the type and condition of the hot surface. Akin and McAdams observed that film boiling began at a higher liquid-solid temperature differential when a steel tube was covered with scale (24). The effect of interfacial tensions on heat transfer has been discussed by Larson (25). His theoretical considerations show that both the solid-liquid interfacial tension and the liquid-vapor tension would influence the heat transfer. It would be reasonable to suppose that the presence of phosphate could materially affect both the liquid-solid and liquid-vapor interfacial tensions and thus influence the rate of heat transfer in the system. This in turn could readily affect the starting activity. However, it is difficult to rationalize why this behavior should be limited to phosphate and not be exhibited by other anionic species such as sulfate or nitrate.

The decomposition efficiency of a silver catalyst was decreased if aluminum, tin, or phosphate were added to SP-90. Thus the volume of oxygen produced per milligram of silver dissolved decreased if any of these materials was present. The observations on the effects of tin were not amenable to quantitative evaluation because of the rapid aging exhibited by stannate in peroxide. The magnitude of the influence of aluminum on this oxygen-to-silver ratio was dependent upon its concentration. When a definite concentration was exceeded, no additional decrease was found. The pattern of increase in the silver loss was similar to the increase in starting activity for SP-90 to which aluminum was added. This could indicate that aluminum affects both of these properties at the same place in the decomposition mechanism. At best this conjecture is highly speculative.

The efficiency of the silver catalyst was sharply reduced by phosphate. This is illustrated in Table 5 where the number of molecules of oxygen evolved per atom of silver going into solution is listed for various phosphate concentrations. Hence, even though it was seen in Fig. 6 that the starting rate for SP-90 exhibited a reversal at 2.0 mg/l of phosphate, the silver loss based on the volume of oxygen continues to rise. It is proposed that, although the phosphate probably increases the starting rate by disrupting the vapor barrier around the catalyst, this anion influences some of the reactions in the decomposition process. In the model mechanism proposed earlier, a decrease in the rate of steps C or an increase in the rate of step D would decrease the ratio of the rates of the chain propagating to chain terminating steps. The net effect would be that which was found experimentally. However, it is also possible that the phosphate could introduce a different chain terminating step so that again the ratios of the rates would be diminished giving the same overall effect.

The experimental results were given for the samples containing two or more additives. It is noteworthy that tin, which is innocuous after a period of aging, can effectively counteract phosphate contamination. Aluminum is also useful in tying up phosphate but falls short of stannate in this respect. The chemistry of these interactions has not been studied and what mechanisms have been suggested are too speculative to be considered here. The three-additive and five-additive systems studied are probably too complex to evaluate even qualitatively at present.

The "crash program" on hydrogen peroxide which has been sponsored by the Bureau of Aeronautics included the comparison of laboratory evaluators with each other and with rocket engines. The two evaluators utilized in this cooperative program were the NRL static evaluator described in this report and a low pressure flow system developed by

TABLE 5
Effect of Phosphate on the Efficiency
of a Silver Catalyst*

Phosphate Concentration (mg/l)	Molecules of Oxygen Evolved per Atom of Silver Dissolved
0.0	9900
0.1	7700
0.25	4500
0.5	4000
0.7	3200
1.0	1900
2.0	700
3.0	500
4.0	300

*2.0-cm length of an 0.020-inch silver wire catalyst
in a 50-ml sample of 90% hydrogen peroxide at 60°C

Becco. Both systems were designed to study the liquid phase decomposition of peroxide on a catalyst at atmospheric pressure. The static evaluator was used in the studies at this Laboratory while Becco, Reaction Motors, and the Naval Air Rocket Test Station made their tests with Becco low pressure evaluators.

Table 6 lists data from these four establishments for samples with the same concentrations of additives and a fine silver catalyst (17). It is seen that the catalyst efficiency for any one sample was of the same order of magnitude at the four laboratories. Furthermore, the decline in efficiency as the phosphate concentration increases was generally the same. It is concluded that the simple static evaluator can give reliable results when only the comparison of the liquid phase decomposition of peroxide sample is of primary concern. On the other hand, the low pressure evaluator is a valuable tool for assessing the quality of plated screen catalysts for engine applications.

The laboratory evaluators can give indications concerning the engine behavior of peroxide samples containing certain contaminants. The best example of this is the phosphate ion which greatly decreases the catalyst efficiency in a laboratory test and also shortens the bed life of a rocket engine catalyst. Tin appears to exert no effect in both systems if aged samples are considered. There is some evidence that nitrate may give trouble in an engine if its concentration is 10 mg/l or higher. The laboratory tests indicated that a concentration of at least 20 mg/l could be tolerated. Clear-cut differences between laboratory experiments and motor tests were found for samples containing

TABLE 6
Comparison of Catalyst Efficiencies for Silver
Obtained at Various Laboratories

SAMPLE	Cubic Feet of Oxygen Evolved per Gram of Silver Lost			
	Static Evaluator NRL	LOW Pressure Evaluator		
		NARTS	RMI	BECCO
SP-90	73	65	77	58
SP-90 + 0.1 mg/l of PO ₄	62	--	--	40
SP-90 + 0.25 mg/l of PO ₄	38	--	--	32
SP-90 + 0.5 mg/l of PO ₄	36	--	--	25
SP-90 + 1.0 mg/l of PO ₄	16	19	18	23
SP-90 + 2.0 mg/l of PO ₄	6	14	10	--
SP-90 + 4.0 mg/l of PO ₄	2	--	0.3	--
SP-90 + 0.25 mg/l of Al	39	--	--	--
SP-90 + 0.5 mg/l of Al	24	--	25	27
SP-90 + 1.0 mg/l of Al	20	28	23	--
SP-90 + 2.0 mg/l of Al	22	30	23	--
SP-90 + 5.0 mg/l of Al	20	32	--	--
SP-90 + 10.0 mg/l of NO ₃	73	~65	64	63
SP-90 + 10.0 mg/l of SO ₄	80	54	69	96

aluminum or sulfate. Aluminum in a concentration of 0.5 mg/l did not affect motor performance but it did cut the catalyst efficiency in the liquid phase decomposition studies. The story was reversed when the contaminant was sulfate. The laboratory runs gave no change from the performance of SP-90 but 3.25 mg/l of sulfate was the limit for satisfactory engine operation.

It thus appears that the presently used laboratory evaluators will not always predict the behavior of a peroxide sample in a rocket engine. Since these systems examine only the liquid phase part of the decomposition, it seems reasonable to expect other factors to play some part in the high-temperature portion of a catalyst bed. For instance, the detrimental effect of sulfate appears to be a physical one in which the high-temperature part of the catalyst bed becomes plugged with a white fluffy deposit of sodium sulfate. In the

laboratory evaluators the sulfate stays in solution because excess liquid is available but in the engine the solvent is decomposed and evaporated leaving the sulfate salt behind on the catalyst bed. This particular salt accumulates in the bed since it is stable at the temperatures involved and apparently is able to adhere to the catalyst. Other deposits which are decomposed by the high temperature or do not stick to the bed are swept out.

The difficulties associated with phosphate contamination can be traced to its ability to increase the solution rate of silver in peroxide. The screens are stripped of their catalyst in a shorter time than normal. If the silver is carried all the way into the rocket exhaust, the catalyst will become depleted more rapidly and eventually incomplete decomposition of the peroxide will be the result. It has also been found in many cases that the silver remains in the bed as a deposit in the lower sections. Frictional forces build up in such circumstances and decrease the flow rate. In either event, the effect of phosphate is highly deleterious.

The redeposition of silver on the catalyst bed may be as small particles or as a thicker plate on the downstream screens. Such behavior is similar to that found in the laboratory tests when the silver reprecipitated as the peroxide concentration decreased.

SUMMARY

The decomposition of high purity 90% hydrogen peroxide on a silver catalyst was found to be sensitive to certain inorganic contaminants. The rate of decomposition and the catalyst loss were altered by minute amounts of phosphate, stannate, or aluminum ions but were immune to sulfate and nitrate ions in the peroxide solution. The effect of tin was subject to aging so that its influence was negligible one day after it was added to the sample. Aluminum increased the starting activity of the silver catalyst as well as its solution rate. These effects were observed at concentrations of aluminum below 0.5 mg/l but were not increased by raising the aluminum concentration above this value. The increased silver loss due to the presence of aluminum was moderate. When phosphate ion was added to hydrogen peroxide, the activity was increased. With concentrations above 2 mg/l, an inhibiting reaction masked this increase and the decomposition rate became slow. Phosphate sharply magnified the amount of silver that dissolved in the peroxide sample. The catalyst efficiency was cut by a factor of 50 at a phosphate concentration of 4.0 mg/l. Attempts to control the undesirable influence of phosphate showed that addition of tin was effective in nullifying the abnormalities due to the phosphate. Addition of aluminum ions or adjustment of the apparent pH to higher values are less satisfactory means of partially counteracting the effects of phosphate.

The NRL static evaluator gave catalyst efficiencies comparable to those found for similar hydrogen peroxide samples in the flow apparatus developed by Becco. Some agreement was also found between this laboratory study and rocket engine tests. The major discrepancy between these two was found for samples containing sulfate ion. In the evaluator, the sulfate salt remains in solution and does not affect the catalyst. In the engine the peroxide is completely changed to gaseous products and the sulfate salt is deposited in the catalyst bed, thereby causing decreased flow rates of propellant.

* * *

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APPENDIX
[Unclassified]DETERMINATION OF INORGANIC MATERIALS
IN HYDROGEN PEROXIDE

In studies of the phenomena associated with the catalytic decomposition of hydrogen peroxide it is often necessary to have reliable analytical methods for determining the concentrations of those ions which affect the catalytic behavior so markedly. The concentrations of interest are low and the standard volumetric or gravimetric procedures of analysis are impractical. Colorimetric methods which have high sensitivities were found to be useful for phosphate, aluminum, nitrate, and tin. Turbidimetric and nephelometric methods are widely used to determine low concentrations of sulfate in aqueous solutions. Although such methods were the best available, they are still not too good because the formation of the barium sulfate precipitate is sensitive to a variety of factors.

Analyses for any of the ions require that the peroxide be decomposed first since it interferes with the formation of precipitates or color. In some methods, peroxide reacts with the organic reagents used, producing undesirable colors. The normal peroxide removal method involves a combination evaporation-decomposition procedure on a steam bath. If permissible, the sample is made alkaline to accelerate the decomposition rate.

In the present study it was found convenient to use the Lumetron Photoelectric Colorimeter, Model 402-E, for all of the analyses. Its sensitivity was acceptable and its design permits the determination of sulfate by the shifting-cuvette procedure. The latter is more sensitive than the turbidimetric method. Burettes were used to add some of the reagents since the concentration of many of them must be carefully controlled. The various analyses are treated separately below.

PHOSPHATE

Place 10.0 ml of hydrogen peroxide in a 100-ml Vycor evaporating dish. Add about 1 ml of 0.1N sodium hydroxide, stir, cover with a "Speedy-Vap," and evaporate to dryness on a steam bath. Wash down the dish and cover with water and again evaporate. Acidify with 0.05N sulfuric acid (about 5 ml is sufficient to neutralize the sodium hydroxide and ensure adequate acidity) and warm for 30 minutes on a steam bath. Transfer with washings to a 50-ml volumetric flask, dilute to 40 ml, and add successively from burettes 2.0 ml of 1.5% ammonium molybdate in 10N sulfuric acid and 1.0 ml of 0.5% stannous chloride in 0.3N hydrochloric acid. Fill to the mark and measure percent transmittance in a 50-mm cell with a photoelectric colorimeter at 660 millimicrons 10 to 20 minutes after final mixing. Determine the phosphate concentration from a calibration curve.

Note - The final concentration of the reagents, the pH of the final solution, and the length of development time are critical in the "molybdenum blue" method for phosphate.* The residue from the evaporation step is heated with sulfuric acid to convert any pyrophosphate to orthophosphate. The stannous chloride reagent should be prepared the same day it is used. If a stronger reagent 3N in hydrochloric acid is prepared, a portion of this may be diluted 1:10 for use every day. This will afford consistent results.

* N.L. Allport, "Colorimetric Analysis," London:Chapman and Hall, 1947, p. 159

ALUMINUM

Place 10.0 ml of hydrogen peroxide and about 1 ml of 0.1N sulfuric acid in a Vycor evaporation dish. Mix, cover with a Speedy-Vap, and evaporate on a steam bath. Wash down the dish and cover with distilled water and again evaporate. Take up in water and transfer to a 50-ml volumetric flask, keeping the volume of washings small. Add one drop of phenolphthalein and make just alkaline by the addition of 8% sodium hydroxide solution. Neutralize the solution with 2N hydrochloric acid and add, from a burette, 2.0 ml in excess. Add 5.0 ml of 25% ammonium acetate, 1.0 ml of 1% thioglycolic acid, and 2.0 ml of 0.1% aluminon reagent from burettes. Make up the volume to just below the mark, immerse the flask in a thermostat at 30°C for 40 minutes, cool to room temperature, and adjust the volume to 50-ml. Measure the percent transmittance in a 50-mm cell at 515 millimicrons, setting a blank containing the same quantities of reagents at 100% transmittance. Read the aluminum concentration from a calibration curve.

Note – The determination of aluminum in peroxide with aluminon reagent was developed by Walkden, Austing, and Cottell.* This was used as a basis for the analytical method used at this Laboratory. The aluminon reagent was prepared by the method recommended by Snell and Snell.† The sampling procedure is important for aluminum since samples stored in aluminum drums frequently have an aluminum oxide sediment. The color development depends on the pH and the dye concentration, hence the reagents were added with burettes.

NITRATE

Place 10.0 ml of hydrogen peroxide and about 1 ml of 0.1N sodium hydroxide in a 100-ml Vycor evaporating dish. Mix, cover with a Speedy-Vap, and evaporate to dryness on a steam bath. Wash down the dish and cover with distilled water and evaporate. Repeat the washing and evaporation steps. Cool to room temperature and add 1 ml of phenol disulfonic acid. Allow to stand 20 minutes, then transfer contents and washings to a 50-ml volumetric flask. Fill to about 30 ml, then make alkaline by dropwise addition of concentrated ammonia. Dilute to the mark, mix thoroughly, cool, place in a 50-mm cell, and read the percent transmittance at 420 millimicrons. It may be necessary to use a blank for 100% transmittance since some batches of the reagent are slightly tan in alkaline solution. The nitrate concentration is determined by reference to a calibration curve.

Note – The nitration of phenol disulfonic acid in anhydrous conditions gives a nitro compound which has a yellow color in alkaline solution.‡ The reagent is very sensitive to oxidation. A drop of 1% hydrogen peroxide solution will produce a brown or black color when in contact with this phenol. Thus, every trace of peroxide must be decomposed and the sample must be shielded from peroxide vapors during the nitration step. The phenol disulfonic acid reagent was obtained commercially but the isomer present in the reagent was not specified.

*J. Walkden, C. E. Austing, and K. Cottell, "Determination of Aluminum in Hydrogen Peroxide," Great Britain, Chemical Inspectorate, Ministry of Supply, Report CI/Memo. 3 (Unclassified), 1951

†F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," New York:Van Nostrand, 1948, p. 248

‡N. F. Allport, op. cite., p. 145

TIN

Place 10.0 ml of hydrogen peroxide in a 100-ml Vycor evaporating dish. Add 1 ml of 0.1N sodium hydroxide, stir, cover with a Speedy-Vap, and put on steam bath. Evaporate to dryness, wash down the dish, and cover with distilled water and again evaporate. Cool, add 5.0 ml of 5N sulfuric acid and then 5 drops of thioglycolic acid. Transfer with washings to a 50-ml volumetric flask and dilute to about 45 ml. Add 2 drops of Santomerse S and mix. Then add 1 ml of dithiol reagent and again mix. Add 8 more drops of Santomerse S, mix, dilute to mark, and re-mix. Place in a 50-mm cell and read percent transmittance in a colorimeter at 550 millimicrons as compared with a blank set at 100% transmittance. Determine the tin concentration from a calibration curve constructed from data for standard stannous chloride samples.

Note - The method for tin is a modification of the one developed by Farnsworth and Pekola.* If catalytic decomposition on platinum in sulfuric acid is used to remove the peroxide, a yellow color frequently interferes with the desired pink tint. This yellow color was not observed when alkaline decomposition was used, hence this method of reducing the peroxide was used. The Farnsworth-Pekola method recommends a final concentration of 1.2N in sulfuric acid. Such an acidity was found to decrease the solubility of the dispersing agent and turbidity was encountered on occasion. A concentration of 0.5N sulfuric acid was found to be suitable. The Santomerse S was used as received from Monsanto. The dithiol (toluene-3,4-dithiol) reagent is prepared by weighing 0.15 g of dithiol into a 100-ml beaker, adding 8 drops of thioglycolic acid, and then adding 50 ml of 2% sodium hydroxide. The mixture is stirred until the dithiol is completely dissolved. The solution is stable for one week if stored in a refrigerator.

SULFATE

Place 25.0 ml of hydrogen peroxide in a 100-ml Vycor evaporating dish, cover with a Speedy-Vap, and evaporate to dryness on a steam bath. Warm the residue with 1.0 ml of 0.05N hydrochloric acid and transfer this with distilled water washings to a 50-ml volumetric flask. Fill to the mark and mix thoroughly. Pour into a 50-mm cuvette and stir moderately as 2.0 ml of 10% barium chloride is added. Continue stirring for 1 minute, then allow sample to stand 10 minutes. Measure the percent transmittance at 420 millimicrons by the shifting-cuvette method. Calculate the sulfate concentration by reference to a calibration curve.

Note - The sulfate method was quite erratic even with standard sulfate samples, but it is recorded here in lieu of any better method at the time the work was done.† The mixing conditions for the precipitation of a uniform and reproducible particle size are very critical and the particles grow with age. Therefore a rigid mixing and aging program must be followed.

* M. Farnsworth and J. Pekola, *Anal. Chem.* 26:735-737 (1954)

† R. N. Hazlett, "A Conductometric Analysis for Sulfate Ion in Hydrogen Peroxide," NRL Memorandum Report 717 (Unclassified), June 1957

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