

CONCENTRATED HYDROGEN PEROXIDE *

By M. E. BRETSCHGER AND E. S. SHANLEY **

ABSTRACT

Some of the properties of concentrated hydrogen peroxide are summarized. Stability and stabilization of hydrogen peroxide solutions are discussed. Special attention is devoted to the compatibility and explosion hazard of concentrated hydrogen peroxide. Mention is made of the actual and potential uses of this newly available material.

STABILITY

Hydrogen peroxide solutions are very stable when pure. The following data show the rate of decomposition of high purity 90% hydrogen peroxide of commerce.

TABLE I

Rate of Decomposition of Hydrogen Peroxide

Temperature		Approximate Time for 1% Loss
25° C	78° F	1 year
66° C	150° F	1 week
100° C	212° F	24 hours
140° C	285° F	Decomposes rapidly

TABLE II

Effect of Certain Metallic Ions on Hydrogen Peroxide Solutions

Contaminant		% Loss in 24 Hr. at 100° C
None		2
Aluminum	10 mg. per L	2
Chromium	0.1 mg. per L	96
Copper	0.01 mg. per L	24
Copper	0.1 mg. per L	85
Iron	1.0 mg. per L	15
Tin	10 mg. per L	2
Zinc	10 mg. per L	10

Hydrogen peroxide solutions are very sensitive to catalysis. Certain metal ions, as soluble salts, were added to a mildly acid 6% com-

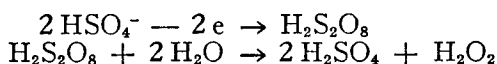
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mercial type hydrogen peroxide solution with the results shown in Table II. This solution by itself was not as stable as the purified 90% hydrogen peroxide described above. However, the effects of intentional contamination were qualitatively similar to those noted with more concentrated solutions.

CONCENTRATED HYDROGEN PEROXIDE

Most of the hydrogen peroxide of commerce is now made by the electrolytic oxidation of sulfuric acid or a sulfate to persulfuric acid or a persalt with subsequent hydrolysis and distillation of the formed hydrogen peroxide. The over-all reactions are as follows:



The preparation of 30% solutions has been a large scale industry for about twenty years. Very highly concentrated solutions have been in large scale production only during the last few years.

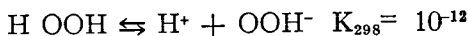
A new process developed by the Buffalo Electro-Chemical Company has made available solutions containing 90% hydrogen peroxide and of a degree of purity heretofore unattained. The purpose of this paper is to discuss some of the properties of this solution.

PROPERTIES^{1*}

A few of the physical properties of 90% hydrogen peroxide are compiled below.

Color	— Clear, Colorless
Odor	— None
Specific Gravity	— 1.396 at 20° F
Viscosity	— 0.0130 poise at 18° C
Freezing Point	— —11° C
Boiling Point	— 140° C with decomposition
Refractive Index	— 1.3998 n_D 20° C
Dielectric Constant	— 95 at 0° C

Hydrogen peroxide solutions are more stable when acid and less stable when made alkaline. Hydrogen peroxide is a weak acid, dissociating according to the following equation:



Acids decrease and alkalis increase the concentration of OOH^- ion and this fact, together with the known effects on stability, suggest that the OOH ion is probably involved in the catalyzed decomposition.

STABILIZATION

Literally, hundreds of materials have been suggested as stabilizers for hydrogen peroxide solutions.² Except for acids it is probable that these materials have no effect on the peroxide, but serve only to in-

* See References at end of paper.

activate decomposition catalysts. Most stabilizers for hydrogen peroxide are either absorbents for heavy metal ions or are capable of forming complexes with heavy metals. In the first category may be mentioned hydrous stannic oxide and antimony oxide, freshly precipitated silica and alumina. In the second category may be mentioned the pyrophosphates, fluorides and cyanides, 8-hydroxyquinoline and acetanilid. There is no one best stabilizer for hydrogen peroxide solutions. The choice is affected by the purity, concentration, pH and intended use of the product. As noted above, hydrogen peroxide solutions of very high purity are quite stable. Present tendency in commercial practice is higher purity and less stabilizer.

SOLUBILITY

Hydrogen peroxide is soluble in all proportions in such materials as ethanol, isopropanol, acetone, pyridine and many other substances with which water is miscible. In addition, hydrogen peroxide is more soluble than water in many organic materials. A few examples are shown in Table III.

TABLE III

Solvent	g. 90% H ₂ O ₂ in 100 ml.	g. H ₂ O in 100 ml.
Methyl Methacrylate	18	1
Allymer CR-39	28	3
Dimethyl Phthalate	28	1.6
Diethyl Phthalate	2.5	1.0
Ethyl Acetate	..	3.5
Aniline	..	3.5

ENERGY

The decomposition of hydrogen peroxide is a strongly exothermic reaction. One kg. of 90% H₂O₂ on complete decomposition yields 620 kg.-cal. Under adiabatic conditions and at 1 atmospheric pressure, the oxygen and steam will be liberated at 750° C and will occupy about 5,000 times the volume of the liquid starting material.

The oxygen can be used to burn a fuel, thus greatly increasing the energy yield per pound of fuel mixture.

The power possibilities of this system have been investigated very extensively both here and abroad. Some of the developments will be mentioned later.

COMPATIBILITY

It is known that concentrated hydrogen peroxide can form explosive mixtures with combustible materials.^{3, 4} This laboratory has carried out extensive studies on the compatibility of concentrated hydrogen peroxide and on explosion hazards connected with the handling of this material.

Compatibility tests were made by pouring a few ml. of 90% hydrogen peroxide on a like quantity of the material for test. Small test tubes or evaporating dishes were used. Tables IV and V contain information obtained in this manner.

TABLE IV

Materials Causing a Reaction Upon Contact with H₂O₂ 90%

Materials	Type of Reaction
Ammonia (liquid)	vigorous decomposition
Aniline containing Cu(NO ₃) ₂	delayed explosion
Calcium hydride	very bright flame
Calcium Permanganate	violent decomposition
Chromium Trioxide	violent decomposition
Copper Metal	very mild decomposition
Hydrochloric Acid 36%	slow gas evolution
Hydrazine Hydrate	violent explosion
Iron Metal	mild decomposition
Lead Metal	vigorous decomposition
Lead Dioxide	vigorous decomposition
Manganese Acetate	vigorous reaction with sparks
Mercury Metal	vigorous decomposition
Potassium Chromate	vigorous decomposition
Sodium Metal	vigorous reaction, flame
Sodium Hydroxide	vigorous decomposition
Asbestos	mild to vigorous decomposition
Boiler Ash	mild decomposition
Cotton Cloth, clean	very mild decomposition
dirty or soiled	fire
Clay Soil	vigorous decomposition
Concrete	vigorous decomposition
Filter Cell	mild to vigorous decomposition
Fullers Earth	mild to vigorous decomposition
Rock Wool	mild to vigorous decomposition
Vermiculite	mild to vigorous decomposition
Wood, clean	very mild decomposition
Wood, dirty	fire

TABLE V

Materials Showing No Visible Reaction with H₂O₂ 90%

<i>Organic Materials</i>	
Acetone	n-Hexaldehyde
Acetic Acid	n-Hexanol
Aniline	Isopropanol
"Carbitol"	Kerosene
"Diethyl Cellosolve"	Lubricating Oil
Diethyl Phthalate	Methanol
Dimethyl Phthalate	Methyl Methacrylate
Dioxan	Paraffin Wax
Ethanol	"Polythene"
Ethyl Acetate	Quinoline
Ethylene Glycol	Silicone Greases
Glycerol	"Teflon"
<i>Inorganic Materials</i>	
Ammonium Nitrate	Phosphoric Acid 85%
Ammonium Sulfate	Sodium Acetate
Nitric Acid (conc.)	Sodium Nitrate
Perchloric Acid (conc.)	Sulfuric Acid (conc.)

Many of these "stable" mixtures have been examined with special regard to possible explosion hazard. Some of the tests are described below.

Rifle Bullet Impact. All of the materials listed above as soluble and non-reactive on mixing with 90% H_2O_2 have been subjected to rifle fire. The mixtures were made up in small glass containers after which a 22 calibre bullet was fired into them. Violent explosions were observed when the reactants were at or near the stoichiometric proportions for complete combustion of the added material.

90% hydrogen peroxide by itself is unaffected by rifle fire.

Drop Weight Tests. Impact studies have also been carried out in a Bureau of Mines type drop weight tester. In this apparatus a small sample of the mixture to be tested is placed in the bottom of a cylinder. A piston is inserted and allowed to rest on the sample, after which a weight is allowed to fall on the top of the piston. The sensitivity of the composition is judged by the energy necessary to cause detonation. It is common to express this energy in terms of kg. cm. for probability of detonation = $\frac{1}{2}$ (5 fires in ten tries).

Hydrogen peroxide solutions, even at 99%+ H_2O_2 , do not detonate in this test. Mixtures containing soluble combustible materials may detonate. The sensitivity is highest when the reactants are in about the right proportions for complete combustion. Actual energy necessary to set off such "stoichiometric" mixtures is in the range of 10 kg. cm. to 100 kg. cm., depending upon the combustible material.

A few insoluble and non-reactive materials have been tested in this apparatus. The insoluble material and the hydrogen peroxide were placed in the cylinder independently and the test made in the usual way. Every combustible material tested in this fashion in combination with 90% hydrogen peroxide detonated. The list includes such materials as kerosene, petroleum lubricating oil and grease, paraffin wax, various silicone fluids and greases.

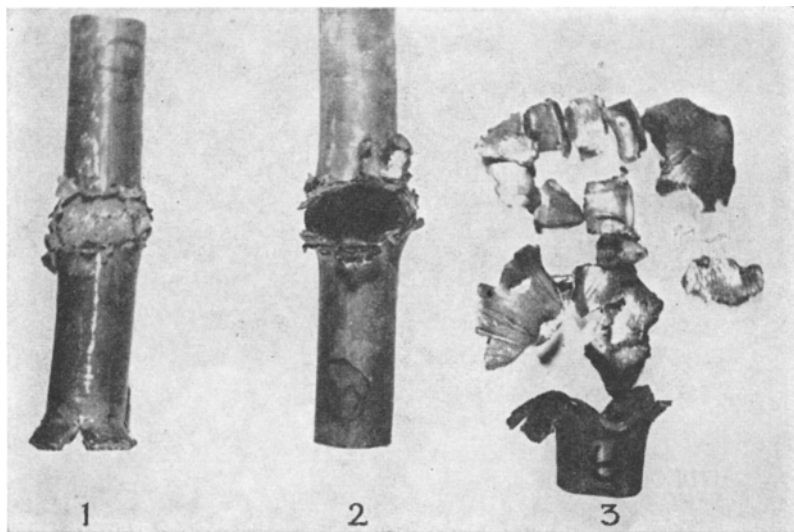


FIG. 1. Lead pipe explosion test. 1. 10 ml. water. 2. 10 ml. H_2O_2 90%. 3. 4 ml. H_2O_2 90%, 6 ml. ethanol.

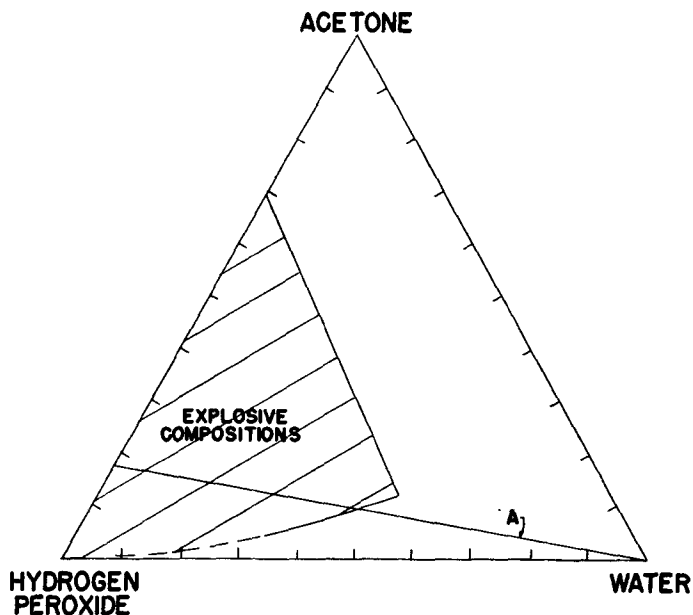


FIG. 2. Explosive compositions in the system—acetone, hydrogen peroxide and water. Line A indicates stoichiometric proportions of acetone and hydrogen peroxide. $C_2H_6O + 8 H_2O_2 \rightarrow 3 CO_2 + 11 H_2O$.

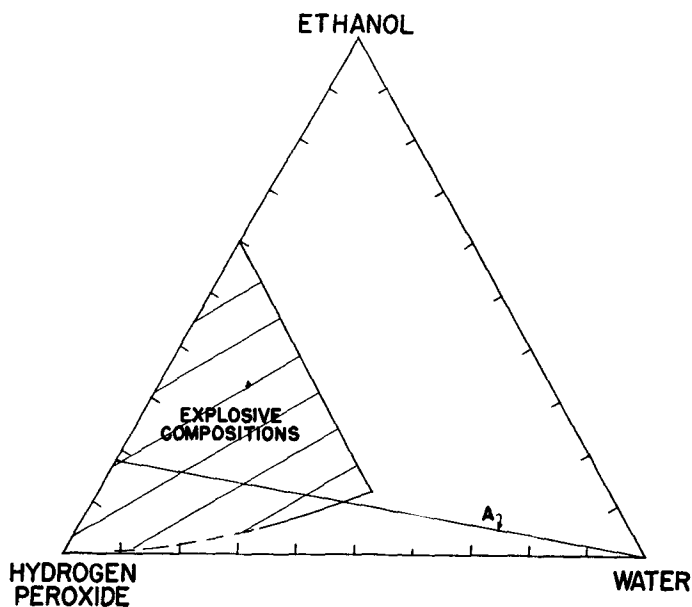


FIG. 3. Explosive compositions in the system—ethanol, hydrogen peroxide and water. Line A indicates stoichiometric proportions of ethanol and hydrogen peroxide. $C_2H_5OH + 6 H_2O_2 \rightarrow 2 CO_2 + 9 H_2O$.

Blasting Cap Tests. A standardized procedure has been adopted for determining the effect of a blasting cap on these mixtures. The procedure is as follows:

The desired quantities of "fuel" and hydrogen peroxide are measured into separate containers and then mixed behind a suitable barricade. The resulting mixture (usually about 10 ml.) in a 15 x 150 mm. pyrex test tube is placed in a 7 in. (17.8 cm.) section of 0.75 in. (1.9 cm.) lead pipe, having 0.25 in. (0.63 cm.) wall thickness. This pipe is supported upright on a 1 in. (2.5 cm.) steel plate. A fuse-ignited #6 blasting cap is then lowered into the test tube and supported in such a way that the shell of the cap is about half immersed. The cap is then set off. The effect can be judged by the sound and by the appearance of the lead pipe. The pipe is only bulged when the test tube contains water. If the lead pipe is broken into fragments, it is considered that detonation has occurred. Fig. 1 shows the appearance of the pipes after some typical trials.

This test, like any other for the purpose, is arbitrary to a certain degree. The impact sensitivity of liquids is particularly dependent on the degree of confinement and widely varying results can be obtained by changing this factor. The test as described is a severe one. Mixtures not detonated by this procedure can be considered immune to detonation under any circumstances likely to arise in practice.

The results of studies on some three component systems are presented in the form of triangular charts. Fig. 2, 3 and 4.

Similar tests have been carried out with a number of additional soluble combustible materials with results analogous to these. Detona-

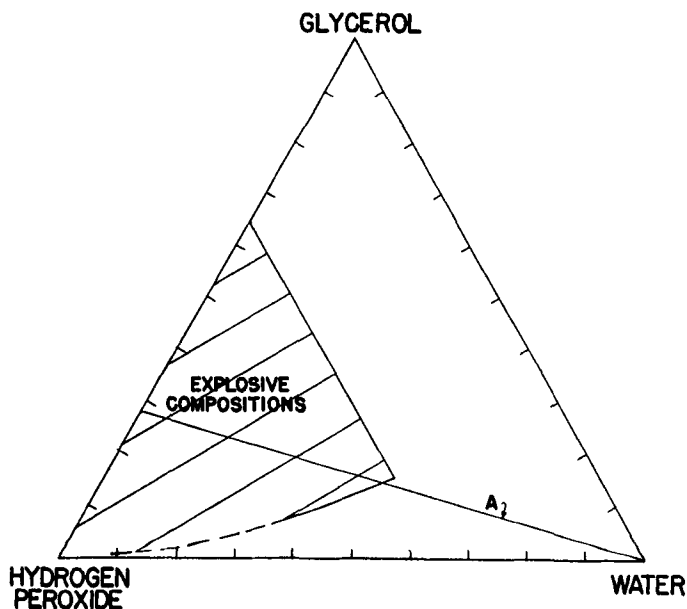


FIG. 4. Explosive compositions in the system—glycerol, hydrogen peroxide and water. Line A indicates stoichiometric proportions of glycerol and hydrogen peroxide. $C_3H_8O_3 + 7 H_2O_2 \rightarrow 3 CO_2 + 11 H_2O$.

tions have been observed only when the 90% hydrogen peroxide formed over 30% by volume of the final mixture (more than 3 ml. of 90% peroxide in 10 ml. total).

In case it is desired to make up hydrogen peroxide-"fuel" solutions which fall within the explosive range, it is advisable to take extensive precautions. Some mixtures may be detonated rather easily, for instance by dropping the container, and the explosion may sometimes be comparable with that of a corresponding quantity of nitroglycerine.

REACTIONS OF CONCENTRATED HYDROGEN PEROXIDE

The following survey is intended to illustrate some of the typical reactions of concentrated hydrogen peroxide.

Organic Oxidations. Some of the following reactions can also be carried out with dilute hydrogen peroxide, but the use of concentrated hydrogen peroxide results in improvements in rate or yields, etc.

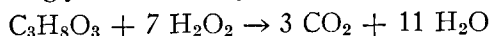
TABLE VI

Lower aliphatic acids	→	peracids
Lower aliphatic aldehydes	→	acids
Secondary amines	→	hydroxylamines
Tertiary amines	→	amine oxides
Paraffin hydrocarbons		not affected under mild conditions
Unsaturated fatty acids	→	hydroxyacids
Benzene	→	phenol
naphthol	→	Carboxy cinnamic acid

Bleaching. Bleaching of several oils, fats, and waxes has been observed with concentrated hydrogen peroxide. 90% hydrogen peroxide is much more effective than dilute aqueous H_2O_2 solutions for certain of these reactions. The increased concentration of oxidant at the interface and the greater solubility of concentrated hydrogen peroxide are both presumed to play a part in this effect.

Polymerization. Hydrogen peroxide has been widely used as catalyst or promoter in emulsion polymerization. It has not been commonly used for bulk polymerization. 90% hydrogen peroxide is soluble at least in catalytic concentrations in several monomers. Polymerization has been carried out in this fashion with several materials including styrene, methyl methacrylate and some partially polymerized polysulfides.

As a Component of Explosives. Explosive compositions can be formed by dissolving certain combustible materials in concentrated hydrogen peroxide. Such mixtures may be quite stable in storage, but detonate violently under the proper stimulus. Some of the data on explosives compounded with glycerol and hydrogen peroxide are outlined below as typical of the sort of performance to be expected from such compositions. The data is for mixtures made up with 90% hydrogen peroxide and glycerol to satisfy the equation:



The maximum power and sensitivity occur near this stoichiometric composition, even though the actual reaction does not go to completion as shown.

TABLE VII

	Glycerol + 90% H ₂ O ₂	Nitroglycerine
Impact Sensitivity (drop weight test)	15 kg. cm.	2 kg. cm.
Total energy released	1.6	1.6
Total gas volume released	1 L/g.	0.7 L/g.
Detonation rate	6,500 m./sec.	8,000 m./sec.

These figures indicate the possibility that useful explosives may be compounded with concentrated hydrogen peroxide.

As an Energy Source. During World War II the Germans made use of concentrated hydrogen peroxide to energize some of the most spectacular secret weapons. Some of the devices utilized hydrogen peroxide and a catalyst to produce a stream of oxygen and steam from which the energy was derived. In other cases, a fuel was burned in the oxygen to increase the energy output. A few of the devices are listed below.*

Me rocket propelled pursuit planes
V1 robot bomb
V2 long range rocket
High speed submarine
High speed torpedo

Many more devices had been proposed and in some cases built by the Germans.

It is to be expected that the new concentrated hydrogen peroxide will prove to be equally useful in the ways of peace.

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3. M. Bamberger and J. Nuszbaum, Z. ges. Schies-Sprengstoffw. **22**, 125-8 (1937).
4. L. Medard, Compt. rend. **222**, 1491-3 (1946).
5. C. H. Ricker, Aviation, p. 190 (November, 1946).
6. Anon, Newsweek, p. 46 (January 28, 1946).

Resumen del artículo: "Peróxido de Hidrógeno Concentrado."

Peróxido de hidrógeno con 10% de agua pero sin otras impurezas es químicamente muy estable a la temperatura del ambiente (Tabla I), pero cantidades minuciosas de ciertos iones metálicos catalizan la descomposición extremadamente (Tabla II).

Ahora se produce peróxido de 90% comercialmente por la evaporación en el vacío de peróxido de 30% producido electrolíticamente. Se añaden sustancias que adsorben o forman iones complejos con los metales pesados para estabilizar el peróxido contra descomposición. Ácidos también estabilizan el peróxido, y por eso se supone que el ión OOH⁻ es de importancia en la descomposición catalizada.

* See also ref. 5, 6.

Se indican muchas sustancias que reaccionan con peróxido (Tabla IV) y otras que no (Tabla V), y las composiciones de mezclas con acetona, etanol, o glicerina que pueden estallar (Fig. 2, 3 y 4).

DISCUSSION

THOMAS ENDICOTT: For a number of years I have been interested in literature reference on the decomposition of strong hydrogen peroxide solutions in contact with various materials, specifically glass and fused quartz. Men at McGill University worked on this some years ago. There has been a recent publication of the National Research Council at Ottawa, and Rice and his coworkers did a lot of work on this at Johns Hopkins some years ago. I understand that the rate of decomposition in glass and fused quartz, for example, comparing one with the other, depends largely upon the presence or absence of dust. I imagine this is another way of saying what the author has stated as to the catalytic effect of metallic impurities. In other words, probably dust acts through the presence of iron, as a rule, in the ordinary atmosphere. Would that be the case?

E. S. SHANLEY: I believe that is true. I think it likely that the heavy metal catalysts play a very important part in the effect that you mention. However, there is another effect which is due to the walls of the containers or, in fact, the surfaces of any solid particle in contact with hydrogen peroxide walls. We believe that some decomposition occurs on a surface, any surface, without any particular specificity.

THOMAS ENDICOTT: As I recall some of these papers, especially prepared glass and quartz surfaces acted a little bit different than ordinary surfaces, but to my mind there was nothing very conclusive to those results. You would say in general that this statement as to the presence of dust and your findings as to the effect on metals would be saying practically the same thing in different words, wouldn't you?

E. S. SHANLEY: I think so.

J. P. MARBLE¹: What is the stability of the 90% hydrogen peroxide toward light? Does it have to be kept in opaque containers or is it more stable toward light than the less concentrated solutions? I am interested in this as a possible chemical reagent in connection with rare earth chemistry.

E. S. SHANLEY: I don't believe I can answer the question exactly, but the solution is at least reasonably stable toward light. Exposure to ordinary daylight, for example, causes only slight decomposition.

¹ 321 U. S. National Museum, Washington, D. C.