# Flammability Characteristics of the Vapor System Hydrogen Peroxide–Xylene–Formic Acid–Water

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AT PRESENT the textile industry is the major single user of hydrogen peroxide in the United States. Other industries use it as a reagent in chemical synthesis, as a source of free radicals to start polymerization, as a foaming agent in manufacturing porous substances, and for its effect on biological processes. Also because highly concentrated hydrogen peroxide is a compact source of energy, it is useful either as a monopropellant or as the oxidizer of a bipropellant system. Large quantities of highly concentrated hydrogen peroxide propellant were used during World War II, particularly by Germany. Since then production of this peroxide has increased rapidly. United States production alone has more than doubled since 1950 (*3*).

Because of its widespread use, increasing interest has been shown in the hazards of handling high-strength peroxide. Although the stability of the reagent (*1*, *4*) and its vapor (*5*, *7*) and the hazards of introducing contaminants and dissolved oxidizable substances in the liquid (*10*) have been studied, apparently little work has been done on vapor-phase reactions of systems involving high-strength peroxide and combustibles.

Since hydrogen peroxide–combustible–water vapor systems are encountered during production of the peroxide by oxidation of organic liquids (*3*), this study was undertaken to determine the limits of flammability of organic vapors in hydrogen peroxide–water vapor mixtures. *o*-Xylene and formic acid, representative of two widely varying classes of possible organic substances, were used.

## APPARATUS

A small-scale version of the apparatus used in determining the limits of flammability of hydrocarbons in air (*11*) was used to obtain the data presented here. This apparatus (F-39) consists of an explosion chamber, an ignition source, liquid-feed devices, and a constant-temperature bath (Figure 1).

The explosion chamber, *A*, of the F-39 apparatus and the adjacent mixing chamber, *B*, were made from a borosilicate glass tube 20 inches long and 1 inch in inside diameter; the explosion chamber is 15 inches long. Indentations were placed spirally around the mixing chamber to facilitate the formation of homogeneous mixtures. Spark electrodes, *C*, are located at the base of the explosion chamber; they are made of 20-gage platinum wire and enclosed in glass, so that only their tips are exposed to the test vapors.

Vaporizing arms, *D* and *E*, were made from 8-mm. borosilicate glass tubing 30 inches long. They were designed to ensure complete vaporization of the liquids added to the system. Tube *D* was packed with borosilicate glass helices and used to introduce the combustibles and the water into the system. The flared fitting at the upper end of this tube received a rubber stopper. A second fitting was added to this tube to permit the addition either of two combustibles or of one combustible and water to the system. A Teflon adapter was used on the upper end of the hydrogen peroxide vaporizing tube, *E*. A wafer held in place by an aluminum

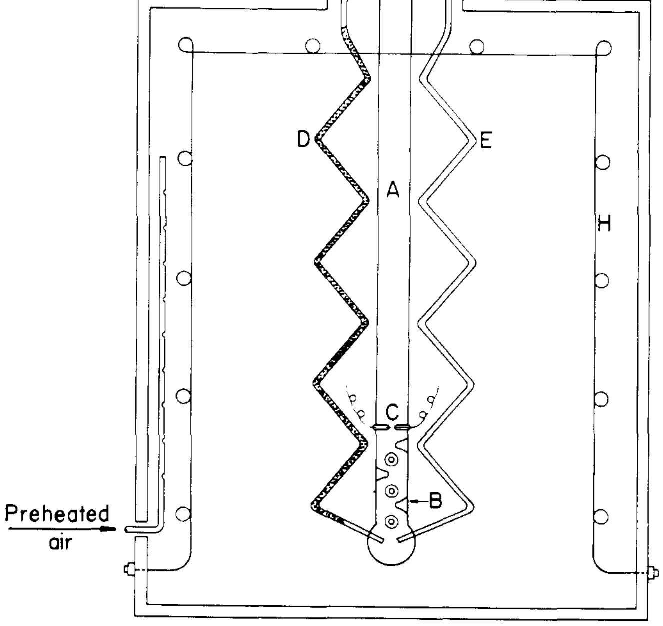

Figure 1. Schematic diagram of the F-39 elevated temperature limit-of-flammability apparatus

screw cap sealed the hypodermic needle used to deliver the hydrogen peroxide.

Each of the constituents was added to the system at constant rate with small hypodermic syringes, *F*. Fractional horsepower motors equipped with built-in gear reducers were used to drive the feed mechanisms, *G*, which depressed the syringe pistons at predetermined rates. The rate of liquid delivery was determined by the syringe and the gears used to drive the feed mechanism.

The ignition source consisted of a 15-kv., 30-ma. luminous tube transformer. A 1/4-inch spark gap between glass-sheathed 20-gage platinum electrodes was used.

The temperatures of the explosion chamber and related parts were maintained constant by a small commercial oven, *H*, equipped with an air circulating system.

## PREPARATION OF EQUIPMENT

Because of the sensitivity of hydrogen peroxide vapor to surface conditions (*8, 9*), passivation of glass surfaces that come in contact with this vapor is extremely important. Various methods of passivation (*7, 8*) tend to minimize the decomposition rate of hydrogen peroxide.

The glass apparatus was first thoroughly cleaned with a detergent, then rinsed and soaked overnight in concentrated nitric acid. After this soaking period, it was flushed with distilled water, rinsed with deionized water, and drained. The final traces of water were removed by slowly passing filtered air through the apparatus at 150° C. All openings in the apparatus were then covered with aluminum foil. The apparatus was also cleaned between tests. The carbon and other deposits were removed by washing with a xylene-acetone mixture and a detergent in water. The vapors from boiling concentrated nitric acid were passed through the apparatus; then it was rinsed and dried as noted above.

The syringes used for the peroxide feed were passivated by soaking in nitric acid and then in hydrogen peroxide; the needles were passivated by soaking in hydrogen peroxide. Attempts to passivate the needles by soaking in 35% nitric acid failed because the connecting ends of the needles were nickel-plated brass, so that treatment with the acid exposed new surfaces on which the peroxide was active. Between tests the syringes were emptied of peroxide and wrapped in tin foil; they were not rinsed.

## PROCEDURE

To test the limit of flammability, the cleaned, passivated apparatus was installed in the oven, and the electrodes were connected to the high-voltage transformer. The Teflon adapter was attached, using Teflon tape to make a gastight connection. The oven temperature was set at 154° C.; this temperature was selected both to ensure complete vaporization of all liquid components and at the same time to minimize decomposition of the hydrogen peroxide as it passed through the apparatus (*8*). The amount of decomposition was not determined except in a few tests in the discussion below.

The hypodermic syringes were filled with either the combustibles or water as required for each test, placed in adapters, and weighed. They were then mounted on individual liquid-feed assemblies so that the hypodermic needle tips touched the inside of the glass feed tubes.

The hypodermic syringe used for the peroxide was filled last, so that the amount of decomposition and leakage could be kept to a minimum. It was weighed and placed on its liquid-feed assembly. In practice, the time between weighing and starting each test was noted and a correction made for the peroxide lost in preparation. The rate of leakage was determined for each size of syringe by performing the preparation without starting the liquid-feed-device motor and then reweighing the syringe. The operator wore a full face shield at all times when handling the peroxide.

All liquid-feed assemblies and the timer were connected to the same electrical starting switch and started together. Enough vapor was passed through the explosion chamber to flush it four times in approximately 20 minutes. The mixture was then tested by passing a spark through it in a darkened room and observing whether a flame traveled uniformly through at least two-thirds the length of the explosion chamber. If a flame traveled through at least this distance, the mixture was considered flammable; otherwise, nonflammable.

The timer and liquid-feed assemblies were turned off, the syringes and adapters were reweighed, and the change in weight was recorded for each constituent. The molar concentration of each constituent added to the mixture was then calculated; an average molecular weight of 31.23 was used for the 90 weight % hydrogen peroxide.

## RESULTS AND DISCUSSION

A flame can be initiated by a spark discharge through the vapors that result when hydrogen peroxide is vaporized at 1 atm. of pressure (*7*). For this reason, combustibile-oxidant systems in, which this peroxide is used as oxidant do not have a lower—that is combustible-lean—limit of flammability. However, lower limits may be formed if enough water vapor is added to the peroxide or if the peroxide decomposes before it is used as the oxidant.

The upper limit of flammability was tested on 90 weight % hydrogen peroxide–*o*-xylene–formic acid mixtures at 154° C. and 1-atm. pressure. Similar tests were conducted with 90 weight % hydrogen peroxide–*o*-xylene–water vapor mixtures and 90 weight % hydrogen peroxide–formic acid–water vapor mixtures. In the latter case, some lower limit-of-flammability tests were also conducted. These data are presented graphically in Figures 2 to 4. Flammable mixtures containing hydrogen peroxide are represented by solid circles and nonflammable mixtures by crosses.

**Hydrogen Peroxide–o-Xylene–Formic Acid System.** The system, 90 weight % (82.6 mole %) hydrogen peroxide–*o*-xylene–formic acid is actually a four-component system and can be represented by a plane in a regular tetrahedron (Figure 5) passing through the 82.6% hydrogen peroxide point and through the line joining the points 100 % *o*-xylene–100 % formic acid. The resultant diagram is an isoceles triangle with the coordinates noted in Figure 2. The flammable and nonflammable regions in this figure are separated by a solid curve which joins the upper limits of flammability of xylene and of formic acid in 90 weight % peroxide. The solid curve was constructed with the aid of the experimental points included in the figure and the observations of the nature of the flames and their propagation rates. There are no lower limits of flammability in this instance.

The upper limit curve calculated from LeChatelier's rule (*2*) is shown as a broken curve in Figure 2. Two other curves are included. The unlabeled solid curve near the base line gives the stoichiometric compositions for the system curves are included. The unlabeled solid curve near the base line gives the strichiometric compositions for the system 90 weight % hydrogen peroxide–*o*-xylene–formic acid. The curve labeled "Oxidant: Decomposed 90 wt. % $H_2O_2$" separates the flammable and nonflammable mixtures of the system in which the oxidant is a mixture of water and oxygen in the ratio formed when 90 weight % hydrogen peroxide is decomposed; flammable mixtures are represented by squares, and nonflammable mixtures by triangles. This, too, is an upper limit curve, so that flammable mixtures exist below the curve. In this instance, however, lower limits of flammability could be formed. They would lie along a curve located below the stoichiometric curve in Figure 2; their compositions were not determined.

**Limits of flammability at 154° C. and 1 atm. of pressure**

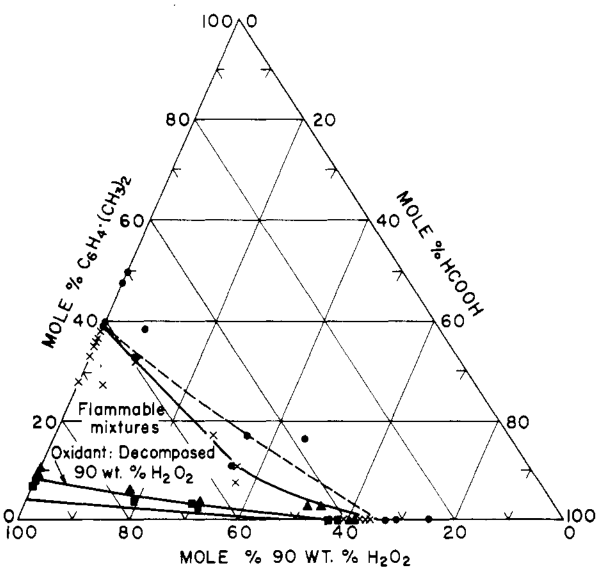

Figure 2. 90 weight % hydrogen peroxide–o-xylene–formic acid

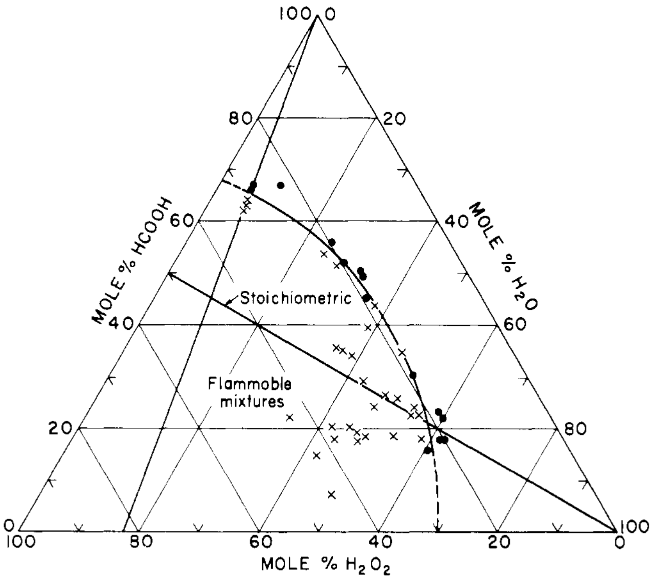

Figure 3. Hydrogen peroxide–formic acid–water

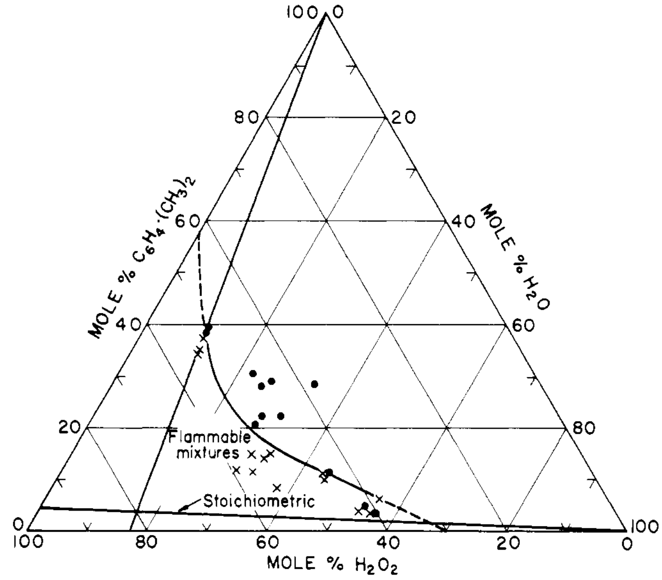

Figure 4. Hydrogen peroxide–o-xylene–water

**Hydrogen Peroxide–Formic Acid–Water System.** The experimental data for this system were recalculated on a 100 % hydrogen peroxide basis (Figure 3). The line joining the 82.6 mole % hydrogen peroxide and the 100 % formic acid points includes all mixture compositions containing 90 weight % hydrogen peroxide. Accordingly, the upper limit of flammability of formic acid and 90 weight % hydrogen peroxide lies on this line. Limit mixtures containing more water vapor lie in the region between this line and the 100 % water vapor point. When enough water vapor is present, a limit mixture containing a stoichiometric quantity of fuel is obtained. Flame propagation through mixtures in the vicinity of this limit mixture was rather erratic. Several combustible-lean mixtures in this region ignited

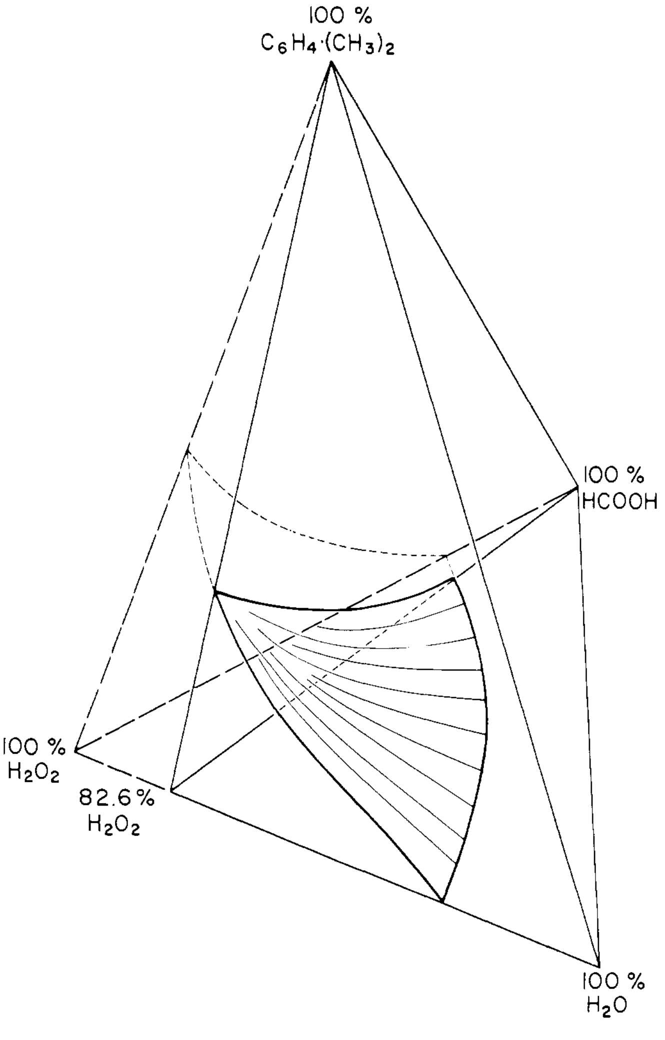

Figure 5. Composite diagram of the four-component system

and burned only in the mixer portion of the apparatus. Analysis of the vapors collected on a cold finger from the upper portion of the explosion chamber during these tests showed that an abnormal amount of peroxide decomposition had occurred. The extent of decomposition increased as the combustible content decreased and the peroxide content increased.

In the various series of tests, the change in surface sensitivity was evidenced by explosions in the explosion chamber before ignition. These explosions became increasingly violent with continued testing. The apparatus had to be replaced twice; it was destroyed on the 33rd test of the first series and on the 38th test of the second series. The amount of peroxide decomposition was determined in the third apparatus after it had been used for approximately 20 tests. This apparatus may have developed an unusual surface condition because it was not possible to determine the limit of flammability for hydrogen peroxide-water vapor mixtures alone. Accordingly, the data of Satterfield and others *(6)* were used to define the lower limit-of-flammability curves in Figures 3 and 4. The value, 30 mole % hydrogen peroxide, was used as the terminal point on the hydrogen peroxide-water vapor line in these figures because the criterion for this value corresponds closely to the criterion used here for flammability. A broken curve was then drawn between this point and the curve. Also, the upper limit-of-flammability curves in Figures 3 and 4 were extrapolated to outline the region of flammable mixtures containing hydrogen peroxide in greater concentrations than those used here.

**Hydrogen Peroxide–Xylene–Water System.** The experimental data recalculated on a 100 % hydrogen peroxide basis are presented in Figure 4, which also contains a 90 weight % line and a stoichiometric composition curve (Figure 3). Unlike the hydrogen peroxide-formic acid-water, system, this system contained very small quantities of combustible in the region where the limit-of-flammability curve approached the stoichiometric curve. Because of this, it was difficult to determine the xylene concentration very accurately in this region without drastically changing the vapor-flow rate of the system; accordingly, lower limit mixtures were not tested for this system.

**Hydrogen Peroxide–Formic Acid–Xylene–Water System.** The data presented in Figures 2 to 4 can be combined in three-dimensional form (Figure 5). Although no special significance should be attached to this particular composite figure, it can be formed from the data obtained in such a study. Furthermore, this type of figure can be used to outline readily the flammable regions of such four-component systems and thus show the effect of the addition of each component on the flammability of the composite system.

## CONCLUSIONS

The system hydrogen peroxide–*o*-xylene–formic acid–water with less than moderate water vapor concentration has no lower limits of flammability. Hydrogen peroxide as oxidant in place of decomposed hydrogen peroxide produces a rather substantial increase in the upper limit of flammability of *o*-xylene and of mixtures of *o*-xylene and formic acid containing an excess of *o*-xylene. Upper limit mixtures of these combustibles in hydrogen peroxide deviated markedly from the values predicted by LaChatelier's rule.

Conventional flow-type apparatus can be used if precautions are taken to passivate the apparatus. However, because of the violent decomposition reaction that may occur in a contaminated system when hydrogen peroxide is used as oxidant, special precautions should be taken to protect the personnel engaged in this type of work.

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