for ignition would be of interest, but authors are not in a position to make them at this time.

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Ignition Limits of Hydrogen Peroxide Vapor at Pressures above Atmospheric

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Explosive characteristics of hydrogen peroxide vapor at atmospheric and subatmospheric pressures, including values for the ignition limit over this pressure range and the effect of the nature of diluent gases and method of initiation on the limit have been reported (*1, 2*). In the present study, ignition limits were determined over the pressure range of 14.7 to 95 p.s.i.a. The term "ignition limit" as used here is defined as the minimum concentration of hydrogen peroxide in a vapor mixture, under specified conditions, below which powerful external ignition cannot initiate a self-propagating reaction.

Experimental

The experimental method involved the batch distillation without rectification of a hydrogen peroxide solution and passage of the slightly superheated vapor through a borosilicate glass ignition bulb. Because water has a much higher relative volatility than hydrogen peroxide, the fraction of hydrogen peroxide present in the vapor stream increases with time, and by repeated attempts to initiate ignition in the bulb at regular time intervals, coupled with analyses of the condensed vapor, it is possible to establish closely the minimum peroxide concentration at which an explosion can be caused to occur. By placing the whole apparatus inside a pressure vessel, it was possible to establish the effect of pressure on the limit.

The apparatus used is depicted schematically in Figure 1. For a run, 125 ml. of approximately 40 mole % hydrogen peroxide solution in water was placed in the borosilicate glass boiler (200-ml. bulb capacity), and the whole system was pressurized to the desired operating pressure with nitrogen. The pressure was measured with a Bourdon-type gage calibrated by means of a dead weight gage tester. Heat for the boiler was supplied through a Glass-col heating mantle.

The vapor mixture evolved on boiling was superheated about 5° to 20° C. to prevent possible condensation and was led to a borosilicate glass ignition bulb. Boiling points for various liquid compositions were estimated by extrapolation of data on total

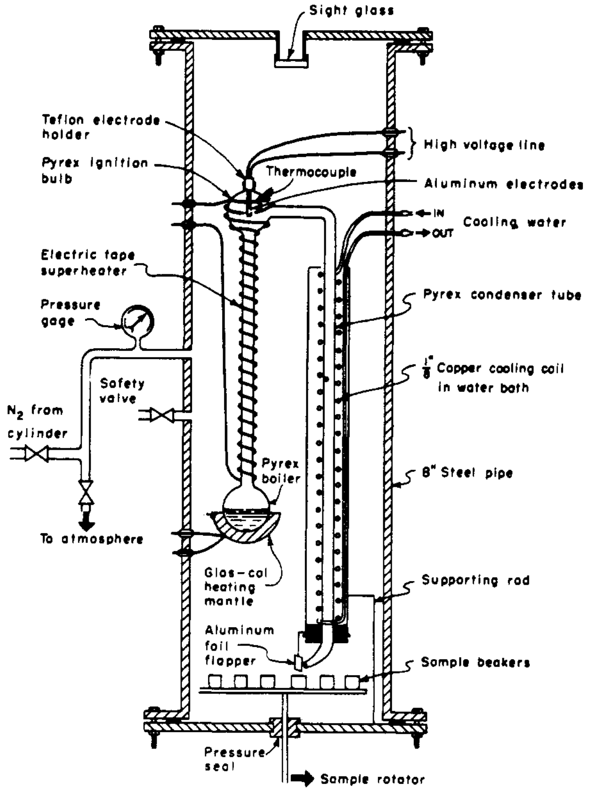

Figure 1. Apparatus for determining ignition limits

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vapor pressure and vapor composition, each *vs.* temperature (*5*). The stem of the apparatus and the ignition bulb were wound with an Electrothermal 6-foot X 2-inch heating tape and further insulated with asbestos tape. The temperature in the ignition bulb was measured with an iron-constantan thermocouple inserted into a small well in the bulb. Ignition was achieved by inducing a high voltage discharge from a Tesla coil between electrodes of aluminum wire 0.032-inch in diameter.

From the ignition bulb the vapor passed to a total condenser consisting of a borosilicate glass tube 2 cm. in diameter, immersed in a cold water jacket and surrounded by a coil of 1/8-inch copper tubing through which cooling water flowed. The condensate was collected consecutively in a series of 10-ml. borosilicate glass beakers mounted on a rotary platform below the condenser.

Much care is required to reduce the heterogeneous decomposition of hydrogen peroxide vapor to an acceptable minimum, particularly at the higher pressures studied. The only materials that came in contact with the hydrogen peroxide vapor were borosilicate glass and the aluminum wire and Teflon used in the sparking electrode assembly. Scrupulous cleanliness is of paramount importance. The borosilicate glass equipment was washed thoroughly, soaked for several hours in a hot caustic soda-Versene solution, and then rinsed thoroughly. It was then soaked overnight in a hot 1 to 3 mixture of concentrated nitric and sulfuric acids and rinsed thoroughly with conductivity water. The equipment was then wrapped in clean aluminum foil and annealed by holding it at 490° to 500° C. for at least 2 hours, followed by slow cooling. Relatively high temperatures and long annealing times reduce the rate of heterogeneous decomposition on glass considerably. Other information concerning the effect of surface treatments of glass on its activity towards hydrogen peroxide has been published (*4*).

For most of the runs a boiling rate of about 3.5 ml. per minute was used; each condensate sample consisted of the distillate resulting from 2 minutes of operation. When close to the expected ignition range, sparking was repeated once every 20 seconds until ignition occurred, this time interval having been chosen so as to allow the vapor in the ignition bulb to be purged completely between subsequent sparkings. Blank runs established that the amount of decomposition caused by the sparking itself was negligible.

After ignition, between 30 seconds and 1 minute was allowed to elapse to purge the decomposition products before condensate collection was continued. From a plot of hydrogen peroxide concentration versus time the vapor composition could be interpolated for each attempted ignition. In some runs, particularly at higher pressures, the flame produced by the ignition propagated back to the boiler and established itself on the liquid there. In such cases the ignition limit was determined by extrapolation from the last sample composition.

In the region of the ignition limit, the question as to whether or not a propagating reaction has been achieved in any given attempt is slightly arbitrary since various criteria can be used to define the limit. Here two independent criteria were used:

Upon ignition, the temperature in the ignition bulb jumps sharply and extensively. In the span of 20 seconds between sparkings, which corresponds to an average increase in concentration of the hydrogen peroxide in the vapor of about 0.4 mole %, the reading from the thermocouple upon sparking would usually change from no temperature increase (or at most a 1° C. jump) to a sudden jump whose peak was usually so high and achieved so fast as not to be readily determinable with the potentiometer used. For the purpose of this work, ignition was considered to have taken place if the temperature as measured with the thermocouple inserted in the small well blown in the side of the bulb, jumped suddenly upon sparking at least 10° C. A few seconds after ignition the temperature would normally return again to a value close to the temperature before the sparking.

Ignition is also accompanied by a sudden volume increase of the ignited gas. To detect it, the outlet of the condenser was curtained by a small sheet of thin aluminum foil hinged along its upper edge. By keeping the hinge diameter very small and the weight of the foil low, the "flapper" could be made very sensitive to a sudden volume change within the apparatus. A distinct lifting of the flapper was an indication that ignition had occurred. At times a white fog was also expelled from the condenser.

In general, the two methods of detecting ignition agreed. Because the temperature jump was more definite, and easier to observe and measure, it was considered the more reliable indication and ignition limit data quoted here are based on this criterion. In earlier work (*2*) the criterion for explosion was the sudden expulsion of fog from the condenser. Because of the construction of the apparatus here, it was difficult to make such observations; hence the earlier criterion could not be used.

In early studies at higher pressures with the initiating system used here, on several occasions visible sparks failed to ignite a mixture that was clearly within the explosive limit. In many cases the vapor shortly thereafter ignited spontaneously with considerable vigor, the flame traveling back and continuing to burn in the boiler. Therefore, a Ford coil first used, which would give a spark of maximum length of about 1 cm. in air at 1 atm. pressure was replaced by a Tesla coil capable of about a 2.5-cm. spark in air. A series of tests with this system at 1 atm. pressure with several different spark gaps showed that reliable ignition was obtained with a 6-mm. gap; a 1-mm. gap seemed to increase slightly the minimum H_2O_2 concentration at which ignition occurred, while a gap as large as 11 mm. produced a thin spark which would not initiate explosions unless the composition was well within the explosive range, the explosions in these cases being extremely violent.

The spark ignition is further complicated by the fact that as the pressure is increased the breakdown voltage for a gap of fixed size needs to be increased. At the same time, the spark gap may not be decreased below the quenching distance. For the current work it was assumed as an approximation that the dielectric constant of the vapor increased directly as the pressure and that the quenching distance decreases directly with pressure. Consequently, in an attempt to eliminate spark gap distance and voltage from affecting the observed limit, the

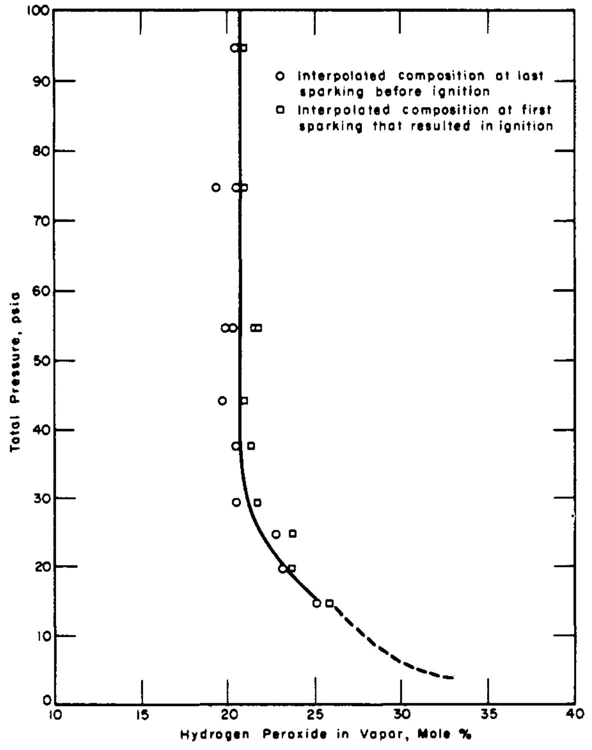

Figure 2. Ignition limit of hydrogen peroxide at pressures above atmospheric

Data for results below 1 atm. taken from (3) electrode gap used was varied inversely with the pressure, becoming, for example, 1.0 mm. at 6-atm. pressure. In earlier work at 1-atm. pressure, the ignition limit was independent of whether initiation was achieved by a hot wire or by a 5 to 6-mm. spark gap supplied by a Ford spark coil.

RESULTS

The ignition limits obtained are plotted in Figure 2. Each run is designated by two points, showing the interpolated or extrapolated vapor compositions at, respectively, the last sparking before ignition and the first sparking that caused ignition. Between 2- and 6-atm. pressure, the ignition limit was found to be constant at 20.7 mole % hydrogen peroxide in the vapor. This value is probably not significantly changed by moderate variations in the ratio of water to oxygen in the vapor (*1*). At atmospheric pressure, the limit was found here to be 25.6 mole %, slightly lower than the previously established value of 26.0 mole % (*2*). This difference may well reflect the fact that different criteria were used in the two studies for determining whether or not ignition had occurred, and that used here is probably slightly more sensitive.

By this technique, the vapor temperature increased slightly with increasing pressure, being about 155° C. at 30 p.s.i.a. and 192° C. at 95 p.s.i.a. Although, in general, increased temperature might be expected to lower the ignition limit, variation of vapor temperature here by 20° C. or so at a fixed pressure gave no noticeable effect on the limit, within the accuracy of determining it by this method.

No theoretical explanation is at present available for the apparent constancy of the limit in the range of 2- to 6-atm. pressure. For mixtures of various combustibles such as methane, carbon monoxide, and hydrogen with air, the ignition limit sometimes decreases and sometimes increases with pressure. In some cases the change with pressure is insignificant over a wide pressure range.

In runs in which a flame did not propagate back to the boiler, an over-all hydrogen peroxide material balance was made. The loss of hydrogen peroxide by decomposition amounted to less than 1 to 2% for all runs at pressures up to about 45 p.s.i., but increased to a maximum of 7% at higher pressures. It is believed that this decomposition occurred primarily in the liquid phase on boiling. This result was indicated by the amount of decomposition obtained in separate tests at various pressures in which H_2O_2 was boiled in a glass bulb surmounted directly by a reflux condenser, the design being such as to minimize the glass area exposed to hot vapors. The increase in decomposition rate with pressure thus represents the usual effect of increased temperature on reaction rate. Decomposition occurring before the ignition bulb causes the true composition in the bulb to be slightly less than the reported composition because of dilution from the oxygen formed in the decomposition. The correction may amount to a few tenths of a percentage point at about 55 p.s.i.a., but is probably less than one percentage point even in the runs in which the greatest decomposition occurred. However, this means that the ignition limit may in fact decrease very slightly with increased pressure.

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Dynamic Loading of Rupture Disks with Detonation Waves

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During the last century large groups of engineers and scientists have investigated the properties of materials under stress. The properties of most materials have been defined completely when the materials are subjected to a static stress. However, comparatively little is known about the behavior of materials subjected to dynamic loads.

This investigation dealt exclusively with dynamic loading of rupture disks. Its objective was to establish the relation between the dynamic bursting pressure and the static bursting pressure.

Several investigators have considered this problem. Campbell, Littler, and Whitworth (*1*), in one of the earliest investigations of gaseous detonations, determined the detonation pressure developed by knallgas ($2H_2 - O_2$) using rupture disks. Their work seemed to indicate that the static and dynamic bursting pressure were approximately equal.

Gerstein, Carlson, and Hill (*2*) performed an interesting series of experiments testing rupture disks in a long detonation tube. The disks tested ruptured at dynamic pressures somewhat lower than the static pressure rating. As large thin disks were used, Gerstein postulated that the disks may have failed partially from vibrational fatigue.

Stewart and Fox (*4*) performed bursting tests on aluminum foil to demonstrate its usefulness in pilot plant development:

Initial pressure atmospheric, pressure applied gradually
Initial pressure atmospheric, pressure applied suddenly
Initial vacuum, pressure applied gradually
Initial vacuum, pressure applied suddenly

He concluded that the ultimate yield stress of the aluminum foil was essentially the same for the different types of loading.

In this investigation belled rupture disks, 1 inch in diameter, were dynamically loaded by detonating a dry stoichiometric mixture of hydrogen and oxygen. The disks were attached to the end of the detonation tube perpendicular to the path of the detonation wave. The materials tested were stainless steel Type 304, nickel, phosphor bronze, and cold-rolled steel.

The ratio of dynamic bursting pressure to static bursting

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