This is an informal report intended primarily for internal or limited external distribution. (The opinions and conclusions stated are those of the author and may or may not be those of the laboratory.) This report is not to be given additional external distribution or cited in external documents without the consent of the author or LLL Technical Information Department.

LAWRENCE LIVERMORE LABORATORY
University of California/Livermore, California

LONG TERM COMPATIBILITY BEHAVIOR OF BRIDGEWIRES IN DETONATORS

C. Colmenares, C. F. Bender, and T. McCreary

May 19, 1975

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.


DISTRIBUTION OF THIS DOCUMENT UNLIMITED
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
LONG TERM COMPATIBILITY BEHAVIOR OF BRIDGEWIRES IN DETONATORS

C. Colmenares, C. F. Bender, and T. McCreary
Lawrence Livermore Laboratory
Livermore, California

(Presented at the 15th meeting of JOWOG-12, June 18-21, 1974, AWRE, Aldermaston, England)

Gold bridgewires in detonators have developed infinite resistance (open circuit) after maintaining them at 165°F for two years. The question has arisen as to whether this will happen during the stockpile life of a given system. We will discuss in this presentation the results of recent experimental and theoretical studies. In particular, we will cover the following areas:

A) The chemical reaction mechanism causing the observed failure and kinetic modeling studies.
B) "Super" detonator experiments.
C) Experiment with large number of detonators at site 300.
D) Discussion of the possible reasons why detonator failures have not been observed in stockpile.

A. Reaction Kinetics and Modeling of Mechanism.

X-ray diffraction analyses of the corrosion products formed on the gold bridgewires held at elevated temperatures (165° to 212°F) revealed the presence of AuCN. Gold reacts with the CN⁻ ion in the presence of oxygen according to the following
Reaction (1) implies that some moisture is necessary for the reaction to take place. This is conceivable in the case of a detonator, because the explosive and plastic components can both supply small amounts of water vapor, particularly as the temperature of the unit is raised to 165°F. Furthermore, detonators do not have gas tight seals and consequently oxygen can easily diffuse into the bridgewire area.

Studies were initiated at LLL and Mound Laboratories in an effort to understand the phenomena involved. Thermally accelerated studies were given particular emphasis. The results of this type of study conducted at Mound showed that corrosion did not occur below 110°F for four months; however, incipient corrosion was observed at 130°F beginning at four months. Severe corrosion and failures were observed between 165° and 212°F as shown in Figure 1.

The gold bridgewire corrosion was followed as a function of time and temperature by resistance measurements. Typical data is presented in Table 1.

**TABLE 1. Detonator Bridgewire Resistance Changes with Time**

<table>
<thead>
<tr>
<th>Time, months</th>
<th>Temperature, °F</th>
<th>ΔR, ohms</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>212</td>
<td>0.006</td>
</tr>
<tr>
<td>4</td>
<td>212</td>
<td>0.085</td>
</tr>
<tr>
<td>9</td>
<td>212</td>
<td>0.434</td>
</tr>
<tr>
<td>13</td>
<td>212</td>
<td>∞</td>
</tr>
<tr>
<td>4</td>
<td>190</td>
<td>0.006</td>
</tr>
<tr>
<td>9</td>
<td>190</td>
<td>0.087</td>
</tr>
<tr>
<td>13</td>
<td>190</td>
<td>0.180</td>
</tr>
<tr>
<td>25</td>
<td>stockpile</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Figure 1. Corrosion of gold bridgewires as a function of temperature.
Assuming that the corrosion of the gold wire is caused by cyanide ion, the rate of reaction is given by

$$\frac{d[\text{Au}]}{dt} \propto A_s [\text{CN}^-]$$  \hspace{1cm} (2)

where $A_s$ is the surface area of gold exposed. For a wire of radius $r$ and length $\ell$, the area is,

$$A_s = 2\pi r \ell$$  \hspace{1cm} (3)

The mass of the gold wire may be expressed in terms of its volume ($V = 2\pi r^2 \ell$) and its density, $\rho$,

$$[\text{Au}] = \rho \pi r^2 \ell$$  \hspace{1cm} (4)

Assuming uniform corrosion of the wire along its surface (change in radius only) we may write equation (2) as follows:

$$\frac{d[\text{Au}]}{dt} = 2\pi r \ell [\text{CN}^-]$$  \hspace{1cm} (5)

$$\frac{d[\rho \pi r^2 \ell]}{dt} = 2\pi r \ell [\text{CN}^-]$$  \hspace{1cm} (5a)

Therefore,

$$\frac{2\pi r \ell}{dt} \frac{dr}{dt} = 2\pi r \ell [\text{CN}^-]$$  \hspace{1cm} (5b)

$$\frac{dr}{dt} = [\text{CN}^-]$$  \hspace{1cm} (6)

Assuming that the concentration of cyanide with time changes according to the expression

$$[\text{CN}^-] \propto t^x$$  \hspace{1cm} (7)
where \( x \) may be a fraction or an integer.

Then,
\[
\frac{dr}{dt} \propto t^x \tag{8}
\]

Between \( t = 0 \) and \( t \), and for an initial wire radius of \( r_0 \),
\[
(r - r_0) \propto t^{x+1} \tag{9}
\]

For a wire with cross sectional area, \( A_c \), and length, \( L \), its resistance is given by,
\[
R = \rho L / A_c \tag{10}
\]
or
\[
R \propto 1/r^2 \tag{11}
\]
and
\[
r^2 \propto 1/R \tag{11a}
\]

Integrating equation (9) and the change in radius by a change in resistance, we obtain the following expression,
\[
(r - r_0)^2 \propto t^{2(x+1)} \tag{12}
\]
\[
\frac{1}{R} + \frac{1}{R_0} - \frac{2}{\sqrt{RR_0}} \propto t^{2(x+1)} \tag{13}
\]

Since we are dealing with a chemical reaction, its temperature dependence is exponential and may be introduced in equation (13),
\[
\frac{1}{R} + \frac{1}{R_0} - \frac{2}{\sqrt{RR_0}} = At^{2(x+1)} \exp(-B/T) \tag{14}
\]
where \( A \) is a constant and \( B \) represents the activation energy.
The data shown in Table 1 has been used to determine A, x, and B. The value of x has been found to be about 1, hence, the production of CN^- obeys zeroth order kinetics. The value of A and B were $6.84 \times 10^{30}$ (ln A = 71) and $2.8 \times 10^{4}$ respectively. Since $B = \frac{E}{R_g}$ ($R_g$ is the ideal gas constant) the activation energy for the process is 55.4 kcal/mol. Figure 2 demonstrates the change of resistance with time according to equation (14). From the latter we have calculated that the 2 year exposure of detonators at 165°F was equivalent to an age of 18 years at 105°F.

B. "Super Detonator" Experiments.

An attempt was made to pinpoint the agent or agents causing the formation of CN^- Four large mock-detonators were built with gold wires about 1 cm long and about 0.3 grams of PETN. Similar units were made with the inclusion plastic wafers of the formulation used to make detonator heads (blue formulation). These units were maintained at temperatures of 80° and 100°C for six months and then raised to 100° and 120°C for another four months. Resistances of gold wires were measured by a pulsed-current technique at one hour intervals as well as the oven temperature. The experiment was carried out under computer control and automatic data acquisition for the length of the experiment. No change was observed in any of the four units tested.

C. Site 300 Experiments.

Since the "super detonator" experiment did not produce positive results, a similar computer controlled experiment using WR detonators has been initiated. Five detonators each of four different types will be tested at temperatures of 40, 60, 80 and 100°C, and their resistance automatically measured at least once a day. Both gold and platinum-gold bridged detonators will be tested. The test will take...
DETONATOR BRIDGE WIRES CHANGE WITH TIME

- DISOLVE IN SOLDER
- CORRODE

\[ \frac{1}{\Omega} + \frac{1}{\Omega_0} - \frac{2}{\sqrt{\Omega_0 \Omega}} = A t^4 e^{-B/T} \]
from one to two years to complete. Units that fail will be removed from the ovens for examination.

D. Possible Causes for the Absence of Failure in Stockpile.

Since oxygen is necessary to produce corrosion of gold bridgewires, we have postulated that this gas is not as available within the real detonator environment as it is in laboratory thermal aging experiments carried out in air. One of the reasons may be that as the oxygen is consumed inside the detonator, nitrogen eventually fills any void volume and oxygen can only be replenished near the gold wire by diffusion through a stagnant layer of nitrogen, which is a very slow process.

To test this theory, several detonators were thermally aged in a nitrogen atmosphere at several temperatures. No change in resistance was observed for several months in these units, thus confirming our postulate.