STABILITY OF DELAY COMPOSITIONS

James E. Rose
Naval Ordnance Station
Indian Head, Maryland

ABSTRACT

The degradation and stability of delay compositions are explored under various temperature and humidity environments. Delay compositions investigated include D-16 (manganese/lead chromate/barium chromate) and T-10 (boron/barium chromate) delays which are components of cartridges for cartridge actuated devices (CADs) used in automated aircrew escape systems, and tungsten-viton delay, a relatively new composition which has found application in the igniter for the 5"/54 gun fired rocket assisted projectile (RAP). Comparison of trends indicates the superiority of T-10 and tungsten-viton delay compositions over D-16 delay.

1. INTRODUCTION

This study was undertaken with the following objectives:

(1) To extend the service life of aircrew automated escape system (AAES) cartridges from the present 18 months to 36 months or better.

(2) To determine the mechanism by which AAES cartridges degrade. Early in the program possible modes of degradation were identified. They are propellant degradation, pyrotechnic ignition composition degradation, pyrotechnic delay composition degradation, and sealant failure. Sealant failure was ruled out as a result of leak tests on fleet return surveillance cartridges, which showed excellent seal integrity after five years elapsed time.

Accelerated ageing at 200°F of the ignition composition indicated no change in cal/gm heat output over 20 weeks storage, ruling out ignition composition degradation. Propellant degradation observed in fleet return surveillance units is small as indicated in changes in output pressures, and does not contribute to system delay time, the parameter in question. This left us with delay composition

degradation to investigate as the mechanism of AAES cartridge degradation.

At present, D-16 delay consisting of manganese/lead chromate/barium chromate is the pyrotechnic delay composition used in Navy AAES cartridges. Consequently, it was decided to investigate the degradation mechanism of this and other compositions. Results of this investigation were to be used as the basis for a decision on whether to improve the existing D-16 composition or substitute other delay compositions so as to extend system service life.

2.   BACKGROUND

2.1 MANGANESE DELAY

D-16 or manganese delay compositions are widely used in aircrew automated escape cartridges with rated service lives of 18 months and some Navy Missile Systems. However, little is known of the mechanism by which these compositions degrade, becoming slower and slower as they age. They consist of varying proportions of manganese, lead chromate, and barium chromate.

It is recognized that the manganese metal powder reacts preferentially with the lead chromate component in a reaction which proceeds very slowly at ambient temperatures. Zimmer-Galler reports that the oxidation potential of manganese is such that complete reduction of the lead salt to metallic lead is achieved during burning.[1] Lopatin[2] reports that from DTA and ignition temperature, the lead chromate-manganese reaction is responsible for initiation of reaction propagation. Lopatin also reports that "TGA indicates that Mn_3O_4 is the stable manganese oxide resulting from air oxidation. Heats of reaction indicate that MnO is is the reaction product with lead chromate in the absence of air. X-ray diffraction studies of residues could not identify any significant species."

Both Zimmer-Galler and Lopatin support the hypothesis that manganese tends to react preferentially with lead chromate, but neither makes mention of a slow, long-term redox reaction of manganese and lead chromate at room temperatures.

Murphy[3] has investigated manganese delay composition and reported on the effect of metal treatment and particle size on

surveillance storage characteristics. A manganese metal of 14.3 microns weight average diameter (WAD) was better than a 27.5 micron WAD manganese with respect to performance at -65°F and reliability of slow burning powders. The 27.5 micron manganese was more susceptible to combustion failure after wet surveillance, and had higher burn time variability.

Murphy noted that "Untreated manganese is far more susceptible to deterioration under wet surveillance than treated manganese. Treated and untreated manganese are not affected significantly by dry surveillance".

Manganese delays burning 10 seconds/inch or faster could resist four weeks of wet surveillance at 71°C (160°F) and 95 percent relative humidity, with 14.5 micron manganese. The wet surveillance resistance of delays burning over 10 seconds/inch varied directly with fuel/ oxidant ratio. A 16.5 seconds/inch delay failed two weeks wet surveillance whether the manganese was 14.5 or 27.6 microns.

Comyn also investigated manganese delay properties, but his more recent findings[4] contradict his earlier work.[5] Comyn's earlier work reported that after 37 weeks' exposure to an accelerated storage cycle, a D-16 delay containing pretreated manganese appeared to have superior storage qualities. His later work indicated that pretreatment of manganese powder would not prevent deterioration of delays in wet storage. Some other significant findings of Comyn's later work are that:

(1) The stability of the delay mixture varies inversely with manganese crystallite particle size. Smaller sizes give better stability.

(2) A preliminary reaction may be necessary to stabilize a manganese delay mix. Apparently stable batches have already undergone this reaction before they are tested.

(3) Slow burning mixtures containing a relatively small amount of lead chromate had much poorer storage qualities than fast burning compositions with large proportions of lead chromate.

(4) Pretreatment of the manganese metal powder is not necessary for delay mixes that will be kept dry.

Comyn and Murphy are essentially in agreement with respect to the

adverse effect of large manganese particle size on delay storage stability and the superior storage stability of fast burning delays. It is the effectiveness of the treatment of the manganese against wet storage deterioration that is in dispute between these authors.

The effectiveness of manganese treatment against humid deterioration can be explained by the degradation mechanism of the delay mix. From Murphy's and Comyn's observation that mixtures kept dry did not deteriorate, we can deduce that water plays a role in delay degradation. Furthermore, on comparing average growth rates for compressed and loose delay powders, we note that compressed powders age faster than loose powders. We therefore deduce that the degradation mechanism involves a reaction between the delay ingredients as opposed to atmospheric oxidation of the delay mix. Compression of the delay mix increased interparticle contact, thereby promoting ingredient reactions. The most likely ingredient reaction is between manganese and lead chromate, as indicated by Lopatin[2] and Zimmer-Galler[1]. Pretreatment, which involves treatment of the manganese metal with dichromate solution, is believed to protect the metal surface against further reaction, possibly by formation of manganese chromate compounds on the surface. Apparently these compounds are sufficiently adherent to protect the manganese particles from further reaction. When the manganese is incorporated into the delay mix by mulling, it can be argued that any protective coating on the manganese particles is worn off by the grinding action of the muller, or nullified when the manganese particles are broken up under the muller wheel's crushing action. However, it is possible that a stabilizing reaction between the freshly exposed surface of the manganese metal and the lead chromate takes place within a few days after mulling. Comyn[4] supports this hypothesis in observing that delay mixtures increased in burn time for about three days of wet storage and then became stable. This indicates that the stabilizing reaction proceeded in the presence of water.

It is noteworthy that both the

protective stabilizing reaction and the degradation reaction proceed in the presence of water and lead chromate. This may explain why Comyn was unable to duplicate his earlier work with manganese delays. The same conditions can lead to either stability or degradation of the delay mix.

Factors determining successful functioning of the delay mixture include manganese particle size and percentage level of manganese metal in the delay mixture. Both Murphy and Comyn note that faster burning manganese delays tend to have better storage qualities and resist the effects of humid surveillance to a greater degree than slower burning delays. The slower burning delays have a smaller percentage level manganese metal and a smaller heat output than fast delays. Delays burning slower than 14 seconds/inch may not ignite at low temperatures, which indicates the marginal heat output of these slow delays. Murphy[3] noted that a 16.5 seconds/inch delay did not pass two weeks of wet surveillance whether the manganese particle size was 14.5 or 17.5 microns. It is possible that the smaller manganese concentration and smaller total surface area of manganese particles in a slow burning delay may explain its poorer resistance

to humidity. On the other hand, the larger total surface area of manganese in fast burning delays may offer a greater resistance to deterioration.

Another possible explanation is that the marginal heat output of a slow delay is more easily affected by moisture than would be the higher heat output of a faster burning delay. The moisture could act to lower heat output either by absorbing heat output equivalent to heat of vaporization or by promoting degradation of some of the manganese fuel. In either case, heat output could be lowered below that required for sustained flame propagation in the delay column, so that the delay composition so affected would not burn.

Calculations of theoretical heat output indicate that there is about a 100 percent difference between the fastest and slowest delays made to OD9360.[6] A 45/55 $Mn/PbCrO_4$ mix had a calculated output of 256 calories/gram. A slower delay mix 29.1/25.9/45 $Mn/PbCrO_4/$

$BaCrO_4$ had a calculated output of 168 calories/gram. As previously hypothesized, the marginal heat output of the slower delay mix could be more easily affected by delay degradation. If both delays experienced equal heat losses due to degradation or other causes, the faster burning delay would not experience as great a percentage heat loss as would the slower delay. Furthermore, the faster burning delay would have less likelihood of having its heat output lowered below that heat output necessary to sustain burning.

Recent work[7] on the high temperature ageing characteristics of manganese delay indicates an oscillatory behavior. Delay time apparently goes up, then down, and then up again for some Mk 4 Cartridges conditioned at $200°F$. In vented units, delay time went up at first as would be expected, then experienced a sharp downturn contrary to expected ageing. In these short-term ca-10 week tests, clear trends in shifts of delay burntime with age do not appear to be established. It appears that an initial "bump" is experienced, after which a gradual rise in delay burntime occurs. In Figure 1, only the initial bump is visible. Conclusions drawn from Figure 1 are that:

(1) Initial upward degradation is practically independent of temperature.

(2) The secondary downward drift of delay time is somewhat accelerated by temperature. In Figure 2 the initial bump is visible in the $70°F$ firings, while the $200°F$ and $-65°F$ show a rise in burntime without the initial bump. On the other hand, the effects of ageing appear more clearly in a Crane report on the ageing of Mk 5 Delay Cartridges over a period of four years.[8] Over this longer time period, a trend towards increasing delay time is clearly evident. Figure 3 shows trends for two cartridge lots. Average growth rate is about .06 second/year for all tests, except for the $-65°F$ test of Lot 3-IHM-0470, where it comes to about .08 second/year. On both $70°F$ tests, a decrease in growth rate is observed with the passage of time. However, in the other tests, an increase of growth rate with time is observed. Thus, while a clearly increasing trend in delay time is observed, it cannot be established that this trend approaches an asymptotic value as might be expected.

In summary, with the present state-of-the-art:

(1) The effectivenss of pretreatment of manganese metal with dichromate and stearate is in dispute.

(2) Manganese is recognized to preferentially react with the lead chromate component.

(3) Smaller particle size manganese tends to give delays with greater storage stability.

(4) Trends in ageing of manganese delay are not established clearly with short-time, high temperature accelerated ageing tests.

(5) Delay times clearly increase in long-term, room temperature surveillance of manganese delay in Mk 5 hardware.

2.2 T-10 DELAY

T-10 delay composition is widely used in Army cartridges. It is composed of boron and barium chromate. Burning rate is controlled by the percentage of boron. Burn time can be adjusted from three and one-half to as low as 0.4 seconds/inch in an obturated cartridge by varying percent boron from three and one-half to 15 percent. Mechanical strength of pressed composition is low in situations where the composition is not mechanically supported.
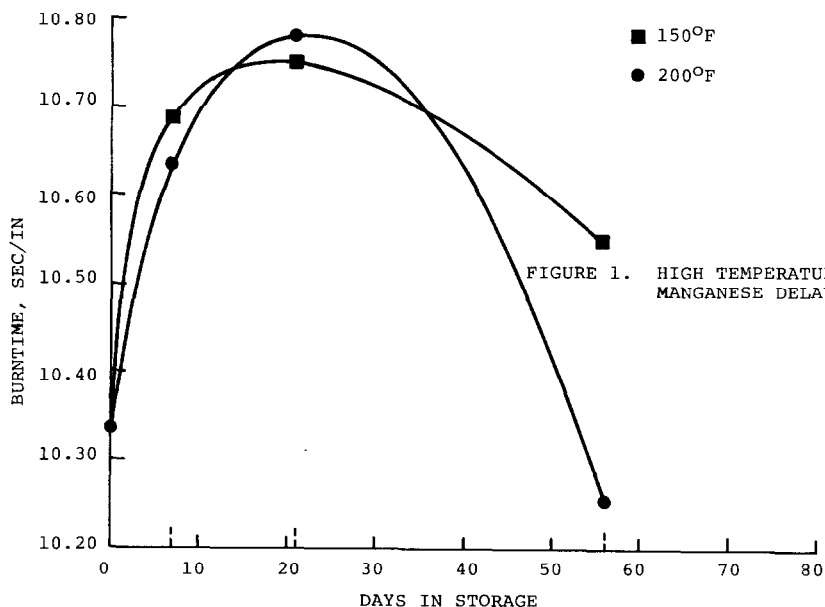

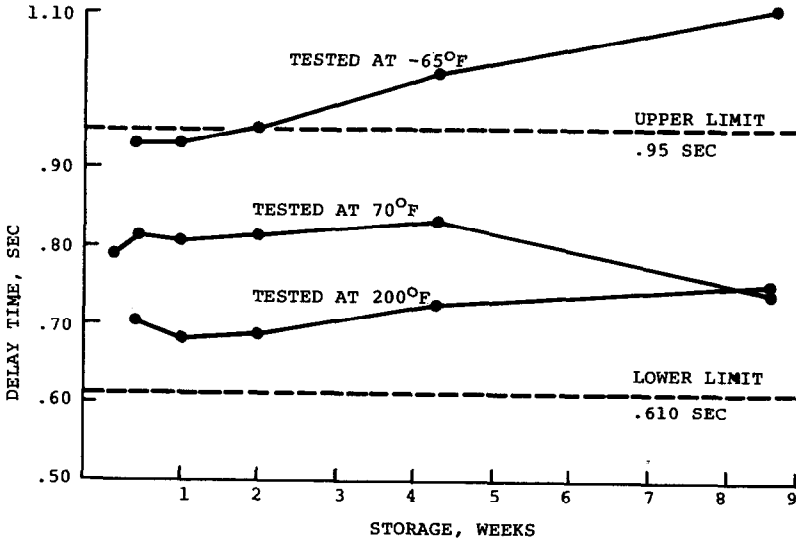FIGURE 1. HIGH TEMPERATURE AGEING OF MANGANESE DELAY

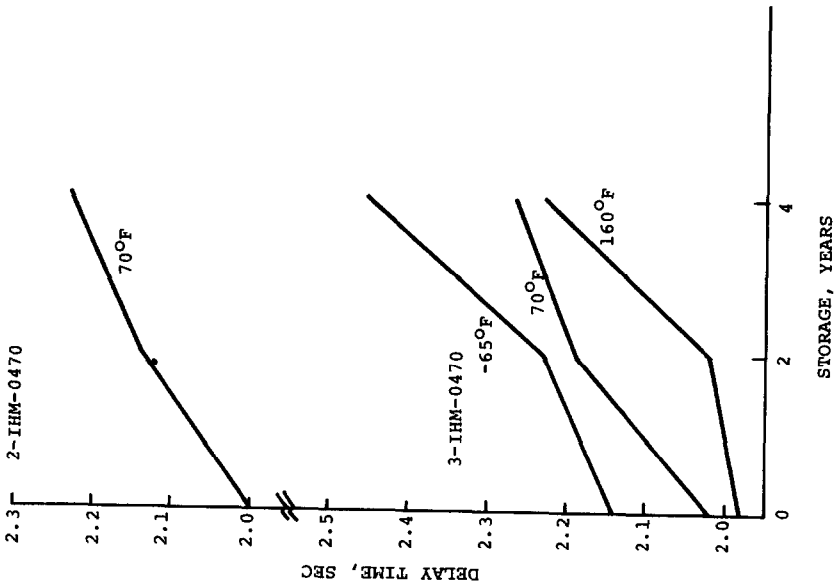FIGURE 2. EFFECT OF 200°F STORAGE ON DELAY TIME OF
MK 4 DELAY CARTRIDGES

FIGURE 3. AGEING OF MK 5 DELAY CARTRIDGES

Picatinny Arsenal has done considerable work in the development of T-10 delay powder.[9] Surveillance of T-10 delay powder loaded into M112 Photoflash Cartridge fuze housings was done at 76°C for a time period up to one year. Storage of 4.2 and 4.0 percent boron mixtures under these conditions resulted in growth of burn times from 1.17 to 1.36 seconds and 0.60 to 0.66 second, respectively. No delay failures occurred. Storage of a 90/10 mixture at 76°C over silica gel resulted in an initial five percent decrease in burn time. After one year's storage, burn time increased almost to the original burn time which was 0.62 second over 1.29 inches. No delay failures were observed.

Further work was done on the burning characteristics of T-10 delay.[10] It was found that:

(1) The curve of burn time versus percent boron is flat over a wide range, i.e., from 10 to 25 percent boron.

(2) As pressure increases, burn time decreases. For pressures up to 500 psi, burn time exponents were -0.13 and -0.043 for 95.4/4.6 and 90/10 compositions, respectively. Below one atmosphere, decreasing pressure had no effect on 81/19 and 90/10 compositions. However, with a 95.4/4.6 composition, a trend toward increased burn time was noted.

(3) Burn time decreases as temperature increases. This is in accordance with expected kinetic behavior according to Arrhenius' rate law. For 90/10 mixtures, the observed effect was 20-30 percent or 0.09 to 0.13 percent per °F over -65 to 160°F. For 95/5 mixtures, it was 20 to 40 percent or 0.09 to 0.18 percent per °F, depending on ingredients used.

(4) Sorbed vapors of water or acetone increase burn time.

Surveillance tests of units loaded with T-10 Delay indicate excellent storage qualities. Two lots of XM64 Initiators loaded with XM148 Delay Cartridges showed no significant differences in delay time over storage times of about 7 and 10 years.

Similar excellent performance was had for RIP-20-41, a lot of M12 Initiators loaded with M71 Delay Cartridges. Over 8-1/3 years, average delay time growth was 0.01 second/year.

Below is listed the results of these tests on Lot RIP-20-41.

	Accept 16 Nov 60	Surv 21 Mar 69	Aver Growth Sec/Yr
$-65^{\circ}F$	1.225 sec	1.305 sec	0.01 sec
$+70^{\circ}F$	1.025 sec	1.106 sec	0.01 sec
$+160^{\circ}F$	0.901 sec	1.002 sec	0.012 sec

Murphy[3] found that a T-10 Delay containing 4.6% boron did not change in delay time under four weeks dry surveillance at $71^{\circ}C$ ($160^{\circ}F$), 15 to 20% RH. After wet surveillance at $71^{\circ}C$ ($160^{\circ}F$) and 95% RH for four weeks, the 4.6% T-10 Delay showed a weight gain of about 20%. After drying the wet surveillance samples, delay times increased by 7% over the room temperature burn time before surveillance. No functioning failures occurred as a result of wet storage.

2.3 TUNGSTEN-VITON DELAY

This delay is a relatively new delay composition. It was developed at NWC, China Lake for the 5"/RAP, a gun projectile igniter application. It is composed of tungsten, barium chromate, potassium perchlorate, silicon dioxide, and one percent viton added. The delay composition is mixed according to a Shock-Gel technique. The viton is first dissolved in acetone and then precipitated on the composition particles by addition of the non-solvent hexane. The composition is then rinsed with additional hexane.

The obtainable burn time range is at present, unknown. However, compositions burning as long as 30 seconds/inch and as quickly as two seconds/inch have been made. Compositions burning even faster and slower may be possible.

Tests of composition per WS 12607[11] in Mk 279 Mod 2 Igniter hardware indicate superior temperature coefficients. Typically, temperature coefficients do not exceed 0.06 percent per $^{\circ}F$. In special tests, Mk 279 Igniters have functioned immediately after $-100^{\circ}F$ conditioning.

Humid surveillance of a tungsten-viton composition for five days at $160^{\circ}F$, 95% RH resulted in 7/10 duds.[12] Results are presented below:

Ambient	28.568 sec/in	18/18
$-65^{\circ}F$	31.162 sec/in	9/9
humid	30.0512 sec/in	3/10

Examination of the duds showed that they had burned part way through the delay column and then extinguished. This may have been due to moisture absorption by the

delay composition and subsequent leading out of potassium perchlorate, the water-soluble component. In such case this would have resulted in propagation failures due to lowered compositional heat content.

Long term storage stability of tungsten-viton delay per WS 12607 looks quite good. Evaluation of Mk 279 Mod 2 Igniters over a four year timespan[12] gave the following results:

Year	1973	1977
Temperature	Igniter Delay Time, seconds.	
20°F	24.23	24.075
70°F	22.94	22.919
120°F	21.72	21.744

This calculates to changes of -.64%, -.09%, and +.11% in delay time for 20, 70, and 120°F respectively.

3. DISCUSSION
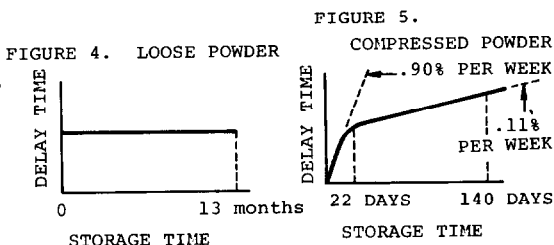
3.1 MANGANESE DELAY DEGRADATION

3.1.1 Loose and Compressed
The degradation mechanism of manganese delay is established. A comparison of delay times of compressed and loose compositions shows that delay time does not change in the loose state, but that it does change over a period of time in the compressed state. Data are presented for, magazine stored and compressed delay powder at 70°F. Results are also shown in Figures 4 and 5.

Table 1. Manganese Delay Degradation at 70°F

| Loose	Compressed at 30 ksi
3/1/76 x = 10.337	0 days x = 10.264
SD = .111	22 days x = 10.540
4/8/77 x = 10.264	
SD = .271	66 days x = 10.5734
No significant change	
	140 days x = 10.7414

FIGURE 4. LOOSE POWDER

FIGURE 5. COMPRESSED POWDER

These data indicates that after 20 days approximately in the compressed state, manganese delay degradation at 70°F levels off. The fact that such degradation did not occur in the loose state while it did in the compressed state indicates that the degradation occurs as a solid-solid reaction between the manganese metal fuel particles and the lead chromate. The fact that degradation levels off after some time indicates the reaction is diffusion controlled and involves only the surface of the manganese particles. After the delay is compressed,

manganese comes into closer contact with lead chromate particles and starts reacting. The manganese increases its protective layer of manganese oxide, which limits the diffusive reaction between lead chromate and manganese. A corresponding increase in delay time occurs, due to the buildup in the oxide layer. When the layer is built up to a sufficient thickness, diffusion is reduced so that degradation decreases and the upward trend in delay time levels off.

3.1.2 High Temperature Degradation
At $200^{\circ}F$, the proposed upper service temperature of Navy CAD's, the degradation mechanism is somewhat more complicated. Data acquired during a 20 week, $200^{\circ}F$ accelerated ageing test indicate this trend:

FIGURE 6. COMPRESSED POWDER, $200^{\circ}F$
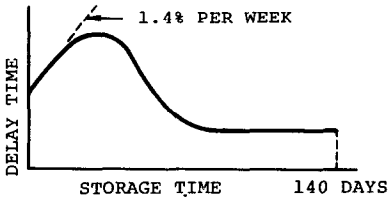
Two distinctly different influences are apparently in effect in high temperature degradation. Upward degradation, similar to that which occurred at $70^{\circ}F$, takes place over a time period up to about 30 days. After this time, a downward trend in delay time occurs. The downward shift in delay time is thought

to occur as a two-stage process. First the stearic acid coating melts off the surface of the manganese particles to expose the oxide surface. Next the freshly exposed surfaces are either (1) more reactive than stearic acid coated particles or (2) another reaction takes place to make them more reactive to cause the downward shift in delay time. This other reaction could be between the freshly exposed manganese oxide surfaces and the aluminum case walls to form free manganese metal at the interface. As the aluminum – MnOx reaction approaches equilibrium, the aluminum surface would build up a diffusion-limiting layer of aluminum oxide. Delay time should reflect this and the trend should level off, as it actually does in Figure 6.

3.1.3 Treated and Untreated Metals
To evaluate the effectiveness of surface treating or coatings, various delays were prepared and underwent high temperature accelerated ageing at $200^{\circ}F$. Nonstandard, untreated metals were used for some delays. One was simply raw, untreated manganese, while another was untreated manganese specially prepared under

mineral spirits. Still another delay powder was prepared in which all ingredients were coated with 1% viton using a Shock-Gel technique similar to that employed for tungsten-viton delay previously mentioned. Results of accelerated ageing are listed below.

Table 2. Initial Degradation at 200°F

Manganese Delay Type	Delay Increase Percent Per Week
Standard	
Dichromate/stearate	1.4
Treated	
Untreated, raw	3.5
Untreated, mineral spirit milled	5.2
Viton coated	0.5

The above results show that the untreated metals gave delay powders which aged significantly faster initially at 200°F. The viton coated delay fared best of all.

High temperature thermal analyses of the manganese metal ingredients have proved informative. Both treated and untreated metals were TGA analyzed. Treated metal gained weight, or oxidized faster than untreated metal at high temperatures up to 600°C. This indicates that treated metal is more susceptible to air oxidation once the stearic acid volatizes off. This result, contrary to the accelerated ageing tests which indicated untreated metal is more susceptible to degradation than the treated, indicates that air oxidation does not play a role in 200°F degradation and probably not at 70°F, either.

3.1.4 Humid Surveillance

As part of its qualification for acceptance, a batch of manganese delay powder is required to withstand five days at 160°F/95% RH without changing its delay time by more than 15.0%.[13] Those delays tested for high-temperature ageing were also evaluated up to eight weeks at 160°F/95% RH to see what effect high humidity had on delay burntime. The results are listed below.

Table 3. Degradation at 160°F/95% RH

Manganese Delay Type	Result
Standard treatment	Withstood eight weeks 3.7% decrease
Raw, untreated	Dudded after one week
Untreated, mineral spirit milled	Dudded after one week
Viton coated	Withstood eight weeks 96% increase

The first three results verified those results of Comyn[5] and Murphy[3] which found the dichromate/stearate treatment to offer significantly better protection against high humidity than no treatment

at all. The viton coating offered
limited protection against humidity,
but delay time increased unacceptably.
Of all treatments evaluated, the standard
treatment came out the best with respect
to protection against high humidity.

3.2 T-10 DELAY DEGRADATION

The study of the stability of T-10 delay
compositions was limited to high
temperature accelerated ageing at $200^{O}F$
for time periods up to 12 weeks. Results
are listed below.

Table 4. 95/5 T-10 Delay Ageing

Temperature	$70^{O}F$	$200^{O}F$
Time, days	Delay time, sec/in	
0	1.7367	
7	1.7137	1.6740
14	1.7644	1.7388
28	1.7348	1.7274
58	1.7684	1.7368
84	1.7469	1.7427

Table 5. 90/10 T-10 Delay Ageing

Temperature	$70^{O}F$	$200^{O}F$
Time, days	Delay time, sec/in	
0	.6710	
7	.6604	.6431
14	.6683	.6576
28	.6603	.6420
57	.6879	.6662
84	.6662	.6626

For both delays a small but
statistically significant decrease
in delay time occurred at one
week, $200^{O}F$. Thereafter delay time
increased back towards its original
value. This may have been due to
an initial moisture loss followed
by some readjustment of the
composition's chemical equilibrium.
The boron ingredient contains
90-92% boron with about 6% magnesium
impurity. Magnesium would be more
active than boron in the presence
of moisture. The reaction would
proceed according to $Mg + 2H_2O \longrightarrow$
$Mg(OH)_2 + H_2$. However, the
overall stability of the T-10 delay
compositions tested appears to be
quite good. Over the 12 week time
period, delay time did not vary
significantly from control This
indicates that in spite of the
potential adverse effect of the
magnesium impurity on delay, delay
time is little affected by $200^{O}F$
accelerated ageing. Apparently
no significant interactions occur
between delay ingredients at room
temperature or $200^{O}F$. In this
respect it is superior to manganese
delay.

3.3 TUNGSTEN-VITON DELAY DEGRADATION

Evaluation of tungsten-viton delay composition stability was conducted in the same way as the accelerated ageing tests on T-10 delay. Results are listed below.

Table 6. Fast Tungsten-Viton Delay

Temperature	$70^{\circ}F$	$200^{\circ}F$
Time, days	Delay time, sec/in	
0	6.1956	
7	5.9535	6.2454
14	6.0191	6.0165
28	6.1837	6.1108
56	5.7863	6.1461
84	6.0186	5.9556

Table 7. Slow Tungsten-Viton Delay

Temperature	$70^{\circ}F$	$200^{\circ}F$
Time, days	Delay time, sec/in	
0	30.6885	
7	29.8586	30.0405
14	29.8285	29.9690
28	29.9271	-
56	30.8279	30.6789
84	29.8721	30.5990

No significant trends were observed for either delay. These results indicate excellent storage stability for compressed tungsten-viton delays at room and elevated temperatures up to $200^{\circ}F$. With respect to storage stability tungsten-viton appears superior to manganese delay.

4. CONCLUSIONS

1. Delay degradation is the service-limiting factor is AAES Cartridges. Present service life with manganese delay is 18 months.

2. Delay degradation of manganese delay does not begin until the delay powder is compressed into a delay cartridge. Manganese delay degradation does not occur in uncompacted powder.

3. Upward trends in delay time are the result of a solid-solid reaction between manganese and lead chromate.

4. Downward trends in delay time are the result of stearic acid coating loss coupled with an electrochemical reaction of surface MnOx species with the aluminum case to produce free manganese.

5. The dichromate/stearate treatment offers excellent protection against the deleterious effects of high humidity on manganese delay.

6. Viton coating manganese delay offers excellent protection against $200^{\circ}F$ degradation, but only limited protection against high humidity.

7. T-10 and tungsten-viton delays are remarkably stable in the compressed state at room temperature and at $200^{\circ}F$ for time periods up to 12 weeks.

8. A 95/5 T-10 delay is stable in loaded units for time periods up to 10 years.

9. Tungsten-viton delays will not withstand humid storage at 160°F/95% RH for five days. Propagation failures can occur.

10. Tungsten-viton delay composition per WS 12607 is stable in loaded units for time periods up to four years.

11. T-10 delay and tungsten-viton delay composition have better storage stability than manganese delay at room temperature in surveillance of loaded CADs and ignition devices, and at elevated temperatures up to 200°F.

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6. AUTHOR'S BIOGRAPHY

J. E. Rose is a project engineer in the CAD/PAD Department of the Naval Ordnance Station, Indian Head. He has nine years experience in R&D involving mixing and formulation of pyrotechnic compositions. He received his BS in Chemical Engineering from Clarkson College of Technology. He is a member of the American Chemical Society, the American Institute of Chemical Engineers, and the American Defense Preparedness Association.