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ARMAMENT RESEARCH DEPARTMENT

DIVISION FOR WEAPONS RESEARCH.

A. R. D. REPORT No. 19/47

STUDIES IN IGNITION IN S.A.A.-PART 3. THE EFFECT OF DETERIORATION OF CAP COMPOSITION OF THE FIRING CHARACTERISTICS.

BY

H. J. YALLOP

Fort Halstead
KENT

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C.I.D. No. 0410-0000
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INTELLIGENCE REPORT

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From: The Military Attache, London, England. (AGENCY OR OFFICER / STATION) Date: 31. Oct. 1947

Source: Armament Research Dept. ARD 19/47 Eval: A-1

Area Reported On: Gt. Brit. Subject: DETERIORATION OF CAP COMPOSITIONS.

Reference: (DIRECTIVE, CORRESPONDENCE, PREVIOUS REPORT, ETC., IF APPLICABLE)

SUMMARY: ENTER CAREFUL SUMMARY OF REPORT, CONTAINING SUBSTANCE SUCCINCTLY STATED. ANSWER QUESTIONS WHERE, WHEN, WHAT, HOW, HOW MANY, AND GIVE DATE OF EVENT. IN A FINAL ONE SENTENCE PARAGRAPH GIVE SIGNIFICANCE. BEGIN TEXT ON PAGE 2.

BRITISH SUMMARY:

A study had been made of the incidence of hangfires in relation to deterioration and charge weight of S.A.A. caps filled with mercury fulminate compositions. It has been found that a simple relationship can be established between the weight of fulminate originally present in the cap, the percentage drop in fulminate content on storage and the incidence of hangfires. It is found that there is an optimum size of cap. Below this size failures will occur progressively sooner as the cap size decreases. Any increase in this size is unnecessary from the point of view of keeping quality though other considerations may call for a larger cap. A mathematical relationship connecting the three variables has been deduced. The meaning of the temperature coefficient of the decomposition of mercury fulminate in cap composition has been reconsidered and certain considerations which affect the accuracy of prediction of service life of S.A.A. are discussed."

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COMMENT: This report is of interest as it shows the deterioration of mercury fulminate used as a pressure sensitive element in primers. The U.S. uses non-corrosive and non-mercuric compounds for small arms primers. It is requested that one copy of this report and its inclosure be transmitted direct to ORDTS.

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ARMAMENT RESEARCH DEPARTMENT

DIVISION FOR WEAPONS RESEARCH

A.R.D. Report No. 19/47

STUDIES IN IGNITION IN S.A.A. - PART 3

THE EFFECT OF DETERIORATION OF CAP COMPOSITION ON THE FIRING CHARACTERISTICS

by

H.J. Yallop

References:- XC (3) 344.

Summary:-

A study has been made of the incidence of hangfires in relation to deterioration and charge weight of S.A.A. caps filled with mercury fulminate compositions.

It has been found that a simple relationship can be established between the weight of fulminate originally present in the cap, the percentage drop in fulminate content on storage and the incidence of hangfires. It is found that there is an optimum size of cap. Below this size failures will occur progressively sooner as the cap size decreases. Any increase on this size is unnecessary from the point of view of keeping quality though other considerations may call for a larger cap. A mathematical relationship connecting the three variables has been deduced.

The meaning of the temperature coefficient of the decomposition of mercury fulminate in cap compositions has been reconsidered and certain considerations which affect the accuracy of prediction of service life of S.A.A. are discussed.

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Studies in Ignition in S.A.A. - Part 3

The effect of deterioration of cap composition on the firing characteristics

Reference: XC(3) 344.

REPORT

Introduction

This report forms the third part of a general study of problems in ignition in S.A.A. The work described is a study of the decomposition of mercury fulminate type caps in relation to the firing characteristics. When ammunition is stored under adverse climatic conditions deterioration of the cap composition takes place until eventually hangfires or missfires occur. The time at which hangfires occur can normally be regarded as the end of the service life of the ammunition and this investigation concerns itself with the consideration of the onset of hangfires. In particular an attempt is made to find a method of assessing the service life of various S.A.A. caps based on an examination of underlying physico-chemical concepts.

Previous work on the Detonation of Mercury Fulminate

Mercury fulminate can be made to explode by two methods; by impact or by heating. Explosion induced by heating has been studied by a number of workers for it is connected with the study of the thermal decomposition of mercury fulminate. It has been found that fulminate will explode simply when heated but the temperatures quoted for this action are not concordant. Berthelot[1] found 187°C, Wohler and Metter[2] give 190°C. while Hoitsema[3] claim to have obtained explosion at 130°C.

A systematic examination of the problem was carried out by Laffitte and Patry[4] and was published in a series of papers in Comptes Rendus, the chief of which was in 1931. They carried out their experiments by placing small quantities of mercury fulminate on the surface of a bath of mercury maintained at a constant temperature. They found that in a certain range of temperature the fulminate did not explode instantaneously but only after an interval which decreased with rising temperature. At 277°C. they obtained explosion without delay and found delays from this temperature down to 135°C. when the delay was nearly 40 minutes. At 133°C. they were unable to obtain explosion even after heating for 2 hours and they observed that fulminate heated to 133°C. or less, decomposes slowly and is no longer capable of explosion when raised to a higher temperature. Since the previous authors do not mention delays it is possible they failed to record them and thus the divergences are explained.

The normal thermal decomposition of mercury fulminate falls into several stages. First there is an almost quiescent period, which is followed by an acceleration leading to a uniform decomposition. The crystals become brown during the acceleration, and this is interpreted as being the period in which the reaction centres are being formed. The end of the acceleration period occurs when the fulminate is between 1/5 and 2/5 decomposed. Garner[5] found that at high temperatures where thermal decomposition led to explosion, it occurred at the beginning of the acceleration period. At lower temperatures the explosion may occur when the crystal is about 1/5 decomposed, but if it is more than 1/5 decomposed it will not explode whatever the temperature. Thus if a sample is heated, two effects are at work; thermal decomposition tending to prevent explosion and heating tending to cause it. If the thermal decomposition causes the fulminate to decompose by 1/5 before the explosion temperature is reached, then no explosion will occur.

This work was carried a stage further by Vaughan, Phillips and Birks[6] while carrying out investigations into safe temperatures for fuze components in bomb disposal work. They observed the induction period before explosion and noted that under fixed conditions of thermal insulation that this period decreases exponentially with increasing temperature. They also found that at constant temperature, for equal weights of fulminate, the induction period varies with the thermal insulation of the sample while with fixed conditions of temperature and thermal insulation the induction period decreases with increasing weight of fulminate. This latter effect may be due in part to the sample controlling its own thermal insulation.

They found also that dilution with other substances not of the detonant type raises the minimum temperature of explosion.

During the induction period they observed that the fulminate sample kept the temperature of the heating bath, but that later its temperature began to rise above that of the bath. This rise finally led to explosion. It seems possible from this, that the acceleration of heating is due to the decomposition of molecules with liberation of energy leading to self heating of the sample. When self heating becomes considerable, that is when a large number of reaction centres have been formed, explosion will follow but if the temperature or conditions of thermal insulation or the partially decomposed state of the fulminate is such as to prevent enough energy liberation, then thermal decomposition will occur but no explosion.

It will be seen from this that there is a close connection between the physical state of the fulminate and its explosion characteristics. When it is used in a cap composition and is exploded by impact we should not expect the mechanism of the explosion necessarily to be the same, but it will be seen that even so a knowledge of the thermal decomposition assists in interpreting the behaviour of decomposed caps.

Methods of Investigation Used

None of the work on which this discussion is based was carried out specifically for this investigation and the results used are derived from a large number of climatic trials on S.A.A. carried out between 1942 and 1945 by the Department's Small Arms Section.

A small arms cartridge is a very complex physical and chemical mechanism which makes the study of the deterioration of one or more of its constituent parts a difficult matter since alternative and competing mechanisms play a part and give rise to great complexity. However by controlling such factors as we are able, such as the conditions of storage, it is possible to examine the process with a measure of success for although single examples may be misleading, some unity and simplicity can be found in the statistical consideration of a sufficiently large number of examples.

The climatic trials concerned were carried out under accurately controlled conditions of temperature and humidity and analytical and firing tests were carried out at regular intervals, often beyond the point at which failures started to appear in the form of hangfires. This provides therefore a considerable body of data connecting the conditions of storage, the deterioration of the cap and the incidence of hangfires. Various conditions of storage have been used but the greatest amount of data comes from Accelerated Tropical Magazine storage. This condition is an accelerated version of the Standard Tropical Magazine conditions and has been used extensively to study the relative keeping qualities of S.A.A. The figures in this report all refer to trials carried out under these conditions, and by thus limiting the data several potential variables are eliminated.

The effect of Deterioration on Firing Characteristics

(a) The effect of size of Cap on incidence of hangfires

The analysis of the data considered is summarised in the table given in the appendix. This table gives results for eight types of S.A.A. (viz. 9mm. .455", 7.92mm. .303", .5" (Vickers), .50" (Browning) 20mm. & 15mm.) and shows the average percentage drop in fulminate required to produce 0%, 1%, 2%, 5%, 10%, 15% and 20% hangfiring rounds. The figures are expressed in the appended graph as a plot of percentage drop in fulminate against the original weight of fulminate present.

It will be seen that at any given percentage of hangfires the curves are essentially similar in shape. The first part of the graph shows a clear linear relationship between fulminate loss and weight of fulminate, but then the curves change direction rapidly to become asymptotic to the x axis. The point at which the rapid change of direction occurs is about at .4 grains original weight of fulminate. We may then divide our caps into two varieties. Those with more than .4 grains of fulminate originally present and those with less.

In the case of the small caps, as the weight of fulminate in the cap increases, so also does the percentage drop required to give a given percentage of hangfires. Thus a cap containing .1 grain of fulminate will give 5% hangfires when the fulminate content has dropped by 17%, whereas a cap containing .2 grain of fulminate will give 5% hangfires when the fulminate content has dropped by 34%. Further analysis shows that where the weight of fulminate is .3 grain or less, then if the weight of fulminate is doubled it requires double the decomposition to give the same percentage of hangfires.

In the case of the larger caps this law does not hold and it will be seen that where the weight of fulminate is .6 grain or more, a given percentage of hangfires will require about the same percentage of decomposition no matter what the original amount of fulminate.

These results have some interesting consequences. It has been established by previous work that the rate of deterioration of caps is independent of their size, other things being equal. Consequently if a number of rounds are subjected to the same conditions for a given amount of time the percentage of fulminate left will in all cases be the same, independent of the actual amounts involved. Let us suppose for example, that 20% of the fulminate has decomposed. From the graph, we may read of the approximate expected incidence of hangfires. 20mm. will give no hangfires, .303" will give about 5% hangfires and 9mm. will give about 15% hangfires. This is of considerable importance since it gives a measure of the keeping qualities of the ammunition. It is clear that to obtain the best keeping qualities a cap must be used which contains at least .4 grain of fulminate. Any increase on this quantity is unnecessary from the point of view of keeping quality, though of course other considerations may call for a larger cap.

Since the initial parts of the curves are approximately linear, it has been found possible to work out a mathematical expression for the relationship. In the case therefore of caps containing .3 grain or less of mercury fulminate, we can use two equations.

$$(1) \qquad P = 25\,W\,(R + 2)$$
$$(2) \qquad \log P = \log W + \frac{R}{67} + 2.28.$$

Where P = percentage drop in fulminate content.
W = weight of fulminate originally present (in grains).
R = percentage of rounds giving hangfires.

Equation (1) applied for values of R of 5 or less and equation (2) applied where R is between 5 and 20.

Garner's experiments on mercury fulminate showed that when a crystal of mercury fulminate is more than 1/5 decomposed it will not explode when raised to a high temperature. It might therefore be expected that 20%

deterioration would mark the beginning of hangfires. An attempt was made to find the point at which hangfires commence, but only a very rough approximation could be made. However it was found that caps containing more than .4 grain fulminate do start to give hangfires somewhere in the region of 20% decomposition.

(b) The Temperature Coefficient

In Studies in Ignition in S.A.A. - Part 2. (A.R.D. Report No. 18/47.) the kinetics of the decomposition of mercury fulminate were examined and it was found that after the first 20% of decomposition the reaction obeyed first order law thereby allowing a temperature coefficient to be calculated. In view of what has been said above however, it is clear that we must reconsider the meaning of the temperature coefficient for S.A.A. caps. Clearly if only the first 20% of the decomposition is of practical value then the first order reaction is of only academic interest. Hence temperature coefficients calculated from the latter are of no use in estimating service lives, and we must consider the time taken to achieve the first 20% of decomposition. Such a "temperature coefficient" will have uncertain physical significance.

Coefficients have accordingly been evaluted both at constant absolute and at constant relative humidity. As might be expected from Farmer's work the results are of the same order of magnitude as the first order coefficient, being about 1.8 for 20°F. In the case of higher humidities a value of 3.5 was obtained but this is approaching the region of high humidities where, as we have seen in the previous report, accelerated decomposition can occur and the normal fulminate decomposition is masked by deliquescence effects.

(c) The Anomolous Results with .50" (Browning)

It will be noticed that there are an anomolous set of results on the graph which are due to the .50" (Browning) cap. This cap produces a given percentage of hangfires with less deterioration than is to be expected from the other results. However as far as can be ascertained it does commence to give hangfires at about 20% decomposition.

It is possible that this apparent anomoly arises from not taking sufficient results on which to base the figures. However, it will be noticed that although this cap does not conform to the type of behaviour characteristic of the larger caps it does behave very much like the smaller ones. If the charge had not been .55 grain but about .1 grain, then the points would fall on the curves. The reason for this is not apparent.

CONCLUSIONS

1. It has been seen that there is a clear relationship between the size of a cap and the percentage of hangfires produced on deterioration of the fulminate. As a consequence of this, if a number of rounds are subjected to the same storage conditions for a given length of time, the smaller the cap the greater the percentage of hangfires that will result. Thus in order to obtain the best keeping qualities, a cap must be used which contains at least .4 grain of fulminate; any increase on this quantity is unnecessary from the point of view of keeping quality, though other considerations may call for a larger cap.

2. It has been seen that in general, hangfires will set in not later than the time when 20% of the fulminate has decomposed and so only this period is of interest from the service point of view. Calculations of the service life of S.A.A. which is generally dependent on the life of the cap, have, since 1922 been calculated on a figure of an increase in the rate of decomposition of 1.8 times per 5°C. as found by Farmer for mercury fulminate. We have seen however, that watervapour in the air may modify this, but in general it may be taken that a rise in temperature of 5°C. will

increase the rate of deterioration by a factor of between 1.5 and 2. There are cases however, where very high humidities can cause deliquescence of some of the constituents of the cap composition leading to an enormously increased "temperature coefficient" possibly up to a value of 300. The possibility of this occurrence must always be borne in mind in predicting the life of a service round.

3. Successful prediction of the service life of S.A.A. with mercury fulminate sensitised caps depends on an exact knowledge of three things. The weight of the fulminate in the cap originally, the previous history of the sample of fulminate used for the filling and the conditions of temperature and humidity which are likely to obtain over the cap. It must be emphasised that the maximum humidity is the factor which is potentially liable to cause the greatest damage.

T A B L E

INCIDENCE OF HANGFIRES WITH DETERIORATED CAPS IN ROUNDS AFTER ACCELERATED TROPICAL MAGAZINE STORAGE

TYPE	Av. Charge Weight of Compo grs.	% $Hg(ONC)_2$	Weight of $Hg(ONC)_2$ grs.	percentage drop in $Hg(ONC)_2$ for						
				0% HF.	1% HF.	2% HF.	5% HF.	10% HF.	15% HF.	20% HF.
9 mm.	.25	26	.065	0	6	8	13	19	22	26
.455"	.40	18	.070	0	5	8	11	16	19	22
7.92 mm.	.50	28	.14	0	10	16	27	38	45	50
.303"	.60	20	.12	0	7	9	15	22	26	31
.5" (Vickers)	1.10	20	.22	0	16	22	38	57	70	77
.50" (Browning)	1.92	37.5	.72	0	27	30	37	43	47	50
20 mm.	2.34	37.5	.83	0	35	44	63	75	80	83
15 mm.	2.75	20	.55	0	35	44	63	75	80	83

ACKNOWLEDGEMENTS

Where research is carried out by a team of workers, the relative contribution of each member is difficult to assess, for much interchange of ideas takes place, making it impossible usually to give credit where it is due. The results from which the conclusions in this report are reached form such a case, and acknowledgement must therefore be made to all who worked in the Small Arms Section during the late war and particularly to those who in any way were engaged on the study of Climatic Trials.

References

1. Berthelot. Comptes Rend. 1880 p.946.

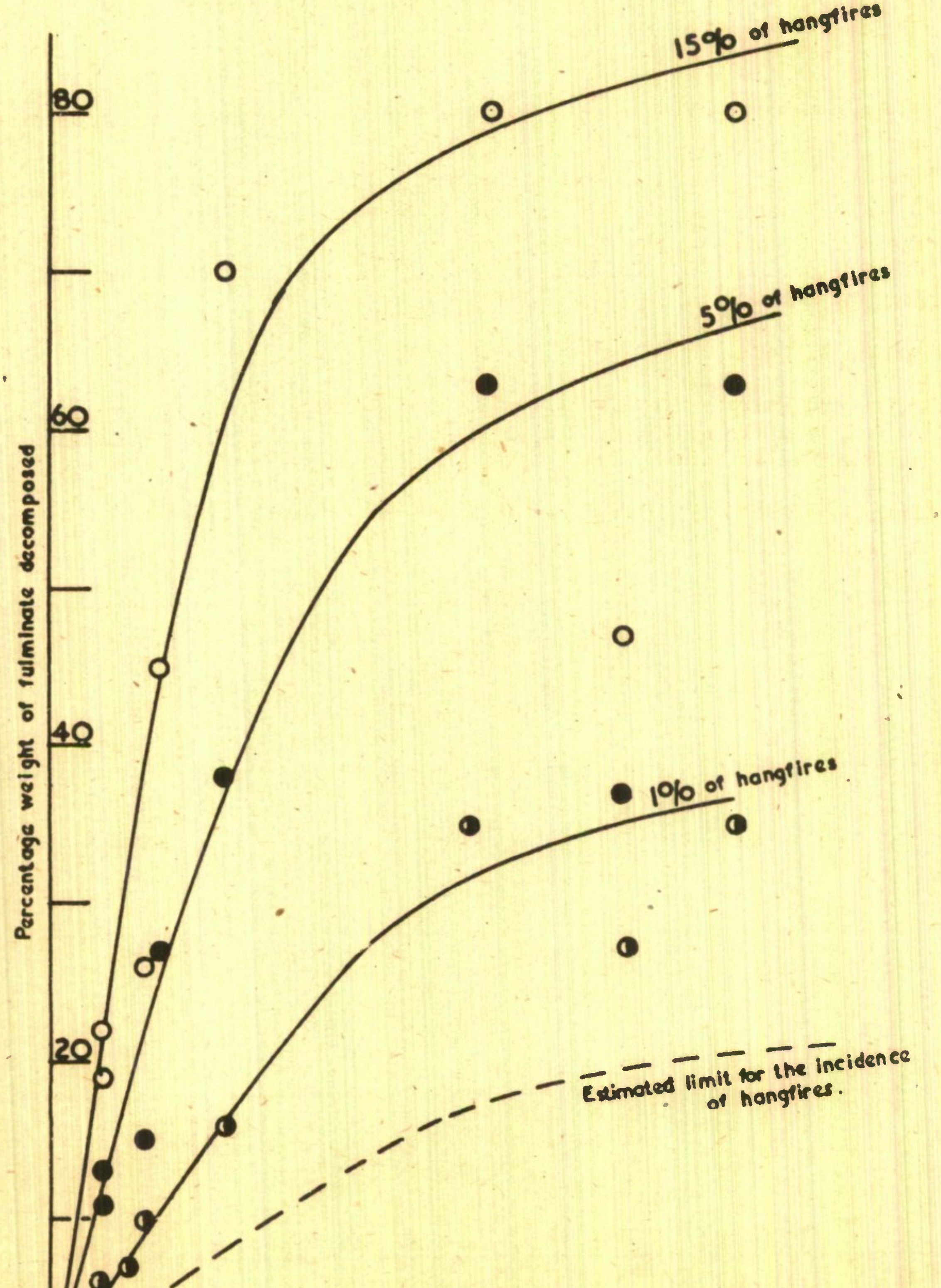
2. Wohler and Metter. Z. Schiess. Sprengst. 1907 p.204.

3. Hoitsema. Z. phys. Chem. 1896 21 p.137.

4. Laffitte and Patry. Comptes Rend. 1931 p.171 and p.948.

5. Garner and Hailes. Proc. Roy. Soc. 1933 cxxxlx p.576.

6. Phillips, Vaughan and Birks. A.R.D. Explosives Report 260/43.



15% of hangfires
5% of hangfires
1% of hangfires
Estimated limit for the incidence of hangfires.
80
60
40
20
·2
·4
·6
·8
1·0
Percentage weight of fulminate decomposed
Original weight of fulminate in the cap — grains.

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