

# Primer mixes composition and behaviour.

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In this short article I tried to assemble some information on small arms primer mixes with regard to the formation of gunshot residues (GSR), a topic not yet well known at least in the forensic domain. Indeed, after the eminent study of the late dr. Basu<sup>1</sup> written more than 30 years ago, as far as I know the problem has never been researched again and quite often inaccurate assertions are found in articles published by academic peer-reviewed journals.

The authors cited are the actual creators of the following pages: I trust they shall forgive me for any mistake in interpreting their scientific production.

*"The most remarkable thing about the history of percussion primers is the total absence of any radical changes or brilliant improvements, since their invention, such as have occurred in the field of propellant powders. Modern primers are very much the same as the first primers made by Forsyth in 1807, containing 70.6 parts of potassium chlorate, 11.8 parts of charcoal, and 17.6 parts of sulphur. Important improvements have been made in the uniformity and reliability of primers, but the priming charge still consists, as it has for the last century, of a heterogeneous mixture of granular substances, capable of taking fire when struck. The remark has frequently been made that primers are still in the "black powder" stage of development."*<sup>2</sup>

In the years following some remarkable progresses, already in development, were accomplished: if barium nitrate continued to be the main oxidizer and antimony sulphide the main fuel the usual "initiator", mercury fulminate, was eliminated through the use of more easily ignited materials, thereby increasing the sensitivity of the mixture, so that it compared very well with mercury fulminate mixtures. Example of this kind of priming was the Winchester, or F.A.70<sup>3</sup>, mixture

Potassium chlorate	53%
Antimony sulphide	17%
Lead sulfocyanide	25%
T.N.T.	5%

Later, as we shall see, a perfect initiating action was obtained with the use of lead styphnate and tetracene: we now leave behind the history of primer mixes and we shall investigate how they operate.

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<sup>1</sup> Basu, S. "Formation of Gunshot Residues" *Journal of Forensic Sciences*, JFSCA, Vol. 27, No. 1, Jan. 1982, pp. 72-91.

<sup>2</sup> Rechel, E.R. *Small Arms Primers* Frankford Arsenal Report n. 10 (1932)

<sup>3</sup> Hatcher, J.S. *Hatcher's Notebook* Harrisburg, 1966

<sup>3</sup>Bydal, B.A. Percussion primer mixes in: *AFTE JOURNAL* (volume 22, number 1) January 1990

Not much is known, except to the few specialists of the subject, on percussion primer mixes and on their chemical-physical behaviour when initiated. Very scarce is the ready available relative written material: dr. Bruce A. Bydal, in one of the few articles the present authors were able to find<sup>4</sup> in the bibliography lists 92 entries but most of them are patent indications. In this work dr. Bydal stated that a complete study he was preparing was nearly ready but, very unfortunately, this book as far as we know has never been published.

*“The function of a priming mixture being to supply a flame of sufficient intensity and heat to ignite propellant powder, the priming composition include two essential ingredients; first, a fuel or substance to be burned, and a second, an oxidizer to furnish oxygen for the combustion of the fuel. A third ingredient, however, is quite universally used, the function of which, stated in very general terms is to initiate the reaction between the oxidizer and the fuel; thus its essential characteristic is that it react under the stimulus of a blow to produce sufficient flame and/or heat to start the combustion of the fuel by the oxidizer.”*<sup>5</sup>

The output characteristics of a percussion primer can best be described as a deflagration of low brisance with the accompanying emission of hot particles, flame and gases. In the past, various physical parameters of the primer's output have been measured in an effort to evaluate or compare the same. Such measurements have included volume of gas produced, impulse imparted to a column of mercury by the pressure pulse, closed bomb data, light and temperature output. Even two standard military explosive tests, namely the sand crush and lead disc tests, been employed with the most brisant primers, in an effort to gain more meaningful information. All the above tests, however, tend to be empirical and non-qualitative in nature and at best provide only limited primer to primer comparison<sup>6</sup>.

The energy output and the flame temperature are critical for the initiation of charge ignition and for the cartridge correct performance. In a study of Lang-Mann Chang and Anthony W. Williams<sup>7</sup> measurements were made for the percentage of combustion products in condensed phases from a no. 41 percussion primer, and the influence of the condensed phases on the charge ignition in the 5.56-mm ammunition was characterized. The studies were carried out in three phases using three different test fixtures. Results showed 34% of the combustion products in condensed phases, including liquid and solid particles. With the residue remaining in the primer cup added together, the percentage increased to 44%.

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<sup>5</sup> US Patent n. 1,862,295 – June 7, 1932, James E. Buns.

<sup>6</sup> Lake, E.R. *Percussion Primers, Design Requirements* Report MDC A0514 30 June 1970.

<sup>7</sup> Lang-Mann Chang and Anthony W. Williams *Characterization of Particle Output From a Percussion Primer* Aberdeen Proving Ground, MD 21005-5066, 2007.

*“A knowledge of the energy output of percussion primers is important in assessing their behaviour as suitable igniters in pyrotechnic trains. Several authors have defined the energy required for ignition of a pyrotechnic composition in terms of not only the physical and chemical properties of the composition but also the heat flow into the composition from the ignition source. This heat flow is related to the temperature of the ignition source (since the pyrotechnic must reach its characteristic ignition temperature before burning) and the rate of heat flow or heat flux. If the flux is not large enough, the time to ignition may be too long to cause ignition in a practical time frame or combustion may start but not be sustained. Clearly there exists a need to know what energy a primer will supply and what energy a pyrotechnic needs to ignite and whether one matches the other.*

*Conventional techniques of measuring primer output have typically relied on one of its output characteristics. These have included light output, radiant energy, volume of gas produced or pressure. Thermal measurements are complex because of the speed of the primer action.*

*Similarly, pressure or volume of gas measurements assume the greater the pressure/time integral the greater the primer efficiency or ignitability. However, this premise is invalid if the primer products contain a large proportion of condensed phase material.”<sup>8</sup>*

Nearly all the work done up to now in the search and identification of GSR has been done taking into consideration primers containing lead, antimony and barium. We believe important to know what happens inside such a primer when the pin crushes the mix between the cup and the anvil and this in order to better understand the formation of the GSR particles.

First of all we shall examine the materials that form this class of primer mixes, materials that include one or more initiators, a sensitizer, one or more oxidizers, one or more fuels, and, especially in rim-fire cartridges, a frictionator.

'Primary explosives' is the expression now more frequently used to describe those explosives formerly known in the United States as 'initiators'; the change has become desirable partly because 'primary explosives' is a more distinctive description of the substances concerned and partly because in United States practice 'initiators' are devices employed to initiate an explosive system.

One of the principal concern of explosives experts working at primer mixes was “...to produce a priming charge which is particularly suited for use with powders as now employed in firearms and particularly small arms, such charge producing an explosion of not to great local pressure, and of sufficient heat, and leaving substantially no harmful residues.”<sup>9</sup>

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<sup>8</sup> de Yong, L.V. *An Evaluation Of Temperature And Heat Flux Gasless And Gassy Percussion Primers* Department of Defence Material Research Laboratory Report MRL-R-971, Melbourne, 1985.

<sup>8</sup> US Patent n. 1,106,343 – August, 4, 1914, William H. Buell

<sup>9</sup> This paragraph is from: Urbanski, T. *Chemistry and Technology Explosives of Explosive* Vol. 3 Warszawa, 1967

Mixtures of mercury fulminate<sup>10</sup>, potassium chlorate (as an oxidizing agent), antimony sulphide and ground glass were widely utilized for many years in percussion caps. The content of mercury fulminate was small so that the mixture had no explosive properties. For the same reasons significant amounts of potassium chlorate were used as an oxidizing agent, thus diluting the fulminate to some extent. Antimony sulphide is a combustible component which gives a hot flame. Ground glass was added in order to increase the internal friction and make it more sensitive to percussion. Some compositions also contained an adhesive, e.g. shellac, gum etc. A German composition of 1883 contained, for example:

Mercury fulminate	27%
Potassium chlorate	37%
Antimony sulphide	29%
Ground glass	7%

To 100 parts of this mixture 0.6 part of shellac were added.

The composition of other caps according to Gorst [128] is given in Table 42.

TABLE 42

Cap	Mercury fulminate	Potassium chlorate	Antimony sulphide
Rifle and pistol	16.5	55.5	28.0
Fuse	25	37.5	37.5
Fuse	50	25	25

The English caps contained a little black powder which elongates the flame produced by the explosion of

Mercury fulminate	by	15%
Potassium chlorate	by	35%
Antimony sulphide	by	45%
Sulphur	by	2.5%
Blackpowder	by	2.5%

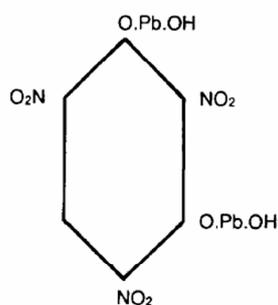
Mixtures containing mercury fulminate, potassium chlorate, and antimony sulphide tend to destroy the inside of firearm barrels, since on decomposition the mercury fulminate

evolves free mercury which causes erosion of the barrel at the high temperatures created inside the bore. Decomposition of the potassium chlorate gives potassium chloride which remains in the bore and strongly corrodes the steel. Sulphur dioxide formed by the combustion of antimony sulphide also helps to destroy the barrel. For a long time therefore, the use of compositions not containing mercury fulminate and potassium chlorate were advocated, but a satisfactory formulation for non corrosive mixtures was found ("Sinoxyd") only when lead styphnate was introduced as their chief component. Since styphnate is hard to ignite by impact it was sensitized by an admixture of tetrazene. At the same time potassium chlorate was replaced by barium nitrate. German compositions for rifle and pistol caps are tabulated below:

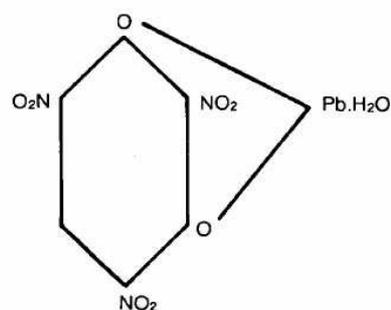
Components	Composition No. 30/40 for rifle and pistol caps	Composition for rifle caps manufactured at Stadeln
Lead styphnate	40	30-35
Tetrazene	3	2-3
Barium nitrate	42	40-45
Lead dioxide	5	5-8
Calcium silicide	10	6-12
Antimony sulphide	—	6-9

### Lead styphnate

As initiator normally it is employed trinitroresorcinol (aka lead styphnate, lead 2,4,6-trinitroresorcinate) but, when used alone, despite a favourable rate of detonation and good power characteristics, this substance is a relatively poor initiator<sup>11</sup>. Two forms of lead styphnate are used



as primary explosives: **basic**



and **normal**

<sup>11</sup> See, for ex. Svadeaba, G. *Impact Sensitivity Of Primary Explosives* (Navord Report 2647).

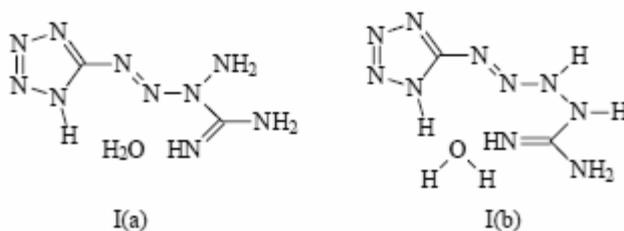
The brute formula is for basic styphnate is  $C_6HN_3O_8Pb$  while the equivalent formula for normal styphnate is  $C_6HN_3O_8Pb$  Both styphnates are deficient in oxygen when decomposing at the time of firing (oxygen balance -18,8%), so that both act as fuel, as well as initiators<sup>12</sup>.

Basic lead styphnate is industrially produced in the US where it is employed as a primer constituent while normal lead styphnate is ordinarily produced and utilized in Europe<sup>13</sup>.

Lead styphnate has a heat of explosion of 460 calories per gram, a flash point of 275°C, and a rate of combustion of 25–30 cm/sec at high density; its detonation velocity at a density of 2.9 is 5200 m/s while the detonation flame temperature is around 2400-2700°C.

Lead styphnate does not react with metals and it is less sensitive to shock and friction than lead azide<sup>14</sup>. For sake of precision we must remember that these information must be considered as an average considering that lead styphnate can present itself, apart as basic and normal, as lead styphnate monohydrate, monobasic lead styphnate, tribasic lead styphnate dehydrate, all with different values of heat of formation and enthalpy of reaction and formation<sup>15</sup>.

**Tetrazene** (aka guanyldiazoguanyl tetrazene and 4-guanyl-1-(nitrosoaminoguanyl)-1-tetrazene; brute formula –  $C_2H_8N_{10}O$ )



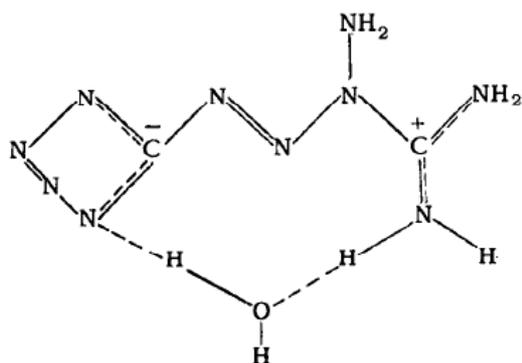
Federoff informs us that other studies show that Tetrazene is “is the zwitterion (guanidinium) of 1-Amino-1-[(1H-tetrazole-5-yl)azol- guanidine Hydrate of structure:

<sup>12</sup> Frost, G.E. *Ammunition Making* Washington, 1990, p. 56

<sup>12</sup> Duguet, J.R. *Les explosifs primaires* Paris, 1984.

<sup>14</sup> Federoff, B.T. et al. *Encyclopedia of Explosives And Related Items* Vol. 1 Picatinny Arsenal, 1960.

<sup>15</sup> .Paynel, J. R. Thermochemistry of lead styphnate *Thermochimica Acta* 242 (1994) 13-21; Malsacheff, M. and D.J. Whelan *Thermochemistry of Normal and Basic Lead Styphnates Using Differential Scanning Calorimetry* Department of Defence Material Research Laboratory Report MRL-R-1000, Melbourne, 1986.



Whichever is the correct nature and formula, Tetrazene (or Tetracene) is rather more sensitive to impact than is mercury fulminate and is of similar power (as measured by the lead block test) but this falls off when it is pressed to higher densities. It is not used alone. However, it has remarkable properties as a sensitizer and this constitutes its principal use in military stores. A comparatively small amount (3 to 5% by weight) markedly sensitizes lead azide to mechanical stimuli (shock, stab and percussion), Similar proportions are frequently added to cap compositions (particularly those based on lead styphnate and lead dinitroresorcinate) to achieve the required degree of sensitivity to percussion, which is maintained even when decomposition of some tetrazene has taken place as a result of exposure to temperatures at which tetrazene is not stable.

The ease with which tetrazene is detonated by ignition depends to an exceptionally great extent on its density. It has been shown that tetrazene detonates most easily when it is poured freely into the capsule; when pressed it gives a much weaker detonation. At a pressure of 200 kg/cm<sup>2</sup> the substance nears the condition of being "dead pressed". In spite of the fact that burning under this condition passes to detonation with difficulty, when greatly compressed the material maintains its ability to be detonated by a cap. Thus, 0.4 g of tetrazene, pressed under a pressure of 200 kg/cm<sup>2</sup>, develops its maximum power, i.e. 21.1 g of sand crushed, when initiated with 0.4 g of mercury fulminate. The difficulty in passing from burning to detonation makes tetrazene unsuitable for detonators and its application is thus limited to ignition caps, where even 2% in the composition results in improved uniformity of percussion and friction sensitiveness and makes it suitable as a sensitizer for friction compositions. The explosion heat of tetrazene is rather low, i.e. 663 kcal/kg. This is characteristic of explosive substances containing a guanyl group in the molecule.

The gas volume produced is 1190cc/g while the heat of explosion. is 658cal/g -

It was found that the thermal decomposition in the temperature range close to its ignition temperature (ca. 140°C / 413 K) of tetrazene is a complex process, the material appearing to soften prior to decomposition and then decomposing exothermically by a two-stage kinetic process. In the initial, more energetic process, the rate of reaction follows an autocatalytic, bimolecular rate law, which proceeds from interaction between either the reactant and a reactive intermediate (formed from its initial decomposition) or the solid in the presence of melt. This is relatively uncommon

amongst organic compounds and may help to explain the effectiveness of tetrazene as a primary booster explosive<sup>16</sup>.

*“The purpose of my invention is to produce a priming charge which is particularly suited for use with powders as now employed in firearms, and particularly small arms, such charge producing an explosion of not too great local pressure, and of sufficient heat, and leaving substantially no harmful residues.”* This are the words of one of the best known primer specialists, William H. Buell, 72, the chemical engineer and prolific inventor connected to the Winchester, who developed a series of primers, primer mixes and tracer bullets. Buell realized that in the primer pocket, at the moment of the explosion, in order to obtain the best flash the heat had to be high while the pressure should not rise to much. Indeed *“The lead styphnate type priming compositions which result in toxic exhaust compounds typically exhibit flame temperatures 2900 to 3400 degrees K.”*<sup>17</sup> and these values (2627/3127°C) are quite higher than those given by Basu at this stage (1500/2000°C). To increase the temperature lend a hand the barium nitrate with its oxygen and, if present, the aluminium powder frequently added to the primer mix. The aluminium powder increases the heat produced upon ignition, i.e., the enthalpy of combustion of aluminium raises the peak temperature of the explosive event. (The added effect is dependent on the Al particle size.) The aluminium powder is assumed to sequentially oxidize, but first the encapsulating Al<sub>2</sub>O<sub>3</sub> coating must be disturbed to allow oxygen to the elemental Al in the core of the powder. This can be done by melting the oxide (2045 °C, melting point), melting the interior elemental Al (660 °C, melting point), or vaporizing the interior Al (2057 °C, boiling point).

Pressures inside the primer are difficult, if not impossible, to appraise but values from 435<sup>18</sup> to 870 PSI have been reported by various authors, values that are quite lower in respect of the 1.400 PSI pointed out by Basu.

Summing up, thermal and pressure conditions when the primer mix explodes seems to be different from those we believed to be: temperatures are higher while pressures are lower. In the complete progression of the primer explosion we can observe, in a few thousands of second, the detonation of lead styphnate and tetrazene, the explosion of barium nitrate and antimony sulphide and the growth of the ignition flame composed of burning gases and solid or liquid droplets. In other words the lead styphnate and tetrazene are the primary explosives meant to convert the shock induced by the firing

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<sup>16</sup> Daniel J. Whelan and Mark R. Fitzgerald *The Kinetics and Thermochemistry of the Thermal Decomposition of the Initiating Explosive, Tetrazene, near its Ignition Temperature (between 385 K and 400 K)* DSTO-TR-0450 Melbourne, 1996.

<sup>17</sup> US Patent No. 4,963,201 Robert K. Bjerke et al. Oct. 16, 1990.

<sup>18</sup> *A study of pressure time curves for small calibre ammunition* Interim Report 64-MDC-A-77 U.S. Army Command, Frankford Arsenal.

pin into the initiation of the primer material. It is very necessary to stress the idea that primer flames are the result of rapid burning rather than detonation.

Primers that detonate are unserviceable in that the cup is usually blown back against the head of the bolt, and leaks develop around the primer pocket. Hardly any "set-back" can be observed with primers that function properly, and so it is assumed that combustion in this case is considerably slower, approaching the progressive burning" of smokeless powders. Furthermore the duration of primer combustion is of the order of  $10^{-3}$  to  $10^{-4}$  seconds, and this certainly rules out detonation phenomena .

The composition of U.S. Army small-caliber primers is well known and unchanged for many years (table 1). This primer composition is used in all of the Army's small- and medium-caliber ammunition.

Table 1. Chemical composition of the number 41 primer mixture.

Name	Formula	Weight-Percent	± Weight-Percent Deviation	Primary Purpose
Lead styphnate	$H_3 C_6 N_3 O_9 Pb$	37	5	Primary explosive
Barium nitrate	$Ba (N O_3)_2$	32	5	Oxidizer
Antimony sulfide	$Sb_2 S_3$	15	2	Fuel, slow
Aluminum powder	Al	07	1	Fuel, fast
Tetracene	$H_8 C_2 N_{10} O$	04	1	Primary explosive
PETN	$C_5 H_8 N_4 O_{12}$	05	1	High explosive

Lawrence Livermore National Labs developed a thermodynamics code for explosives called Cheetah<sup>19</sup> which includes the option for a gun calculation. The gun calculation is done under conditions of constant specific volume and enthalpy, which are meant to simulate a gun firing. Of special interest to the IB community is the ratio of specific heats (frozen) called  $\gamma$ , along with the thermodynamically predicted temperature and pressure.

Primary explosives detonate or explode upon shock or added heat. High explosives detonate under the influence of the shock of the explosion of a suitable primary explosive. Explosives do not necessarily combust; in some cases, explosives do not have the necessary ingredients to combust. Propellants are materials which contain sufficient amount of oxygen to burn without exploding, but provide gas which thereafter may produce an explosion. Fuels are similar to propellants, but they

<sup>19</sup> Fried, L. E.; Glaesemann, K. R.; Howard, W. M.; Souers, P. C.; Vitello, P. A. Cheetah Code, Version 4.0, UCRL-CODE-155944, 2005.

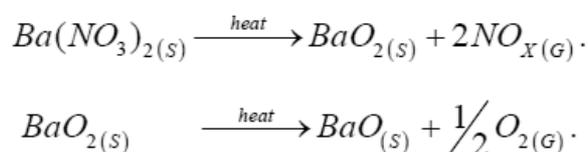
need oxygen from another source to burn. Oxidizers are materials with excess oxygen which when liberated can be used by a fuel.

The lead styphnate and tetracene are primary explosives meant to convert the shock induced by the firing pin into the initiation of the primer material. Tetracene is the more impact sensitive of the two and is important in order to keep stability in the sensitivity of the small-caliber primer<sup>20</sup>. Davis<sup>19</sup> points out that as little as 2 weight-percent is enough to improve the sensitivity of primers. The impact sensitivity of tetracene is given as 1 N-m, and lead styphnate as 2.5–5 N-m

The PETN (pentaerythritoltetranitrate) is a high explosive added to the primer mix to increase brisance (the shock produced) and heat produced. The impact sensitivity is given as 3 N-m<sup>21</sup>.

The aluminium powder increases the heat produced upon ignition, i.e., the enthalpy of combustion of aluminium raises the peak temperature of the explosive event. (The added effect is dependent on the Al particle size.) The aluminium powder is assumed to sequentially oxidize, but first the encapsulating Al<sub>2</sub>O<sub>3</sub> coating must be disturbed to allow oxygen to the elemental Al in the core of the powder. This can be done by melting the oxide (2045 °C, melting point), melting the interior elemental Al (660 °C, melting point), or vaporizing the interior Al (2057 °C, boiling point). It is interesting to note that an explosive mixture consisting of only liquid oxygen and porous aluminium was invented in 1895 the products of which are only solid aluminium oxide, the excess oxygen gas, and much heat. The aluminium powder is a fuel which burns quickly once ignited due to a cascading effect of the large amount of heat released.

The barium nitrate is an oxidizer which undergoes a chain of decomposition reactions which first produce NO<sub>x</sub> and barium peroxide. The NO<sub>x</sub> goes into the gas phase where it can supply oxygen to the fuels. The barium peroxide decomposes to barium oxide with further heating during the primer initiation. Barium nitrate produces a green flame when burned in air.



The antimony sulphide, also known as stibnite, is a slow fuel. Davis<sup>22</sup> describes, as a constituent of percussion primers, “antimony sulphide (a combustible material which maintains the flame for a longer time) ...” Antimony sulphide produces a blue flame when burned in air.

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<sup>20</sup> Fox, W.; Vogelsang, K.; Harris, J.; Lathrop, A. Investigation of Tetracene Decomposition Variation Using Taguchi Methodology. In *Military Mathematical Modeling (M3)*; Arney, D. C., Ed.; Department of Mathematical Sciences: United States Military Academy, West Point, NY, 1998.

<sup>21</sup> Meyer, R.; Kohler, J.; Homburg, A. *Explosives*; 5th ed.; Wiley-VCH Publishing Co, Weinheim, 2002.

<sup>22</sup> Davis, T. L. *The Chemistry of Powder and Explosives*. John Wiley & Sons, Inc.: New York, NY, 1943.

## Primer Firing Event

The action of the firing pin hitting the primer cup causes the detonation of the primary explosives (tetracene and lead styphnate) and the high explosive (PETN). The mechanical energy of the firing pin is to be transformed into heat concentrated in a small zone forming a so called "hot spot": the thermal ignition of the explosive starts at the hot spot and rapidly spreads in every direction.

Hot spots can be produced in three primary manners:

- by the adiabatic compression of gas bubbles entrapped in the solid explosives;
- by friction, especially if grit is present;
- by viscous heating of the rapidly flowing explosive as it escapes from between the impacting surfaces<sup>23</sup>.

This assumption has been, and still is, widely but not unanimously accepted notwithstanding it has been constantly validated by all the experimental work carried out so far.

*During detonation produced by impact, the physical phenomena involved seem to differ according to the intensity of this impact. In the case of a very weak induced shock, e.g. that generated by impact in sensitivity tests of explosives (fall of a mass weighing a few kilos from a height of approximately one meter), the detonation seems to be of thermal origin. In particular the "hot spots" hypothesis seems to have received a clear experimental confirmation by the work of Bowden and his collaborators. Likewise, when the detonation is brought about by heat or by light, the explosive is subjected to a physical-chemical evolution in which the thermal phenomena seem to play a large role.*<sup>24</sup>

The mechanism of detonation in solid explosives may be conveniently considered from two broad aspects-viz., the surface properties and the bulk properties of the explosive. The various possible detonation reaction mechanisms then include the following:

### Grain Burning

- (1) Gaseous diffusion is rate determining.
- (2) Bulk decomposition is rate determining.
- (3) Surface decomposition, evaporation, or sublimation is rate determining.

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<sup>23</sup> Bowden, F.P. and Y.D. Yoffe *Initiation and growth of explosion in liquids and solids* Cambridge, 1952.

<sup>24</sup> Bernier, H. - *Contribution To The Study Of The Initiation Of Detonation Produced By Impact On An Explosive* Picatinny Arsenal Technical Translation 9, 1966.

## Unimolecular Bulk Decomposition From Shock Compression

- (1) Unimolecular, first-order, bulk decomposition is rate determining,
- (2) Gaseous diffusion is rate determining.

In the grain burning theory (originally due to Eyring and co-workers<sup>25</sup>), the initiation and propagation of detonation in heterogeneous explosives is considered on a microscopic scale to proceed through a mechanism whereby chemical reaction is induced in and spreads from "hot-spots" produced by localized stress from impact (e.g., shock or mechanical impact).

. The detailed mechanism of energy release in the grain burning theory need not be known to evaluate detonation reaction times; it is only necessary to isolate the rate determining step. Eyring and co-workers concluded that  $k_r$  had only a small temperature dependence and thus involved a smaller activation energy than would normally be expected for first- or second-order kinetics. They suggested that a diffusion process, either of heat or matter, was possibly rate controlling. Unfortunately, it has never been possible to numerically calculate the specific rate constant of the rate controlling reaction with any confidence using this suggestion.<sup>26</sup>

In a publication of 1981 C. Stephen Coffey e Ronald W. Armstrong wrote<sup>27</sup>:

*Hot spots have long been acknowledged to have a decisive role in producing ignition in explosives and propellant materials when they are subjected to low level stimulations. The hot spot concept arose because of an abundance of experimental evidence which has shown that ignition can occur in an explosive/propellant under conditions in which the energy supplied to the sample was insufficient to raise its bulk temperature to the levels required to cause ignition.*

*To account for ignition under these conditions it is necessary to postulate that some mechanism(s) are operating which act to concentrate the energy of a low level stimulation into limited regions or hot spots where the local temperatures and energy densities are sufficient*

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<sup>25</sup>. Eyring H, RE Powell, GH Duffey, and RB Parlin, The Stability of Detonation, *Chem. Rev.* 1949, 45, 69 ± 179

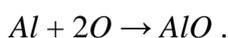
<sup>26</sup> Cheselske, F.J. *Investigations Of The Mechanisms Of Decomposition, Combustion, And Detonation Of Solids* Report 0372-O1F - Aerojet-General Corporation.

<sup>27</sup> Coffey C. S. e and R. W. Armstrong *Description Of "Hot Spots" Associated With Localized Shear Zones In Impact Tests* Naval Surface Weapons Center, NSWC TR 80-499.

*to ignite the explosive/propellant sample. To date these mechanisms have never been clearly elucidated nor have the hot spots themselves been adequately described. In this report we present some recent efforts to address these latter two issues and obtain a true physical understanding of hot spots and their origins.*

Some doubts are cast by only few authors: Mellor and Boggs assert that “*It is generally accepted that initiation in the sample begins at localized ‘hot spots’ whose origins have not been fully determined. Speculation is that hot spots may be caused by adiabatically heated gas in voids or in naturally occurring porosity. Another theory holds that hot spots may be highly sensitive particles. e.g., nitrocompounds, which are plastically deformed at rates high enough to cause ignition.*”<sup>28</sup>

The aluminium is a fuel which burns very quickly. The outer surface of the Al powder is actually Al<sub>2</sub>O<sub>3</sub>, up to 30 % by weight. Burning occurs when the inner Al (that is not oxidized) is exposed to oxygen. This can be done by either melting the solid particles or vaporizing it (sublimation). Oxide cracking would also provide an avenue for oxygen to reach the aluminium. The convection currents in the melted Al particles would assure fresh un-oxidized aluminium would be supplied to the surface. Once at the surface it would react with available oxygen and release a generous amount of heat. This heat would increase the convection currents supplying more un-oxidized aluminium at the surface, and a cascading effect takes place. After a suitable amount of energy is produced by this process the particles could then vaporize, which would burn (oxidize) in the vapour phase. The first reaction of aluminium with oxygen produces AlO. The largest spectral signature from burning aluminium powder is Al O .



From the open-air experiments and analysis of Williams et al.<sup>21</sup>, the aluminium containing particles are mostly in the submicron size range. This indicates that the aluminium containing particles nucleated from the vapour phase into the solid phase upon cooling. This supports the supposition that the aluminium powder is a fast burning fuel.

The barium nitrate is an oxidizer with the primary purpose of ensuring that the fuels have enough oxygen containing compounds in the vapour phase to react to completion. The decomposition of barium nitrate is highly endothermic<sup>29</sup> and burns with a green flame<sup>30</sup>.

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<sup>28</sup> Mellor, A.M. and T.L. Boggs *Energetic Materials Hazard Initiation: DoD Assessment Team Final Report* Engineering Sciences Division - U.S. Army Research Office, 1987.

<sup>29</sup> Ellern, H. *Modern Pyrotechnics, Fundamentals of Applied Physical Pyrochemistry*. Chemical Publishing Co., Inc.: New York, NY, 1961.

<sup>30</sup> Brauer, K. *Handbook of Pyrotechnics*; Chemical Publishing Co., Inc.: New York, 1974.

The decomposition process is described in detail by Bordon and Campbell<sup>31</sup> As previously stated, the barium nitrate decomposes with heat to oxygen containing nitrogen compounds which can then give up their oxygen in the gas phase. The barium peroxide will (with additional heating) decompose to barium oxide and oxygen. The oxygen is then available for the fuels in the gas phase. The analysis<sup>32</sup> indicates that there may be some BaO present after the open air firings, but that was inconclusive. Kaste's analysis of the products of the closed chamber packed with inert propellant grains, primer firing showed a marked decrease in the nitrates. This is consistent with the higher pressure, temperature, and time of exposure to which the primer products (including barium nitrate) would be exposed in a closed chamber with an inert propellant bed.

The antimony sulphide is also a fuel similar to the aluminium powder, but the reaction takes a longer time. The solid antimony sulphide melts with added heat; the liquid drops must absorb more heat to vaporize, only once it reaches the vapour phase can the antimony sulphide produce appreciable amounts of antimony oxide. The analysis of both the open air and inert propellant experiments of Williams et al<sup>33</sup> indicates that this reaction is slow, as no antimony oxide peaks were detected by Fourier Transform Infra Red (FTIR), which would have been readily apparent if there were any substantial amounts. It is possible that the antimony sulphide also serves a secondary purpose during the initiation phase of the primer. That is while the firing pin is impinging on the primer cup, the secondary purpose is to make the mixture more sensitive to percussion. A similar function is provided by ground glass in some percussion primers mixes, especially for .22 rim-fire cartridges. Of note is that high-speed films of the no. 41 primer open air firings were compared to the open air firings of a primer without antimony sulphide as an ingredient. The primer no. 41 firing showed a definite blue hue near the end of the firing event, where the primer without stibnite failed to show a blue hue. This indicates that there was some burning of the antimony sulphide.

A very interesting work of Lang-Mann Chang and Anthony W. Williams<sup>34</sup> describes the flow of the material (solid, liquid and gaseous) generated from the explosion of a no. 41 primer.

What follows is the summary of the results obtained during a complex experimentation.

*Tests were conducted in three test phases to measure the mass percentage of primer combustion products in condensed phases and to characterize their effect on charge ignition. In phase I, five tests were performed. The results showed that a minimum*

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<sup>31</sup> Bordon, S.; Campbell, C. *Differential Thermal Analysis of Inorganic Compounds, Nitrates and Perchlorates of the Alkali and Alkaline Earth Groups and Their Subgroups, Analytical Chemistry*; 27, 1102–9, 1955.

<sup>32</sup> Williams, A. W.; Brant, A. L.; Kaste, P. J.; Colburn, J. W. Experimental Studies of Primer Ignition in 5.56 Ammunition. *Proceedings of the 53rd JANNAF Propulsion Meeting*, 5–8 December 2005, Monterey, CA.

<sup>33</sup> Williams, A. W.; Brant, A. L.; Kaste, P. J.; Colburn, J. W. Experimental Studies of Primer Ignition in 5.56 Ammunition. *Proceedings of the 53rd JANNAF Propulsion Meeting*, 5–8 December 2005, Monterey, CA.

<sup>34</sup> Lang-Mann Chang and Anthony W. Williams *Characterization of Particle Output From a Percussion Primer* ARL-TR-4188 August 2007.

*average percentage of 34% of the combustion products is in condensed phases. These products entered the charge system in the 5.56-mm ammunition. When including the residue recovered from the postfire primer, the percentage increased to a minimum of 44%. It was noted that this is a minimum because it was unclear whether all of the primer residue was recovered. Also, although it was a very small portion of the total, the mass of the paper was unknown. In phase II tests, a specially-configured channel was connected to the primer exit nozzle. The channel was used to produce a flow with or without particles, depending on whether or not the channel walls were lined with adhesive tape. Images from high-speed photography revealed that*

*during the early time period, numerous fine particles were accompanying the primer gases*

*exiting the channel either with or without adhesive on the channel walls. Later, a large stream of particles (medium and large size) appeared only in the flow from the channel, without adhesive on the channel walls.*

*Tests in phase III were conducted with a small closed chamber loaded with live WC844 propellant. The pressure rises in the entrance section of the chamber for the two flow conditions (with and without particles present) were monitored and compared. Analysis based on the pressure and photographic data suggested that the presence of condensed phases did not significantly influence the initiation of the charge. However, it may have helped accelerate the charge ignition process and possibly reduce the time needed to complete a ballistic cycle. At cold temperatures, the contribution to propellant ignition could be appreciable but will not be investigated.*

*Fine particles (possibly burning and hot) exiting from the primer during the very early time may have a significant contribution to effective charge ignition.*

*A remark should be made that for a given mass of constituents, a primer without producing a large number of particles may have a stronger gas flow and thus may achieve similar ignition enhancement as achieved by condensed phases. A further investigation on this is needed.*

It looks indeed that Basu theory on the GSR formation is accurate and that the only correction involves the estimation of pressure and temperature inside the primer pocket: pressures result lower while temperature are estimate higher in respect to the 1982 values described in “*Formation of Gunshot Residues*”.