

A Reappraisal of Silver Fulminate as a Detonant

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Die Neubeurteilung von Silberfulminat als Zündmittel

Die Darstellung und Eigenschaften von Silberfulminat wurden untersucht zur Abschätzung seiner Leistungsfähigkeit als Initialsprengstoff. Die Verbindung ist ein außerordentlich wirksames Zündmittel, scheint aber als stoßempfindliches Material nicht verwendbar zu sein. Es wird der Schluß gezogen, daß Silberfulminat wegen seiner extremen Empfindlichkeit und der Gefahren und Schwierigkeiten, die mit der Darstellung verbunden sind, nicht für den militärischen Einsatz geeignet ist. Es findet gewerbsmäßige Anwendung bei der Herstellung von Spielzeug und Feuerwerkskörpern, da es dort normalerweise nur in kleinen Mengen und in feuchtem Zustand verarbeitet wird.

Une nouvelle évaluation du fulminate d'argent comme composition d'amorçage

On a étudié la préparation et les propriétés du fulminate d'argent en vue d'évaluer ses possibilités d'emploi comme explosif primaire. Cette substance est, en effet, une composition d'amorçage extrêmement efficace mais ne semble pas être utilisable pour réaliser des amorces sensibles à la percussion. On conclut qu'en raison de sa sensibilité extrême, des dangers et des difficultés liés à sa préparation, l'emploi du fulminate d'argent n'est pas envisageable pour des besoins militaires. Il est utilisé dans la fabrication de jouets et de pétards pour feux d'artifice où il est normalement traité en petites quantités et à l'état humide.

Summary

The preparation and properties of silver fulminate have been examined to assess its potential for use as a primary explosive. It is an extremely effective detonant but does not appear promising as a stab-sensitive material. It is concluded that its extreme sensitiveness and the hazards and difficulties associated with its preparation render it unsuitable for military applications. It does find commercial use in the manufacture of toys and crackers when it is normally handled exclusively in small quantities and in the wet state.

1. Introduction

Silver fulminate was first prepared by Brugnatelli⁽¹⁾ in 1798, was later recognized by Gay-Lussac⁽²⁾ to have an identical composition to silver cyanate and thus became the first known example of isomerism. It is a white crystalline material which darkens on exposure to light, is non-hygroscopic, only slightly soluble in water (0.075 g in 100 ml at 13 °C / 0.25 g in 100 ml at 100 °C), insoluble in nitric acid and is decomposed by hydrochloric acid. It has long been known to be a sensitive explosive with good detonating properties⁽³⁾ but detonators containing silver fulminate have apparently been used only by the Italian Navy⁽⁴⁾. It is used in small quantities in pyrotechnics, fireworks and toys such as "snaps", "pull crackers" and paper caps for toy pistols⁽⁵⁾. For these applications it is produced in the UK (by only one manufacturer as far as the authors are aware), USA, USSR and South Korea among other countries.

In general, the combination of its extreme sensitiveness⁽⁶⁾, alleged poor stability and the high cost of silver as a raw material⁽⁷⁾ have precluded the use of silver fulminate in commercial or military priming and detonating devices. However, silver azide has found uses in military stores so that the cost is not necessarily a deterrent and with regard to stability, Peter⁽⁸⁾ has reported that a sample of silver fulminate stored under water for 40 years had darkened in colour but otherwise, showed no signs of change in physical or chemical properties. Martin and Wöhler⁽⁹⁾ examined the initiating properties of various fulminates and found that the Ag, Cd and Cu salts have stronger initiating power than mercury

fulminate. Mercury fulminate, long used as the standard primary explosive, is now obsolete in UK and USA, replaced in the detonant role by lead azide and by other explosives in priming compositions. It has poor stability and is susceptible to hydrolysis but is still used in many countries. Silver fulminate is about fifteen times as efficient as mercury fulminate for exploding tetryl (2,4,6-trinitrophenylmethyl nitramine) but only about 30 per cent more efficient for exploding trinitroxylene⁽³⁾. The average velocity of detonation⁽¹⁰⁾ of silver fulminate is of the order of 1700 m · s⁻¹ (measured for an ~ 0.5 mm thick unconfined film ignited by a hot wire). Its brisance, as judged by the sand test, is essentially the same as that of mercury fulminate⁽¹⁾.

At PERME, silver fulminate has been examined as part of a general survey of potentially useful detonants. In this paper, the method of preparation and properties are evaluated with a view to possible practical applications.

2. Experimental

2.1. Preparations and analysis

Preparations were generally carried out on a small scale with the aid of a master-slave manipulator. Details of a representative experiment are as follows:

6.8 g silver nitrate were dissolved in 4 ml water and 20 ml nitric acid (S.G. 1.42) were added. 36 ml ethanol were added and the mixture heated to 40 °C in a water bath. The temperature rose to 62 °C over twenty minutes and the reaction was allowed to proceed for a further 30 minutes, the temperature rising to 68 °C and subsequently falling to 43 °C at which point 100 ml water were added. The precipitate of fine needles was filtered off, washed with water and dried on a steam table. The yield obtained was 4.5 g (75% of theoretical).

A temperature of at least 60 °C appears to be desirable for the reaction. The temperature in the reaction flask is best controlled by use of hot and cold water baths. Destruction of unwanted material and reaction liquors can be effected

with hydrochloric acid or sodium thiosulphate solution.

Factors including the effect of temperature to start the reaction, the reaction time before drowning out with water, variation of the amount of alcohol and/or nitric acid were all examined.

Microanalysis was carried out on a CHN analyser and additionally, analysis for silver content was carried out by atomic absorption spectroscopy (Ag lamp, 328 nm) on a Perkin-Elmer 370 instrument. This technique was checked against an electrodeposition method for accuracy. X-ray powder patterns were examined for a number of silver fulminate samples.

2.2. Performance and sensitiveness testing

Detonative performance was assessed in 1.5 gr detonators (1 gr = 0.0648 g) according to methods described by White and Williams⁽¹¹⁾. For some samples tests were also carried out in the larger No. 6 type detonator. In general a pressing load of 17 MPa was used but several samples were evaluated at various pressing loads in the range 17 MPa to 33 MPa.

A limited number of 1.7 gr stab igniters were loaded with commercial silver fulminate at 250 MPa and tested for stab sensitivity. 100 mg of this material could only be loaded by pressing in two increments. Other pressing loads were not investigated.

The impact, friction and electrostatic sensitiveness and the temperature of ignition of commercial silver fulminate were all determined using standard PERME procedures⁽¹²⁾.

3. Results and Discussion

3.1. General

It is worth noting that in much of the early literature, the nature of the bonding was not understood and thus silver fulminate is often found written as AgONC, which can lead to confusion. It is also important to realize that fulminates (salts of fulminic acid) are quite distinct from fulminating compounds (see Ref. 3, p. 400). Fulminating silver is a black solid which is extremely sensitive and can detonate when moist. Its structure has so far not been determined.

There are many preparative methods for silver fulminate described in earlier literature^(3, 4, 7). For example, details of the procedure employed at Picatinny Arsenal are given by Livingston⁽¹⁾. Nearly all the literature methods are analogous to those used for mercury fulminate and involve the reaction of alcohol with silver or a silver salt in nitric acid. The mechanism of formation of fulminate ions from alcohol and nitric acid has been discussed by Wieland⁽¹³⁾. An examination of the various methods, that given by Rinckenbach⁽¹⁴⁾ being typical, was used as a basis for our investigations.

The reaction was found to have poor reproducibility in that a consistent yield could not be obtained. The time of reaction before drowning out was very difficult to decide and it appeared to be critical to the yield to quench at the right moment. Matters were further complicated in that the reaction product was inconsistent. In some instances pure silver fulminate was formed but in other preparations a more complex material, perhaps a solid solution or a double salt, was obtained (see analytical and X-ray data). This material

Table 1. Analytical Data

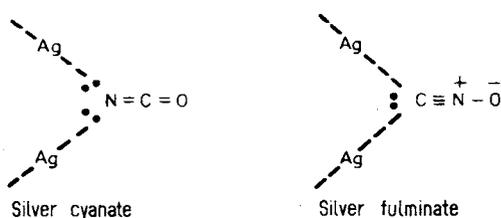
<i>Theoretical</i>						
	MW	% of	C	N	H	Ag
AgCNO	149.9		8.0	9.34	0	72.0
"AgCNO · AgCN"	283.8		8.5	9.87	0	76.0
"(AgCNO) ₂ · AgCN"	433.7		8.3	9.68	0	74.6
"AgCNO · AgNO ₃ "	319.8		3.75	8.76	0	67.5
<i>Experimental</i>						
		% of	C	N	H	Ag
KSF 2/73			8.2	9.5	0	71.3
KSF 3A			8.0	9.35	0	70.0
KSF 4/73			8.5	9.5	0	69.7
Material soluble in 3 M NH ₄ OH			8.3	9.4	0	69.8
Commercial (UK origin)			8.0	9.3	0	71.2

was readily converted to silver fulminate by recrystallisation from ammonia solution, either by evaporation of the ammonia or neutralising with nitric acid.

Analytical data for a number of preparations and theoretical values for silver fulminate and hypothetical complexes are given in Table 1. Silver figures quoted are averages of three determinations.

The commercial material analyses were very close to the theoretical for silver fulminate and our preparations deviate only slightly from expected values. Unfortunately the analytical data is insufficiently discriminating to distinguish the nature or amount of impurities. Infrared spectra were run and showed that no nitrate was present but CN bands would be masked by the CNO group absorption bands.

The crystal structure of silver fulminate was subjected to examination by Singh⁽¹⁵⁾ whose conclusions were not entirely correct. Subsequently a more detailed study was performed by Britton and Dunitz⁽¹⁶⁾ who investigated two polymorphic forms of AgCNO. They were unable to find an amorphous form and it seems extremely doubtful whether a truly amorphous form of the material exists. The two polymorphs are orthorhombic and trigonal (rhombohedral) with the former containing infinite $-C-Ag-C-Ag-C-$ chains and linear fulminate ions and the latter involving cyclic hexameric units with Ag-Ag separations which are slightly shorter than those in metallic silver. Crystals were grown from 6M ammonia and a mixture of needles and multiple growths of leaf-like habit resulted. Both polymorphs appeared as both types of crystal and they could not be distinguished under the microscope. The crystals warped under exposure to X-rays during structure determination which explains the rather poor data. The structures show certain novel features and suggest strongly that the bonding does not entirely consist of ionic interactions but has considerable covalent character. This view is supported by optical and infrared studies on fulminates and isoelectronic azides and cyanamides⁽¹⁷⁾. Figure 1 is a diagrammatic representation of the bonding in silver cyanate and silver fulminate.



In the present study, some of the X-ray powder patterns gave lines in agreement with single crystal predictions, whilst other samples (e.g. KSF 3 A and KSF 4/73) had some lines shifted, which supports the presence of some impurity as postulated above. The commercial material gave a similar pattern to our preparations of relatively pure silver fulminate with additionally three weak lines not apparently attributable to any phase of silver fulminate. There was also evidence of metallic silver and/or other impurities in some samples submitted for analysis.

With regard to the performance testing, pure silver fulminate was found to be as effective as lead azide in the No. 6 detonator, 60 mg being sufficient for maximum output from the RDX base charge. 120 mg of commercial material was required to achieve similar efficiency at the same pressing load and it was found to “dead-press” at loads above 33 MPa. In the 1.5 gr detonator, it was not possible to load more than 40 mg of the complex material (KSF 3 A) compared with 60 mg of service lead azide and tests over a range of pressing loads showed this to be insufficient for more than low order detonations.

1.7 gr stab igniters containing 100 mg of silver fulminate failed to function even with input energies up to 25 inch ounces (~ 176 mJ). The only positive response achieved was with 60 mg pressed in one increment, this firing at 10 inch ounces.

The relative stab insensitivity of silver fulminate is rather surprising (cf. mercury fulminate is quite sensitive to stabbing) but may be as a result of the very small crystal size of the material tested (see below) or, the use of an inappropriate pressing load. The phenomenon of dead-pressing was shown to take place in the detonator testing.

Sensitiveness data for commercial silver fulminate is given in Table 2. A comparable set of data is not available for material of PERME manufacture as a batch was being prepared for this purpose when an accidental ignition occurred (see section 3.2) and preparative work on this material was terminated.

The outstanding feature of the data in Table 2 is the extremely low energy required for electrostatic initiation which renders silver fulminate very hazardous to handle, particularly when dry. Additionally, propagation seems especially good with this material.

Shepherd⁽¹⁸⁾ stated that silver fulminate has too high a sensitiveness to accidental impact for practical usage. It is instructive to make comparisons with other initiatory

materials, in particular with mercury fulminate and lead azide. Davis⁽³⁾ stated that mercury fulminate will tolerate a higher temperature and is much less sensitive to shock and friction than silver fulminate. In fact, mercury fulminate (F of I = 10) is more sensitive to impact than silver fulminate, but it is not so friction sensitive (50% fires for emery friction at 4.5 ft/s, ~ 1.37 m/s) and is far less sensitive to electrostatic discharge metal/metal (m/m) electrode: 150 μ J at 5000 pF). Rosenberg⁽¹⁹⁾ gave the T of I for silver fulminate as 170 °C (210 °C for mercury fulminate). The T of I's were variously reported elsewhere e.g. Andreev⁽²⁰⁾ gives 169 °C–175 °C (heating rate 20 °C/min). Schumacher⁽²¹⁾ reported that on heating silver fulminate rapidly on a metal plate in vacuum, it detonated, causing indentation or penetration of the plate. Lead azide behaved similarly but mercury fulminate invariably decomposed without detonation. The T of I of the complex (KSF 3 A) is 224 °C–228 °C i.e. 20 °C higher than that of the pure commercial material.

Lead azide (SLA) is less sensitive to impact (F of I = 30, ball and disc 50% point = 17.5 cm), friction (emery 50% point = 4.5 ft/s), temperature (T of I > 300 °C) and electrostatic initiation (m/m 2 μ J at 520 pF, r/m (rubber/metal) 225 μ J at 1200 pF).

Rinkenbach⁽²²⁾ has stated that silver fulminate as normally produced consists of fine colloidal aggregates but suggests that the generally observed high sensitiveness is due to small clusters of crystals being present. The formation of the two polymorphs was first pointed out by Pandey⁽²³⁾ who carried out recrystallisations from ammonium acetate at controlled pH values and Britton and Dumitz⁽¹⁶⁾ suggested that the variation in sensitivity results from the presence or absence of the second form. The suggestion made above of a complex or solid solution may furnish an alternative explanation. It is known that silver fulminate can form double salts⁽¹⁾ e.g. with NH_4^+ or K^+ . The salt $\text{Ag}(\text{NH}_4)(\text{ONC})_2$ which can be prepared by the action of ammonium iodide on silver fulminate is a less violent explosive than the silver salt.

The hazards involved in handling silver fulminate are highlighted by the data in Table 2 and the comparisons made with lead azide and mercury fulminate. When heated, silver fulminate decomposes to a gas and silver. The thermal decomposition at different temperatures and explosive properties have been studied and mechanisms put forward^(24–26). Bowden and Yoffe⁽²⁷⁾ suggested that silver fulminate will only explode on heating when its crystals are above a critical size and this provides a possible explanation of the less sensitive so-called “amorphous” material which is really microcrystalline. Small crystals have apparently been seen to melt just prior to explosion. DTA studies showed no evidence of phase changes⁽²⁶⁾ between 20 °C and 145 °C. Relatively recently, ignition of silver fulminate under reduced pressures has been studied by Urbanski⁽²⁸⁾. Ignition by exposure to intense light (from a Xe-filled electron flash bulb) has been reported⁽²⁹⁾, the electrical energy required in the discharge for explosion to occur being similar to that for lead azide. Explosion after brief irradiation with sparks (sudden heating) has also been examined⁽³⁰⁾.

The sensitiveness to electrostatic discharge is particularly noteworthy and may possibly be enhanced in partially decomposed samples by the presence of particles of metallic silver. A number of accidental ignitions have been reported during preparations of silver fulminate and some of these are discussed further below.

Table 2. Sensitiveness Test Data for Silver Fulminate (Commercial)

Impact (Rotter Test):	Figure of Insensitiveness (F of I) = 22 (RDX = 80)
Temperature of Ignition (T of I):	Exploded at 200 °C and 204 °C
Electrostatic:	metal/metal electrodes 0.04 μ J at 48 pF rubber/metal electrodes 0.3 μ J at 48 pF
Ball and Disc:	14 cm 6/10 fires 13 cm 6/10 fires 12 cm 4/10 fires 11 cm 4/10 fires 10 cm 3/10 fires 9 cm 1/10 fires 8 cm 0/20 fires
Friction (Emery Paper):	2.5 ft/s (~ 0.76 m/s) 7/10 fires 2.0 ft/s (~ 0.6 m/s) 5/10 fires 1.5 ft/s (~ 0.45 m/s) 0/10 fires

3.2. Accidents during preparation of silver fulminate

Several accidents have occurred due to experiments resulting in the accidental formation of silver fulminate. An example of this is an accident which occurred during the preparation of AgBF_4 by a literature method⁽³¹⁾. A less surprising explosion occurred in reclaiming Ag residues when silver nitrate crystals obtained from HNO_3 solution were rinsed with ethanol. In this case, about 1/4 lb of the alcohol moist crystals in a beaker exploded violently on being touched with a porcelain spatula⁽³²⁾.

Three ignitions have occurred during preparations at PERME. The first of these was during a reaction closely following the method outlined in section 2.1.⁽³³⁾ The reaction had just been quenched and a thermometer was turned in the solution. The input of external energy was extremely small but resulted in an explosion and complete fragmentation of flask and thermometer. The cause of the ignition was not determined although the possibility of a spontaneous explosion resulting from rapid nucleation and crystallisation on addition of water (which decreases solubility of silver fulminate in the reaction liquor) cannot be ruled out.

A second incident occurred when a small (wet) sample of material from a preparation was placed on a glass slide for microscopic examination. Ignition resulted and the slide was shattered. Electrostatic initiation was the most likely cause of this event.

Most recently, an accident occurred during the preparation of a sample for sensitiveness testing. The reaction was complete, had been drowned out and the product (approx. 4 g) was being filtered off under suction. An explosion resulted as the empty reaction flask was being withdrawn, shattering both funnel and reaction vessel, scattering debris over a wide area and causing minor injuries to the experimenter. The most probable cause of this event was an electrostatic discharge, as the experimenter was wearing conducting footwear and standing on an antistatic floor whilst funnel and filter flask were non-conducting. It is nevertheless surprising that initiation took place as the sample was all in the wet state. Silver fulminate is regularly handled wet commercially, apparently without incident, although a critical particle size condition as discussed earlier may operate. The use of vacuum filtering seems inadvisable as there is some evidence that application or removal of vacuum can cause initiation of very sensitive materials.

The authors have also received details of an incident in an Australian laboratory where ignition occurred whilst a wet precipitate of silver fulminate was being tipped from one vessel into another.

4. Conclusions

Due to the numerous problems and hazards involved in preparing and handling silver fulminate, it is not considered suitable for large-scale use in detonators. In general, it is felt that risks are likely to outweigh possible advantages over alternative materials. However, because of the very high efficiency as a detonant it may find future use in specialised roles. Silver fulminate shows no promise as a stab-sensitive material.

It is emphasised that any work undertaken on silver fulminate should take particular account of the electrostatic

and frictional hazards. It is obviously preferable to handle the material in the wet condition as far as possible but as shown by our experience and that of other workers, this is no guarantee of safety.

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