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REPORT No. 37/48

APPLIED RESEARCH DIVISION

Co-ordination Compounds as Sensitizers for
Percussion Cap Compositions

C. M. Bean

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Co-ordination Compounds as Sensitizers for
Percussion Cap Compositions

C. M. Bean

Summary

The possibility of using co-ordination compounds as sensitizers of percussion cap compositions has been investigated. Fairly promising results have been obtained which are regarded as an indication that there is scope for much further work on similar lines.

No recommendations are made for Service use of the compositions described.

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More Detailed Summary

(a) It has been found that the following mixture, provisionally called mixture 300 (b) gives very sensitive caps and has certain noteworthy properties:

Mixture 300 (b)

Potassium chlorate (120 - 170 BSS)	50%
Antimony sulphide (grist as for Q3 mixture)	35%
Dipyridinoethylenediamino cupric perchlorate (passing 120 BSS)	10%
Tetrazene	5%

In .303 inch S.A. caps this mixture is 1.7 times as powerful as the present Service S.A.A. fulminate composition, is on the average, over a complete range of critical and unfavourable assemblies, about 5 inches/ $\frac{1}{4}$ lb. more sensitive than the Service mixture; unlike any other composition known, is little affected by dimensional changes in the anvil assembly. Although more sensitive in the pressed state than the Service mixture, when loose the composition is relatively very insensitive to impact and friction. Under hot dry storage conditions the stability is greater than that of the Service fulminate mixture but there are doubts as to its stability under hot moist conditions (see para.4.3.2.5) although no loss in sensitivity has been found. Owing to this fact the composition is not recommended for Service.

Sensitivity and gun trials (the latter by C.S.A.R., Swynnerton) have also been done on 20 mm. caps filled mixture 300 (b).

(b) A new class of copper co-ordination compounds is described in which a polynitrophenol is linked by co-ordination to a divalent copper atom thus producing (in conjunction with neutral co-ordinating groups) a non-ionized complex. Among this class of bodies dipyridinodipicrato copper has been found to possess useful sensitizing properties for chlorate mixtures and a mixture ("Pypicu 10") has been developed, which in unfavourable assemblies is more sensitive than the present Service mixture:

Mixture "Pypicu 10"

Dipyridinodipicrato copper	10%
Potassium chlorate (grist as for A.1 mixt.)	54%
Antimony sulphide (grist as for Q3 mixt.)	36%

Although not as sensitive as mixture 300 (b) this mixture has the advantage that it does not contain tetrazene.

It has not been possible on account of other work to carry investigations on this mixture to completion.

(c) Some new thioureo cuprous complexes have been prepared and promising preliminary results have been obtained with mixtures containing both dipyridinodipicrato copper and dithioureo cuprous picrate.

(d) Attempts have been made to prepare for use in cap compositions complex azides with co-ordinatively linked azide groups resistant to hydrolysis under moist conditions.

(e) Attempts have been made to develop "rustless" cap compositions containing chlorate by making use of lead hypophosphite as a fuel and reducing the percentage of chlorate to 10 per cent., but obtaining compensation for the reduced weight of chlorate by increasing the total surface of this ingredient present by fine grinding. No compositions sufficiently sensitive to be of practical use have been found but further work in this direction might yield useful results.

(f) It has become obvious that there is a wide field for further investigation into the application of co-ordination complexes to cap compositions and also possibly to pyrotechnics.

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Drawing A.R.D. No.8720 showing the sensitivity of .303 inch caps filled mixtures 300 (a) and 300 (b) in a variety of critical assemblies.

1.0 Introduction

The present report is an account of work done in the period 1945-1947 on the application of complex co-ordination compounds as sensitizers of percussion cap compositions.

On account of pressure of other work, further work on the lines described has had to be put into abeyance, so the present report is an interim one describing what has already been done and indicating some possibilities of future work. It has not been possible to explore in detail the sensitizing properties of all the compounds described but three mixtures in particular have shown promise and their behaviour in caps has been investigated in some detail although there remain several points requiring further elucidation.

2.0 Properties desirable in a cap composition. Rustlessness. Summary of present position

The chief desiderata in a cap composition, in addition to sensitivity and stability are - virtual smokelessness, power, ignitory ability, freedom of the finished caps from liability to explode en masse, good mixing properties (absence of tendency to segregate), absence of muzzle-flash promoting properties and safety in handling. The most difficult of these requirements to fulfil is sensitivity and thus the achievement of adequate sensitivity must be the primary point of attack on the problem even if some of the other desirable qualities have to be foregone.

Rustlessness (that is absence of any tendency of the products of explosion to cause rusting of the barrel) is, other things being equal, also desirable, but experience has shown that the development of a non-rusting mixture is an altogether more difficult problem than that of producing a rusting one. The reason for this is that rusting properties are entirely controlled by the presence or absence of halogen and in general mixtures containing potassium chlorate are very much more sensitive and powerful than those without it, due presumably to the fact that the reaction $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$ is slightly exothermic. The difficulty lies in finding an oxidising agent in place of chlorate which is free from halogen, non-hygroscopic, stable, yet not too reluctant to yield up its oxygen on heating and, moreover, containing a fairly high proportion of available oxygen. In practice the choice narrows down to potassium and barium nitrates (or a double salt of these two) in neither of which is the yielding up of oxygen sufficiently facile for them to give sensitive and powerful mixtures without the aid of relatively large proportions of powerful quick burning and flash sensitive agents such as lead styphnate. Lead styphnate, unfortunately, makes the finished caps liable to explode en-masse, while barium nitrate promotes muzzle flash in certain guns.

When this work was started rustlessness was not a Service requirement, indeed the fulminate mixtures which had been used in S.A. caps since their introduction over a hundred years ago were all of the rusting type and all the mixtures described in this report are also of the rusting type. Quite recently, however, the Ordnance Board (Proc.No.34036) after trials with VH2 rustless caps, laid down rustlessness as an additional requirement; in view of this decision none of the work described in this Report has any immediate Service application.

As far as can be seen at present there are only two general types of possible rustless mixtures, (a) those based on the German Sinoxyl patents, e.g. VH2 and D.I.L. mixtures and (b) those based on dinitrodiazophenol (D.D.N.P.).

Type (a) contains lead styphnate, tetrazene, barium nitrate, calcium silicide, lead peroxide (with or without a small amount of antimony sulphide to give extra sensitivity). Type (b) is similar except that the lead styphnate is replaced by a smaller amount of D.D.N.P. and ground glass is often added to enhance the sensitivity.

The great disadvantage of mixtures of type (a) is that the presence of lead styphnate (which is exceedingly sensitive to flash) makes the loose filled caps liable to explode en masse when a paper disc is used as a closure. If tinfoil is used in place of paper the liability to mass explosion is reduced but the sensitivity is reduced as well - a sacrifice which can ill be afforded as there are no great reserves of sensitivity in hand. It appears in fact as if the very property of lead styphnate which makes it useful (i.e. its flash receptivity) is the property which also makes it dangerous.

The disadvantage of the rustless D.D.N.P. mixtures lies in the dubious stability of D.D.N.P.; it is decomposed by light and catalytically by contact with copper and certain samples appear to contain an impurity which so reduces the stability that gross decomposition has been observed in 12 hours at 120°F. and 95 per cent. R.H.

Now although most of the co-ordination complexes described in this report are neither sensitive nor powerful enough to form useful mixtures in the absence of chlorate it is quite possible that further work on the same lines might reveal a co-ordination complex with the desired properties. Stable complex azides appear to be the most promising line of approach (see para.6.2, also para.4.4).

3.0 The application of co-ordination complexes to cap compositions

3.1 General considerations. Complexes containing oxidizing and fuel functions

In spite of the large amount of labour which has been expended in the search for improved cap compositions, not only in this country but abroad (in Germany in particular), the search still has to be conducted along largely empirical lines owing to lack of knowledge of the fundamentals involved and to the complexity of the problem. It has been possible, however, in the last few years to obtain some insight into the problem and to discern some general principles.

Of these one of the most important is that the inherent friction or impact sensitivity of the substance added as a sensitizer to a mixture of oxidizing agent and fuel has little relation to the sensitivity it confers on the mixture. It is true that some of the best sensitizers are in themselves very sensitive, mercury fulminate for example, but this inherent sensitivity is incidental and probably only indirectly related to the sensitizing ability. The lack of correlation between sensitivity and

sensitizing power is illustrated by results which were reported in A.R.D. Expl. Report 373/43 on the sensitization of mixtures of potassium chlorate and antimony sulphide by the addition of various third components; it was found, for example, that lead azide, in spite of its high sensitivity particularly to grit friction has very little sensitizing power - less indeed than tetryl and very much less than PETN. It is not in fact necessary for the sensitizer to be an explosive at all and it was found that elementary sulphur in certain optimum proportions (6 per cent.) produced slightly greater sensitization than mercury fulminate and, apart from tetrazene, was the most powerful sensitizer of chlorate mixtures encountered.

In addition to elementary sulphur, certain non-explosive compounds containing divalent sulphur, such as lead and cuprous thiocyanates are moderately good sensitizers; both in fact have been so used in American Service compositions. The disadvantage, however, of using non-explosive sensitizers is that the mixtures tend to "fizzle" when used in caps of small charge weight or in conjunction with small pointed anvils. This fact precludes their use in small arms caps although they are perfectly satisfactory in primer caps, which have a large charge weight relative to the amount of venting and also large hemispherical anvils. If the normal amount of venting is increased caps of this type also "fizzle" in primers.

The tendency to "fizzle" is really a manifestation of lack of vigour of the composition and its reluctance to burn up rapidly to explosion without the aid of suitable confinement and may be regarded as being due to the total segregation in separate particles of the mixture of the oxidizing and fuel functions.

The earliest experiments described in this report arose out of attempts to exploit the sensitizing action of sulphur compounds and to render it of use in small arms caps; in an endeavour to improve on the sensitizing action of sulphur and to overcome the difficulty of "fizzling" the ultra-accelerator tetramethyldithiuram disulphide ($\text{Me}_2\text{N}.\text{CS}.\text{S}.\text{S}.\text{CS}.\text{NMe}_2$), used as a source of active sulphur in the vulcanization of rubber, had been tried but, although it was a powerful sensitizer, compositions containing it "fizzled" in small arms caps. Attention was then turned to co-ordination compounds containing both divalent sulphur and oxidizing groups in the same molecule, in the hope of combining the beneficial sensitizing effects of the sulphur with a certain amount of intra-molecular fuel oxidation, which it was thought, might reduce the tendency to "fizzling". What may be described as the "anti-fizzling" role is usually played by substantial proportions of initiators or near initiators, but the number of substances suitable to fill this role is somewhat limited since it is found that the addition of large proportions of non-sensitizing or weakly sensitizing initiators or near initiators in order to reduce the tendency to "fizzling" often reduces the sensitivity as well and there are other objections to those (e.g. mercury fulminate, lead styphnate or D.D.N.P.) which do not reduce the sensitivity. Possible reasons for this effect were discussed in A.R.D. Expl. Report 373/43.

Since the field of possible co-ordination compounds which can fairly readily be made is so large it appeared to be of interest to extend the work on sulphur compounds to other types, particularly when it was found that the most efficient of the sulphur bodies were hardly stable enough to be of practical use. The main types investigated were simple

co-ordination complexes of oxy-acids, chiefly perchlorates, and the primary objective was to find such bodies, which when added to the extent of about 10 per cent. to mixtures already sensitized by say tetrazene, would have an "anti-fizzling" effect. Dipyrindinoethylene-diamino cupric perchlorate showed itself to possess this property to a fairly marked extent and mixture 300 (b), whose properties are described in para.4.3, was developed along these lines. The possibility, however, was not ruled out that there might be a sulphur-free co-ordination complex of similar type which would function without the auxiliary sensitizer; dipyridinodipicrato copper showed some promise of success in this respect as described in para.6.3.2.

Co-ordination complexes almost inevitably contain a large excess of fuel in relation to the amount of available oxygen in their molecules so are hardly to be described as initiators - at least they are mostly very mild and their typical behaviour on ignition is to deflagrate gently. Their impact and friction sensitivity is low and local ignitions at the point of impact generally do not propagate themselves throughout the mass. These remarks apply to the perchlorates, nitrates, picrates, etc. (The chlorates are much more sensitive and more unstable). The fuel-oxygen unbalance is not disadvantageous because sufficient potassium chlorate can be added to the composition to form a nearly balanced mixture, and the volume of the gaseous products of combustion of such a balanced mixture is larger than with the standard compositions. The effect of this extra volume of gas is to increase the apparent power of the compositions as measured by the ballistic pendulum (see para.4.3.2.3.) and it also probably assists by increasing the effective confinement.

3.2 The use of co-ordination complexes not depending on intra molecular fuel oxidation

In addition to intra molecular fuel oxidation complexes the possibility was considered of using an inherently explosive radical, e.g. azide in the complex, as for instance in the unionised complex dipyrindino-diazido copper $[\text{Py}_2\text{Cu}(\text{N}_3)_2]$. In this case all the fuel groups would be available for reaction with the chlorate while the azide group would provide a certain amount of power; looked at from another point of view this device seemed to afford a method of toning down the violence of the azide group which, in simple salts such as cupric azide, is far too violent to be of practical use in caps. It was also thought that by holding the azide radical by co-ordinative as opposed to ionic bonds the tendency to release hydrazoic acid under moist conditions (a tendency common to most simple ionic azides) might be obviated. Actually it was found that the above mentioned complex azide did liberate hydrazoic acid under moist conditions, but a certain complex cobaltic azide did not do so. This topic is discussed further in para.6.2.

3.3 The choice of metal to act as co-ordination nucleus

Several metals were considered as possible co-ordination nuclei, in particular Ag, Cu, Ni, Co, Fe, Pb, Hg, Cd, Zn, but most attention was given to copper. Other things being equal, a metal of fairly low equivalent or atomic weight is preferable, since it is desirable to reduce what may be described as ballast weight to a minimum because the metal itself will have no useful contribution to make to the combustion mechanism.

In this respect lead and mercury compounds stand at a disadvantage. Those silver cadmium and zinc compounds which were prepared tended to be of poor crystalline form, i.e. rather light and "fluffy" and so unsuitable for incorporation in mixtures to the extent of more than a few per cent. A few nickel, cobaltous and cobaltic salts were investigated but there is probably a good deal of scope for further work in this direction; more often than not their crystalline form was well adapted for admixture in cap compositions.

4.0 Compositions based on co-ordinated cupric perchlorates

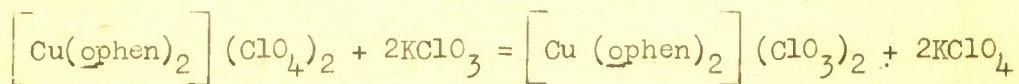
The following complex cupric perchlorates were made and their ability to sensitize a 60/40 mixture of potassium chlorate and antimony sulphide investigated:

- (a) Diorthophenylenediamino
- (b) Polymeric paraphenylenediamino
- (c) Ethylenediaminoorthophenylenediamino
- (d) Tetrapyridino
- (e) Ethylenediaminodipyridino
- (f) Diethylenediamino
- (g) Diamminodipyridino
- (h) Diamminoethylenediamino
- (j) Tetraammino
- (k) Diaquoethylenediamino

In general it was found that these salts had but moderate sensitizing power being about equal in this respect to lead thiocyanate. The most effective were (a) and (c).

4.1 Orthophenylenediamino cupric perchlorates

The sensitizing power of (a) and (c) was so good that at first there were some hopes that it might be possible to obtain with them sufficiently sensitive 3 component mixes. The reason underlying the choice of orthophenylenediamine as a co-ordinator was that it was thought that enhanced sensitivity might be obtained on account of the reducing properties of the diamine since it would not be merely a case of oxidising an inert fuel as in most of the other compounds but a case of an oxidising mixture (chlorate and perchlorate) acting on a moderately strong reducing agent. It was expected that such systems would be more readily initiated than those with no reducing agent on account of the greater oxidation-reduction potential between the components. The mixtures, however, proved to be useless because the orthophenylenediamino salts underwent a slow oxidation (possibly accelerated catalytically by the copper) when in contact with chlorate. It is probable that when diorthophenylenediamino cupric perchlorate is in contact with potassium chlorate (particularly under moist conditions) there is a certain amount of double decomposition owing to the sparing solubility of potassium perchlorate and leading to the formation of the complex chlorate.



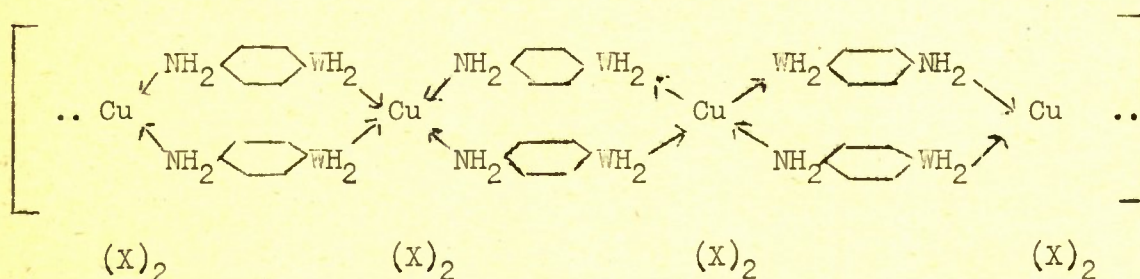
This chlorate was actually prepared and found to be exceedingly sensitive but unstable; when freshly prepared it was blue-violet in colour, but two days later it had become dark grey and after a few months at room temperature was tarry and inert. In contrast, the corresponding perchlorate (which was a lilac-coloured crystalline body) was stable for long periods at room temperature.

Some sensitivity figures for orthophenylenediamine complexes are given in Appendix I.

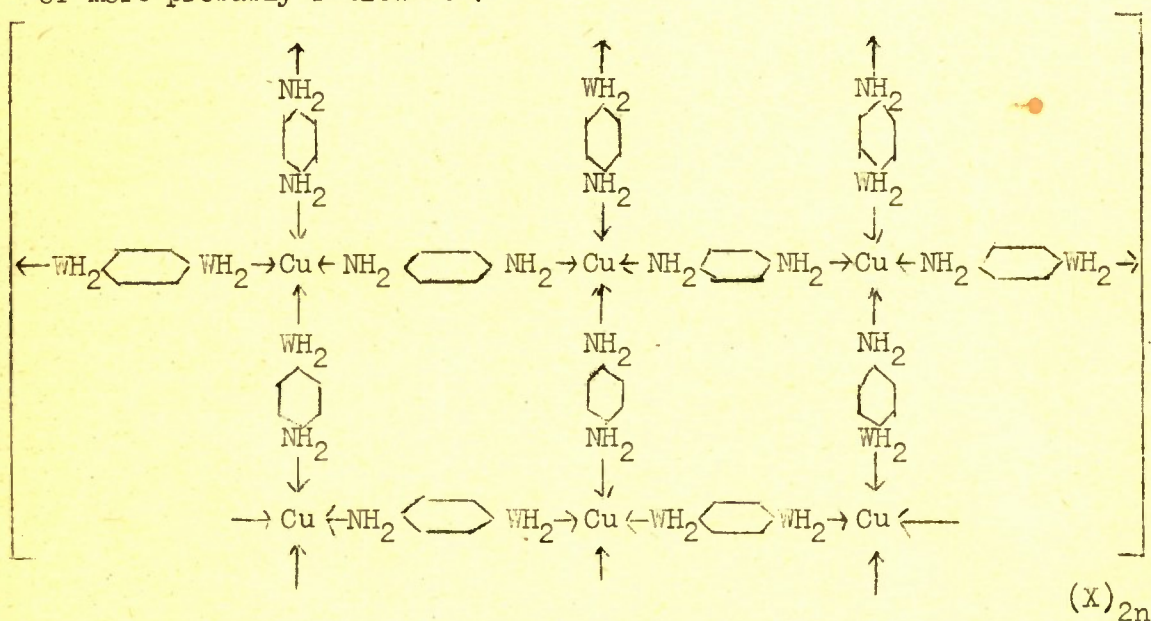
Although the orthophenylenediamine complexes had shown some promise as regards sensitivity, further work on them was abandoned owing to the above mentioned instability in the presence of chlorate and also because orthophenylenediamine is somewhat inaccessible in quantity.

4.2 Paraphenylenediamine cupric salts

The action of aqueous solutions of p-phenylenediamine on solutions of cupric salts is to precipitate an amorphous very finely divided black substance which may be a co-ordination polymer either linear:-



or more probably reticulate:-



On adding an aqueous solution of p-phenylenediamine to cupric chlorate and cupric perchlorate solutions the complex black amorphous chlorate and perchlorate respectively were obtained. Both salts deflagrated gently with a smoky flame when ignited; the chlorate was very sensitive

to impact and the perchlorate less so, but the former (like the corresponding ortho-phenylenediamino chlorate) became inert after standing at room temperature for a few months. The sensitizing ability of the amorphous complexes was poor possibly owing to their excessively large specific surface.

It was hoped that it might be possible to restrain the formation of the amorphous polymeric complexes with p-phenylenediamine by using ethylenediamine as a blocking group to prevent the extension of the chain or net, but on adding an equimolecular mixture of ethylenediamine and p-phenylenediamine to cupric perchlorate solution the black substance was at once precipitated while a portion of the copper remained in solution as purple ethylenediamine complex.

4.3 Ammino, ethylenediamino and pyridino cupric perchlorates

The following compounds are dealt with in this section.

- (a) $[\text{Py}_4 \text{ Cu}] (\text{ClO}_4)_2$
- (b) $[\text{Py}_2 \text{ en Cu}] (\text{ClO}_4)_2$
- (c) $[\text{en}_2 \text{ Cu}] (\text{ClO}_4)_2 \cdot \frac{1}{2} \text{H}_2\text{O}$
- (d) $[\text{Py}_2(\text{NH}_3)_2 \text{ Cu}] (\text{ClO}_4)_2$
- (e) $[\text{en}(\text{NH}_3)_2 \text{ Cu}] (\text{ClO}_4)_2$
- (f) $[\text{Cu en}(\text{H}_2\text{O})_2] (\text{ClO}_4)_2$
- (g) $[(\text{NH}_3)_4 \text{ Cu}] (\text{ClO}_4)_2$

of which the first two were found to be the most useful. Both are stable and readily prepared in good crystalline form; their preparation and properties are described in Appendix I, paras.1.1 and 1.2 respectively.

4.3.1 Sensitizing properties. Mixtures 300 (a) and 300 (b)

Measurements of the sensitizing power of compounds (a) and (b) in 60/40 potassium chlorate antimony sulphide mixes were made but it was found, as was anticipated from their high ignition temperatures (which lie in the region 240-250°C.), that their sensitizing ability was only moderate, being about equal to that of lead thiocyanate. It appears probable that the sensitizing properties of these compounds in mixtures containing potassium chlorate is due, at least in part, to an interface reaction between the potassium chlorate and the complex whereby a much more sensitive complex chlorate is formed. Confirmation for this view was found in the fact that if the potassium chlorate in a mixture of the complex perchlorate, potassium chlorate and antimony sulphide were replaced by potassium perchlorate the resulting mixture was very insensitive, although normally the loss in sensitivity in replacing the potassium chlorate of a sensitive mixture by potassium perchlorate is but small. The complex chlorates supposed to be formed at the potassium chlorate-complex perchlorate interfaces in the pressed mixture were actually prepared in a crystalline condition (by reaction between the complex perchlorates and potassium chlorate in aqueous solution and also directly from cupric chlorate) and found to be sensitive to impact and very soluble in water.

Although no usefully sensitive three-component mixtures were found containing (a) or (b) or (c) it was found that by incorporating 5 per cent. of tetrazene, mixtures having unusual and interesting properties could be obtained. Of such mixtures two in particular were investigated in detail, namely:

<u>Mixture 300 (a)</u>		<u>Mixture 300 (b)</u>	
Potassium chlorate (120-170 BSS)	50%	Potassium chlorate (102-170 BSS)	50%
Antimony sulphide *	35%	Antimony sulphide *	35%
Tetrapyridino cupric perchlorate (passing 120 BSS)	10%	Dipyridinoethylenediamino cupric perchlorate (passing 120 BSS)	10%
Tetrazene (passing 120 BSS)	5%	Tetrazene (passing 120 BSS)	5%
	100%		100%

* = Grist as for antimony sulphide in Q.3 primer cap compositions, i.e. 50% 120-170 B.S.S. 50% blended as for A.1 mixture. (A.1 antimony sulphide all passes 120 B.S.S. and approximately 20% is retained on 170 B.S.S.).

The proportion of copper salt used (10 per cent.) was found to be the optimum - larger proportions, i.e. 15 per cent. or 20 per cent. tended to cause "fizzling" - smaller proportions did not give maximum power.

4.3.2. Experimental results on mixtures 300 (a) and (b) in .303 inch S.A. caps

4.3.2.1. Method of filling and varnishing

Some preliminary experiments to determine the best method of filling and closing showed that a pressing load of 900 lb. with a flat ended drift gave satisfactory results and this load was adopted for all the experimental fillings described below. The normal Service load is 600 lb. but it is considered that in general a rather heavier load than this gives better results with non-fulminate mixtures.

As a preliminary, three methods of closure were tried, namely

- (a) 1 drop of varnish R.D.1198C on Colne Valley parchment paper,
- (b) 2 drops of Service shellac varnish on Service lead-tin foil and
- (c) 1 drop of R.D.1198C on Service lead-tin foil.

Sensitivity results are given in Table I, all caps having been tested in Kynoch type cases with hemispherical anvils, dimension C = 58-60 * - the most unfavourable value allowed by the Service specification.

* Dimension C is the distance in thousandths of an inch between the tip of the anvil and the outside base of the cap in the assembled round.

TABLE I

Method of closure	Sensitivity * inches/ $\frac{1}{4}$ lb.
1 drop R.D.1198C on C.V.P.	14
2 drops Service shellac on lead tin foil	> 19 (all firings irregular)
1 drop R.D.1198C on lead tin foil	> 15

On these results Colne Valley parchment paper and 1 drop of R.D.1198C was chosen as the most suitable form of closure.

4.3.2.2 The sensitivity behaviour of .303 inch caps filled with mixtures 300 (a) and (b) under adverse conditions of assembly

It is found that in .303 inch assemblies the main factor which controls the sensitivity is the value of dimension C which ranges in Service assemblies from L43 to H60; in general the smaller dimension C the greater the sensitivity. The sensitivity of Service fulminate caps for instance is greatly influenced by this dimension falling in certain cases to as much as 30 inches/ $\frac{1}{4}$ lb. and in favourable assemblies rising to about 9 inches/ $\frac{1}{4}$ lb.

It was found with some surprise that caps filled mixtures 300 (a) and 300 (b) were not only much more sensitive than Service fulminate caps over the whole range of assembly conditions but mixture 300 (b) in particular was only slightly affected by changes in dimension C; it was the first time that this behaviour had been observed. Actual results of sensitivity measurements over the whole gamut of critical assemblies are shown in the attached graph (Drg. No.A.R.D.8270) for caps filled mixtures 300 (a) and (b) together with the corresponding results for Service caps filled fulminate mixture for comparison.

Caps filled mixture 300 (a), although on the average about $5\frac{1}{2}$ inches/ $\frac{1}{4}$ lb. more sensitive than Service caps over the whole range of conditions of assembly (including eccentric as well as central strikes) are actually affected by variations in dimension C to about the same extent as Service caps, i.e. the two curves run very roughly parallel to one another. The lowest sensitivity recorded for Service caps was 30 inches/ $\frac{1}{4}$ lb. (R.L. conical anvils, eccentric strike C = 60) while the lowest sensitivity recorded for caps filled 300 (a) was 22 inches/ $\frac{1}{4}$ lb. (Kynoch hemispherical anvils, eccentric strike C = 60).

Caps filled mixture 300 (b) were found to be on an average about 5 inches/ $\frac{1}{4}$ lb. more sensitive than Service caps, but their sensitivity was very much less affected by the adverse conditions (high values of dimension C and eccentric strikes) which so seriously affect the sensitivity of Service caps. Thus the lowest sensitivity recorded for caps filled mixture

* In this report all sensitivity figures (unless otherwise stated) represent the minimum height of drop in inches of a $\frac{1}{4}$ lb. ball necessary to fire a run of 20 rounds without failure.

300 (b) was 18 inches/ $\frac{1}{4}$ lb. against the value of 30 inches/ $\frac{1}{4}$ lb. recorded for Service fulminate caps. These points are made clear to the eye in the attached graph and there is no doubt that composition 300 (b) in particular is much superior as regards sensitivity to Service fulminate mixtures in .303 inch caps; in fact this mixture is by far the most sensitive (in the filled condition) that has yet been encountered, since it has previously been difficult even to equal the sensitivity of the Service fulminate caps.

Strangely enough (but perhaps on account of the interface reaction on pressing to form an organic chlorate as mentioned above), these compositions, although very sensitive to strike in the pressed condition, are remarkably insensitive in the loose state. This is illustrated by the following Ball and Disc and Friction Test results in which the two mixtures are compared with Service A.1 mixture:

TABLE II

Composition	Ball and disc test *	Emery paper friction test *
Service A.1	2 oz./3 inches	< 3 ft./sec.
Mixture 300 (a)	‡ 8 oz/15 inches	5 ft./sec.
Mixture 300 (b)	‡ 8 oz/15 inches	7 ft./sec.

* These figures represent the strongest blows at which it is possible to obtain failure to fire in each of 10 successive trials.

* Figures obtained on the A.R.D. friction machine in which the explosive (resting on fine emery paper on a flat steel plate) receives a nearly tangential blow from a fixed boxwood wheel covered with emery paper and attached to the end of a swinging arm. The figures quoted represent the greatest tangential velocities of strike at which it is possible to obtain failure to fire in each of 10 successive trials.

4.3.2.3 Power of compositions 300 (a) and (b) in .303 inch caps. Ballistic Pendulum measurements

Ballistic pendulum measurements in which capped cases were fired from a cut-down rifle showed that volume for volume the new compositions are roughly 1.7 times as powerful as the Service fulminate composition. This result (which is not to be interpreted as implying that the ignitory power of the caps for propellants is necessarily superior to that of the Service caps) is probably due to the relatively large amounts of gas evolved by the combustion of the organic fuel in the co-ordination compound.

Some of the actual ballistic pendulum results are given in the next section dealing with Storage Trials.

4.3.2.4 Preliminary hot dry storage trials on .303 inch caps
filled mixtures 300 (a) and (b)

The two varieties of caps were subjected to a rapid hot dry storage trial side by side with Service caps at a temperature (180°F.) at which the Service caps have a useful life of only a few days. After trials sensitivity and ballistic pendulum regularity and power were measured. The results are shown in the following table.

TABLE III

Time elapsed (hours)	Mixture	Sensitivity* (inches/ $\frac{1}{4}$ lb.)	Ballistic Pendulum *	
			Power coefficient	C. of V. of trace lengths (%)
0	{ Service 300 (a)	20	1.00	6.6
		13	1.74	3.5
92	{ Service 300 (a)	>21 (all firings weak and irregular)	0.64	30.4
		13	1.70	18.5 ϕ
164	{ Service 300 (a)	>31 (all rounds "fizzled")	0.03	87.6
		12	1.70	4.7
0	{ Service 300 (b)	20	1.00	14.0
		13	1.79	7.2
336	{ Service 300 (b)	----- Caps practically inert -----		
		12 †	1.74	4.8

* All sensitivity figures in this table are for Kynoch cases, central strike, dimension C = 58 - 60.

* The rounds for ballistic pendulum work were fired in a cut-down Service rifle, the assembly being Kynoch cases, dimension C = 50-52. The power co-efficient is obtained by dividing the average trace length for 10 of the caps under trial by the average trace length for 10 Service caps. The C. of V. quoted is based on the 10 results in each instance.

ϕ A single low result occurred in this series resulting in a high C. of V. The trace lengths as measured were as follows: 8.25, 8.30, 4.55, 10.65, 9.55, 9.00, 8.46, 8.42, 8.21, 8.34 inches. The control Service caps gave the following results: 4.20, 2.60, 2.11, 4.15, 3.34, 2.71, 3.32, 4.68, 2.89, 1.42 inches.

† All paper discs bulging slightly and red dye in varnish bleached at end of this trial.

It is not possible to assess from these results the relative lives of the two new compositions as compared with the Service fulminate mixture because they resisted the severe conditions of the test so well. It will be seen, however, that after 91 hours the Service caps had deteriorated to such an extent as to seriously impair their usefulness, while after 336 hours caps filled mixture 300 (b) were actually slightly better in regard to sensitivity and regularity than they were when the trial started and in power were unchanged. The trials with mixture 300 (a), although they did not continue for so long as those with 300 (b), did not reveal any deterioration except for 1 wild round which had the effect of increasing the C. of V. to 18.5 per cent. for the caps which had been on trial for 92 hours.

4.3.2.5 The stability of mixtures 300 (a) and 300 (b) under hot moist conditions

Storage trials of the compositions under hot moist conditions were unfortunately not so encouraging as those under hot dry conditions.

The loose compositions were exposed to moist atmospheres at 115°F. and the percentage loss in weight determined, the compositions being dried in each case before the final weighing. The results are shown in tabular form below.

TABLE III(a)

Mixture	Relative humidity (per cent.)	Duration of trial (days)	Loss in Weight (per cent.)
300 (a)	75	18	4.2
300 (a)	100	7	5.0
300 (b)	75	18	2.8
300 (b)	100	4	3.8
300 (b)	100	11	4.4

.303 inch S.A. caps filled mixtures 300 (a) and 300 (b) were also tested under hot moist conditions; after 2 days at 115°F. and a relative humidity of 75 per cent. the foils were bulging, indicating that a certain amount of gas had been evolved from the compositions - an effect which had also been observed in the dry trial with mixture 300 (b) after 336 hours at 180°F. (see Table III). The moist trial of the filled caps was, however, continued for a total time of one month at 115°F. and 75 per cent. relative humidity and at the end of this time all the caps fired satisfactorily in the "weak" rifle.

A possible explanation of the evolution of gas from these mixtures on moist storage is that the tetrazene (a diazo body) is decomposed catalytically by the copper salts giving nitrogen and complex bases which co-ordinate with the copper and displace pyridine. Although it was shewn (vide Appendix I, paras. 1.1 and 1.2) that disengagement of pyridine did not take place when the complex perchlorates were stored alone at 120°F. and 100 per cent. relative humidity for long periods, there is evidence that this may take place when the compositions themselves are stored at high humidities. Even if rustlessness were no longer a Service requirement it is considered that the deleterious effects which pyridine might have on propellants in contact with the caps would preclude the present mixtures from being recommended for Service, at least until much more extended trials had been carried out.

4.3.3.1 Sensitivity trials of 20 mm. caps filled mixtures 300 (a) and 300 (b)

20 mm. caps were filled to the Service dimensions with mixtures 300 (a) and 300 (b) using a Service type pipped drift and a pressing load of 1200 lb. The caps were disced with Colne Valley parchment paper and varnished with two drops of R.D.1198C. Sensitivity results on the caps

assembled into Hispano cases (dimension C = 105) are shown in Table IV below, together with results for Service caps filled A.1 mixture under the same conditions of assembly, which are actually the most unfavourable allowed by the Service specification.

TABLE IV

Caps	Sensitivity (inches/l lb.
Filled mixture 300(a)	17
Filled mixture 300(b)	18
Service, filled A.1 mixture	22

Both the new mixtures are seen to be superior in sensitivity to the fulminate mixture.

4.3.3.2 Gun trials of caps filled mixtures 300 (a) and 300 (b) in 20 mm. Oerlikon gun

20 mm. caps filled as described above with the two compositions were forwarded to C.S.A.R., Swynnerton who fired them in a 20 mm. Oerlikon gun at normal temperature and at -40°F. His results for recoil and clearance between breach block and gun body were as follows:

Gun S 40085 Age 372 rounds
 Barrel B 15900 " " "
 Ammunition:- 20 mm. Oerlikon ball filled 435 grs. MA1222
 Type A ... caps filled mixture 300 (a)
 Type B ... caps filled mixture 300 (b)

TABLE V

Amm.	T°F.	Recoils beyond sear in order (mm.) *	Recoil		Rate of fire (rounds per min.)
			High	Low	
A	normal	[50.0, 37.0, 44.0, 42.0, 44.5] [50.5, 34.5, 44.0] [52.0, 34.5, 45.5, 41.5] [51.5, 33.0, 46.0, 41.0, 43.5, 42.5 42.5, 42.0, 43.5, 40.5, 43.5 42.5, 44.0]	52.0	33.0	462 459
A	-40	[50.0, 44.0, 36.0] [47.0, 33.5, 42.0] [47.0, 26.5, 43.5] [47.5, 27.5, 42.0, 34.0, 38.5 40.0, 37.5, 38.0, 40.5, 40.0 37.5, 40.5, 53.5]	53.5	26.5	416
B	normal	[51.5, 35.5, 46.0] [50.5, 37.5, 43.5] [51.5, 33.5, 47.5,] [51.0, 37.5, 44.0] [51.0, 34.5, 46.0, 41.0, 45.5, 41.5, 45.0, 41.5, 43.5, 40.0, 44.5, 42.0, 45.0] [47.5, 26.5, 42.5]	51.5	33.5	456
B	-40	[47.5, 18.5, 46.5] [48.5, 26.5, 42.5] [49.0, 24.0, 42.5, 36.5, 39.5, 37.5, 38.5, 39.0, 39.5, 36.5, 38.0, 35.5, 39.5]	49.0	18.5	417

* Square brackets indicate the beginning and end of bursts of automatic fire.

TABLE VI

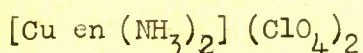
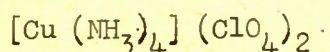
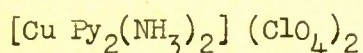
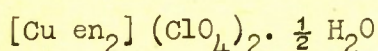
Double loading stop marks*
(mm. from base of case)

Ammunition	Temp. °F.	High	Low	Mean
A	Normal	61.5	57.0	58.8
A	-40	58.0	53.0	55.7
B	Normal	60.5	57.5	59.0
B	-40	58.0	54.0	55.5
Service (typical)	Normal	62.0		61.0
"	-40	61.5	54.0	60.5

* The difference between 48 mm. and the distance of the double loading stop mark from the base of the case gives the clearance between the breach block and the gun body; the greater the clearance the better.

4.3.4 Functioning tests on the analogues of mixtures 300 (a) and (b) with different co-ordinating groups

The following compounds were prepared and made up into mixtures analogous to mixtures 300 (a) and (b):



The grists and proportions were the same as in 300 (a) and (b) but the 10 per cent. of tetrapyridino and diethylenediaminodipyridino salts were replaced by 10 per cent. of one of the salts above listed. Sensitivity and Power tests were done on all four compositions in .303 inch caps under the same conditions as those under which caps filled mixtures 300 (a) and (b) had been tested and the results are shown in the following table:

TABLE VII

Copper salt used in cap composition type 300	Sensitivity* inch/ $\frac{1}{4}$ lb.	Power coefficient	C. of V. of Ball. Pend. trace lengths
1. $[\text{Cu en}_2] (\text{ClO}_4)_2 \cdot \frac{1}{2} \text{H}_2\text{O}$	> 17	1.5	11.8%
2. $[\text{Cu Py}_2(\text{NH}_3)_2] (\text{ClO}_4)_2$	11	1.4	10.7%
3. $[\text{Cu}(\text{NH}_3)_4] (\text{ClO}_4)_2$	13	1.4	12.0%
4. $[\text{Cu en}(\text{NH}_3)_2] (\text{ClO}_4)_2$	15	1.4	13.6%
Service caps filled fulminate mixture	20	1.0	13.6%

* Kynoch cases; dimension C = 58 - 60.

These compositions appear to have no advantages over 300 (a) or (b) and some disadvantages. The diethylenediamino salt is excessively soluble in water and generally inconvenient to handle besides giving rather poor sensitivity relative to the other mixtures. The amino perchlorates are in general less well defined and more soluble than the pyridino or ethylenediamino salts and in general perhaps ammonia compounds are best avoided in cap compositions.

The preparation and properties of the complex salts mentioned in Section 4 are given in Appendix I.

4.4 Attempts to develop rustless cap compositions based on complex cupric perchlorates

It was not found possible to achieve any useful degree of sensitivity by replacing the chlorate in mixtures of the type of 300 (a) and 300 (b) by barium nitrate, in fact most such mixtures appeared to be quite inert. Since, however, according to the theories of cap sensitivity put forward in A.R.D. Expl. Report No. 373/43, a factor controlling the effect on sensitivity of any ingredient of a cap composition is the relative surface area of that ingredient present, it seemed possible that a fairly sensitive non-rusting mixture might be made by starting with a mixture of the type of 300 (b) and reducing the amount of potassium chlorate from about 50 per cent. to about 10 per cent. but compensating for the lesser quantity by increasing the specific surface. It was then proposed to make up the deficiency in oxygen by adding a suitable amount of coarse potassium nitrate, and to neutralize the rusting characteristics of the reduced amount of halogen present by replacing the antimony sulphide by lead hypophosphite.

Corrosion experiments in which various experimental caps were fired at mild steel discs which were then stored at room temperature at 100 per cent. R.H. showed that the phosphate present in the products of combustion of cap compositions of this type did in fact reduce the corrosion to negligible proportions relative to ordinary Service caps, although the results were not so good as with the completely halogen-free VH2 mixture*.

Several mixtures were tried containing various proportions of tetrapyridino cupric perchlorate (or dipyridinoethylenediamino cupric perchlorate), tetrazene, lead hypophosphite, potassium nitrate with 10 per cent. of fine potassium chlorate, but all showed a tendency to "fizzle". Somewhat unexpectedly it was found that the addition of ground glass in substantial amounts to the most promising mixtures reduced the tendency to "fizzle" - the optimum addition appeared to be 20 per cent. which is an unprecedentedly large amount. Actual firing results with increasing proportions of ground glass are shown in the table below:

* Other experiments on similar lines have shown that the presence or absence of chlorate is the sole factor controlling rusting properties; calcium silicide, antimony sulphide, barium nitrate and potassium nitrate single or in various combinations have no appreciable effect one way or the other on rusting properties, neither does substitution of barium chlorate for potassium chlorate.

TABLE VIII

Composition (per cent.)						Firing results in "weak" rifle *
[Cu en Py] (ClO ₄) ₂ passing 120 BSS	Tetrazene passing 120 BSS	Potassium chlorate passing 300 BSS	Lead hypo- phosphite 120-180 BSS	Potassium nitrate 120-180 BSS	Ground glass (as for Q.F. mixture)	
10	5	10	50	25	0	13F2F*
10	5	10	45	25	5	24F2F*
10	5	10	40	25	10	26FF*
10	5	10	35	25	15	25F
10	5	10	30	25	20	27F

* All caps were pressed at 1000 lb. dead load, disced with Colne Valley parchment paper and left unvarnished. They were fired in the most unfavourable assembly (Kynoch anvils C = 59 - 60) in a "weak" rifle representing the worst Service conditions for strength of blow, eccentricity of strike, etc.

F = satisfactory firing. F* = fired but "fizzled"

The last composition in the table, being the most promising, was given a more extended trial, the caps this time being varnished with one drop of varnish R.D.1198C. The sensitivity results in various assemblies together with the sensitivity of Service caps under the same conditions for comparison are shown in the following table:

TABLE IX

	Assembly and Strike (Kynoch cases)		
	C = 58 - 60 Central strike	C = 51 - 53 Central strike	C = 58 - 60 Eccentric strike
Hypophosphite caps	> 25 inch/ $\frac{1}{4}$ lb.*	16 inch/ $\frac{1}{4}$ lb.	27 inch/ $\frac{1}{4}$ lb.
Service caps	20 "	12 "	24 "

* 8 firings and 1 "fizzle" in "weak" rifle.

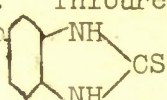
As might be expected from the large proportion of ground glass there was some tendency to press explosions and one cap fired in the press during the pressing of 130.

Although this mixture is less sensitive than the present Service mixture and probably not sensitive enough to be of practical use it is possible that further work on similar lines might lead to a satisfactory rustless mixture sensitized in part by small amounts of finely divided chlorate.

5.0 Complex cuprous salts having co-ordinating groups containing divalent sulphur

5.1 Introduction

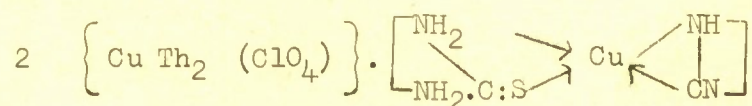
Since sulphur is one of the best sensitizers of chlorate cap compositions it appeared to be of interest to construct some compounds having both divalent sulphur and chlorate (or perchlorate) in the same molecule.

It is a remarkable fact that if certain compounds containing divalent doubly bonded sulphur atoms are brought into contact with a cupric salt immediate reduction of the cupric ion to the cuprous state takes place, followed by the co-ordination of the thio body with the cuprous ion. The colourless complex formed is usually very stable to acids but decomposed by alkalis with the formation of copper sulphide. Thiourea (Th), ethylene-thiourea (etu), $\text{CH}_2\text{NH} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{CS}$ CH_2NH o-phenylenethiourea  and even sodium

thiosulphate behave in this way with cupric salts. The reactions taking place and the products formed are complex and often binuclear - for instance from copper sulphate and thiourea the compound $[\text{Cu Th}_3] [\text{Cu Th}_2(\text{H}_2\text{O})] (\text{SO}_4) + \text{H}_2\text{O}$ is reported in the literature to be formed. A curious property of many of the cuprous thiourea complexes is that on dissolving them in hot water they come out on cooling in the form of oily droplets which crystallize slowly.

5.2 The cuprous complex formed from cupric perchlorate and thiourea.

By the interaction of 1 mol. of cupric perchlorate and 2 mols. of thiourea in water a total yield (calculated on the perchlorate) of 57% of a white crystalline body, moderately soluble in water was obtained, which on ignition burned very vigorously with a dark red flame and had outstanding sensitizing properties for 60/40 chlorate-sulphide mixtures. It was not possible to obtain this substance from cuprous salts, as for instance by dissolving a mixture of cuprous oxide and thiourea in perchloric acid, by treating $[\text{CuTh}_3] \text{Cl}$ with perchloric acid nor by dissolving copper powder in dilute perchloric acid containing thiourea. Analysis of the body for Cu, ClO_4 , N and S showed that it contained 12 atoms of nitrogen to 5 of sulphur thus making it impossible to formulate it as a simple thiourea complex. The most probable structure assigned to it on the analytical results was the following:-



the second and unionized nucleus being a thiourea complex of cuprous cyanamide formed by the abstraction of H_2S from the thiourea. Although the sensitizing properties of the complex for chlorate mixtures were comparable with those of tetrazene, work on this substance was discontinued when it was found that chlorate mixtures containing it were not very stable. There was a marked decomposition and blackening of the originally white complex after a few days' storage at 120°F and 75% R.H. of mixtures of it with potassium chlorate and antimony sulphide.

5.3 Cuprous chlorate thiourea complexes

As a matter of interest an attempt was made to prepare a chlorate analagous to the perchlorate described in paragraph 5.2. By adding thiourea to an aqueous solution of cupric chlorate a white crystalline salt was obtained which was excessively sensitive to impact and when placed on a surface at 106°C. exploded at once with a loud report. .303 inch caps filled with the salt alone could be fired in a Service rifle (cp. Appendix I paragraph 1.9). The unusually low ignition temperature of this body is probably the explanation of both the instability of chlorate mixtures containing the corresponding perchlorate and of the excellent sensitizing properties of the perchlorate (cp. paragraphs 4.1 and 4.3.1).

5.4 Miscellaneous thio complexes

Complex cuprous perchlorates were made from *o*-phenylenethiourea and ethylene thiourea but only cursorily examined. They were white crystalline bodies, sparingly soluble in cold water but more soluble in hot from which they separated in the form of oily droplets which slowly crystallized to felted or cheesy masses. Both the ethylene and the *o*-phenylene complexes were almost completely insensitive to steel-to-steel impact and when ignited they smouldered away leaving much black ash.

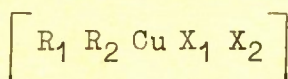
By adding 4 mols. of thiourea to one of lead perchlorate in hot water a beautifully crystalline complex was obtained. It was not a very good sensitizer of potassium chlorate-antimony sulphide mixtures and was not further investigated. (Some further thiourea cuprous salts of rather special type are described in paragraph 6.3.4 below).

6.0 Non-ionized copper complexes

6.1 Introduction

There are certain ionic groups with potentially useful explosive properties which have a co-ordination affinity for copper and thus permit non-ionized copper complexes with explosive or sensitizing properties to be prepared. Among such groups are the following:-

thiocyanato, nitrito, azido, and (as emerged during the work) picrato and styphnato, all of which yield with cupric copper unionized and generally very insoluble complexes of the general form:



where R_1 and R_2 are neutral co-ordinating groups and X_1 and X_2 ionic co-ordinating groups with unit charge. The normal ionized cupric co-ordination compounds are, as is well known, generally intense blue to violet in colour, and the unionized bodies are readily distinguished from them not only by their insolubility but by their greenish hue which varies from a vivid green (e.g. the precipitate produced in the well known pyridine thiocyanate test for copper) to a dark olive green. Exceptions are ethylenediaminedipicrate copper, which is buff-coloured, and the hydrazine body, which is yellow. A further characteristic of this class of compound is the tendency to form surface skins on water similar to that formed by nickel dimethylglyoxime.

6.2 Attempts to make complex azides which are resistant to hydrolysis

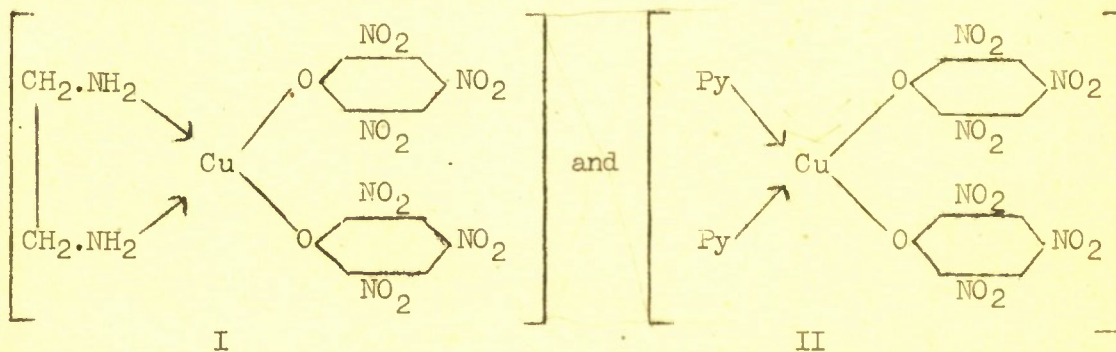
Lead azide and even copper azide are fairly readily hydrolysed under conditions of high humidity giving hydrazoic acid; thus, lead azide in contact with or near copper is liable to give rise to very dangerous corrosions of copper azide on the copper, a fact which renders the use of normal ionic azides undesirable in cap compositions. It was hoped that by actual co-ordination of the azido group in a non-ionic complex its resistance to hydrolysis might be increased owing to the firmer binding of the azido group and thus enable the explosive properties of this group to be used in caps. Actually, however, it was found that the non-ionic complex copper azides for example dipyridinediazide copper yielded up their azide under moist conditions about as readily as copper azide itself, the only difference being that the pyridine as well as the azide disengaged itself with the result that the original compound was built up again as a corrosion on a piece of bright copper suspended over dipyridinediazide copper in a moist atmosphere. This new type of corrosion, although not as powerful nor probably as sensitive, as ordinary copper azide, was nevertheless objectionable. On heating in a flame a piece of copper corroded in this way there was only a slight flash and not the shattering crack which would have resulted from the same amount of normal copper azide; much azide radicle was, however, detected chemically in the corrosion.

Although hydrazoic acid disengaged itself fairly readily from the complex copper azides it was possible to prepare a complex ethylenediamine cobaltic azide (see Appendix 4.0) which did not liberate any detectable amount of hydrazoic acid during 60 hours at 120°F. 100% R.H. Owing to lack of time this substance was only cursorily examined but further work on it might have useful results.

6.3 Complex copper picrates and styphnates

6.3.1 General

When a dilute solution of a co-ordinating base is added to a dilute solution of cupric picrate an extremely insoluble complex is precipitated; with ammonia the precipitate is a dirty yellowish green and is amorphous,* with ethylenediamine it is flesh or buff coloured and can, by careful precipitation from boiling solutions, be obtained as crystalline plates; with hydrazine the precipitate is amorphous and yellow in colour while with pyridine it is a bright green. Special attention was given to the complexes derived from ethylenediamine and from pyridine since they were fairly readily obtained in a crystalline condition. Their compositions were found to agree with the following structures:-



*The formation of this body has been proposed (A. Zacharov, J. Appl. Chem. Russia 1933, 6, 998; A 1934, 40) as a method for estimating picric acid but analogues with co-ordinating bases other than ammonia do not appear to have been previously reported.

in which the picrate ion functions as a co-ordinating group. It does not appear to have been previously recorded that the picrate ion has this property. A very insoluble green compound similar to II was also obtained by the action of pyridine on copper styphnate solution and obtained (with some difficulty owing to its very sparing solubility) in a crystalline form (see paragraph 7.3.3 below).

I is in many ways an anomalous body - its colour for instance is buff or flesh coloured while most of the other complexes of supposed similar structures are dark green in colour, and on ignition it deflagrates much more mildly than II although it does not contain such an excessive amount of fuel. Since the sensitizing properties of I were negligible and mixtures containing more than about 5% of it "fizzled" badly, further work on it was abandoned.

6.3.2 Caps compositions based on Dipyridinodipicrate copper ("Pypicu")

This picrate was found to be quite a good sensitizer of chlorate-antimony sulphide mixtures alone and without the aid of any tetrazene. Several mixtures containing it were tried in .303 inch S.A. caps but the most satisfactory was found to be the following:-

Mixture "Pypicu 10"

Dipyridinodipicrate copper	10%
Potassium chlorate (as for A.1 mixture)	54%
Antimony sulphide (as for Q.3 mixture)	36%

Time did not permit a complete investigation of the sensitivity over the whole range of critical assemblies as had been done with caps filled mixtures 300 (a) and (b), but the determinations which were carried out (shown in the table below) indicate that on the average caps filled "pypicu 10" are more sensitive than the present Service caps although not quite as sensitive as caps filled mixtures 300 (a) and (b). Climatic trials and power measurements have not yet been done; the power appeared to be good judged by auditory standards and the flash was strong.

TABLE X

Showing the sensitivity of .303 inch caps filled mixture
Pypicu 10, pressed at 1000 lb. dead load, disced Colne
Valley Parchment paper and varnished with 1 drop of varnish
R.D. 1198

Conditions of Assembly			Sensitivity *	
Dimension C	Type of anvil	Blow	Service caps	Caps filled Pypicu 10
44	Kynoch	Central	11	15
51	"	"	12	12
59	"	"	20	15
59	R.L.	"	22	15
59	Kynoch	Eccentric	24 - 25	23

* = minimum height of fall of $\frac{1}{4}$ lb. ball required to fire 20-25 rounds successively without failure.

6.3.3 Sensitizing properties of Dipyridinostyphnate copper

This body is not nearly such a good sensitizer as the corresponding picrate; the composition obtained by replacing picrate in mixture "pypicu 10" by the styphnate had a sensitivity greater than 17 inch/ $\frac{1}{4}$ lb. in unvarnished caps compared with 14 inches/ $\frac{1}{4}$ lb. for "pypicu 10" (Kynoch anvils, central strike C = 59).

The sensitizing power of an ammonia - pyridine - styphnate copper complex prepared was even less than that of the simple pyridine derivative. The sensitivity under the conditions mentioned above was greater than 23 inches/ $\frac{1}{4}$ lb.

6.3.4 Thiourea cuprous picrate complexes. Development of a sensitive mixture containing dipyridinostyphnate copper and thiourea cuprous picrate

The addition of a soluble picrate to a solution of trithiourea cuprous chloride results in the formation of a sparingly soluble and stable complex probably best formulated as dithiourea picrate copper. It was hoped that it would be a better sensitizer of chlorate mixtures than dipyridinodipicrate copper because it contains divalent sulphur in addition to picrate. As initially precipitated this body forms brick red needles and is anhydrous but on re-crystallization from aqueous thiourea it appears in the form of very dark garnet-red free-flowing tablets of a monohydrate. On the whole the anhydrous form appeared to give the better results in .303 inch caps. It was a moderately good sensitizer, for instance, 9 parts of a 60/40 potassium chlorate-antimony sulphide mixed with 1 part of the complex gave a sensitivity of 11 inches/ $\frac{1}{4}$ lb. in .303 inch caps (pressing load 1000 lb., disc - Colne Valley Parchment paper, varnish - nil, anvil - Kynoch, C = 58-60). Although the sensitizing effect was promising the firings sounded rather irregular and variable, which is a sign of incipient "fizzling". Attempts were made to offset this effect by the addition of dipyridinostyphnate copper; calling the later body A for the time being, and the pseudomorphous form (see Appendix 2.2) of the thiourea cuprous picrate complex B, the following mixtures were tested:

1.	A	10	2.	A	10	3.	A	5
	B	5		B	10		B	10
	KClO ₃ (.1)	51		KClO ₃ (.1)	48		KClO ₃ (.1)	51
	Sb ₂ S ₃ (.3)	34		Sb ₂ S ₃ (.3)	32		Sb ₂ S ₃ (.3)	34

Mixture 1. gave the most promising results.

2. tended to fizzle more than the original mixture containing 10 of B alone although, if a "fizzle" were counted as a success, it was fairly sensitive.

3. did not fizzle but was about 2 inches/ $\frac{1}{4}$ lb. less sensitive than 1.

The sensitivity characteristics of mixture (1) were therefore examined in more detail in various unfavourable assemblies with the results shown in the table below.

TABLE XI

Conditions of Assembly and strike			Sensitivity (inches/ $\frac{1}{4}$ lb)	
Anvils	Strike	Dimension C	Caps filled mixture (1) ϕ	Service Caps
Kynceh	Central	43 - 45	13	11
"	"	51 - 53	12	12
"	"	58 - 60	19	20
"	Eccentric*	58 - 60	22	24
R.L.	Central	58 - 60	18	22

* Blow 0.026 inches off centre.

ϕ Pressing load 1000 lb. disced Colne Valley Parchment Paper, varnished 1 drop R.D. 1198C.

Except for the favourable assembly Ky. C = 43 - 45 the caps filled mixture (1) are more sensitive than the Service caps.

In point of time the above results are the latest dealt with in this report and at this stage the work unfortunately had to be broken off but it is considered that it might be worth while investigating the above composition further when opportunity offers.

6.4 Dipyridinodithiocyanato copper

The well known complex dipyridinodithiocyanato copper $[\text{Py}_2\text{Cu}(\text{SCN})_2]$ which is used for the estimation of copper is normally obtained as a bright green amorphous powder, but it may be obtained in the form of dark green compact crystals by slow evaporation of ammonia from its solution in aqueous ammonia. The complex has moderately good sensitizing power for chlorate mixtures being about as good as lead thiocyanate for addition of between 5 and 10 per cent to 60/40 potassium chlorate antimony sulphide mixture. (Maximum degree of sensitization = 6 inch/lb.)*

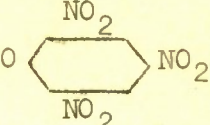
6.5 Dipyridinodinitro copper

This complex $[\text{Py}_2\text{Cu}(\text{NO}_2)_2]$ may be obtained in good yield in the form of dark green free-flowing crystals by treating a solution of copper sulphate with the calculated amounts of pyridine and sodium nitrite. It is not a very good sensitizer of chlorate mixtures and the compositions fire rather weakly and erratically.

*See Appendix II.

6.6 Miscellaneous unionized pyridine copper complexes

Since the azide, nitrite and picrate ions can co-ordinate with copper the possibility arises of making the following interesting compounds.

- I. $[\text{Py}_2\text{Cu}(\text{NO}_2)(\text{Pi})]$
II. $[\text{Py}_2\text{Cu}(\text{N}_3)_2]$
III. $[\text{Py}_2\text{Cu}(\text{N}_3)(\text{Pi})]$
IV. $[\text{Py}_2\text{Cu}(\text{N}_3)(\text{NO}_2)]$
- Pi = 

The general method of preparing them is to add as required the calculated amounts of sodium nitrite, azide or picrate in aqueous solution together with the calculated amount of pyridine to the calculated amount of aqueous copper sulphate.

In preparing II there is serious risk of obtaining either copper azide itself or a product containing free copper azide. It has previously been described in the literature. In contrast to copper azide II is insensitive to impact but is violent when ignited. It was obtained as a dark brownish green powder.

III, the double azide-picrate is a dark green crystalline body, extremely sensitive to impact and very violent.

IV is interesting owing to the possibility of the mutual destruction of the azido and nitrito groups. It is a dark greenish brown body which dissolves with effervescence in dilute acetic acid.

APPENDIX I

Preparation and properties of the more important complex salts mentioned in the report

1.0 Complex cupric chlorates and perchlorates

1.1 Tetrapyridino cupric perchlorate $[\text{CuPy}_4](\text{ClO}_4)_2$

Preparation. This salt may be made by the action of pyridine on an aqueous solution of cupric perchlorate or more expeditiously from copper sulphate, ammonium perchlorate and pyridine. 12.5 grs. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 11.75 grs. of ammonium perchlorate were dissolved in 100 cc water and added dropwise during half an hour and with vigorous stirring to 100 cc water containing 15.8 grs. pyridine. The blue crystals (21 grs.) were filtered off and washed in water followed by alcohol. Yield 73%. Found Cu 10.8%, $[\text{Cu}(\text{C}_5\text{H}_5\text{N})_4](\text{ClO}_4)_2$ requires 10.9%. The salt forms lilac blue lozenge shaped tablets similar in shape to mercury fulminate crystals.

Solubility. Very sparingly soluble in cold water, more soluble in hot water and may be recrystallised from hot water.

Ignition Temperature.* 254°C. (mild explosion with secondary pop).

Behaviour on Ignition. Melts to a black liquid which deflagrates spasmodically.

Sensitizing power for 60/40 pot. chlorate-antimony sulphide. The maximum increase in sensitivity was 7 inches/1 lb. produced by the addition of 10% of the complex.[/]

Sensitivity. Can be fired only with difficulty by impact between steel hammer and anvil and then only partial firing is obtained.

Stability. A sample was kept at 120°F. 100% R.H. for 6 months without any apparent change. A piece of red litmus paper kept in the bottle during this test did not go blue and there was no smell of pyridine. (For stability of mixture 300 (a) see paragraphs 4.3.2.4. and 4.3.2.5 of report).

Miscellaneous. On treatment with the equivalent amount of an aqueous solution of potassium chlorate, KClO_4 is precipitated and the corresponding chlorate may be isolated from the mother liquor in the form of violet needles which are very soluble in water and very sensitive to impact.

1.2 Dipyridinoethylenediamino cupric perchlorate. $[\text{CuPy}_2\text{en}](\text{ClO}_4)_2$

This salt is most conveniently prepared from copper sulphate, ammonium perchlorate, ethylene diamine and pyridine, but may also be made direct from cupric perchlorate. To a cold solution of 25 grs. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

*Unless otherwise stated all Ignition Temperatures quoted in this report have been determined by the A.R.D. slow heating method (temperature rise 50°C. per minute).

[/]See Appendix II.

(1 mol) in 100 cc. water was added 16 grs. of pyridine (2 mols) and 6.0 grms. of ethylenediamine (1 mol.). The resultant deep blue solution was added dropwise during half an hour and with vigorous stirring to a nearly saturated cold aqueous solution of 26 grms. (2.3 mols.) of ammonium perchlorate. The resultant deep blue crystals (41 grms; 85% yield) were filtered off and washed with the minimum amount of cold water followed by alcohol. Approximately half of the total quantity of the complex obtained was retained on a 120 B.S.S. sieve. Found Cu, 13.1, 13.5% $[\text{Cu}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)(\text{C}_5\text{H}_5\text{N})_2](\text{ClO}_4)_2$ requires 13.24% Cu. The salt forms purplish-blue rectangular tablets which tend to form aggregates.

Solubility. 100 ml. of a saturated aqueous solution of the salt at 20°C. contains 0.55 grams. The salt is much more soluble in hot water and may readily be re-crystallised from it.

Ignition Temperature. 238°C. (violent explosion)

Behaviour on Ignition. Deflagrates with moderate vigour.

Sensitivity. Can be fired by impact of a steel hammer on a steel anvil only with difficulty; ignition does not spread to the whole mass.

Stability. A sample was kept at 120°F. 100% R.H. for 6 months without any apparent change. A piece of litmus red paper kept in the bottle did not go blue and there was no smell of pyridine. There was no loss in weight on prolonged heating at 50°C.

1.3 Diethylenediamino cupric perchlorate $[\text{Cu en}_2](\text{ClO}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$.

This salt is best made by treating cupric perchlorate with the calculated amount of ethylenediamine. 3.18 grams (1 atom) of copper in the form of $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ was dissolved in the minimum amount (approximately 10 cc.) of hot 60% perchloric acid. On cooling, 20 cc. of alcohol was added to the solution of cupric perchlorate followed by 6 grams. of ethylenediamine (2 mols) in the form of its dihydrate dissolved in 20 cc. alcohol. The purple red solution deposited 13.5 grams (70% yield) of mauve needles which were washed with 95% alcohol; a further crop was obtained by evaporation of the mother liquor. Found Cu 16.31% $[\text{Cu}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2](\text{ClO}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ requires 16.23% Cu.

The salt forms purplish-red needles or reddish blue fibrous tablets which are very soluble in water but less so in alcohol. At 22°C 100 ml. of a saturated aqueous solution contains 12.7 grams.

Ignition Temperature. 251°C. with violent explosion.

Behaviour on ignition. Deflagrates with some violence in the loose state; if pressed in pellet form and ignited by a fuze, the pellet, deflagrates as long as it is in contact with the hot surface of the fuze but is extinguished as soon as the fuze is removed.

Sensitivity. Can be fired by impact between steel hammer and anvil but not readily and the ignition does not communicate to the whole mass.

Stability. Probably very stable.

By treatment of an aqueous solution of the perchlorate with the calculated amount of potassium chlorate or by direct reaction between ethylenediamine and cupric chlorate the corresponding chlorate is obtained on slow evaporation in the form of Egyptian blue crystals, very soluble in water.

Ignition temperature. 170°C.

Behaviour on Ignition. Exploded with loud bang.

Sensitivity. A very light blow (steel to steel) caused a loud explosion.

Ball and Disc Test.* 5 inches/4 oz. 0% point.

Emery Friction Test.* 5 ft./sec. 0% point.

Although very sensitive it was not sufficiently so to function as a single-ingredient cap composition; .303 inch caps containing a charge of the neat salt pressed at 800 lb. and not varnished could not be fired in a Service rifle under the most favourable conditions of assembly.

1.4 Dipyridinodiammino cupric perchlorate $[\text{CyPy}_2(\text{NH}_3)_2] (\text{ClO}_4)_2$

A fairly concentrated aqueous solution of cupric perchlorate was divided into two equal portions; to the first aqueous ammonia was added dropwise till the precipitate of cupric hydroxide just dissolved. The solution was then warmed gently and the other portion of cupric perchlorate was added, the resultant precipitate being taken up by the dropwise addition of pyridine. On cooling, a crop of blue hexagonal crystals was obtained. (Found Cu 12.2% $[\text{Cu}(\text{C}_5\text{H}_5\text{N})_2(\text{NH}_3)_2] (\text{ClO}_4)_2$ requires 14.0%).

On evaporation of the mother liquor a crop of large blue cubical crystals, similar in shape to those of potassium bromide, with re-entrant faces was obtained (Found Cu 14.08%, required 14.0%).

The salt is moderately soluble in water but is unstable in hot water, readily yielding a precipitate of copper hydroxide. On ignition the salt deflagrates with moderate violence.

1.5 Ethylenediaminodiammino cupric perchlorate $[\text{Cu en} (\text{NH}_3)_2] (\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$

This salt was prepared by adding the calculated quantity of ethylenediamine together with a slight excess of aqueous ammonia to a strong solution of cupric perchlorate and precipitating by the addition of alcohol. (Found 16.26% Cu $[\text{Cu} (\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)(\text{NH}_3)_2] (\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ requires 16.19% Cu.) Long reddish purple needles, moderately soluble in water. On ignition burns vigorously.

*See paragraph 4.3.2.2. of report.

1.6 Cuprammonium perchlorate $[\text{Cu}(\text{NH}_3)_4] (\text{ClO}_4)_2$

This salt was made by adding aqueous ammonia dropwise to a fairly concentrated solution of cupric perchlorate till the precipitate just dissolved; an equal volume of alcohol was then added to the clear blue solution, then a large excess of .880 ammonia. A vivid blue crystalline precipitate of a higher ammino perchlorate was formed and filtered off. On drying at 100°C . it lost ammonia and became dull violet-blue in colour and granular in appearance. The salt crystallised from water in rectangular tablets or octahedra. (Found Cu. 19.9% $[\text{Cu}(\text{NH}_3)_4] (\text{ClO}_4)_2$ requires 19.2% Cu.). On ignition the salt burned with moderate vigour.

1.7 Di-o-phenylenediamino cupric perchlorate

2.5 grams. of $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (= 1 atom Cu) was dissolved in the minimum amount of hot 60% perchloric acid and on cooling a saturated aqueous solution containing 4.32 grams of o-phenylenediamine was added. 8.6 grams of purple platy crystals of the complex perchlorate were filtered off and washed with a small volume of water. (Found Cu 14.1%; $\text{C}_{12}\text{H}_{16}\text{O}_8\text{N}_4\text{Cl}_2\text{Cu}$ requires 13.3% Cu).

The salt is sparingly soluble in cold water; it still retained its purple colour after a year's storage at room temperature showing that no appreciable oxidation of the o-phenylenediamine had taken place.

Ignition Temperature. 268°C .

Behaviour on ignition. "Popped" gently giving much black smoke and a "phenolic" smell.

Sensitivity. Can easily be fired by impact between steel hammer and anvil.

Ball & Disc Test.* 0% point = 4 inches/8 oz.

Friction Test.* 0% point = 4 ft./sec.

Sensitizing power for 60/40 potassium chlorate - antimony sulphide mixture - is an excellent sensitizer but the compositions are somewhat unstable.

1.8 Di-o-phenylenediamino cupric chlorate

2.16 gram (2/100 mol.) o-phenylenediamine dissolved in 20 cc. of warm alcohol was added to 1/100 mol. cupric chlorate dissolved in 10 cc. water. 3 grams of purple plates crystallised out and were filtered off and washed with water.

Ignition temperature. 145°C .

Behaviour on Ignition. Application of a lighted fuzee caused a loud explosion.

Sensitivity. A very light blow (steel to steel) caused a loud explosion.

*See paragraph 4.3.2.2. of report.

Ball and Disc Test.* 0% point = 5 inches/2 oz.

Emery Friction Test.* 0% point = <3 ft./sec.

Sensitizing power for 60/40 potassium chlorate-antimony sulphide mixtures - is a good sensitizer.

Stability. Is unstable; decomposes to a grey inert mass in a few days at room temperature.

1.9 Ethylenediamino-o-phenylenediamino cupric chlorate

To .01 mol. o-phenylenediamine and .01 mol. ethylenediamine dissolved in 20 cc. alcohol was added .01 mol. cupric chlorate dissolved in 10 cc. of water. Compact dark purple crystals were formed and were filtered off and washed with alcohol.

The product was excessively sensitive and fired when struck (steel-steel) under water. A .303 inch S.A. cap filled with the neat salt pressed at 900 lb. and closed with paper fired when struck in a Service rifle.

Ignition Temperature - 117°C. The Induction Period to explosion at various temperatures was measured with the following results:

<u>Temperature</u> °C.	<u>Induction Period</u> (Secs.)
103.5	15
106.2	10.5
111	5.5
122	1.5

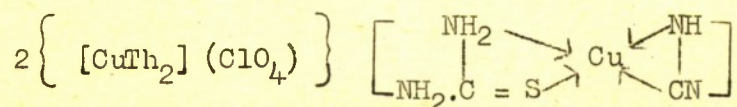
Stability. The salt is unstable at room temperature.

1.10 p-phenylenediamino cupric perchlorate and chlorate

These two polymeric salts were prepared by adding an aqueous solution of p-phenylenediamine to cupric perchlorate and chlorate solution respectively. Both were black amorphous bodies resembling carbon black in appearance and both were insoluble in the usual solvents. The perchlorate was sensitive to steel-steel impact and the chlorate extremely sensitive, but neither was very violent. The perchlorate appeared to be stable and retained its activity after about a year under damp conditions of storage at room temperature. The chlorate however soon became inert - presumably due to intra molecular oxidation-reduction. The sensitizing ability of these compounds for 60/40 potassium chlorate-antimony sulphide mixtures is not marked.

2.0 Thiourea cuprous complexes

2.1 Thiourea cuprous perchlorate - cuprous cyanamide complex



*See paragraph 4.3.2.2. of report.

Cupric perchlorate hexahydrate (55.5 grams; .15 mols) was dissolved in 75 cc. of cold water and poured slowly over 22.8 grams (.3 mols) of thiourea in a small beaker. The thiourea rapidly dissolved and discharged the blue colour of the cupric salt; before half the cupric salt had been added the solution was clear and had a faint yellow colour. As the second half of the cupric salt was added the solution took on a faint apple green colour. The now strongly acid solution was scratched vigorously and cooled on ice when it became syrupy and finally deposited 27 grams of colourless crystals which were filtered off and washed with a mixture of alcohol and ethyl acetate. Yield 57 per cent, calculated on the cupric perchlorate taken.

Found Cu = 23.23%, (ClO₄) = 24.60%, N = 21.07%. S = 19.85%

C₆H₂₁O₈N₁₂S₅Cl₂Cu₃ requires Cu = 23.52%; (ClO₄) = 24.56%.
N = 20.74%. S = 19.75%.

It was very difficult to recrystallize the complex from hot water or from alcohol-water mixtures because it tended to form supersaturated syrups and losses were great. The sample used in sensitization experiments was not recrystallized; considerable acidity is produced by the reduction of the cupric ion during the preparation of the body but it was shown that aqueous solutions of the complex used in the experiments were neutral or even slightly alkaline to litmus. The sample used was granular and free-flowing and consisted of rectangular tablets or stellate aggregates.

Behaviour on ignition. Deflagrates fiercely with a dark red flame and little smoke.

Sensitizing power for 60/40 potassium chlorate-antimony sulphide. Is an excellent sensitizer with sensitizing power almost equal to that of tetrazene.

Sensitivity. Is not easily fired by steel-steel impact.

Stability. The complex alone is stable at room temperatures but in contact with potassium chlorate it is not stable.

2.2 Thiourea cuprous picrate complex (Dithiourea picrate copper)

When a solution of cupric picrate is treated with thiourea a very insoluble red-brown cuprous complex is precipitated; the same body may be obtained in a more pure form and also more conveniently by treating trithiourea cuprous chloride with a solution of sodium picrate when the complex is obtained in the form of reddish-brown needles unsuitable, however, for incorporation in cap compositions on account of the low bulk density and tendency to felt together. A free-flowing form of the complex was obtained by recrystallizing the needles from a hot aqueous solution of thiourea, one of the few media in which it is appreciably soluble. The resultant garnet-red tablets are a hydrate of the original complex and contain one molecular of water to each atom of copper.

Both the hydrated and anhydrous forms of this complex were found to be moderately good sensitizers of potassium chlorate-antimony sulphide mixtures but the anhydrous form was the better; it was obtained in a form suitable for incorporation in cap compositions by drying the free-flowing mono-hydrate at 95°C. when it lost its water and became considerably lighter in colour but retained its original crystalline shape. These crystals, which were used in the sensitization experiments described in paragraph 6.3.4 of the report are regarded as pseudomorphic; the original dark red tablets of the hydrate showed sharp extinction under crossed nicols but there was no orientation of the dried form which gave extinction.

16.3 grams of trithioureic cuprous chloride was dissolved in 500 cc. of boiling water and to it was added rapidly and with vigorous stirring 200 cc. of an aqueous solution of sodium picrate obtained from 11.5 grams of picric acid. Momentarily a light yellow precipitate was formed but after a few seconds it suddenly became maroon coloured and a mass of needle shaped crystals separated out: they were filtered off, washed with water. Found - Cu 14.2%, S = 14.1%. $[\text{CuTh}_2\text{Pi}]$ requires Cu 14.3%, S = 14.4%.

Properties

The anhydrous complex is fairly soluble in acetone and if re-crystallized from moist acetone the dark red hydrate is obtained. The complex is split up by concentrated hydrochloric acid and becomes colourless but on moderate dilution it is reformed and crystallizes out again unchanged.

2.3 Thiourea cuprous azide

By treating one molecular proportion of trithioureic cuprous chloride in aqueous solution with one of sodium azide, colourless felted needles of a thiourea cuprous azide were obtained whose constitution has not yet been investigated.

The azide group in this body is so diluted with explosively inert material that on ignition the body burns very slowly and with a green flame.

3.0 Unionized copper complexes

3.1 Ethylenediaminedipicrate copper

To a boiling dilute aqueous solution of cupric picrate a dilute solution of ethylenediamine was added drop by drop; ethylenediaminedipicrate copper was precipitated as flesh-coloured plates.

On boiling the complex with an excess of ethylenediamine solution no trace of a blue or purple colour was observed, showing that the co-ordinated picrate groups could not be easily expelled from the nucleus and replaced by a further molecule of ethylenediamine, in spite of the great affinity of this co-ordinator for the cupric ion. Found Cu 9.94% $[(\text{NH}_2.\text{CH}_2.\text{CH}_2.\text{NH}_2) \text{Cu} (\text{C}_6\text{H}_2\text{N}_3\text{O}_7)_2]$ requires Cu 9.91%.

Solubility. Very sparingly soluble in water.

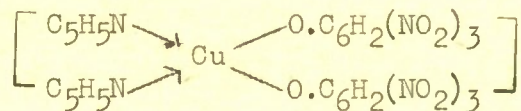
Behaviour on Ignition. Deflagrates mildly.

Sensitivity. Relatively insensitive to steel-steel impact.

Sensitizing Power. Slight. More than 5 per cent added to 60-40 potassium chlorate-antimony sulphide mixture causes "fizzling".

Miscellaneous. The bulk density of the sample prepared was very low and the crystalline form unsuited for incorporation in cap compositions.

3.2 Dipyridinodipicrate copper



This body can be prepared by the action of pyridine on an aqueous solution of cupric picrate or, more expeditiously, from copper sulphate, sodium picrate and pyridine.

Picric acid (23 grams) was added to 300 cc. of boiling water and neutralized with sodium hydroxide. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (12.5 grams) dissolved in water was added to the boiling solution of sodium picrate and the whole made up to 600 ccs. If necessary any slight precipitate of copper hydroxide was cleared by the addition of a few drops of sulphuric acid and then 100 ccs. of an aqueous solution of pyridine containing 8.0 grams of pyridine was added dropwise during 15 minutes with vigorous stirring to the solution of copper salt which was maintained at boiling point throughout. On cooling, the heavy dark green crystals of the complex were filtered off, washed with water and dried. Yield, 33 grams (97 per cent).

Found Cu 9.57 per cent; $[(\text{C}_5\text{H}_5\text{N})_2 \text{Cu} (\text{C}_6\text{H}_2\text{O}_7\text{N}_3)_2]$ requires Cu 9.38 per cent.

In contrast to ethylenediaminodipicrate copper, this complex reacts with an excess of its co-ordinator, pyridine, giving a dark green solution from which may be isolated dark green crystals of a higher complex salt containing more than two molecules of pyridine, for on exposure to air the excess pyridine disengages itself leaving the original dipyridino body in the form of an amorphous light green powder.

On treatment of the crystalline dipyridino body with aqueous thiourea the link between copper and pyridine is broken, and the copper is reduced to the cuprous state, the green crystals being converted in situ to garnet-red plates of cuprous dithiourea picrate hydrate. (See paragraph 2.2 of this Appendix).

Solubility. Sparingly soluble in boiling water, insoluble in cold water.

Behaviour on Ignition. On heating melts to a black liquid which deflagrates fiercely out spasmodically.

Sensitizing power for 60/40 potassium chlorate - antimony sulphide.
Is a good sensitizer, 10 per cent addition being the optimum amount. The mixtures are powerful and do not readily fizzle in .303 inch caps. (For further details see paragraph 6.3.2. of report).

Stability. Not yet investigated.

3.3 Dipyridinostyphnato copper. $[\text{Py}_2\text{Cu}(\text{C}_6\text{H}_8\text{N}_3)]$

When pyridine is added to an aqueous solution of normal copper styphnate (or to equivalent amounts of normal sodium styphnate and copper sulphate) an amorphous bright green precipitate is formed which is extremely insoluble in water and on ignition deflagrates with some vigour; it is dipyridinostyphnato copper.

Many attempts were made to obtain this body in crystalline form, for instance, by adding dilute aqueous pyridine to a boiling solution of disodium styphnate and copper sulphate, by adding an aqueous solution of sodium styphnate and pyridine to dilute boiling copper sulphate solution and finally by adding a mixture of sodium styphnate and pyridine to a solution of cuprammonium sulphate. By this last method dark tea-green needles were obtained which contained both pyridine and ammonia and were presumably pyridino amino styphnato copper. This substance on ignition burned vigorously.

The required dipyridino body was finally obtained in a crystalline condition by the following process:-

Styphnic acid (3 grams) was dissolved in 200 cc. of boiling water and half neutralized with sodium hydroxide. An excess (4 grams) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was then added to the hot solution which was brought to the boil and a dilute aqueous solution of pyridine was added dropwise until the yellow precipitate formed at each addition just failed to dissolve. The solution was then cooled to 70°C . and maintained at this temperature while a stream of air which had passed through a wash bottle containing 50/50 aqueous pyridine was bubbled through the liquid. Soon a heavy dark green crystalline deposit was formed, and passage of the pyridine-laden air was continued as long as the crystals continued to form. (When pyridine laden air was passed through a hot solution of copper sulphate and styphnic acid the first effect was to precipitate yellow crystals of pyridine styphnate; on continued passage of pyridine this was converted into dipyridinostyphnato copper).

Dipyridinostyphnato copper - Found Cu 13.57% $[(\text{C}_5\text{H}_5\text{N})_2\text{Cu}(\text{C}_6\text{H}_8\text{N}_3)]$ requires Cu 13.68%. Dark green square plates insoluble in water.

Behaviour on Ignition - deflagrates with moderate vigour.

Sensitizing power of 60/40 potassium chlorate - antimony sulphide - moderate. (For details of actual compositions investigated see paragraphs 6.3.3. and 6.3.4. of report).

3.4 Miscellaneous unionized copper complexes

3.4.1 Picrates

When ammonia is added to an aqueous solution of cupric picrate, an extremely insoluble light green amorphous precipitate is formed which could not be obtained in a crystalline state. It is interesting that if the reaction liquid is boiled in a glass vessel a copper mirror is sometimes deposited on the glass. On ignition the dry body deflagrates mildly.

By the action of triethanolamine on aqueous cupric picrate a sparingly soluble bright green amorphous precipitate is produced. The sparing solubility of this complex is remarkable in view of the high solubility of most triethanolamine salts in water. On ignition the body smoulders.

On adding an aqueous solution of hydrazine to cupric picrate a yellow amorphous precipitate is produced which evolves nitrogen on boiling with water and which when dry burns vigorously on ignition.

All the above mentioned complexes form persistent surface skins on water, even on the surface of the reaction mixture in which they are formed; this is taken as evidence of their non-ionic nature.

4.0 Ethylenediamine cobaltic azide

This azide (whose composition has not yet been determined) is that mentioned in paragraph 6.2 of the report as not yielding any detectable amount of hydrazoic acid under hot moist conditions.

To a nearly saturated aqueous solution of cobaltous nitrate four molecular proportions of sodium azide in water were added and then to the clear purple red solution an aqueous solution of ethylenediamine drop by drop till the purple amorphous precipitate just dissolved. On aeration the dark red solution became brown yellow in colour and deposited dark red compact crystals of the complex azide. On ignition the body burned vigorously with a smoky flame.

No azide could be detected on a bright copper strip suspended in a weighing bottle over a sample of the azide after 60 hours storage at 120°F. and 100% relative humidity - conditions under which all other azides which have been tested release considerable amounts of hydrazoic acid.

5.0 Complex lead salts containing triethanolamine

The three triethanolamine lead salts described below appear to be of little or no use in cap compositions but their existence is recorded for sake of completeness.

5.1 Basic Lead triethanolamine nitrate $[\text{Pb}(\text{OH})(\text{C}_6\text{H}_{15}\text{O}_3\text{N})](\text{NO}_3) \cdot \text{Pb}(\text{OH})_2$

To a hot 5 per cent aqueous solution of triethanolamine an aqueous solution of lead nitrate was added until there was a faint permanent precipitate. The basic triethanolamine lead nitrate crystallized as a heavy microcrystalline powder. Found Pb 62.0%, NO_3 10.1%, $\text{C}_6\text{H}_{18}\text{O}_9\text{N}_2\text{Pb}_2$ requires Pb 61.2%, NO_3 9.2%.

The complex which was very sparingly soluble in water smouldered vigorously when ignited, giving beads of metallic lead.

5.2 Basic triethanolamine lead perchlorate and picrate

The perchlorate was made in an analogous way to the nitrate described above; it formed heavy colourless crystals sparingly soluble in water. It was moderately sensitive to steel-steel impact and on ignition deflagrated vigorously.

Found Pb 61.3% (ClO_4) 15.3%

On mixing warm aqueous solutions of lead acetate and triethanolamine picrate and cooling, canary yellow free-flowing crystals of the double picrate were obtained. The body had little sensitizing power when added to chlorate-antimony sulphide mixtures and was relatively insensitive to steel-steel impact. On ignition it deflagrated; when thrown on to Wood's metal at 270°C . it exploded immediately.

The above triethanolamine salts were not investigated further since they appeared to show little prospect of usefulness in cap compositions.

APPENDIX II

The Degree of Sensitization of 60/40 Potassium Chlorate - Antimony

Sulphide Mixture produced by the addition of various Sensitizers

Various percentages of the sensitizer under investigation were mixed with a basic mixture consisting of 60 percent Potassium Chlorate (grist as for Al mixture) and 40 percent of Antimony Sulphide (grist also as for Al mixture). The sensitivity of the resultant mixtures was determined by filling into Service (copper) primer caps under a dead load of 750 lb.; the filling was covered with a disc of varnished lead-tin foil as used in Service primer caps but no further varnish was applied. The charge in each cap was adjusted so that the distance from foil to lip of cap fell within the limits 0.100 - 0.106 inches, a radiused drift having been used in the pressing. The caps were assembled in No. 1 Mk.II primer bodies with two-holed anvils but no closing plug or seal and were tested for sensitivity in the ball-dropping apparatus using a 1 lb. ball. The sensitivity was taken as the minimum height of fall required to produce a run of ten successive firings, a "fizzle" being counted as a failure.

Sensitization figures for many of the more common explosives determined in this way were published in ARD Expl. Rep. 373/43 and the present figures are comparable with those results. For sake of comparison the following figures, abstracted from that report, are given:-

Sensitizer	Maximum Degree of Sensitization Observed (inch/lb)
Tetrazene	10
Sulphur	10
D.D.N.P.	8
Mercury Fulminate	8
Picrite	7
PETN	7
Lead Thiocyanate	6
Lead Styphnate	5.5
C.E.	5.25
Stannous methylene-bis (nitrosyhydroxylamine)	5
Lead Azide	5
Ground Glass	4
RDX	3

The following figures for Service and other cap compositions are also of interest for purposes of comparison:-

	Amount by which (under the standard conditions) the sensitivity of the composition exceeds that of unsensitized 60/40 mixture. (inch/lb.)
Al Mixture	9
Q.F. Mixture	5
Q.3. Mixture	9
Mixture 300(a)	9

It should be noted that a good sensitization figure in the present test does not necessarily imply that the mixture would be suitable for use in .303 inch caps since it has been found that there is a greater tendency to "fizzling" in these smaller caps than in primer caps. In general, however, a poor figure in the present test goes hand in hand with poor sensitivity in .303 inch caps.

The table does not include results on all the sensitizers mentioned elsewhere in the report since many of the more recent compounds were tested directly in .303 inch critical assemblies, the requisite .303 inch cartridge cases with extreme dimensions having become readily available. The table does, however, include results on sundry sensitizers other than co-ordination compounds not previously reported and now given for sake of completeness.

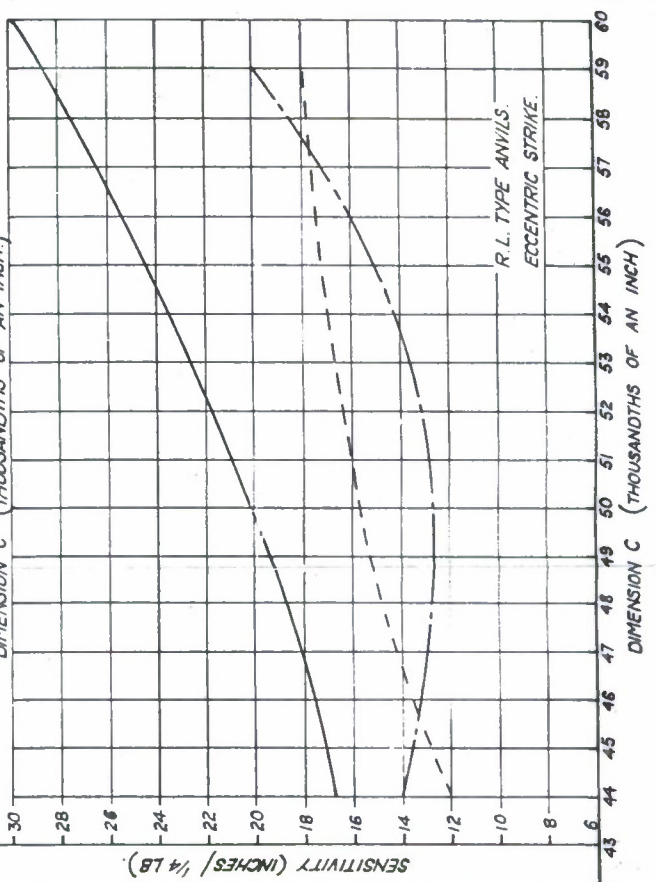
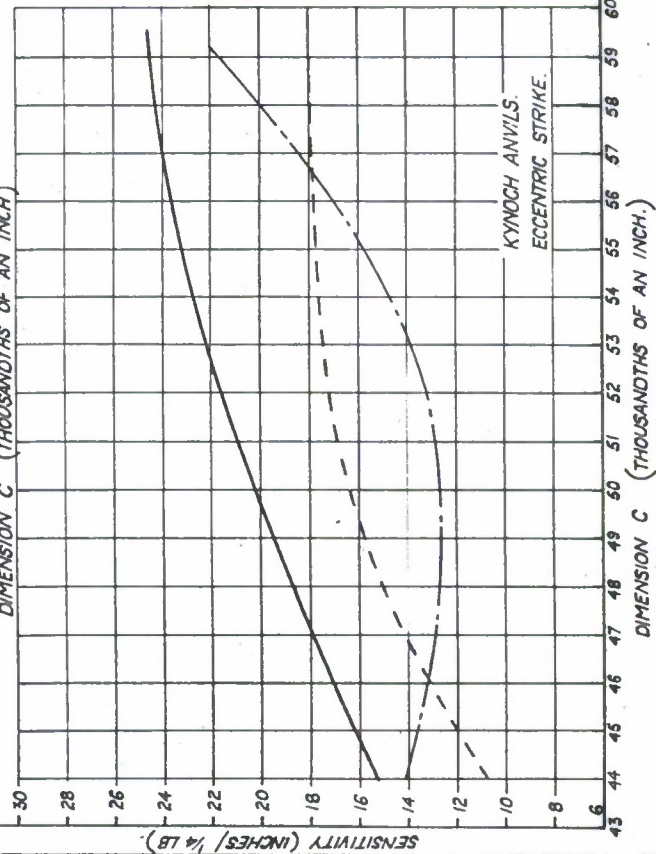
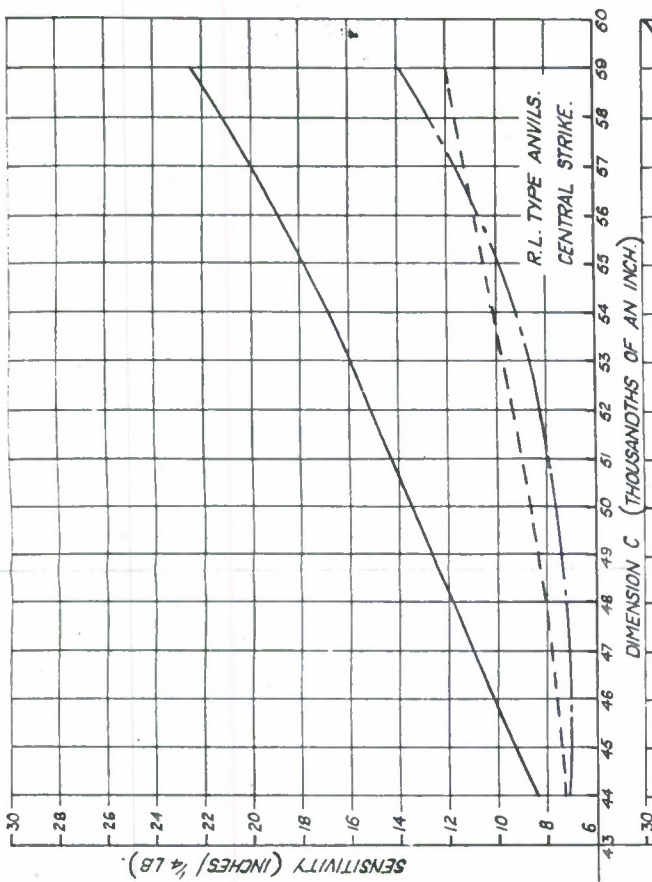
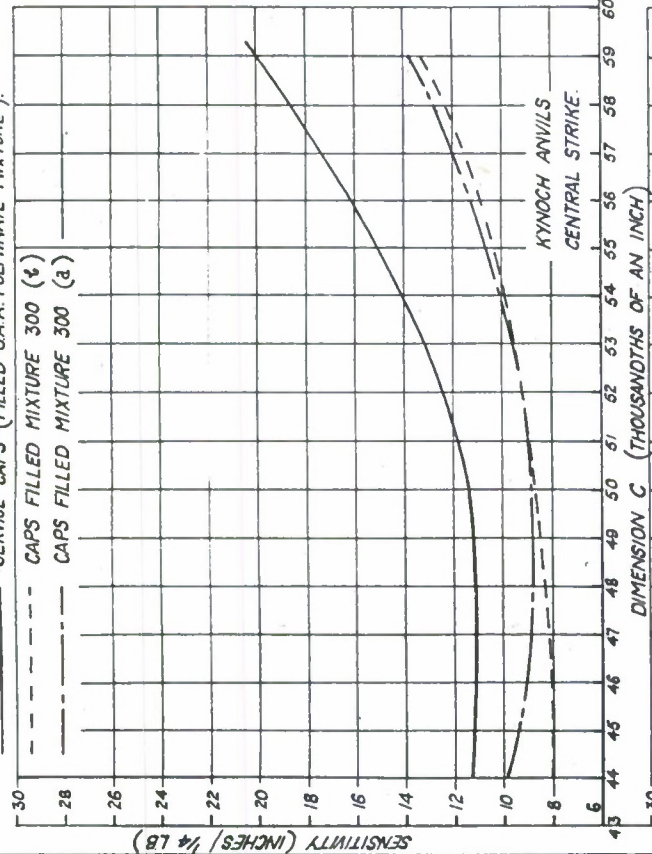
Sensitizer	Percentage added	Degree of Sensitization (inch/lb)
<u>Lead Compounds</u>		
[Pb Th ₄] (ClO ₄) ₂	16	6
Basic triethanolamine lead perchlorate	16 8	3 1
Lead Hypophosphite	16 8 4	5 5 4
Lead Hypophosphite - Lead Nitrate double salt	24 16 8 4	6 7 6 5
Lead 3,6 dinitrobenztriazole	5	2
Lead dinitroquinol	16 8	4 4
Basic lead trinitro- <u>m</u> -cresylate (R.D.1322)	16 8	5 5
Lead nitronitrosaminoguanidine	16 8 4 2 1	4 3 3 3 1
<u>Diazo oxides</u>		
2,6 dinitro-4-diazophenol (" <u>para</u> D.D.N.P.")	16 8 4 1	8 9 7 4
2-nitro-4-diazophenol (R.D.1310)	20 10 5	7 8 7
4-nitro-2-diazophenol (R.D.1314)	16 8 4 2	10 10 9 7

Sensitizer	Percentage added	Degree of Sensitization (inch/lb)
<u>Misc. Compounds</u>		
Nitrocotton (Service, pulverized)	16	1
	8	0
Erythritol tetranitrate	16	< -10
	8	3
	4	3
	2	3
Ethylenedinitramine	16	4
	8	4
	4	4
	2	3
Thiourea	20	0
	10	4
Tetramethyldithiuram disulphide	12	0
	8	7
	4	9
	2	7
	1	3
<u>Copper Compounds</u>		
[Cu Py ₄] (ClO ₄) ₂	16	3
	10	7
	8	6
	5	5
	4	4
	2.5	5
	1.6	5
[CuPy ₄] (Mn ₂ O ₈)	15	< -2
CuN ₆	5	7
[CuPy ₂ (SCN) ₂]	16	3
	10	6
	5	6
	2.5	5
	1.25	3
[CuPy ₂ (NO ₂) ₂]	16	< -2
[Cu en ₂] (NO ₃) ₂	16	< 2

Sensitizer	Percentage added	Degree of Sensitization (inch/lb)
$[\text{Cu on}_2](\text{ClO}_3)_2$	16 8 4	6 5 6
$[\text{Cu Th}_3](\text{NO}_3)$	16	6
$[\text{Cu Th}_2(\text{H}_2\text{O})](\text{NO}_3)$	16	< -2
Cuprous cyanamide-thiourea cuprous perchlorate complex	16	8
Cupric β -aminoethyl dithiocarbamate	16	4
$[\text{Cu}(\text{o-phen})_2](\text{ClO}_4)_2$	10	7
<u>Cobalt Compound</u>		
$[\text{Co}(\text{NH}_3)_6](\text{ClO}_4)_3$	16	1
<u>Mercury Compounds</u>		
$[\text{Hg Py}_2](\text{ClO}_4)_2$	30 20 10 5	5 8 5 5
$[\text{Hg}(\text{NH}_3)_4](\text{ClO}_4)_2$	15	2
<u>Silver Compound</u>		
Silver salt of nitro- guanidine	16 8	< -2 < -2
Potassium dinitrobenzofurozen oxide	16 8	4 3
Sodium dinitrobenzofurozen oxide	16 8	4 3
Barium Styphnate	16 8 4	3 2 1

SERVICE CAPS (FILLED S.A.A. FULMINATE MIXTURE).

--- CAPS FILLED MIXTURE 300 (4)
--- CAPS FILLED MIXTURE 300 (3)



GRAPHS SHOWING THE RELATIONSHIP BETWEEN DIMENSION C.
(DISTANCE FROM TIP OF ANVIL TO OUTER BASE OF CAPS)
& SENSITIVITY IN 303 S.A. CARTRIDGE CASES.

DRG. NO. A.R.D. 8270.

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