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PROCEEDINGS OF THE SYMPOSIUM ON LEAD AND COPPER
AZIDES HELD ON 25TH-26TH OCTOBER 1966

Explosives Research and Development Establishment
Waltham Abbey, England

26 October 1966

MINISTRY OF TECHNOLOGY

EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT

Proceedings of the
Symposium on
Lead and Copper Azides

E.R.D.E., 25th - 26th October 1966

UNLIMITED

**WALTHAM ABBEY
ESSEX**

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SUMMARIES AND CONCLUSIONS

SYMPOSIUM ON LEAD AND COPPER AZIDES
HELD ON 25th - 26th OCTOBER, 1966

at E.R.D.E., Waltham Abbey, Essex.

The purpose of the Symposium was to survey the present state of knowledge of the chemistry of lead azide as it affects preparation and use of the substance as an initiating explosive. Discussion includes the crystallography of lead and copper azides, the effect of environmental conditions, analytical problems and the hazards in preparation and handling.

The programme was arranged as follows:

25th October, 1966:

        Introduction

        Session A Polymorphism of Lead Azide

        Session B Decomposition and Chemical Analysis
                  of Lead Azide

26th October, 1966:

        Session C Copper Azides, Occurrence and Prevention

        Session D Hazards in the Manufacture of Lead Azide

        Summary and Conclusions

ATTENDANCE

Chairman: Dr. I. Dunstan E.R.D.E.

Overseas

Mr. J. Clay	Department of Supply (Australia)
Mr. S.E. Harris	Australian Army Staff, London
Mr. E.B.H Dubois	Fabrique Nationale d'Armes de Guerre, Zutendaal, Limburg, Belgium
Mr. R.M. Ferguson	Canadian Arsenals Ltd., Montreal
Mr. S. Ek	Forsvarets Forskningsanstalt, Sundbyberg, Sweden
Mr. S. Lamnevik	Forsvarets Forskningsanstalt, Sundbyberg, Sweden
Mr. S.A. Rask	Forsvarets Fabriksverk, Zakrisdalsverken, Karlstad, Sweden
Dr. J.V.R. Kaufman	U.S. Army Munitions Command, New Jersey, U.S.A.
Mr. E.W. Van Patten	U.S. Army Munitions Command, New Jersey, U.S.A.

U.K.

Mr. J.P. Leslie	I.C.I. Ltd., Stevenston
Mr. L.E. Medlock	I.C.I. Ltd., Stevenston
Mr. J.D. Howie	A.D.C.F. (Amm.) (F. and D.) Nottingham (M.O.D.)
Mr. E.A.G. Thomas	A.D.O.F. (Amm.) (F. and D.) Nottingham (M.O.D.)
Mr. A. Daykin	R.O.F., Chorley
Mr. O. Robertson	R.O.F., Chorley
Mr. P.K. Sen	C.I., Chorley
Mr. P.E. Wythes	C.I., Woolwich
Dr. F.E. Ball, O.B.E.	R.A.R.D.E.
Mr. R. Eather	R.A.R.D.E.
Mr. R.C. Harris	R.A.R.D.E.
Mr. J.T. Heron	R.A.R.D.E.
Dr. B.H. Newman	R.A.R.D.E.
Mr. T.H. Quarry	R.A.R.D.E.
Dr. D.F. Runnicles	R.A.R.D.E.
Dr. G. Todd	R.A.R.D.E.
Dr. J. Wilby	R.A.R.D.E.

/Mr. G.K. Adams .....

Mr. C.K. Adams   E.R.D.E.
Mr. N.J. Blay   E.R.D.E.
Mr. J.R.C. Duke   E.R.D.E.
Mr. J.T. England   E.R.D.E.
Mr. K.J. Holloway   E.R.D.F.
Dr. A. Lovecy   E.R.D.E.
Mr. J.L. McDougall   E.R.D.E.
Mr. C.H. Miller   E.R.D.E.
Mr. D.A. Salter   E.R.D.E.
Mr. J.F. Sumner   E.R.D.E.
Mr. G.W.C. Taylor   E.R.D.E.
Mr. E.G. Whitbread   E.R.D.E.
Mr. R.J.E. Williams   E.R.D.E.
Dr. R.M.H. Wyatt   E.R.D.E.

              Secretaries: Mr. G. Packman E.R.D.E.
                             Mr. J.R. White E.R.D.E.

A welcoming address was given by Mr. G.K. Adams in the absence of
Dr. L.J. Bellamy (Director, A.R.D.E.) who was on his way to Australia.
Mr. Adams extended a welcome to all visitors, especially those from
overseas, and said that from the number of papers written on the subject
matter, this was an important field of work. He went on to say how
essential it was to have standardised materials and weapons, and to find
out as much as possible about the sensitiveness of all materials and the
hazards they might present in manufacture and subsequent handling and
storage.

Dr. I. Dunstan, as Symposium Chairman, then gave details of the
programme to be followed, stating that the security grading of the
information given and work discussed was UNCLASSIFIED. The purpose of
the Symposium was to bring together the people concerned with manufacture,
performance, and stability of the materials concerned, to survey the
status of the work, and to record its progress. He concluded by saying
that a report of the symposium would be published as soon as possible.

Session Chairman: Mr. G.W.C. Taylor

Contributors: Mr. G.W.C. Taylor
                      Mr. J.R.C. Duke
                      Dr. R.M.H. Wyatt

Session Secretary: Mr. J.R. White

The __Chairman__ opened the session by extending cordial greetings to visitors
from so many different countries and organisations with a common interest in
lead azide. He had met them individually in their own laboratories and
factories and was glad of this unique opportunity to meet collectively at
E.R.D.E. The proceedings of the symposium were non-proprietary as well as
unclassified for security purposes; this was no disadvantage, as the emphasis
would be on the essential chemical and physical properties of lead azide as a
substance.

The __Chairman__ continued that in view of the considerable military and
industrial applications of lead azide, no excuse was needed to account for
the time spent on the ensuing programme. He then reminded the audience that
polymorphism was defined as being the ability of a substance to exist in more
than one crystalline arrangement; each form has a different absolute density,
and can be identified optically and by its x-ray diffraction pattern. Some-
times variation in crystal habit was mistaken for polymorphism, and in lead
azide work pseudomorphism (where conversion from one polymorph to another has
taken place without apparent change in shape) was apt to cause confusion.
Polymorphism becomes apparent during preparation by metathesis, when the size
and shape of intermediates can be studied. There is a strong interest in
polymorphism and it is desirable to understand the conditions favourable for
the formation of each type, since it could perhaps be related to sensitiveness
or to the occurrence of unexplained explosions. Identification by X-ray
diffraction is especially important when additives are incorporated. A full
knowledge of polymorphism could lead to the effective control of crystal size
and shape during production processes. Existing known polymorphs are the
alpha or common rhombic form with a Δ of 4.7; the beta monoclinic form of
Δ4.9 (Miles 1931); the gamma monoclinic form of Δ4.7, first isolated in
E.R.D.E. in 1956 and confirmed in Sweden in 1960; and finally the delta
triclinic form of Δ4.6 isolated recently in Sweden.

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THE CRYSTALLOGRAPHY OF LEAD AZIDE

J.R.C. Duke

Crystallographic methods have been used in this Establishment over a long period for purposes of characterization and identification, and have been extensively used in studies of initiatory explosives.

One of the fundamental requirements of an explosive is reproducibility of performance, and in practice this is achieved by employing as ingredients suitable pure chemical substances in as reproducible a physical form as can be secured. A further requirement is that the method of preparation adopted should consistently result in the formation of the desired physical and chemical individual, even if the conditions of preparation vary in some degree, since in practice it is impossible to avoid some variations of this kind.

Much of our application of crystallographic methods has been within this general framework of practical requirements, and we are here concerned with a survey of the accumulated crystallographic data in the lead azide system.

Four polymorphic forms of lead azide are at present known, and are designated as the alpha- beta- gamma- and delta- forms. Miles, in his pioneer work in the 1930's, described the alpha- and beta- forms, but unfortunately the axial labels, and in the case of the beta- form the cell, which he chose were unconventional. Some subsequent authors have adhered to Miles's choices, but others have changed some or all of these to more conventional ones; nevertheless, the resulting descriptions are equivalent. All descriptions are here given in terms of the cells adopted by Lamnevik and Söderquist, who have made what are probably the most accurate measurements of cell dimensions and powder patterns which are available in this system.

/Alpha- .....

Alpha- lead azide, $Pb(N_3)_2$

Crystal system   : Orthorhombic
Space-group   : $Pc2_1n$ probably
Unit cell dimensions:

a	b	c	Ref.
11.34 Å	16.25 Å	6.64 Å	Miles (1931)
11.312	16.246	6.628	Pfefferkorn (1948)
11.42	16.30	6.65	Duke (1951)
11.31	16.25	6.63	Azaroff (1956)
11.41	16.31	6.66	Hattori and McCrone (1956)
11.330	16.271	6.636	Lamnevik and Söderquist (1963)

X-ray powder data published by:

Hattori and McCrone (1956), contains cubic pattern
Lamnevik and Söderquist (1963)

In the course of our work, we indexed the powder pattern of both
alpha- and beta lead azide, and on a few patterns found a series of extra
lines which could be indexed accurately on the basis of a face-centred
cubic cell, a = 7.860 Å. This pattern is also present in the data published
by Hattori and McCrone for the alpha- form; it will be referred to again
later.

/Beta .....

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Beta lead azide, $Pb(N_3)_2$

Crystal system: Monoclinic

Two choices of unit cell have been made,
with the following unit cell dimensions
and space-groups:

I-centred cell, space-group I2/m, Im or I2

a	b	c	Beta	Ref.
17.60 Å	8.83 Å	5.10 Å	90.8°	Miles (1931)
17.508	8.844	5.090	90.2°	Pfefferkorn (1948)
17.569	8.837	5.113	90.29°	Lamnevik and Söderquist (1963)

C-centred cell, space-group C2/m, Cm or C2

18.37 Å	8.89 Å	5.11 Å	106.3°	Duke (1951)
18.49	8.84	5.12	107.6°	Azaroff (1956)
18.31	8.88	5.23	107.5°	Hattori & McCrone (1956)
18.323	8.837	5.113	106.5°	Lamnevik and Söderquist (1963)

X-ray powder data published by:

Hattori and McCrone (1956)
Lamnevik and Söderquist (1963)

It should be emphasised that the above two descriptions are not in
conflict; they are merely different ways of describing the same thing.

A point requiring clarification in the powder data is that Lamnevik
and Söderquist report a very strong powder line at 7.94 Å in the powder
pattern. We have never observed such a line, and it is not reported by
Hattori and McCrone.

/Gamma- .....

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Gamma- and delta- Lead Azides

The formation of these two polymorphs is favoured by low pH and/or presence of polyvinyl alcohol, at appropriate rates of crystallization.

Gamma- lead azide, $Pb(N_3)_2$

Crystal system: Monoclinic
Unit cell dimensions and space-group

a	b	c	Beta	S-g	Ref.
12.17 Å	10.51 Å	6.55 Å	98.5°	$P2_1/a$	Duke (1957)
12.060	10.507	6.505	95.75	$P2_1/m$ or $P2_1$	Lamnevik & Söderquist (1964)

X-ray powder data published by:

Lamnevik & Söderquist (1964)

Delta- lead azide, $Pb(N_3)_2$

Crystal system: Triclinic
Unit cell dimensions

a	b	c	Alpha	Beta	Gamma	Ref.
13.163 A	10.532 Å	6.531 Å	90.53°	98.12°	112.67°	Lamnevik & Söderquist (1964)

X-ray powder data published by:

Lamnevik and Söderquist (1964)

We have confirmed the single crystal results for delta-lead azide and our powder data for both forms agree with those of Lamnevik and Söderquist

We think, however, that there is an anomaly in the results for gamma lead azide, since we think that our value for the beta-angle is not likely to be in error by more than a few tenths of a degree, while Lamnevik and Söderquist quote an e.s.d. for this angle of ± 0.03°; furthermore our space-group assignment was made on the basis of well-exposed photographs of good crystals. A possible explanation may be that these two forms are related as polytypes, and that some degree of variability exists in the crystals.

/The .....

The "cubic phase"

This has been referred to previously. The experimental observation is that sometimes an X-ray powder pattern of alpha- or (less frequently) beta-lead azide may show this pattern; a repeat specimen made from the same sample may not show it. The frequency of occurrence is very low, but despite attempts at variation of degree of grinding, temperature and humidity, and application of heat or pressure, it has not been possible to obtain this phase in a reproducible manner or in a pure state. Its identity is not known; it may or may not be lead azide; it is not lead nitrate (primitive cubic lattice, a = 7.856 Å).

Details of the x-ray pattern are as follows:

The "cubic phase" - composition unknown

Observed		Calculated f.c.c., a = 7.860 Å	
Intensity	d Å	d Å	Index
m	4.529	4.538	111
w	3.938	3.930	200
w	2.776	2.779	220
m	2.370	2.370	311
w	2.266	2.269	222
w	1.963	1.965	400
w	1.806	1.803	331
w	1.758	1.758	420
v.w	1.606	1.604	422
w	1.513	1.513	511
v.w	1.389	1.389	440
w	1.328	1.329	531

Ref: Duke (1951) (1953)

/Basic .....

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Basic Lead Azide

One of the forms of basic lead azide has been observed, sometimes as well-formed crystals, on alpha lead azide pellets after exposure to hot moist conditions; the same substance has been identified in well crystallised preparations of basic lead azide, whose analysis agrees with the composition PbN_3OH.

Basic lead azide, PbN_3OH

Crystal system: Monoclinic
Space-group : probably $P2_1/c$
Unit cell dimensions:

a	b	c	Beta
15.25 Å	5.75 Å	14.47 Å	114.7°

Powder data obtained

Density 6.10 observed (A.T. Thomas), 6.14 calculated

References

1. Azaroff, L.V., Z. Krist., 1956, 107, 362

2. Duke, J.R.C., Ministry of Supply reports (unpublished)

3. Hattori, K. and McCrone, W., Anal. Chem., 1956, 28, 1791

4. Lamnevik, S. and Söderquist, R. (1963)
   Forsvarets Forskningsanstalt, Sweden. FOA Report A 1105 - F110

5. Lamnevik, S. and Söderquist, R. (1964)
   Forsvarets Forskningsanstalt, Sweden. FOA Report A 1174 - F110

6. Miles, F.D., J. Chem. Soc., 1931, 2532

7. Pfefferkorn, G., Z. Naturforschg., 1948, 3a, 364

by S. Johansson, S. Lamnevik and R. Söderquist

Group 4(B)

$Pb(N_3)_2$

In group 4(B), the structure is known only for lead azide. Four polymorphs are known, alpha, beta, gamma and delta-lead azide.

Miles[22] appears to have been the first to discover alpha- and beta-$Pb(N_3)_2$. He determined the unit cell constants of alpha-$Pb(N_3)_2$ with an X-ray spectrometer and optical goniometer:

$$a = 6.64 \text{ Å}, \quad b = 11.34 \text{ Å}, \quad c = 16.25 \text{ Å}, \quad Z = 12$$

From rotation photographs he determined the cell constants of beta-$Pb(N_3)_2$ (I-centered monoclinic unit cell):

$$a = 17.60 \text{ Å}, \quad b = 8.83 \text{ Å}, \quad c = 5.10 \text{ Å}, \quad beta = 90°49', \quad Z = 8$$

In 1934 Sutton[23] gave a c-value twice that of Miles for alpha-$Pb(N_3)_2$. A redetermination by Pfefferkorn[24] in 1948 (rotation photographs) gave the values:

$$a = 6.628 \text{ Å}, \quad b = 11.312 \text{ Å}, \quad c = 16.246 \pm 0.002 \text{ Å}$$

in agreement with the values given by Miles. The possible space groups are Γ_{2h} (1, 5, 13, 16), that is Pmmm, Pcmm, Pmmn, Pcnm.

For beta-$Pb(N_3)_2$ Pfefferkorn obtained:

$$a = 17.508 \pm 0.002 \text{ Å}, \quad b = 8.844 \text{ Å}, \quad c = 5.090 \text{ Å}, \quad beta = 90°10' \pm 2'.$$

The possible space groups are D_{2h} (1-5), that is P2/m, P2$_1$/m, C2/m, and P2$_1$/a.

/Using .....

Using a precession camera with MoK_{alpha} and AgK_{alpha} radiation, Azaroff[25] obtained:

alpha-Pb$(N_3)_2$: a = 11.31 Å,   b = 16.25 Å,   c = 6.63 Å,   Z = 12

beta-Pb$(N_3)_2$: a = 18.49 Å,   b = 8.84 Å,   c = 5.12 Å, beta = $107^\circ 35'$

Z = 8 (C-centered monoclinic cell)

a = 17.70 Å,   b = 8.84 Å,   c = 5.12 Å,   beta = $90^\circ 10'$

(I-centered monoclinic cell)

The space-group of the lead atoms in alpha-Pb$(N_3)_2$ is Pcmn or Pc2$_1$n. The position of the azide ions could not be determined. The positions of lead atoms are (space group Pcmn):

8 Pb at X = 0.130,   Y = 0.085,   Z = 3/8

4 Pb at X = 0.870,   Y = 1/4 ,   Z = 1/8

Azaroff assumes the azide group to be nonsymmetric in Pb$(N_3)_2$, a suggestion which is supported by IR measurements. However this leads to a contradiction with reference to the space group. Pc2$_1$n is the possible space group for non-symmetric azide ions, but calculations based on geometry indicate the space group Pcmn. Azaroff points out that a definite structure determination will have to wait until neutron diffraction data are available.

Hattori and McCrone[26], using an X-ray powder diffractometer, obtained the following cell constants for alpha-Pb$(N_3)_2$:

a = 11.41 Å,   b = 16.31 Å,   c = 6.66 Å

/A neutron .....

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A neutron diffraction study of alpha-$Pb(N_3)_2$ was undertaken by Glen[27] in 1963. He reports that Saha, in a personal communication, found $Pc2_1n$ to be the correct space group of alpha-$Pb(N_3)_2$. Glen showed that the azide ion is nonsymmetric and the distances Pb-N are 2.48 Å and 2.92 Å. Two lead atoms with the co-ordinates

	X	Y	Z
Pb(2)	0.344	0.121	0.415
Pb(3)	0.333	0.122	0.092

have 7 closest N-neighbours. A lead atom with the co-ordinates

	X	Y	Z
Pb(1)	0.064	-0.140	0.247

has 8 closest N-neighbours.

In 1963 the cell constants of alpha- and beta-$Pb(N_3)_2$ were carefully determined by Lamnevik and Söderquist[28]. Using a Guinier powder camera and CuK_{alpha} radiation they obtained for alpha-$Pb(N_3)_2$:

$$a = 11.330 \text{ Å}, \quad b = 16.271 \text{ Å}, \quad c = 6.636 \text{ Å}$$

and for beta-$Pb(N_3)_2$

$$a = 17.569 \text{ Å}, \quad b = 8.837 \text{ Å}, \quad c = 5.113 \text{ Å}, \quad beta = 90.29° \quad \text{(I-centered cell)}$$

$$a = 18.323 \text{ Å}, \quad b = 8.837 \text{ Å}, \quad c = 5.113 \text{ Å}, \quad beta = 106.50° \quad \text{(C-centered cell)}$$

They showed also that beta irreversibly transforms to alpha-$Pb(N_3)_2$ at about 160°C.

Lamnevik and Söderquist[29] discovered two new polymorphs of lead azide which were named gamma- and delta-lead azide. From single crystal and powder data they determined the cell constants for gamma-$Pb(N_3)_2$, (monoclinic unit cell containing eight formula units):

$$a = 12.060 \text{ Å}, \quad b = 10.507 \text{ Å}, \quad c = 6.505 \text{ Å}, \quad beta = 95.75°$$

/The .....

The space-group is $P2_1/a$. For delta-Pb$(N_3)_2$ a body-centered triclinic unit cell has been chosen with:

$$a = 13.163 \text{ Å}, \quad b = 10.532 \text{ Å}, \quad c = 6.531 \text{ Å}$$

$$\text{alpha} = 90.53°, \quad \text{beta} = 98.12°, \quad \text{gamma} = 112.67°, \quad Z = 8$$

gamma-Pb$(N_3)_2$ has also been obtained by Taylor[30] who obtained:

$$a = 12.17 \text{ Å}, \quad b = 10.51 \text{ Å}, \quad c = 6.55 \text{ Å}, \quad \text{beta} = 98.51°$$

Pb$(N_3)_2$, abstract

The values given are arithmetic means. The limits indicate the highest and the lowest literature value.

	alpha-Pb$(N_3)_2$	beta-Pb$(N_3)_2$	beta-Pb$(N_3)_2$	gamma-Pb$(N_3)_2$	delta-Pb$(N_3)_2$
Lattice type	o-rh.	mon.	mon.	mon.	tric.
Space group	Pc2$_1$n	I-center.	C-center.	P2$_1$/a	I1 or I$\overline{1}$
a, Å	11.340^{+7}_{-3}	17.559^{+41}_{-51}	18.374^{+116}_{-64}	12.060 ± 3	13.163 ± 3
b, Å	16.265^{+45}_{-19}	8.837 ± 7	8.852^{+28}_{-15}	10.507 ± 3	10.532
c, Å	6.639^{+11}_{-11}	5.101^{+12}_{-11}	5.154^{+76}_{-41}	6.505 ± 2	6.511
alpha	–	–	–	–	90.53°
beta	–	90.42°	107.53^{+2}_{-3}	95.75°	98.12°
gamma	–	–	–	–	112.67°
Z	12	8	8	8	8
N-N, Å	–	–	–	–	–
Me-N, Å	2.48-2.92	–	–	–	–

References

22. F.D. Miles, "The formation and characteristics of crystals of lead azide and of some other initiating explosives", J. Chem. Soc. (London) 1931, 2532.

23. T.C. Sutton, "Mechanism of detonation in lead azide crystals", Nature, 1934, 133, 463

24. G. Pfefferkorn, "Zur Struktur von Bleiazid", Z. Naturforsch, 1948, 3 A, 364.

25. L.V. Azaroff, "Structural investigation of lead azide", Z. Krist. 1956, 107, 362.

26. K. Hattori, W. McCrone, "Lead azide, $Pb(N_3)_2$", Anal. Chem., 1956, 28, 1791

27. G.L. Glen, "Neutron diffraction study of alpha-lead azide" J. Amer. Chem. Soc., 1963, 85, 3892

28. S. Lamnevik, R. Söderquist, "On lead azides. 1. Refinement of the unit cell dimensions of alpha- and beta- lead azide. On a transformation of beta- to alpha- lead azide in the solid state", FOA 1 Report A 1105-F 110, Stockholm, Dec. 1963.

29. S. Lamnevik, R. Söderquist, "On lead azides. 2. Synthesis and crystal data of two new polymorphs of lead azide", FOA 1 Report A 1174 - F 110, Stockholm, Oct. 1964

30. G.W.C. Taylor, 1964, personal communication

Discussion on Paper (A-1)

The **Chairman** thanked Mr. Duke and Mr. Lamnevik, who had supplied a literature survey on crystal data and structures of metal azides, an extract from which has been reproduced.

Mr. Lamnevik said that regarding the point raised by Mr. Duke about the strong line at 7.94 Å in the x-ray powder pattern of beta lead azide, this was in fact a misprint and should have read "a very weak line". With reference to the cubic pattern, he had seen it mentioned before in a paper dealing with thermal decomposition of lead azide and thought it could be the first emergent state in the decomposition by heat. He went on to ask if anyone had examined the decomposition products of lead azide under vacuum.

Mr. Duke said that the cubic pattern mentioned by Mr. Lamnevik was a different one [Ref. Stammler, Abel, and Kaufman. Nature 1960, 185, 456], where a cubic phase (a = 12.25 Å) is formed by heating alpha lead azide at 175°C for 215 hours. **Dr. Lovecy** asked if it could be interstitial lead and if it had been treated with hydrazoic acid to see if it was due to superficial damage. Mr. Duke did not think that the presence of the cubic pattern was due to the presence of interstitial lead, but thought it would be a good idea to try the effect of hydrazoic acid.

Mr. Lamnevik then referred to the differences between beta and gamma lead azide. He said he had prepared gamma lead azide both with and without the use of additives, and asked if the gamma lead azide prepared by E.R.D.E. was pure. The **Chairman** said that no P.V.A. could be detected by analysis and work had been started using radio-active labelled P.V.A. **Mr. Duke** said he did not think the presence of P.V.A. in a crystal would affect its parameters.

Mr. R.C. Harris asked if the samples for x-ray examination were ground in air, and if so could this "cubic pattern" be carbonate. **Mr. Duke** replied that the patterns of the usual lead carbonates were quite different. In fact CO_2 usually reacted with lead azide to give, initially, basic azides.

Dr. Lovecy asked if the residues of reagents could be responsible. **Mr. Duke** said there was insufficient present; from the relative strengths of the patterns it appeared that in a typical case there might be about twenty-five per cent of the "cubic" azide present.

Dr. Dunstan asked if there would be enough sample available on which to do a chemical analysis. **Mr. Duke** replied that only one milligramme was used.

/The Chairman .....

The **Chairman** said that E.R.D.E. had experienced difficulty in making beta lead azide entirely free from alpha, using Miles' diffusion process. Mr. Thomas at Woolwich has devised a method by which this can be achieved. Into a three litre beaker containing two litres of distilled water, from burettes situated diametrically opposite, twenty five ml each of solutions containing ten ml of lead nitrate and forty ml of sodium azide are added over a period of one hour. The resulting product is pure beta lead azide.

Dr. Lovecy remarked that the suppressing effect of dextrin has been known for 35 years and asked if anyone had any idea of the mechanism of this effect. He added that one would think the only effect of an added colloid would be to increase viscosity, which by slowing diffusion should favour the formation of the beta polymorph.

The **Chairman** replied that there were other materials that favoured beta, e.g. eosin, which did not increase viscosity, and that the mechanism was not known.

THE SENSITIVENESS OF THE POLYMORPHS
OF LEAD AZIDE

R. M. H. Wyatt

Of the three polymorphs of lead azide, the alpha form has received considerable attention with regard to sensitiveness studies because of its military application. The beta form has not been studied very much, largely because of the difficulty in preparing sufficient of it to carry out enough trials. The gamma form, though easily prepared, has not been systematically investigated.

The opportunity of carrying out comparative tests on all three polymorphs arose recently, mainly because of the discovery by Mr. A.T. Thomas of a method of making beta lead azide on a relatively large scale, and free from contamination by alpha lead azide.

Statements in the literature have suggested that beta lead azide is more sensitive and dangerous than alpha lead azide. Doubts expressed about these statements led to the determination by Gray and Waddington (Nature 1955, 176, 653) of the enthalpy change of the transformation:

alpha crystalline $Pb(N_3)_2 \rightarrow$ beta crystalline $Pb(N_3)_2$
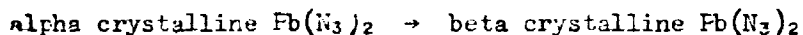
by an E.M.F. method. They found

$$\Delta H = 0.30 \pm 0.05 \text{ Kcal/mole},$$

giving values for the heats of formation of the alpha and beta forms of -115.5 and -115.8 Kcal/mole respectively. Though the energy content is not the only factor, this result suggests that the sensitiveness of the two polymorphs should not differ by very much. The enthalpy change for the transformation to the gamma polymorph is not known.

Comparative tests have been carried out to assess the sensitiveness to impact, friction and electrostatic discharge. Details of these tests are outlined in the appendix.

Table I contains the results for the three polymorphs. In the case of alpha and beta lead azide, very similar results are obtained in all three tests, the differences being quite insignificant. There is no difference in the sensitiveness of alpha and beta lead azide. The gamma polymorph shows an increase in impact sensitiveness and a decrease in friction sensitiveness, but sensitiveness to electrostatic discharge is very similar to that of the alpha and beta forms. The differences found with the gamma polymorph may be caused by a different heat of formation or differences in physical properties. In view of the very similar electrostatic ignition results, the latter explanation is more likely.

/Appendix .....

The Ball and Disc Impact Test

This apparatus is described in the Proceedings of the International Conference on Sensitivity and Hazards of Explosives, London, 1 - 3 October, 1963, and is based on that described by Ubbelohde et al. (Phil. Trans Roy. Soc. 1948, A.241, 287). It employs a 95 g ball as the falling weight, and a striker of 96 g to which is fitted a 5/32 inch steel ball as the impacting surface. The sample of explosive is prepared on a $\frac{1}{4}$ inch steel roller by means of a filling plate of 0.018 inch thickness having a hole of 0.157 inch diameter. A brass disc, of thickness 0.025 ± 0.005 inch, is placed on top of the explosive. A fifty shot up and down test is carried out using a logarithmic distribution of heights with an increment of 0.075.

The Emery Paper Friction Test

With this apparatus one frictional surface is caused to move relative to another by means of a blow from a pendulum bob. The stationary frictional surface is a $\frac{1}{4}$ inch steel roller to which a 11/16 inch diameter circle of O grade emery paper is stuck on the underside. The moving surface is a $2\frac{1}{2} \times 15/16 \times \frac{1}{4}$ inch mild steel slide to which a piece of the same type of emery paper, $1\frac{1}{2} \times \frac{5}{8}$ inch, is stuck towards one end. A sample of explosive (of the same volume as used in the impact test) is spread out very carefully by means of a rubber spatula so that, by the use of a paper guide, it occupies a circle of 11/16 inch diameter towards one end of the emery paper. The slide is placed into the holder of the pendulum machine and centred so that the explosive is lined up with the hole for the stationary surface, and so that the pendulum will collide squarely with its end. The roller with the emery paper face down is lowered carefully into the hole by means of a magnet on to the top of the sample. The loading arm is lowered, giving a load of 15 kg on the sample. The pendulum is then allowed to fall from an angle selected to give the appropriate strike velocity. A fifty shot up and down test is carried out using a logarithmic distribution of velocity with an increment of 0.100.

/The .....

The Electrostatic Spark Test

In this test samples of loose explosive are subjected to two types of discharge, (a) a discharge between two metallic electrodes using capacitances usually of 250 and 500 $\mu\mu F$ under conditions such that the upper electrode can approach and touch the lower electrode upon which the explosive is placed and (b) a discharge between a metallic electrode using capacitances over a wider range, under similar conditions except that the lower electrode is covered by a piece of conducting rubber. The discharges used in (b) simulate those from the finger of a charged person. For some description of the test see Proc. Roy. Soc. 1958, A.246, 189. The sample of explosive is prepared by the same filling plate as used in the impact test.

In (a) fifty trials are carried out at various energy levels with the two capacitances so that a result can be quoted as the minimum or threshold ignition energy which is the energy for 0 ignitions in 50 trials, with one or more ignitions in 50 trials as the next highest level.

In (b) fifty trials are carried out at various energy levels with at least three capacitances, so that a graph can be plotted of the threshold ignition energy against capacitance, from which can be estimated the minimum capacitance for ignition, and the minimum energy at the optimum capacitance.

/TABLE I .....

TABLE I

Sensitiveness of Lead Azide Polymorphs to Impact, Friction, and Electrostatic Discharge

	Service Lead Azide		beta Lead Azide		gamma Lead Azide	
		s		s		s
Impact	50%		50%		50%	
	15.24 cms	0.106	15.04 cms	0.078	7.35 cms	0.121
Friction	4.46 ft/sec	0.184	4.39 ft/sec	0.185	6.29 ft/sec	0.194
Electrostatic discharge						
N/N needle 250 - 500 μμF	20 ergs		12 ergs		11 ergs	
P/N minimum capacitance	~400 μμF		~400 μμF		~400 μμF	
minimum energy	2250 ergs at 1500 μμF		2500 ergs at 1000 μμF		3000 ergs at 1000 μμF	

N.B. The standard deviations have been calculated according to eqn (2) of Dixon & Mood.
J. Amer. Statistical Assoc. 1948, 43, 109.

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Discussion on Paper (A-2)

Dr. Ball asked if the sample of beta lead azide tested was of mixed or controlled crystal size, as he thought it might have some bearing on the results.

Dr. Wyatt said that the sample was broken up with a rubber spatula and was therefore of mixed particle size including broken crystals. **Dr. Ball** then said he thought it might be significant that broken crystals were included in connection with rogue explosions. **Dr. Kaufman** asked if there really was a significant difference between 12 and 20 ergs. **Dr. Wyatt** said there was not, since samples of alpha lead azide of differing particle size had given this sort of range of values.

Mr. Duke asked if 0.3 Kcal difference in heat of formation was significant; if the difference had instead been 3.0 Kcal, would this be sufficient to show marked differences in sensitiveness? It was known that ΔH for polymorphic transformations had a maximum value of ~ 3-5 Kcal/mole, and cases were known where polymorphs undoubtedly showed marked differences in sensitiveness. **Dr. Wyatt** said that 0.3 Kcal difference would not be reflected in difference in sensitiveness, but he thought that 3 Kcal difference would be just discernible.

Dr. Lovecy said Miles and Garner gave different activation energies but he thought that the difference would show up in thermal decomposition but not in a crude test such as this. He went on to ask if, in view of these results, all the effort put into the suppression of beta was justified.

The Chairman said that there was a strong case for the suppression of beta, as it was desirable to have a pure, reproducible product and that some confusion had occurred which associated beta lead azide with spontaneous explosion; this was, of course, incorrect.

G.W.C. Taylor

The common alpha (orthorhombic) normal lead azide is readily prepared free from other modifications although the beta (monoclinic) polymorph is often observed during the early stages of crystallisation. This occurs especially where mixing of reactant solutions is poor so that conditions of slow diffusion are very favourable to beta formation. The isolation of gamma (monoclinic) lead azide is much more difficult which accounts for the comparatively recent discovery of this polymorph.

By the use of selected additives the isolation of the polymorphic modifications of lead azide is simplified. Eosin favours the formation of beta lead azide, and most hydrophilic colloids, of which dextrin is the best known, suppress beta in favour of alpha. The most striking example of a polymorph inducer is polyvinyl alcohol, which favours the gamma polymorph at low temperatures (below ca. 25°C) and alpha at higher temperatures. There is some evidence that at a very critical intermediate temperature beta lead azide is formed. No other additive has been found which is as effective as polyvinyl alcohol in promoting gamma formation; the presence of unhydrolysed polyvinyl acetate interferes seriously with this process. The mechanism by which polyvinyl alcohol operates to give gamma lead azide is a matter for speculation but it is of interest that further study in E.R.D.E. has shown that a new polymorph of barium styphnate can be isolated with polyvinyl alcohol as an additive and that beta lead styphnate formation is suppressed very strongly by it, an observation which is important technically.

Therefore gamma lead azide can be prepared reproducibly and in quantity (450 gm batches) using as an additive polyvinyl alcohol which is free from unhydrolysed polyvinyl acetate. The degree of polymerisation does not appear to be critical. An effective procedure is to add simultaneously and slowly solutions of sodium azide and lead acetate to a stirred solution of polyvinyl alcohol containing a small advance of sodium azide. The temperature preferably should not exceed 15°C for the reason given above.

Gamma lead azide can be prepared also by the action of hydrazoic acid gas on lead acetate solution containing 0.2 per cent polyvinyl alcohol. It can be recrystallised from ammonium acetate solution in order to obtain larger and better formed crystals. It can be prepared also by dissolving alpha or beta lead azide in five per cent aqueous solution of ammonium acetate containing polyvinyl alcohol and allowing to crystallise. When crystallising from ammonium acetate solutions the temperature should not exceed 40°C.

/Discussion .....

The Chairman said that gamma lead azide could be prepared without the use of additives, as had been indicated by Mr. Lamnevik. Dr. Lovecy asked Mr. Lamnevik if there were any special features of his method of preparation. Mr. Lamnevik replied that it was essential to employ the use of a buffer of hydrazoic acid/sodium azide solution of pH 3.0 to 5.0.

Dr. Wyatt gave the results of sensitiveness tests carried out on gamma lead azide (Table I in paper (A-2)) and on mechanical mixes of 90% service lead azide with 10% beta, and 90% Service lead azide with 10% gamma (Table II).

TABLE II

Effect of Beta- and Gamma- Lead Azide on the Sensitiveness of Service Lead Azide to Impact and Friction

	Service Azide		90% Service Azide/ 10% Beta lead azide		90% Service Azide/ 10% Gamma lead azide	
	50%	S	50%	S	50%	S
Impact	15.24 cm	0.106	11.91 cm	0.081	10.31 cm	0.149
Friction	4.46 ft/sec	0.184	3.61 ft/sec	0.206	3.57 ft/sec	0.242

These showed that the addition of either beta or gamma lead azide caused an increase in sensitiveness to impact and friction.

/Mr. Medlock .....

Mr. Medlock asked if the tests on the mixtures could really be showing differences in hardness rather than the true characteristics of the material, and said he would like to see the results of tests carried out on a mixture of 90% gamma and 10% Service lead azide. He thought this might be more sensitive even than gamma on its own.

Dr. Wyatt said that this might be the case, and tests on other mixtures would be carried out.

Mr. Clay said that as a user he was very interested in these results and he looked forward to seeing the results of future tests.

Dr. Lovecy said that beta lead azide had very different "physical features" from alpha and gamma, and asked if the manner in which sensitiveness at the 0% point varies could be a clue to the individual types.

The Chairman said that this point was more appropriate to session D, but as gamma lead azide was less stable than either alpha or beta it was unlikely to have any technical application. Mr. Lamnevik agreed. From his experience gamma and delta fairly readily turned yellow when exposed to light, and this was a method that could be used to detect their presence.

The Chairman said that Dr. Bowden's laboratory at Cambridge had found the gamma form too easily decomposed by electron bombardment at normal temperatures for profitable study, but he thought that gamma and delta lead azide were good subjects for research at low temperatures. It was possible to prepare either alpha, beta, or gamma lead azide simply by altering the temperature conditions of one process. However, it had not been possible to prepare delta lead azide by this process, although it can be made in the presence of P.V.A., and its preparation will be further investigated.

Mr. S.E. Harris asked if any variation in results of sensitiveness tests would be expected on samples of the same material but of various uniform crystal sizes.

The Chairman replied that tests had been carried out on pure alpha lead azide over a range of sizes, and that similar results were obtained. The only exception was in the electrostatic spark test on colloidal material which proved to be more sensitive. However, grinding large crystals did not affect their sensitiveness. He thought that method of preparation was more likely to affect sensitiveness than was crystal size.

/Basic .....

Basic lead azide was then discussed. The Chairman said that it sometimes appears as traces in, and is a component of, Service lead azide. Mr. Thomas at Woolwich had prepared it in a pure crystalline form corresponding to the formula $Pb\ N_3(OH)$ by crystallisation from a 5% ammonium acetate solution containing free ammonia to a pH of 8.7. Mr. Duke had examined this material, and had found it present as well-formed, white crystals on pellets of alpha lead azide stored under moist conditions. The Chairman asked Mr. Duke if he thought that various basic lead azides described in the literature were forms of different crystal habit and not polymorphs. Mr. Duke said that further work would be required before this could be settled, but he thought there might be fewer forms of basic lead azide than had sometimes been suggested.

Dr. Kaufman said that work had been carried out at Picatinny, Arsenal on formation of basic azides by the action of hydrazoic acid on lead oxide, but the results did not indicate any possible use for these materials in ammunition.

The Chairman said that as basic lead azide did not hydrolyse, mixtures with normal azide had been tested for potential application. However, the basic azide did not suppress the hydrolysis of the normal salt even when present in large excess.

This brought session A to a close and the Chairman thanked all those who had participated.

Decomposition and Chemical Analysis
of Lead Azide

Session Chairman: Dr. I. Dunstan

Contributors: Mr. N.J. Blay
                     Dr. G. Todd
                     Mr. S. Lamnevik

Session Secretary: Mr. G. Packman

The **Chairman** opened the session by referring to the various ways in which decomposition of lead azide could occur. The principal modes were:

(i)   Direct breakdown into the elements:

$$Pb(N_3)_2 \rightarrow Pb + 3N_2$$

This reaction had been studied extensively.

(ii) Hydrolysis:

$$Pb(N_3)_2 \xrightarrow{H_2O} \text{basic lead azide} + 2HN_3 + PbO$$
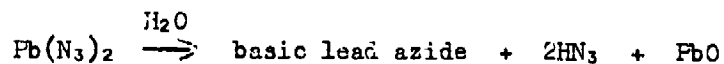
Fundamental investigations of this reaction had received less detailed attention in the open literature, but such degradation was of great practical significance from the Service aspect.

(iii) Oxidation (e.g. by ceric compounds):

$$Pb(N_3)_2 \rightarrow Pb^{++} + 3N_2 + 2e$$
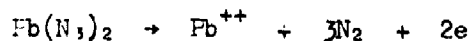
(iv) Reaction with nitrite ion:

$$Pb(N_3)_2 + 2NO_2^- + 4H^+ \rightarrow Pb^{++} + 2N_2O + 2N_2 + 2H_2O$$

(v) Metathesis:

$$Pb(N_3)_2 + 2X^+Y^- \rightarrow PbY_2 + 2XN_3$$
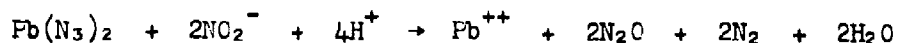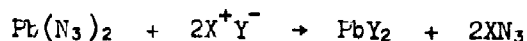
/Analysis .....

Analysis of lead azide was of importance not only for production purposes but also for following the behaviour of lead azide under various conditions arising during climatic trials and other investigations.

The Chairman introduced the first speaker, Mr. N.J. Blay, who was followed by Dr. G. Todd and Mr. S. Lamnevik. Mr. Blay then gave a further paper.

/Paper (B-1) .....

Paper (B-1)   THE EFFECTS OF ENVIRONMENTAL CONDITIONS ON THE
                     DETERIORATION OF LEAD AZIDE

N.J. Blay

The many papers which have been published describing the thermal
decomposition reactions of lead azide when heated in vacuum all indicate
that this mode of decomposition ($Pb(N_3)_2 \xrightarrow{\text{heat}} Pb + 3N_2$) is of little
importance in relation to the behaviour of the substance during storage
at near normal temperatures. The data of Jack[1] can be extrapolated to
show that the period of induction, which is commonly observed in gas
evolution experiments, and which precedes the accelerated reaction leading
to complete decomposition, would last for a period in the region of
100 years if the experiments were conducted at 60°C, or for about 5 years
at 90°C.

Reitzner[2], at Picatinny Arsenal, found that the thermal decomposition
reactions were greatly affected by the presence of water, which in trace
amounts appeared to react with the nuclei from which the thermal decomposition
reactions developed, and thus tended to inhibit the decomposition, but which,
when present in larger quantities, resulted in hydrolysis of the azide with
formation of hydrazoic acid and ammonium azide.

Thornley[3] and others at the University of Utah have used electron
microscopy to study the reactions occurring on the surfaces of lead azide
crystals kept in various environments. It was found that high humidity was
essential to obtain any measurable reaction with carbon dioxide, and that
without added water vapour only slight effects were produced even after
64 hours exposure at 100°C.

There is much evidence to suggest therefore that the long term
stability of lead azide in stored ammunition is largely governed by its
reactivity to water, and the influence which other substances in its
environment may have on this reactivity. These reactions have received
comparatively little attention hitherto, and in this paper some quantitative
information is presented, which indicates the extent to which hydrolysis may
affect lead azide.

Briefly the methods used were as follows:

/Specimens .....

Specimens of lead azide (in most cases British Service Lead Azide), weighing 0.3 grams, were placed in small (2 cm × 2 cm) open glass beakers and stored in air at the temperatures and relative humidities listed in Table I. The storage containers were laboratory vacuum desiccators 7" in diameter, containing saturated salt solutions chosen to produce the required relative humidities. After storage, the azide contents of the specimens were determined, usually by the method described by Sen[4] and others, in which the lead azide is allowed to react with an excess of ceric ammonium nitrate solution; unreacted reagent is then measured by titration with standard ferrous sulphate solution.

The results of these tests are summarised in Table I which, in most cases, gives the average results obtained for several experiments under each set of conditions.

/TABLE I .....

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TABLE I

Decomposition of Lead Azide

(Fall in Azide Content - of Service Lead Azide, Except where Stated)

Trial Conditions				Decomposition Rate Loss of Azide Per cent per month
Temperature °C	Humidity % R.H.	Other Variables	Duration Months	
I.S.A.T.	(A)	-	12	0.15
I.S.A.T.	(A)	R.D.1333	12	0.4
60	Ambient	-	12	0.03
60	Ambient	R.D.1333	12	0.03
60	95	-	6	0.25
80	95	-	1	4 to 5
80	77	-	2	1
80	Ambient	-	1	0.05
90	50	-	0.5	5
90	Ambient	-	1	0.5 to 1.0
80	95	In proximity to sodium carbonate	1	55
80	95	In carbon dioxide	1	40

/The .....

The results demonstrate the very high thermal stability of lead azide in the absence of added water. At 60°C for 12 months and 80°C for 1 month the effects were scarcely detectable, and even at 90°C only a minor degree of deterioration was observed.

When the humidity was increased, an obvious increase in degree of decomposition was produced, although the actual reductions in azide content, bearing in mind the extreme conditions, were not excessive, indicating that lead azide could withstand conditions such as the ISAT(A) cycle, or continuous storage at 60°C and 95% RH. for surprisingly long periods without suffering an unacceptable degree of deterioration. The conclusion from all except the last two results in the Table must be that the reaction between lead azide and water vapour, in the absence of other complicating factors, and in a static situation, is not likely to cause a very serious deterioration of lead azide. This is in line with Service experience, where the principal problem associated with the hydrolysis reaction has usually been the advent of azide corrosion of copper or brass, rather than the extent of the deterioration of lead azide, and the consequent loss of its explosive power.

The increased degrees of decomposition observed in the last two experiments recorded in the Table indicate factors which can greatly affect the extent of hydrolysis of lead azide. This reaction is reversible and an equilibrium condition is attained:

$$Pb(N_3)_2 + H_2O \rightleftharpoons Pb(N_3)OH + HN_3$$

Introduction of an absorbent for hydrazoic acid, such as sodium carbonate, produces a shift in equilibrium to the right and increases the amount of lead azide which decomposes. In the presence of carbon dioxide the equilibrium is again affected, since basic lead azide reacts to give basic carbonate and a new equilibrium is established, requiring the decomposition of more lead azide.

In most of its military applications lead azide has to exist for long periods in a mainly static environment, and it is worth considering what design parameters may influence its behaviour in these circumstances. Clearly the presence of materials capable of releasing substantial quantities of water is undesirable. However, even if considerable amounts of water are introduced the effects may not be too serious, provided that other factors do not affect the equilibrium between lead azide and water, and produce an enhanced degree of hydrolysis.

/The .....

The presence of alkaline absorbents for hydrazoic acid, or of metals which are corroded by it, is an obvious example, but many other possibilities exist. As is suggested by the effect of carbon dioxide, acids or acid gases capable of forming lead salts can be expected to accelerated the decomposition. This effect has been observed with mineral acids and with acidic substances released from shellac lacquers under moist conditions. The practical importance of controlling acidity and alkalinity of materials used in proximity to lead azide is quite evident.

The effects of volatile organic bases will not be very different from those of other alkalies. However, the azides of these compounds often possess an appreciable volatility, and can sometimes be produced as vapours by metathetic reactions between lead azide and their salts. The formation of ammonium azide from lead azide and ammonium nitrate or acetate is a well known example of this. A similar reaction has been observed with mono-ethanolamine hydrochloride, and contaminations by this class of compound in the vicinity of lead azide are undesirable.

None of the reactions so far mentioned involves the actual destruction of the azide ion. However, numerous reactions of hydrazoic acid have been reported,[5][6] which, if occurring in proximity to lead azide, would affect the hydrolysis equilibrium. Among the more important of these are reactions with most common oxidising and reducing agents, mineral acids, alcohols, aldehydes, ketones, sulphur and sulphides. In fact, the reported reactivity of hydrazoic acid is so considerable that the probability of its remaining unreacted in the atmosphere surrounding a detonator in a conventional weapon assembly during long periods of storage begins to appear rather small. It is also true that as the designs of fuzes etc. become more complex, and as more and varied materials become available for their construction, the probability of such reactions occurring will increase.

The substances most closely associated with lead azide in Service use are the metals used to manufacture detonator cases, and other explosives used in incremental filling of detonators. Among the more common metals, those which have been found to be free from serious compatibility objections are surprisingly few in number, being limited to aluminium and certain of its alloys, tin, lead and silver.

Of the explosives which might be used in conjunction with lead azide, tetryl and R.D.X. appear to have no effect and pentaerythritol tetranitrate has only a very slight effect under our test conditions. However, some lead salt of nitroresorcinols do appear capable of influencing the hydrol   of lead azide. Evolution of hydrazoic acid from moistened mixtures   lead azide with three types of lead styphnate has been assessed from the amounts of corrosion produced on copper foil placed in proximity.

/Normal .....

- 31 -

Normal lead styphante ($C_6H(NO_2)_3O_2Pb \cdot H_2O$) markedly increased the amount of acid evolved, monobasic lead styphnate ($C_6H(NO_2)_3(OPbOH)_2$) appeared to have no effect, while tribasic lead styphnate ($C_6H(NO_2)_3(OPbOH)_2 \cdot 2PbO$) greatly reduced the acid evolution. In these instances a reasonably simple explanation can be offered correlating the observed effect on lead azide with the ability of the particular lead styphnate either to yield styphnic acid by hydrolysis, or to absorb hydrazoic acid by reaction with the excess basic lead which it contains. A.T. Thomas[7] has observed that if normal lead dinitroresorcinate (LDNR) or monobasic lead styphnate is covered with a little water, and left in a closed vessel containing a 4 per cent solution of hydrazoic acid, for a few hours, crystals of alpha lead azide and dinitroresorcinol or styphnic acid appear in the water surrounding the LDNR or lead styphnate. A reaction in which hydrazoic acid displaces the much stronger styphnic acid from its lead salt may appear unexpected. However, in the circumstances of the experiment, the reaction:

$$4 \; HN_3 \;\; + \;\; C_6H(NO_2)_3(OPbOH)_2 \;\; \rightleftharpoons \;\; 2 \; Pb(N_3)_2 \;\; + \;\; C_6H(NO_2)_3(OH)_2 \;\; + \;\; 2H_2O$$
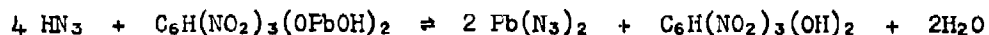
involves four substances, of which three have limited solubilities, and a fourth, hydrazoic acid, which being soluble, is probably present in considerable excess in the liquid phase surrounding the styphnate and LDNR sample, and is constantly replenished.

The reaction, which in other circumstances is reversible, will under these conditions be expected to produce the observed results. The likelihood of such reactions influencing the behaviour of lead azide in service, though difficult to assess, may not be very great. In most instances the reactions would presumably be secondary effects rather than the primary cause of azide deterioration.

Physical conditions may also influence the hydrolysis of lead azide. The equilibrium between lead azide and water produces a partial pressure of hydrazoic acid as calculated by Feitknecht and Sahli[8]. In a closed static system, therefore, the extent of the hydrolysis will depend on the relative sizes of the container and of the azide specimen. In a practical situation, the extent of hydrolysis will be affected by any loss of hydrazoic acid from the container by diffusion or by "breathing" through leaks during temperature variations.

These factors will of course influence the results of experiments of the type which are reported in this paper, and such effects have indeed been observed.

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8. W. Feitknecht and M. Sahli, *Helv. Chim. Acta.*, 1954, 1431-6

Paper (B-2)   THE DECOMPOSITION OF LEAD AZIDE
                                  UNDER STORAGE CONDITIONS

G. Todd
R. Eather
T. Heron

(Paper presented by Dr. G. Todd)

Although lead azide is a relatively stable compound under normal
conditions, it is decomposed by heat, by hydrolysis, by ionising radiations
and by attack with other chemical compounds, and under storage conditions
must be protected against these agents which can modify its performance.

It is difficult to find in the literature precise information on how
sensitivity to impact and friction is affected by the presence of decomposition
products. However, changes in practically every other property such as critical
temperature, delay time and velocity of detonation seem to have been measured,
and are all modified, usually disadvantageously. As an example, may be cited
the work of McLaren at Cambridge (1) (Figure 1). This figure shows how pre-
heating at 250°C in the presence of water vapour has an effect upon the
detonation velocity of compressed sheets of lead azide, the detonation
velocity being reduced to half its value by pre-heating for five minutes
under these conditions.

The importance of the presence of water cannot be over-emphasized in
any context and seems to accelerate most decomposition processes. McLaren
found that if the azide were heated in a vacuum so that water was excluded
and only lead produced, heating times had to be increased 80 fold to achieve
the same reduction in detonation velocity.

It may be useful to summarise some of the known data regarding the
effect of water upon lead azide. For instance, at room temperature, lead
azide is soluble in water to the extent of 0.02% w/w. From a knowledge of
the dissociation constants of lead hydroxide and hydrazoic acid, we may
calculate that only 1.0×10^{-5} grams of lead hydroxide per 100 grams of
water are present at equilibrium. Now 100 grams of water at room temperature
can dissolve 1.5×10^{-2} grams of lead hydroxide, 1500 times more than results
from hydrolysis; so that considerable loss of hydrazoic acid must occur to
shift the reaction far enough to the right for lead hydroxide to be pre-
cipitated. However, this seldom, if ever, occurs in practice since basic
lead azides always intervene. Two of these are readily recognised by
X-ray diffraction as common products of hydrolysis of lead azide under
alkaline conditions. One is slightly richer in basic component than given
by the formula

$$Pb(N_3)_2 \quad . \quad PbO \quad . \quad xH_2O$$
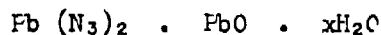
/and .....

and is very well known. An initiator of lower sensitivity to impact and heat than alpha lead azide (2), it may be prepared in the pure form by adding a mixture of one mole of sodium azide and one mole of caustic soda to one mole of lead acetate (3). Its solubility and dissociation parameters are generally not well known, although E.R.D.E. may have them available. In any event, when a saturated solution of lead azide loses sufficient hydrazoic acid, basic lead azide of this type commonly begins to precipitate as the first decomposition product.

The chemistry of the basic azides is very complex, Feitknecht and Sahli[4] claim to have distinguished nine types. During the present work only two of them were encountered, none of these being the common low temperature form just described. This may have been because the temperature of hydrolysis was rather high at 50°C or 60°C. In subsequent discussion it is proposed to give the generic term basic lead azides to all of these products.

In the presence of carbon dioxide the situation is rather different. At normal temperatures water in contact with normal air assumes a pH of about 5.7, which drops to 3.7 as the carbon dioxide content of the contact gases is enriched towards 100%. Neglecting bicarbonate, these pH figures may be taken to mean that water in contact with normal to highly – CO_2 – enriched air may contain from 10^{-6} to 10^{-4} gram-ions of carbonate per litre. We have already noted that the lead azide content of a saturated solution is 0.02% w/w or 6.9×10^{-4} gram-ions of lead per litre. Since the solubility product of lead carbonate is only 3.3×10^{-14}, it follows that the carbonate ion content has only to rise above 10^{-10} gram-ions per litre for lead carbonate to be precipitated.

However, conditions such as these seldom obtain in practice. Lead azide under storage is very carefully protected and ambient conditions would have to be very wet and carbon dioxide-rich for the various barriers to fail and for any appreciable decomposition to occur by the above processes.

From time to time exceptions do seem to occur, and recently at R.A.R.D.E. we have had occasion to examine a very large number of azide samples, many of which had dropped appreciably in azide value. They had all been stored ostensibly in 1/3 of an atmosphere of normal air in a closed container together with other normal items of hardware. All defective azide samples were found to be contaminated with normal carbonate and little else. In fact, if carbonate content was plotted against azide value, a smooth curve was obtained (Figure 2).

We had previously encountered only basic lead carbonates as slow hydrolysis products in air, and we felt that the consistent return of normal carbonate pointed to a prolific source of carbon dioxide.

/Using .....

Using the time-of-flight mass spectrometer based at the Chemical Inspectorate/Woolwich (whose co-operation we gratefully acknowledge), we investigated the carbon dioxide content of the containers of the azide. The argon content was taken as constant and Figure 3 shows a calibration curve for the instrument, in which the carbon dioxide to argon weight ratios of a number of standards are plotted against the ratios of the relative signal strengths obtained from the mass-spectrograms. This calibration yields a factor, which, when multiplied by any signal ratio, gives a value which we term the enrichment factor. This represents the number of times the atmosphere is richer in carbon dioxide than normal air (Figure 4). For example, panel (1) shows a spectrogram for a sample of air to which a few milligrams of solid carbon dioxide have been added. From the calibration curve we may calculate the enrichment factor to be 300 times.

It will be noted that the carbon dioxide to argon ratio is the same in this synthetic sample as that in the ambient atmosphere of an actual azide sample together with its attendant hardware kept for some time under storage conditions as shown in panel (2). The situation in this respect is therefore of the right kind for the decomposition to lead carbonate which had been observed in this sample of azide.

To determine possible sources of carbon dioxide all the materials of construction of the storage hardware were separately tested at 60°C with the representative results shown in panels (3), (4) and (5). It will be noted that where the carbon dioxide content goes up, the oxygen content goes down. Enrichment factors were calculated for a number of components as shown in Table 1. Although polythene and bakelite were satisfactory, the rubber items were prolific sources of carbon dioxide as was the polythene vessel with its content of oxidising fluid.

This item also proved to be the most likely source of the water necessary for decomposition, for, as subsequent tests will show, carbon dioxide without water is relatively innocuous. Figure 5, a graph relating relative humidity to temperature, was obtained by placing an electronic relative humidity sensor inside a canister containing the polythene vessel and evacuating the air in the canister to 1/3 of atmosphere. Signals from the R.H. sensor were received externally. Water permeated the polythene and, during the temperature fluctuations of the ISAT(A) cycle to which the canister was subjected, raised the R.H. at one stage to the point where a coating of liquid water on the azide was feasible. Subject to failure of protective coatings the situation seemed appropriate for decomposition of the azide to lead carbonate, according to the scheme previously outlined.

/A few .....

A few tests were carried out in glass vessels to determine in greater detail the effects of carbon dioxide and water separately and in concert upon lead azide at temperatures of 50°C - 60°C. Calculated masses of water were introduced into a series of vessels to give 25%, 50%, 75% and 100% R.H. at 60°C. All vessels contained a sample of Service lead azide together with air containing an arbitrary 70 times enrichment of carbon dioxide. After storing for seven days at 60°C, X-ray analysis showed that the carbonate content had increased appreciably at the highest humidity only. Little decomposition occurred at lower humidities.

A supplementary test was also carried out in which 3 ml of water were sealed inside a polythene capsule and placed together with a sample of milled Service lead azide in a carbon dioxide-enriched atmosphere at 60°C. The pressure was also reduced to a 1/3 of atmosphere. After seven days a substantial amount of lead carbonate had formed.

When this test was repeated at saturation using a wad of water-soaked filter papers as a humidity source so that water condensed freely on all surfaces, a large proportion of azide was converted to <u>basic</u> lead carbonate after one day and conversion appeared complete after seven days.

These results should be compared with those of parallel trials in which Service lead azide was subjected to a temperature of 60°C for one month at an R.H. of 30% - 40% in air enriched 70 times with carbon dioxide. No decomposition was observed.

Similarly, a sample of Service lead azide was subjected to a temperature of 60°C in normal air saturated with water. Substantial decomposition to basic azides occurred in a few days.

In summary, at 60°C in normally dry atmospheres, whether carbon dioxide is present to excess or not, lead azide appears to be reasonably stable. At humidities approaching 100% R.H., air with normal carbon dioxide content rapidly produces essentially basic lead azides. Where both the humidity and carbon dioxide content are abnormally high, lead carbonates are the decomposition product. Whether the product is <u>normal</u> carbonate or <u>basic</u> carbonate depends upon the relative availability of carbon dioxide and water.

The effects of certain acids and bases upon lead azide have also been studied. In the corrosion field it is generally agreed that organic acids such as formic and acetic accelerate the corrosion of lead to carbonate by forming, initially, formates and acetates. These have a high vapour pressure and low stability, dissociating first to basic salts which undergo conversion into carbonates by uptake of carbon dioxide. It seems reasonable to postulate a similar effect upon the decomposition of lead azide in the presence of packaging materials such as wood and paper, which, together with rubbers,

/evolve ......

evolve these acid on storage. Furthermore, acetic acid and nitric acid are often present as impurities in the cellulose nitrate lacquers used to seal detonators, and, in the course of analysing trace impurities present in the ambient atmospheres of stored detonator systems, hydrochloric acid has occasionally been detected. Dinitroresorcinol may also come in contact with lead azide as a result of liberation from LDNR by the action of various acids including hydrazoic acid from decomposing lead azide.

Certain bases may also be present, and ammonia and hydroxylamine have been detected in certain containers. N-phenyl-β-naphthylamine (PBNA) is used liberally as an anti-oxidant for rubber components.

Table 2 (p. 42) illustrates results obtained when Service lead azide was exposed for 14 days to various acid and basic fumes in air at a R.H. of 30% to 40% and a temperature of 50°C. In the acid series, hydrochloric acid was the most agressive, then followed acetic acid and nitric acid, and a mixture of Service lead azide and solid DNR appeared to give no reaction. As expected, no basic azides or carbonates of lead were observed.

With regard to the bases, ammonia encouraged slight decomposition, and hydroxylamine was inactive.

When this trial was repeated in the presence of N/100 solutions of the acids, only basic azide was observed and no acid salts were obtained (Table 3) (p.43).

Of the strong acids, only hydrochloric acid seemed to exercise a definite enhancing effect, producing much more decomposition than water alone. With the weaker acids, acetic acid and dinitroresorcinol, there was little evidence for change of rate of decomposition, compared with the effect of water alone. However, acetic acid did not affect the nature of the decomposition product whereas DNR eliminated basic azide and produced the basic salt of LDNR (D compound) instead.

In the case of acetic acid the experiment was repeated in an enriched atmosphere of carbon dioxide. There was no enhancement of decomposition but the basic azide normally produced by water was converted into the basic carbonate.

Ammonia had a definite enhancing effect upon the decomposition, producing basic carbonates. This could have been due to two mechanisms. Ammonia vapour would be expected to dissolve in surface water and rapidly collect from the air an equivalent concentration of carbonate ions, thus enhancing carbonate precipitation. There may be an alternative effect due to ammonia vapour removing hydrazoic acid from the reaction and shifting the hydrolysis equilibrium to the right.

/With .....

With PBNA only the second mechanism is possible, for, although enhancement of decomposition occurs, only basic azides are formed. Solid PBNA was mixed with azide for this experiment; the effects of this base will be reinvestigated using only its vapour.

In summary, although fumes of ammonia, nitric and acetic acids, and particularly hydrochloric acid, all decompose lead azide under dry conditions at 60°C, the decomposition products are not carbonates or basic azides and can be recognised by X-ray diffraction. We have never observed these products in Service stores. Under wet conditions only hydrochloric acid fumes enhance decomposition of azide at 60°C, compared with the effect of water alone; the product is basic azide.

Although DNR does not enhance decomposition, it does lower the azide value by converting the basic azide normally produced into a basic salt of LDNR. Bases such as ammonia and substituted ammonias definitely appear to have an enhancing effect. Ammonia in particular has a serious effect since it not only enhances decomposition of lead azide but lowers the azide value even further by converting basic azide into basic carbonate.

This work is continuing.

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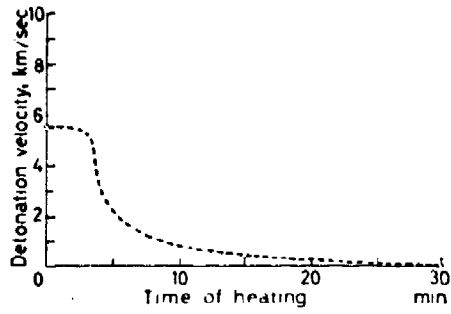
The effect of pre-heating at 250 C in the presence of water vapour on the subsequent detonation velocity of compressed sheets of lead azide

FIG. 1
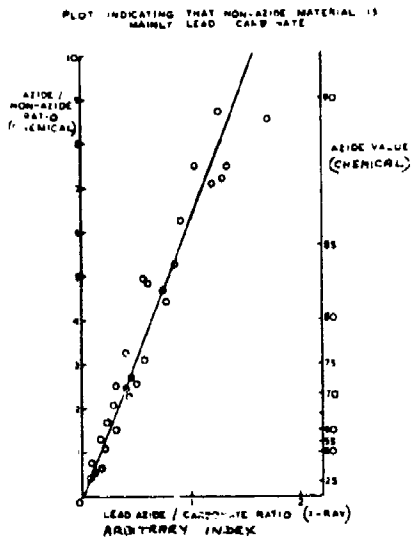
FIG. 2
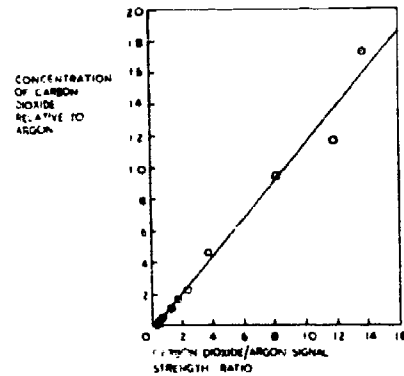
FIG. 3
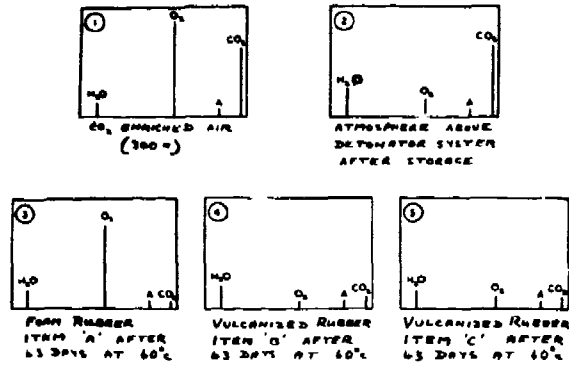
/FIG. 4 .....

FIG. 4
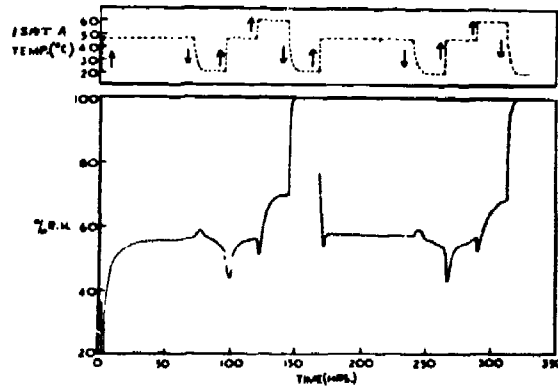
FIG. 5

/TABLE 1 .....

TABLE 1

Description	CO_2 enrichment factor per 28 days
Foam rubber item 'A'	3.0
Vulcanized rubber item 'B'	5.4
Vulcanized rubber item 'C'	6.1
Polythene item 'D'	negligible
Bakelite item 'E'	negligible
Oxidising Solution sealed in polythene	56.6

TABLE 2

Contact atmosphere	Compounds identified by X-ray diffraction			
	Residual lead azide	Basic lead azides	Lead carbonates	Others
Air (30 - 40% R.H.)	mainly	nil	as S.L.A.	nil
Air + hydrochloric acid	trace	nil	-	mainly PbCl$_2$
Air + acetic acid	mainly	nil	as S.L.A.	considerable unknown
Air + nitric acid	mainly	nil	as S.L.A.	some unknown
Air + dinitroresorcinol	mainly	nil	as S.L.A.	nil
Air + ammonia	mainly	nil	as S.L.A.	some unknown
Air + hydroxylamine	mainly	nil	as S.L.A.	nil

TABLE 3

Contact atmosphere	Duration of trial	Compounds identified by X-ray diffraction			
		Residual lead azide	Basic lead azides	Lead carbonates	Others
Air + water	4 weeks	trace	mainly	–	–
Air + water + nitric acid		trace	mainly	–	–
Air + water + hydrochloric acid		some	much	–	–
Air + water	5 days	some	much	as S.L.A.	–
Air + water + dinitroresorcinol		some	nil	as S.L.A.	D compound
Air + water	1 day	much	much	as S.L.A.	nil
Air + water + acetic acid		much	much	as S.L.A.	nil
Air + water	1 day	much	much	as S.L.A.	nil
Air + water + acetic acid		much	much	as S.L.A.	nil
Air + water + acetic acid + carbon dioxide		much	trace	much[*]	nil
Air + water	1 week	some	mainly	as S.L.A.	nil
Air + water + ammonia		nil	trace	mainly[*]	nil
Air + water	1 week	some	mainly	as S.L.A.	nil
Air + water A N-phenyl-β-naphthylamine		nil	mainly	as S.L.A.	trace

[*] Basic lead carbonates

MECHANISM FOR THE BREAKDOWN OF LEAD AZIDE

S. Lamnevik

1. Reaction with Moisture

This reaction has been studied at our Institute for a long time. Concentrations of the products involved can be calculated from the conditions of chemical equilibrium. The overall reaction is:

$$Pb(N_3)_2(s) \; + \; H_2O(l) \; \rightleftharpoons \; Pb(OH)N_3(s) \; + \; HN_3(g) \qquad (1)$$
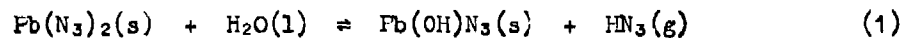
$$K_A \; = \; P_{HN_3}$$

For the calculation the following equilibria must be taken into account:

$$Pb(N_3)_2(s) \; \rightleftharpoons \; Pb^{2+} \; + \; 2N_3^- \qquad (2)$$

$$K_1 \; = \; (Pb^{2+})(N_3^-)^2$$

$$Pb(OH)N_3(s) \; \rightleftharpoons \; Pb^{2+} \; + \; OH^- \; + \; N_3^- \qquad (3)$$

$$K_2 \; = \; (Pb^{2+})(OH^-)(N_3^-)$$

$$HN_3(aq) \; \rightleftharpoons \; H^+ \qquad N_3^- \qquad (4)$$

$$K_3 \; = \; \frac{(H^+)(N_3^-)}{HN_3}$$

$$HN_3(aq) \; \rightleftharpoons \; HN_3(g) \qquad (5)$$
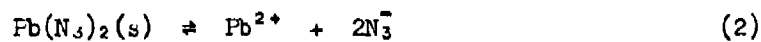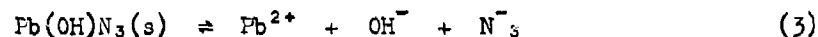
$$K_4 \; = \; \frac{P_{HN_3}}{(HN_3)}$$

/Equation .....

- 45 -

$$H_2O(l) \rightleftharpoons H^+ + OH^- \qquad\qquad (6)$$

$$K_5 = (H^+)(OH^-)$$

Combination of equations 2 - 6 give the expression for the equilibrium constant K_A of the overall reaction (1):

$$K_A = K_1 \cdot K_4 \cdot K_5 / K_2 \cdot K_3$$

The accuracy of the value of K_{H_2O} is of course dependent of the accuracy of the individual values K_{2-5}.

K_1, the solubility product of lead azide, has been determined by Feitknecht and Sahli[1] from solubility measurements: $1.8 \cdot 10^{-9}$ at 20°C and by Suzuki[2] from EMF measurements: $2.58 \cdot 10^{-9}$ at 25°C.

K_2, the solubility product of the basic lead azide formed has been determined by Feitknecht and Sahli[1] from solubility measurements: $5 \cdot 10^{-15}$ at 20°C but should be verified by redetermination.

K_3, the dissociation constant of hydrazoic acid, has been determined by various methods. The value of $-\log K_3$, used by us, is 4.79 at 25°C determined from titrations of sodium azide with a glass electrode in 3 M sodium perchlorate ion medium. This work was done at the Royal Institute of Technology in Stockholm by Lamnevik (1960).

K_4, the partition constant of hydrazoic acid between air and water, has been determined by Feitknecht and Sahli[1]: 51 mm Hg/M at 18°C, and by Lamnevik[3]: 84 mm Hg/M at 25°C, and 120 mm Hg/M at 35°C, by a dynamic method described by Ostwald-Luther[4]. The values of K_4 should preferably be checked by another method.

K_5, the dissociation constant of water, has been determined with great accuracy and can be taken from any handbook of chemistry[5]: $-\log K_5 = 14.1669$ at 20°C and 13.9965 at 25°C. The numerical value of K_A, using the values above, is $4.5 \cdot 10^{-2}$ mm Hg at 25°C corresponding to a concentration of hydrazoic acid in water phase of 0.54 mM. At 20°C K_A is $1.4 \cdot 10^{-2}$ mm Hg (0.27 mM HN_3 in water phase).

/Attempts .....

Attempts to confirm these values experimentally have been made by Feitknecht and Sahli and by Lamnevik and co-workers at our Institute. 0.3-0.5 g lead azide and 2-15 ml water in separate small glass beakers were placed in a glass container which was evacuated and thermostated at $20^{\circ}C^1$ and $25^{\circ}C^3$. The concentration of hydrazoic acid in the water phase was determined colorimetrically with iron (III) from time to time. Equilibrium was reached after a long time, 1 - 3 months, giving a concentration of 0.35 mM at $20^{\circ}C^1$ and 0.47 mM (mean) at $25^{\circ}C^3$. The differences between several runs were rather large. Therefore another method was tried. An air pump, one washing bottle with a lead azide-water suspension and one with water only were connected in series to a closed system and placed in a thermostat at $25^{\circ}C$. The aqueous hydrazoic acid concentration in the water bottle was determined as before. Now equilibrium was reached in a few days with much smaller spread in different runs. 0.42 mM in the water phase corresponding to a partial pressure of $3.5 \cdot 10^{-2}$ mm Hg was obtained in this way.

Further work has to be done, and in fact is planned, at our Institute to confirm these values and extend the temperature range. The equilibrium must also be approached from the other side to verify that an equilibrium really exists.

There are indications that the reaction of dextrinated lead azide with water is more complicated owing to side reactions with dextrin or degradation products of dextrin. Abnormally high values (up to 1 mM in the water phase) have sometimes been observed in the equilibrium experiments. Tests for lead in the water (contamination with lead azide) were negative.

2. Reaction with Carbon Dioxide

This reaction can be considered in the same manner as the hydrolysis reaction of lead azide. The overall reaction is:

$$3Pb(N_3)_2(s) + 4H_2O(l) + 2CO_2(g) \rightleftharpoons Pb_3(OH)_2(CO_3)_2(s) + 6HN_3(g) \qquad (7)$$

$$K_B = P^6_{HN_3}/P^2_{CO_2}$$

/Besides .....

Besides reactions (2), (4), (5) and (6) the following equilibrium conditions are to be considered:

$$H_2CO_3(aq) \rightleftharpoons H^+ + HCO_3^- \tag{8}$$

$$K_6 = (H^+)(HCO_3^-)/(H_2CO_3)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \tag{9}$$

$$K_7 = (H^+)(CO_3^{2-})/(HCO_3^-)$$

$$Pb_3(OH)_2(CO_3)_2(s) \rightleftharpoons 3Pb^{2+} + 2OH^- + 2CO_3^{2-} \tag{10}$$

$$K_8 = (Pb^{2+})^3 (OH^-)^2 (CO_3^{2-})^2$$

$$H_2CO_3 aq \rightleftharpoons CO_2(g) + H_2O(1) \tag{11}$$
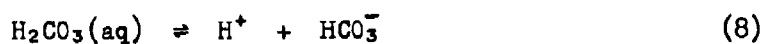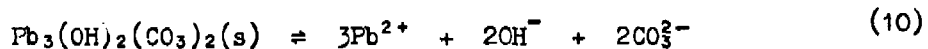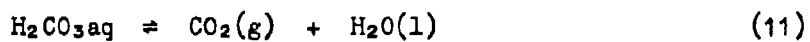
$$K_9 = P_{CO_2}/(H_2CO_3)$$

By combination of these reactions the following expression for the equilibrium constant K_{B_2} can be deduced:

$$K_{B_2} = K_1^3 \cdot K_4^6 \cdot K_5^2 \cdot K_6^2 \cdot K_7^2/K_8^6 \cdot K_8 \cdot K_9^2$$

/Using .....

- 48 -

Using
$$K_6 = 4.30 \cdot 10^{-7} \quad (25°C)^5$$

$$K_7 = 5.61 \cdot 10^{-11} \quad (25°C)^5$$

$$K_8 = 3.5 \cdot 10^{-46} \quad (18°C)^6$$

$$K_9 = 2.25 \cdot 10^{4} \quad (25°C)^7$$

the numerical value of K_B will be $8.7 \cdot 10^{-11}$ at 25°C. Therefore the partial pressure of hydrazoic acid tends to rise with increasing partial pressure of carbon dioxide to, for instance, $2.1 \cdot 10^{-2}$ mm Hg at a carbon dioxide pressure of 1 mm Hg.

There has been no experimental work at our Institute to investigate the exact value of the equilibrium constant, but basic lead carbonate has been detected by X-ray diffraction in lead azide stored in open containers.

3. Reaction with Hydrogen Sulphide

Lead azide reacts with hydrogen sulphide:

$$Pb(N_3)_2(s) + H_2S(g) \rightleftharpoons PbS(s) + 2HN_3(g) \tag{12}$$
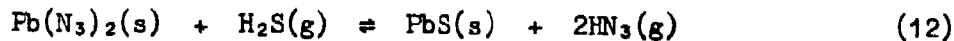
$$K_C = P^2_{HN_3}/P_{H_2S}$$

The following equilibrium conditions exist:

$$PbS(s) \rightleftharpoons Pb^{2+} + S^{2-} \tag{13}$$

$$K_{10} = (Pb^{2+})(S^{2-}) = 1.0 \cdot 10^{-29} \text{ at } 25°C^7$$

$$H_2S(aq) \rightleftharpoons H^+ \ HS^- \tag{14}$$

$$K_{11} = (H^+)(HS^-)/(H_2S) = 1.2 \cdot 10^{-7} \text{ at } 25°C^7$$

/Equation .....

$$HS^- \rightleftharpoons H^+ + S^{2-} \tag{15}$$
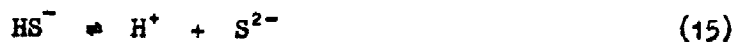
$$K_{12} = (H^+)(S^{2-})/(HS^-) = 1.0 \cdot 10^{-15} \text{ at } 25°C^{[7]}$$

$$H_2S(aq) \rightleftharpoons H_2S(g) \tag{16}$$

$$K_{13} = P_{H_2S}/(H_2S) = 8.3 \cdot 10^3 \text{ at } 25°C^{[7]}$$

$$K_C = K_1 \cdot K_4^2 \cdot K_{11} \cdot K_{12}/K_3^2 \cdot K_{10} \cdot K_{13} = 1.0 \cdot 10^8 \text{ at } 25°C$$

The numerical value of K_C indicates that hydrogen sulphide reacts almost quantitatively with lead azide.

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THE CHEMICAL ANALYSIS OF LEAD AZIDE

N.J. Blay

This paper is concerned principally with the methods of analysis which have been or might be used for the determination of azide content of lead azide as required by the specifications for this substance. The first question which could be asked is whether this test is really essential for proper control of the material, or whether the control of impurities and of performance requirements would alone be adequate. Not all specifications for explosives include a chemical assay, but in general some test of chemical purity, such as setting point or melting point, is required. In the case of lead azide the purity is dependent upon the precise control of crystallisation conditions. The possibility of contamination with one of the basic azides or lead carbonate, neither of which is normally required to be estimated directly by the specifications, increases the desirability of the test and it is therefore unlikely to cease to be a requirement.

The accuracy and precision which are necessary can be judged by considering some current specifications given in Table I.

/TABLE I .....

TABLE I

Compositions Containing Lead Azide

	A Lead Azide (British Military Service Lead Azide)	B Dextrinated Lead Azide	C R.D.1333	D R.D.1343	E R.D.1352
Specification	C.S. 2222 C	C.S. 2423	C.S. 2637	C.S. 5382 A	C.S. 5426 A
Azide Value	< 95.5	< 92.0	< 97.0	< 96.5	94.0 ± 1.0 (on dry)
Pb %	–	–	70.0 ± 1.0	71.0 ± 0.5	68.0 ± 0.5 (on dry)
Carboxy methyl Cellulose %	–	–	0.90 ± 0.30 (as Pb salt)	0.30 ± 0.15 (as Pb salt)	–
Volatile Matter %	> 0.2	> 1.0	> 0.5	> 0.1	> 1.0

B – Precipitated in presence of dextrin.

C – Precipitated in presence of sodium salt of carboxymethyl cellulose.

D – Precipitated in presence of sodium salt of carboxymethyl cellulose and sodium hydroxide.

E – Precipitated in presence of dextrin and an anionic dispersing agent.

After allowing for the proportions of phlegmatising agents and other substances which are present it is obvious that the permitted tolerances on azide content are quite small, and that the analytical methods have to be correspondingly accurate and precise.

Numerous methods have been suggested in the past for the determination of azide content. One of the first, referred to by Marshall[1] in 1917, was the measurement of the volume of nitrogen evolved by reacting lead azide with ceric ammonium nitrate. This method is still used by both the U.S. and U.K. in some of their specification tests, and its retention after so many years indicates its value. Other early methods, none of which are now favoured, were based upon:-

(i)   Gravimetric determination as silver azide.

(ii)   Titration with iodine.

(iii) Reaction with nitrous acid.

(iv)   Oxidation by permanganate.

Another method which has been used more recently, for the analysis of organic azides rather than lead azide, is based upon reaction with a solution of sodium iodide in trichloracetic acid, to give iodine, which can then be titrated.

$$RN_3 \; + \; 3HI \; \rightarrow \; RNH_3^+I^- \; + \; N_2 \; + \; I_2$$
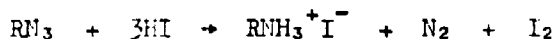
A method which has been found very useful for the analysis of small quantities of lead azide has been contributed by Higgs and Batten of R.A.R.D.E. and appears as Appendix I. It is a spectrophotometric procedure in which the decrease in absorption at 390 millimicrons produced by adding the sample to a standard ceric ammonium nitrate solution is measured.

The principal features of most of the methods which are or have been used or suggested for specification testing are shown in Fig. 1. With one exception, they all involve either reaction with ceric ammonium nitrate (ammonium hexanitratocerate) or precipitation of silver azide. The exception is based upon distillation of hydrazoic acid from a solution of the sample in a known quantity of nitric acid, followed by estimation of residual acid. It has some obvious drawbacks (interference by carbonates and the hazard of evaporating hydrazoic acid) and has not been widely used; it will not be further considered.

The remaining methods will be discussed in more detail.

/Method I .....

- 59 -

Method I. Gas Volumetric Method using Ceric Ammonium Nitrate

As already mentioned, this method was one of the first brought into use
and appears in two specifications (2, 3). The two procedures differ in the
sample weight which is taken (0.15 gram in C.S.2423, and 1.7 gram in the
U.S. Method); also, in the American procedure the evolved gas is passed
through a carbon dioxide absorber. The latter modification makes the method
more widely applicable, and it is the U.S. procedure which will be discussed
more fully. It has some disadvantages, which have been commented on; these
are:-

(a)   the large sample size, which makes the consequence of any accident
       more serious, but which could be expected to increase the accuracy
       of the results, and

(b)   the complexity of the apparatus (Fig. 2) and the time taken to assemble
       it;

In other respects the method appears very good. It can be used without
modification on all the current types of lead azide. It is free from hazard
as soon as the sample and reagent are mixed. Once the apparatus has been
assembled the analysis procedure is simple and rapid, and the published results
indicate that the method is capable of producing adequately accurate and precise
data.

Method II. Ceric Ammonium Nitrate Titration

In this method the azide sample (about 0.3 g.) is allowed to react with
an excess of ceric reagent, and the excess is back-titrated with standard
ferrous sulphate solution.

The method was at one time used by the U.S. Navy, and has been studied in
detail by P.K. Sen (4). It is also the method which is used most frequently
at E.R.D.E. Its main drawback is that it is subject to interference by some
organic additives to lead azide - in particular, dextrin and polyvinyl
alcohol - which are oxidised by the reagent, and it was probably for this
reason that the method lost favour in the U.S. Not all organic additives
behave in this way, however; we have found, for example, that gelatin and
carboxymethyl cellulose do not interfere with the estimation.

Apart from its limited applicability, the method is free from other
objections. It is simple and rapid, free from hazard, once the sample and
reagent have been mixed, and requires no special apparatus. Its accuracy
and precision, as judged from our experience and the results reported by Sen,
are very good.

- 4 -

Method III. Distillation of Hydrazoic Acid into Ceric Ammonium Nitrate Reagent

In this method (3), at present recommended by the U.S. Navy Laboratories, hydrazoic acid is distilled from the sample in hot, dilute perchloric acid, and absorbed in a known quantity of ceric ammonium nitrate solution. Titration of the excess of reagent with sodium oxalate solution enables the azide content to be determined.

The procedure appears more complicated and lengthy than methods I and II and requires the assembly of distillation apparatus. The distillation must inevitably present some hazard. Nevertheless, the method has given reliable results, and is not limited in its applicability.

Method IV. Precipitation of Silver Azide from Ammonium Acetate Solution

This is the British Chemical Inspectorate Method (5), required by specification to be used for all types of military lead azide except "Dextrinated Lead Azide". It suffers from three main drawbacks: in comparison with the first two ceric methods it is very lengthy; also, it involves the precipitation, filtration and finally the destruction of silver azide, and there is a further danger that if the procedure is not closely followed some hazard may arise from the solution of lead azide in ammonium acetate. However, it is fair to point out that the accident record through many years' constant use of the method is very good, and it is not regarded as unduly dangerous. The third objection to the method is that it tends to give low results. This inaccuracy has long been recognised in Britain and the specifications are phrased accordingly to limit the "azide value", as determined by the specified method, rather than the true azide content which is thought to be somewhat higher. In other respects the method is quite good, it requires no special apparatus, is applicable to all types of lead azide (although with some surface active colloids present in the sample the filtration of silver azide is more difficult) and gives highly reproducible results.

Two other methods are mentioned in Fig. 1 which are rather similar and involve the distillation of either ammonium azide from the sample in ammonium nitrate solution or of hydrazoic acid from the sample in nitric acid.

/The .....

The distillates (in the latter case collected in sodium hydroxide solution) are carefully neutralised, and titrated with silver nitrate using potassium chromate as indicator. These procedures are fully discussed by Sen(4) and, until 1943, the ammonium nitrate method was the official Chemical Inspectorate Method. Although sound in theory, the end point of the titration is difficult to observe and the methods are somewhat hazardous.

The disadvantages of the four most important methods are indicated (X) in Table II.

<div align="center">TABLE II</div>

Method	I Gas Evolution with C.A.N.	II Volumetric using C.A.N.	III Distn. of HN_3, followed by C.A.N. Titration	IV Ammonium Acetate British CI Method
Large Sample Size	X			
Complexity of apparatus	X(a)		X	
Time/complexity of operations			X	XX
Hazards			X	X
Inapplicability		XX		
Inaccuracy				X
Precision		No significant difference		

(a) Not applicable if numerous analyses have to be made.

It is apparent that the best two methods are I and II, although method I would be most inconvenient if only one or two samples were to be analysed. Method II is very convenient where it is applicable, but its non-applicability to certain types of lead azide restricts its use.

Data relating to the precision of all four methods from the work of Croom and Pristera[6], and of Sen, show that there is little difference between them, the usual value for standard deviations being about 0.2%.

It is of some interest to consider the difference between results obtained by the British ammonium acetate method IV and those by the remaining methods, I, II and III.

In Sen's report, results of 10 groups of analyses (between 6 and 20 determinations in each group) of various types of lead azide using methods II and IV are given, and in all cases the D.C.I. method IV gave results lower than method II. The differences ranged from 0.3 to 1.4 per cent with an average of 1.0 per cent. There is also evidence in his report to indicate that method II gives results close to the true azide content. Our experience at E.R.D.E. of the two methods is very similar. For example, recent tests of the two methods on R.D.1333 gave results which differed by an average of 1.3%. Results given by Croom and Pristera[6] and some more recent data from Picatinny Arsenal lead to a different conclusion. These authors compared methods I, III, and IV and obtained very reproducible results which differed by only 0.3% between methods I and IV and 0.1% between methods III and IV. These tests were made on dextrinated azide, polyvinyl alcohol-treated lead azide, and synthetic mixtures of sodium azide and lead nitrate. In the last case the average result obtained by the D.C.I. method IV was 99.85%.

The differences in analytical procedures and the results obtained are particularly important in the case of R.D.1333, where great stress has been placed on the necessity for carefully controlled conditions of manufacture in order to obtain a standard product. One might expect therefore that all specifications would require the same minimum azide content. However, whereas the British specification C.S.2637 (see Table I) has a limit of 97.0% (min.), the corresponding U.S. specification (3) requires 98.5% (min.). What has already been said about the respective methods of analysis makes it clear that in the British view some difference in requirements is appropriate, although 1.5% seems rather excessive and 1.0% would probably be more reasonable. However, an opinion based on American trials of the methods would not be expected to agree with this conclusion.

/R.D.1333 .....

R.D.1333 contains 0.9 ± 0.3% of lead carboxymethyl cellulose, quite apart from other extraneous impurities, and the limit of 98.5% for azide content obviously leaves only a very small margin for error either in analysis or manufacture. In comparison with the British specification, this requirement is, in the author's opinion, significantly more restrictive.

References

1. Marshall, Explosives, Vol. II, London, 1917, p. 688

2. (U.K.) Specification C.S.2423

3. (U.S.) Purchase Description PA-PD-2825

4. P.K. Sen, Chemical Inspectorate Report (Unpublished)

5. (U.K.) Chemical Inspectorate Lab. Method M.401/63

6. Croom and Pristera, Pic. Arsenal Tech. Report 2486, Mar. 1958

OXIDATIVE REACTION
using Ammonium Hexanitratocerate (AHC)

Dissolve in AHC(a)

FORMATION OF SILVER

	Dissolve in AHC(a)	Distil with HClO₄ (b)		

Gas Volumetric
(Measure evolved
Nitrogen)

Titrate excess
Ce⁺⁺⁺⁺ with Fe⁺⁺

Absorb HN₃ in
AHC(c). Titrate
excess Ce with
Na oxalate

Dissolve in NH₄ acetate
Ppt. AgN₃ with AgNO₃(d).
Titrate excess Ag⁺
with NH₄CNS

Distil NH₄N₃ f...
mixed with NH₄...
Neutralise. T...
with AgNO₃

(I)   (II)   (III)   (IV)

Reactions Involved:

(a) $2(NH_4)_2Ce(NO_3)_6 + Pb(N_3)_2 \rightarrow 4\ NH_4NO_3 + 2\ Ce(NO_3)_3 + Pb(NO_3)_2 + 3\ N_2$

(b) $2\ HClO_4 + Pb(N_3)_2 \rightarrow Pb(ClO_4)_2 + 2\ HN_3$

(c) $2(NH_4)_2Ce(NO_3)_6 + 2\ HN_3 \rightarrow 4NH_4NO_3 + 2\ Ce(NO_3)_3 + 2\ HNO_3 + 3\ N_2$

(d) $AgNO_3 + N_3^- \rightarrow NO_3^- + AgN_3$

(e) $2\ NH_4NO_3 + Pb(N_3)_2 \rightarrow Pb(NO_3)_2 + 2\ NH_4N_3$

(f) $2\ HNO_3 + Pb(N_3)_2 \rightarrow Pb(NO_3)_2 + 2\ HN_3$

NOTES

(I) Method favo
     investigati
     version was

(II) Investigate
      Has recentl

(IV) Standard D.
      D.401/63)

Fig. 1.

E - METHODS FOR DETERMINATION OF AZIDE VALUE

FORMATION OF SILVER AZIDE (AgN₃)   OTHER REACTIONS

| Dissolve in NH₄ acetate ppt. AgN₃ with AgNO₃(d). Titrate excess Ag⁺ with NH₄CNS | Distil NH₄N₃ from sample mixed with NH₄NO₃(e). Neutralise. Titrate with AgNO₃ | Distil HN₃ from sample mixed with HNO₃(f). Collect in NaOH, neutralise and titrate with AgNO₃. | Heat with HNO₃ to remove HN₃(f). Determine residual HNO₃ with KI, KIO₃ and Na₂S₂O₃. |

(IV)

$Pb(NO_3)_2 + 3 N_2$

$2 HNO_3 + 3 N_2$

NOTES

(I) Method favoured by U.S. (PA-PD-2625) and currently under investigation by D.C.I. and D/E.R.D.E. (A simplified version was used for Dextrinated Lead Azide in Specn. C.S.2423)

(II) Investigated by D.C.I. Has recently been used by D/E.R.D.E.

(IV) Standard D.C.I. method (see, e.g. Lab. Method M.401/63)

Fig. 1.

THERMOMETER

3 WAY T
STOPCOCKS

N⁰.2
POS. B

N⁰.1
POS.A

50 ML BURETTE

SMALL BORE
GLASS TUBING

LEVELING
BULB

ZERO

GAS
BURETTE

6 CM

VIAL

4·5 CM

1·4 CM

450 ML

ABSORPTION
FLASK

REACTION
FLASK

WATER RESERVOIR

WATER JACKET

500 ML.

CIRCULATING
PUMP.

Fig. 2

A Spectrophotometric Method for the Determination of Milligram Quantities of Lead Azide

By H.G. Higgs and H. Batten (R.A.R.D.E.)

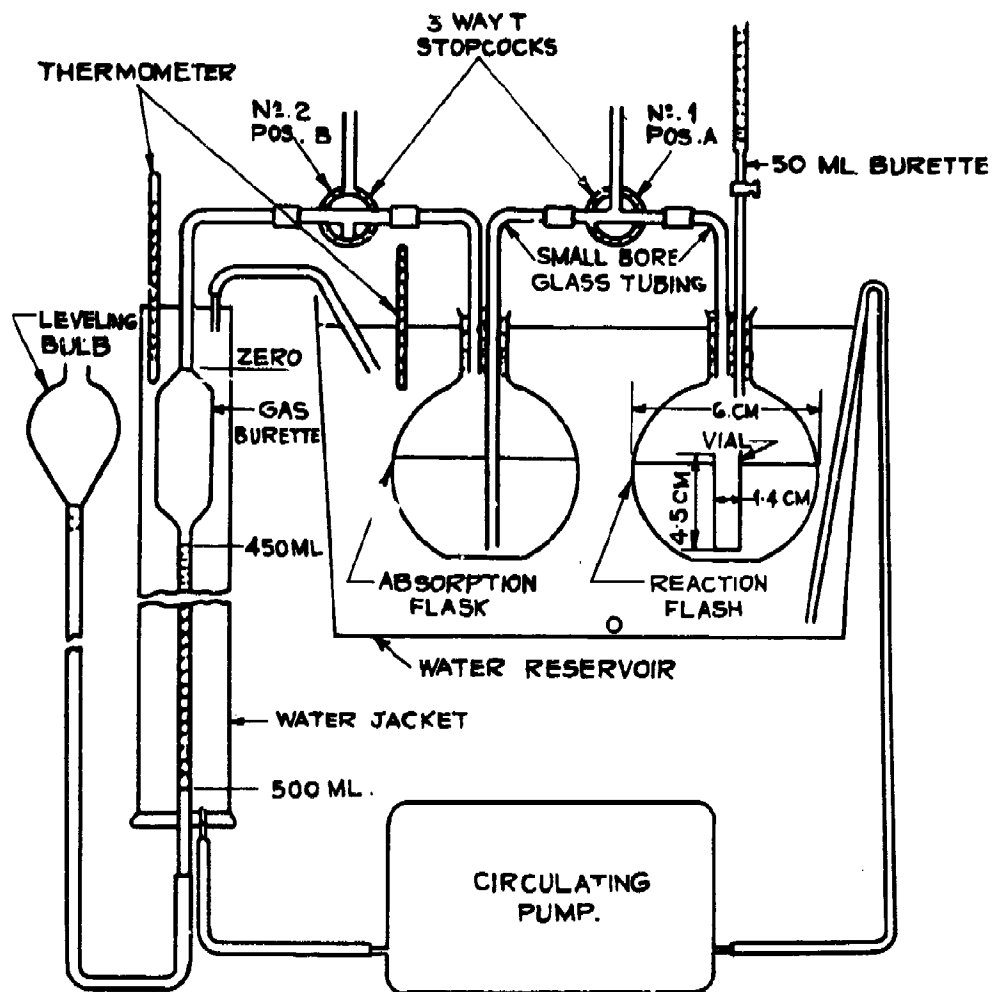To the weighed sample contained in a 50 ml beaker add a few ml of distilled water to wet the sample, followed by 10 ml of 0.025 N ammonium hexanitratocerate containing 3% (v/v) of free nitric acid. Agitate the mixture and leave to react for five minutes. Transfer the contents of the beaker to a 100 ml standard flask and measure the absorbance of the unreacted cerate, using 1 cm cells and a wavelength of 390 millimicrons.

Measure the absorbance of a similar quantity of 0.025 N AHNC in the absence of lead azide, and relate the difference between the two absorbance values to a calibration graph prepared from pure sodium azide, or lead azide of known analytical purity.

Over the sample range: 0.010 - 0.025 g. the observed precision was found to be ± one per cent and the overall accuracy ± 2 - 3 per cent, irrespective of the azide source used for calibration.

Reagent:

Dissolve about 7 g. of C.P. grade ammonium hexanitratocerate in water containing 15 ml of nitric acid (sp. gr. 1.42) and dilute to 500 ml with water.

The lead azide used was of 98.61% purity (Volhard method).

Author's Note

In Appendix II results are given of current work at E.R.D.E., relating to these methods but not available at the time of the symposium.

A Comparison of Methods of Analysis of Lead Azide[*]

By N.J. Blay, J.L. McDougall and D.A. Salter

The following three macro-scale methods for the determination of the azide content of lead azide were compared:

(a) D.C.I. Method M. 401/63

(b) Volumetric method using ceric ammonium nitrate reagent. (Ref 4)

(c) Gasometric method (measurement of nitrogen evolved with ceric ammonium nitrate reagent) as described in U.S. Purchase Description PA-PD-2825.

The three methods were each used to analyse the three materials Service Lead Azide (Specn. CS 2222C), lead azide RD 1333 (CS 2637) and sodium azide, and the results obtained are given in the Table.

/TABLE .....

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[*] Note added in proof. Pristera and his co-workers at Picatinny Arsenal have recently published a report on similar work (Picatinny Arsenal Report No. 66-VG1-177; 29 Dec. 1966).

TABLE OF RESULTS

	D.C.I. Method N 401/63	Volumetric Method C.I. Tech. Paper 167	U.S. Method PA-PD-2825
Service Lead Azide Batch CY 5844/65	96.3, 96.2, 96.5, 96.4 97.2, 97.1, 96.8, 96.6 96.7, 96.7 Average = 96.65% σ = 0.32	96.6, 96.5, 96.8, 96.8 97.2, 96.9, 96.8, 96.4 96.5, 96.5, 96.4, 96.2 96.4, 96.6, 96.6, 96.5 96.6, 96.2 Average = 96.58% σ = 0.25	97.0, 97.0, 97.2, 96.6 96.8, 96.9, 96.7, 96.8 96.8 Average = 96.87% σ = 0.18
RD 1333 Batch 5/66	97.2, 97.4, 97.2, 97.0 97.9, 97.8, 98.3, 97.9 98.3, 98.5 Average = 97.75% σ = 0.53	99.0, 98.8, 99.2, 99.1 98.4, 98.6, 98.6, 98.6 99.0, 98.2, 98.0, 98.1 Average = 98.63% σ = 0.40	98.0, 98.0, 98.0, 98.1 98.2, 98.1, 97.9, 98.2 97.9, 98.1, 98.2 Average = 98.06% σ = 0.12
Sodium Azide	99.8, 99.6, 99.7, 99.8 99.9, 99.6, 99.5, 99.2 99.6, 99.7, 99.7, 99.4 Average = 99.62% σ = 0.18	99.8, 99.6, 99.7, 99.8 99.8, 98.8, 100.0, 99.4 99.2, 99.7, 99.1, 98.9 99.2, 99.4, 99.6, 99.5 99.0, 99.6 Average = 99.46% σ = 0.35	99.5, 99.1, 99.6, 99.2 99.0, 99.6, 99.6, 99.7 99.3, 99.6 Average = 99.42% σ = 0.25

/Discussion ......

Discussion of Results

1. In only one case is the difference between averages of results obtained by the three methods greater than 0.3 per cent. This is for RD 1333, where the volumetric oxidation method gave significantly higher results than the other two methods. The obvious explanation for this is oxidation of the carboxymethyl cellulose in the sample by the ceric reagent, although tests made with carboxy methyl cellulose solutions, both alone and added to Service Lead Azide have failed to show that it has any noticeable effect on the reagent. It is not certain however that these tests can adequately simulate the reactivity of C.M.C. in RD 1333, and in the absence of any other explanation, the possibility of its oxidation cannot be entirely ruled out.

2. The precision of the gasometric (U.S.) method is better in the case of the two lead azides than the other methods. This is perhaps to be expected in view of the much larger sample which is used and the consequent reduction of errors in measurement. The results for sodium azide by the U.S. method include some marginally low figures which were among the first obtained after setting up the apparatus, and it is likely that the method is capable of slightly better precision than is indicated. It was hoped that sodium azide would give results closer to 100 per cent, but repeated recrystallisations failed to produce better material of higher azide content. By analysing portions of lead azide RD 1333 to which 3 per cent by weight of sodium carbonate was added, it was confirmed that the U.S. gasometric method was fully applicable to carbonate-containing samples; and no interference was observed. Further checks were made, after introducing a bubbler containing ceric ammonium nitrate solution immediately after the reaction vessel. No difference was observed in results on sodium or lead azides, confirming that no hydrazoic acid vapour was being swept out of the reaction vessel by the rapid evolution of nitrogen.

3. The D.C.I. method M 401/63 gave very reproducible and apparently accurate results on sodium azide, but was less satisfactory for the two types of lead azide. It is possible that some co-precipitation or other interference may result from having lead ions and carboxymethyl cellulose in the solution from which silver azide is precipitated. This could cause the lack of precision, and also perhaps be responsible for the method giving slightly lower results than the U.S. method on the two lead azides, but not on sodium azide.

/4. .....

4. The difference in requirements for azide content of RD 1333 between the U.S. and U.K. specifications appears quite anomalous in view of these results. The actual difference, attributable to the difference in methods of analysis, here amounted to only 0.3 per cent, and it is noteworthy that the RD 1333 sample made at R.O.F. Chorley failed the U.S. specification test by an average margin of 0.44 per cent.

Mr. Sen, whose extensive work on the analysis of lead azide was referred to by Mr. Blay, said that the ammonium acetate method (see Ref. 5 - Paper B-4), which has since 1943 been the standard method used by D.C.1. for most azide determinations, was adopted as the result of trials and discussions between the (then) Chief Chemical Inspector, Ministry of Supply, (now Director of Chemical Inspection, Ministry of Defence), the Armament Research Department and others. Certain shortcomings were recognised, but it was considered, in spite of a trend towards low values and hence to the specifying of "azide values" instead of azide content, to give fairly constant results and to serve the requirements of testing to the usual specifications. A good deal of work had since been done on alternative methods, and he considered that there was much to recommend the "ceric" method (see Ref. 4 - Paper B-4) which gave results of nearly 100 per cent with sodium azide. There were, however, limitations to its applicability to some types of lead azide. He was interested in the gas volumetric procedure favoured in the U.S. (see Ref. 3 - Paper B-4) and thought that the relatively large sample involved favoured accuracy.

Mr. Blay, replying to a question by Mr. Dubois, confirmed that the ceric method would be inapplicable to dextrinated lead azide on account of reaction of the oxidant with organic matter.

Mr. Taylor said that there was a growing requirement for a reliable method for determining azide to cover the investigation of storage, stability and compatibility problems, apart from control of manufacture. The latter application was regarded with rather less concern in the U.K. (on account of the particular circumstances of manufacture) than in the U.S.A.

Dr. Kaufman agreed that the manufacturing situation in the U.S. was such that accurate azide figures were of considerable importance and he was anxious to improve the reliability of the determination.

Mr. Blay said that the accuracy obtainable by combustion methods was not adequate for present purposes.

Dr. Lovecy expressed surprise that the gas volumetric method was not invariably used. Possibly the U.S. apparatus could be simplified. Was close control of azide content really necessary?

Dr. Kaufman said that at present he was relying largely on a close watch on impurity content, coupled with a minimum of 95 per cent azide.

/Dr. Ball .....

Dr. Ball emphasized the point made by Mr. Taylor, viz: the reliance placed on proved manufacturing methods; azide content was regarded as a check only. He agreed, however, on the importance of improving methods for investigational purposes.

Dr. Newman asked why thermal decomposition was not employed in analysis, as it appeared simple and direct, but Dr. Lovecy pointed out that there were considerable difficulties and hazards in handling explosives by such methods.

Dr. Dunstan mentioned that one of the points which it was important to settle in the gas volumetric method was its ability to deal with samples containing carbonate. This matter was being studied at E.R.D.E.

Mr. Taylor said that consideration was being given to the revision of specification methods for azide determination, and he was very interested in U.S. ideas on this topic.

Dr. Kaufman replied that lead azide testing in the U.S. was mainly to the Army specification and he did not think there was at present any intention of changing this.

Session Chairman: Dr. R.H.H. Wyatt

Contributors: Mr. R.C. Harris
                        Mr. S. Lamnevik
                        Mr. K.J. Holloway
                        Mr. L.E. Medlock
                        Mr. J.R.C. Duke

Session Secretary: Mr. G. Packman

   The **Chairman** opened by remarking that hazards attending the use of lead azide in copper or brass containers, or in proximity to copper or brass components, were well-known.

   When hydrazoic acid, liberated from moist lead azide, reacted with copper, a large number of products may be formed – cuprous, cupric and basic salts, all of differing properties and sensitivenesses.

   With this deliberately short introduction (because of the larger number of contributions received than originally envisaged), he asked Mr. R.C. Harris to give the first paper. He was followed by Messrs. S. Lamnevik, K.J. Holloway, L.E. Medlock and J.R.C. Duke. Mr. Lamnevik then gave the final paper.

THE FORMATION AND DETECTION
OF COPPER AZIDES CORROSIONS

R.C. Harris

Lead azide was first proposed for British Service in 1915, its properties were re-assessed and confirmed in ca. 1925, and it was progressively brought into Service in ZY detonators from then onwards. The possibility of azide corrosion was not overlooked in those early days and the fact that the extent of hydrolysis of lead azide was not recognised was due to the application of an upper limit of 75 per cent for relative humidity tests, giving, as is now known, a false confidence in the stability of lead azide to hydrolysis.

The first example of a sensitive corrosion occurring as a result of a climatic trial was with a completely sealed round containing RDX/TNT fitted with a No. 11 gaine; after 11 months alternating trial at 120°F (dry), copper azides corrosion was found on the detonator. In this instance the moisture from the hydrolysis could have come only from the filling. As a result of this finding and the report then compiled, stores were recalled from Service for examination and the occurrence of copper azides corrosion in No. 11 gaines was confirmed. It is to be noted that azides corrosion trouble with ammunition only became apparent after the last war when ammunition was returned to this country after overseas storage, and later, after storage in this country. As far as is known, there was no incident due to copper azides corrosion in Service ammunition during the war.

The first visual indication of the occurrence of copper azides corrosion is the appearance of a whitish bloom which subsequently develops into a film of cuprous azide. This is the most sensitive form but it is unstable, undergoing rapid oxidation, especially in the presence of light, to cupric azide and ultimately to basic cupric azide. It was stated in early literature that basic cupric azide was the most sensitive salt; in fact, it is less sensitive than the cuprous and normal salts.

The first literature reference to copper azide is in Berichte, 1913. Results of an investigation by a commercial firm in ca. 1924 were published in 1937. More recent open publications appear in Z. Anorg. Chemie, 1943, and Trans. Faraday Soc. Jan. 1959

Copper (cupric) azide is prepared by precipitation methods; there are difficulties in this preparation due to the colloidal nature of the precipitate. Cuprous azide exists in several crystallographic modifications, all of which are very sensitive. Cupric azide is also very sensitive; basic cupric azide is less sensitive, comparable with lead azide itself.

/It .....

It is comparatively easy to reproduce corrosions similar to those encountered in ammunition by the action of hydrazoic acid generated from lead or sodium azides on copper or brass components or foils. Such corrosions have been much used in R.A.R.D.E. in the study of analytical methods of detection and estimation, and in the investigation of properties, e.g. sensitiveness to friction. Unless deliberately incorporated, such corrosions lack the presence of other copper salts, e.g. copper carbonates, often encountered in corrosions found in ammunition. It is important, also, in simulating the corrosions found in ammunition, that the concentration of hydrazoic acid presented to the copper or brass surface should be carefully controlled.

In general, the reagent used for detection of copper azide corrosion is a 1 per cent aqueous solution of ferric chloride, and it is considered important that this concentration is not greatly exceeded as acid attack on the metal substrate or on carbonates present can then occur to an indeterminate degree.

For special purposes a pyridine solution of ferric chloride can be used, and pyridine or ammonium hydroxide can be used as a discriminatory solvent for copper azides.

The much more sensitive reagent ammonium hexanitrato cerate (ceric ammonium nitrate - C.N) has also been used in R.A.R.D.E. laboratory investigations. With this reagent the so-called "invisible film" - which at least in its early stages probably consists of an adsorbed film of hydrazoic acid - can readily be detected. R.A.R.D.E. considered that C.N is far too sensitive a reagent for general use. However, in response to a recent request for a test which could anticipate the likely formation of copper azide corrosion, a feasibility trial is to take place, in which the successive application of this reagent over a period, on similar ammunition similarly stored, will be used in an attempt to trace the growth of copper azide corrosions.

S. Lamnevik

1.   "Copper Azide" Compounds

Copper azide is known to exist as normal copper(I) azide[1] and copper(II) azide[2]. Two more azides, both basic copper(II) azides, are described in the literature[2]. In addition we have discovered two new basic azides and a new polymorph of copper(I) azide. They have been prepared in our laboratory and have been identified by X-ray diffraction as corrosion products on copper and brass exposed to aqueous or gaseous hydrazoic acid of varying concentrations.

Unidentified copper-and azide-containing corrosion products have been observed in short run corrosion tests on brass. These products have not been detected in corrosion products from ammunition containing lead azide.

The following compounds have been made and found as corrosion products:

Formula	Colour	Corrosion Conditions		
$Cu(N_3)_2$	brown-red	HN_3 pressure high.	Oxidants	present
CuN_3 form I	white-grey	" low-high.	"	absent
CuN_3 form II	white	Aqueous 0.2 M HN_3.	"	"
$Cu(N_3)_2 \cdot Cu(OH)_2$	brown-yellow	HN_3 pressure low.	"	present
$Cu(N_3)_2 \cdot 2Cu(OH)_2$	yellow-green	" very low.	"	"
$Cu(N_3)_2 \cdot 3Cu(OH)_2$	blue-green	" "	"	"
$Cu_x Zn_{1-x}(OH)N_3$	light-green	" "	On brass 63% Cu only	

In order to investigate the stability ranges of the copper azides in terms of partial pressure of hydrazoic acid, equilibrium experiments similar to those described in Paper (B-3) were run. Results are summarised in Figure 1. Of course, the limiting partial pressures have to be checked against calculated values of the corresponding hydrolysis constants, but this cannot be done until the solubility products of the basic azides have been determined.

/FIG. 1 .....

FIG. 1
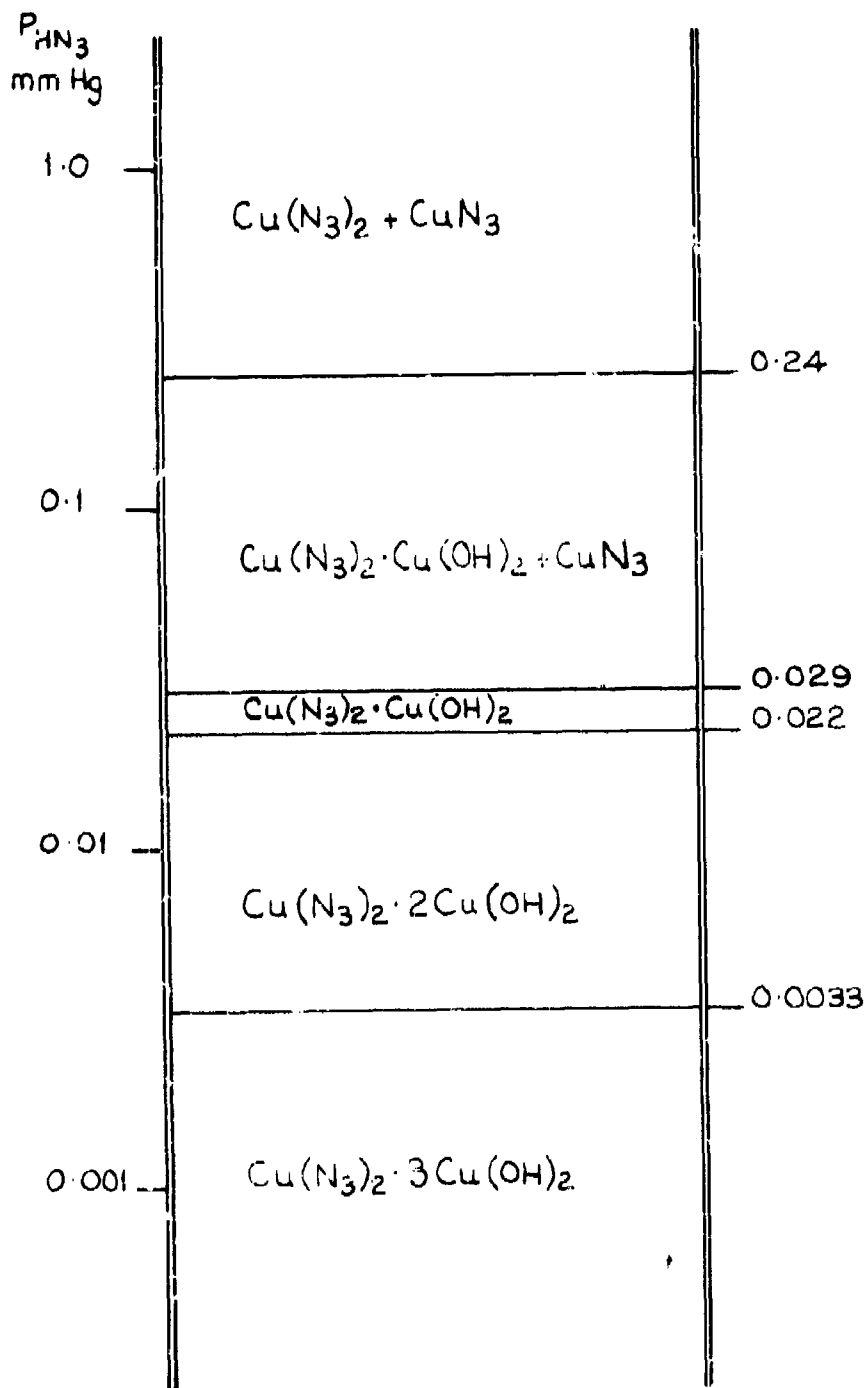
STABILITY RANGES OF THE COPPER AZIDES

From equilibrium measurements at 25°C.
Existence of CuN₃ is possible only in absence
of oxidizing agents.

P_{HN_3}
mm Hg

1·0 — $Cu(N_3)_2 + CuN_3$

———— 0·24

0·1 — $Cu(N_3)_2 \cdot Cu(OH)_2 + CuN_3$

———— 0·029
$Cu(N_3)_2 \cdot Cu(OH)_2$ ———— 0·022

0·01 — $Cu(N_3)_2 \cdot 2Cu(OH)_2$

———— 0·0033

0·001 — $Cu(N_3)_2 \cdot 3Cu(OH)_2$

/2. .....

2.   Preparation

The pure compounds can be prepared in different ways. Copper(II) azide is best made by slow precipitation from a 0.05M sodium azide-hydrazoic acid buffer at pH 4.5 - 5.5 with 0.1M copper perchlorate. The precipitate, which consists of clusters of copper(II) azide needles, is washed with water and ethanol as rapidly as possible to avoid hydrolysis. The dried product must be stored in a desiccator.

Copper(I) azide, form I, is made by precipitation with sodium azide from a reduced (with sodium sulphite) copper perchlorate solution, acidified with acetic acid. The conditions are not critical.

Copper(I) azide, form II, is formed in well shaped crystals when ca. 0.3 g. fine copper powder and 100 ml 0.2M hydrazoic acid react under nitrogen in an airtight glass container. The reaction is slow and usually takes a month. It is advisable to protect the containers from light to prevent discolouration of the product. Both forms of copper(I) azide are rather photo-sensitive.

The first basic copper(II) azide, $Cu(N_3)_2 \cdot Cu(OH)_2$, is prepared by hydrolysis of copper(II) azide suspended in water at 50°C. The time required is about 24 hours. The product has a very small crystal size. It may also be prepared from a copper tetrammine perchlorate solution by adding one mole sodium azide/mole copper, heating the solution to $50^\circ - 60^\circ$C and adding quickly with stirring 2 - 3 moles of perchloric acid/mole copper. Best results are obtained with a solution initially 0.05M in copper tetrammine and azide ion concentration.

The second basic copper(II) azide, $Cu(N_3)_2 \cdot 2Cu(OH)_2$, is best prepared according to Straumanis and Cirulis[1] by hydrolysis of copper diammine azide at 80°C.

The third basic azide, $Cu(N_3)_2 \cdot 3Cu(OH)_2$, is precipitated by blowing air through a stirred equimolar solution of copper tetrammine perchlorate and sodium azide at 60°C. The precipitation must not be continued too long, however, because of danger of contamination with $Cu(N_3)_2 \cdot 2Cu(OH)_2$, which is formed in a second stage when the ammonia concentration has fallen sufficiently.

"Brass azide", $Cu_x Zn_{1-x}(OH)N_3$, has a variable composition due to solid solution formation as indicated by X-ray powder photographs and chemical analysis of different samples. It can be prepared by mixing a suspension of basic zinc azide with dilute copper and zinc perchlorate solutions and ageing the crystals in the mother liquor for at least 6 months. Best results were obtained with 0.6 g. basic zinc azide + 9.5 ml 0.1M zinc perchlorate + 1.5 ml 0.1M copper perchlorate + 90 ml water. Basic zinc azide was prepared by precipitation of 1M sodium azide with an equal volume of 0.5M zinc perchlorate at $80^\circ - 90^\circ$C.

/3.   .....

3. Mechanism of Copper Azide Formation in Ammunition

Hydrazoic acid from reaction of lead azide with water and carbon dioxide in the air attacks copper and brass parts:

$$2Cu \text{ (s)} + 3HN_3 \rightarrow 2CuN_3 \text{ (s)} + NH_3 \text{ (g)} + N_2 \text{ (g)} \tag{1}$$
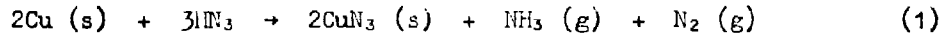
In a second stage copper(I)azide is oxidised by air:

$$2CuN_3(s) + 1/2O_2(g) + H_2O(l) \rightarrow Cu(N_3)_2 \cdot Cu(OH)_2(s) \tag{2}$$

We have confirmed that hydrazoic acid alone cannot oxidise copper(I) azide at any concentration, in agreement with the statements of Straumanis and Cirulis.

The hydrazoic acid partial pressure is not sufficient to be the cause of normal copper(II) azide formation. By studying corrosion layers on copper and brass by X-ray diffraction we found that both copper(I) azide and the first basic copper(II) azide are formed. Copper(I) azide is located as a thin layer nearest the metal surface and has an outer coating of basic copper(II) azide.

If the hydrazoic acid pressure cannot be raised to its full equilibrium value (as for instance in ventilated constructions) the corrosion products are the second or the third basic copper(II) azides.

4. Sensitivity of the Copper Azides

In the FOA ball impact test the sample is placed on a polished metal cylinder and subjected to the impact from 130 g. steel ball falling from a height of up to 70 cm.

/Impact .....

Impact Test Values

Sample	cm.	explosion frequency
CuN_3, form I	10	40%
"	12.5	80,
$Cu(N_3)_2 \cdot Cu(OH)_2$	10	60,,
"	12.5	78,,
$Cu(N_3)_2 \cdot 2Cu(OH)_2$	70	0,,
$Pb(N_3)_2$ Brit. Service	20	50,,

Friction tests were carried out in the Julius-Peters machine where a sample is rubbed between a stationary rough porcelain disc and a moving rough porcelain plug at different loads.

Friction Test Values

Sample	load	explosion frequency
CuN_3, form I	30 g.	50,,
"	40 g.	80,,
$Cu(N_3)_2 \cdot Cu(OH)_2$	120 g.	75,,
"	150 g.	100%
$Cu(N_3)_2 \cdot 2Cu(OH)_2$	60 g.	15,,
"	120 g.	60,,
$Pb(N_3)_2$, Brit. Service	80 g.	50,,

The electrical sensitivity was tested on samples placed in a fixed spark gap of two electrodes. Voltages and capacitances necessary to cause explosions were determined. All samples of copper azide exploded at the minimum energy value obtainable with the apparatus, 1 millijoule.

From other experiments and from investigations of accidents we have estimated the minimum energy to cause explosion to be 1 - 10 microjoules.

/Our .....

Our opinion is that "copper azide" is not significantly more sensitive than lead azide to mechanical stresses but is much more sensitive to electrical fields, discharges 'tc.

Friction tests with non-conducting friction materials are probably a measurement of mechanical and electrical sensitivities in combination. Friction tests with earthed metal friction materials indicate a much lower sensitivity.

Experiments to measure the electrical properties of single crystals of the various copper azides are planned. This will perhaps give an understanding of the mechanism of electrical ignition.

The copper azides are rather heat sensitive with explosion temperatures at <u>ca.</u> 180°C. Behavior varies when the salts are exposed to open flames:

Sample	Behavior
$Cu(N_3)_2$	detonates
CuN_3, both forms	detonates
$Cu(N_3)_2 \cdot Cu(OH)_2$	detonates
$Cu(N_3)_2 \cdot 2Cu(OH)_2$	flashes like black powder
$Cu(N_3)_2 \cdot 3Cu(OH)_2$	burns rapidly
$Cu_x 2n_{1-x}(OH)N_3$	burns rapidly

The most characteristic property of copper(I) azide and the first basic copper(II) azide is the ability to detonate in very thin layers[3]. Detonation propagates in layers thicker than 0.85 mg/cm^2.

<u>References</u>

1. Straumanis, Cirulis, <u>Z. anorg. Chem</u>, 1953 <u>251</u>, 315: 1954 <u>252</u>, 9, 121.

2. Wilsdorf, <u>Acta Cryst.</u>, 1948 <u>1</u>, 115

3. Eriksson, Lamnevik, FOA 1 report A1131-F1101, April 1964 (in Swedish).

/<u>Paper (C-3)</u> .....

THE PREPARATION, IDENTIFICATION AND SENSITIVENESS OF COPPER AZIDES

K.J. Holloway

The preparation of various "copper azide" compounds has been undertaken in order to assess their reproducibility, stability and sensitiveness in relation to corrosions occurring during storage of copper components exposed to hydrazoic acid. Using a master-slave manipulator, chemical analysis and electrostatic spark sensitiveness tests have been carried out immediately after isolation of the various compounds.

The results have shown that products which are extremely sensitive to ignition by electrostatic spark (1 - 2 ergs) can be prepared either by metathesis from solution or by exposure of metallic copper to hydrazoic acid.

Five compounds, namely, cuprous azide (I), cupric azide (II), monobasic cupric azide (III), dibasic cupric azide (IV) and tribasic cupric azide (V) have been prepared and their constitutions confirmed by chemical analysis.

Examples of typical preparations are:

I. Cuprous azide

Method (i). Kartar Singh, Trans. Faraday Soc., 1959, 55, 124

2.8 g. cuprous chloride dissolved in 70 ml. saturated sodium chloride solution at $25^{\circ}C$, 0.28 g. sodium bisulphite ($NaHSO_3$) and one drop of glacial acetic acid added. To the stirred solution. 1.82 g. sodium azide, dissolved in 35 ml. water, was added in 15 minutes.

$$CuCl + NaN_3 = CuN_3 + NaCl$$

Yield 1.5 g. (50% theoretical)

/Method (ii) .....

Method (ii)

2.86 g. freshly prepared cuprous oxide (obtained by the reduction of cupric hydroxide with hydrazine) and one drop of hydrazine were stirred in 200 ml. water at 25°C.

2.6 g. sodium azide in 150 ml. solution $\left.\right)$
1.9 g. sulphuric acid in 150 ml. solution $\left.\right)$ added simultaneously in 30 minutes.

$$Cu_2O + 2NaN_3 + H_2SO_4 = 2CuN_3 + Na_2SO_4 + H_2O$$
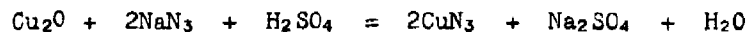
Yield 6.75 g. (theoretical)

On being allowed to stand in air, cuprous azide was found to turn brown rapidly and the resulting material was shown by X-ray diffraction to be monobasic cupric azide.

II. Cupric azide

Method (i)

0.8 g. finely divided cupric oxide (through 120 mesh B.S.S.) was left to stand, with occasional shaking, for several days in 50 ml. of 3.6% (w/v) hydrazoic acid solution (this represents a 100% excess of hydrazoic acid) at room temperature.

$$CuO + 2HN_3 = Cu(N_3)_2 + H_2O$$
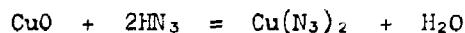
Yield 1.5 g. (theoretical)

Method (ii)

4 g. cupric acetate monohydrate in 100 ml. solution was stirred at 25°C and 2.6 g. sodium azide in 60 ml. solution was added in 60 minutes.

$$Cu(CH_3COO)_2 H_2O + 2NaN_3 = Cu(N_3)_2 + 2Na(CH_3COO) + H_2O$$
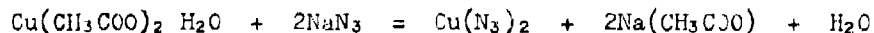
Yield 2.2 g. (75% theoretical)

III. Monobasic cupric azide

2.6 g. sodium azide in 100 ml. solution was stirred at 25°C

10 g. cupric sulphate pentahydrate in 150 ml. solution) added simultaneously
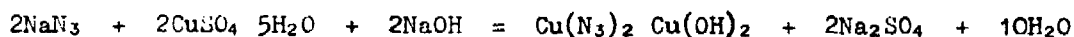1.6 g. sodium hydroxide in 150 ml. solution) during 40 minutes.

$$2NaN_3 + 2CuSO_4\,5H_2O + 2NaOH = Cu(N_3)_2\,Cu(OH)_2 + 2Na_2SO_4 + 10H_2O$$

Yield 4.9 g. (theoretical)

Cupric acetate solution can be used in place of cupric sulphate solution.

IV. Dibasic cupric azide

2.63 g. sodium azide in 100 ml. solution was stirred at 25°C
(1. excess of sodium azide)

12 g. cupric acetate monohydrate in 200 ml. solution) added simultaneously
3.2 g. sodium hydroxide in 200 ml. solution) during 50 minutes.

$$2NaN_3 + 3Cu(CH_3COO)_2\,H_2O + 4NaOH = Cu(N_3)_2\,2Cu(OH)_2 + 6Na(CH_3COO) + 3H_2O$$
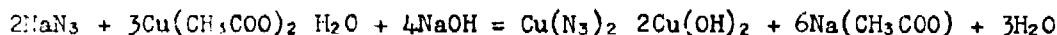
Yield 6.8 g. (theoretical on cupric acetate)

V. Tribasic cupric azide

2.86 g. sodium azide in 100 ml. solution was stirred at 25°C (10 excess of
sodium azide)

16 g. cupric acetate monohydrate in 250 ml. solution) added simultaneously
4.8 g. sodium hydroxide in 250 ml. solution) during 90 minutes.

$$2NaN_3 + 4Cu(CH_3COO)_2\,H_2O + 6NaOH = Cu(N_3)_2\,3Cu(OH)_2 + 8Na(CH_3COO) + 4\,H_2O$$
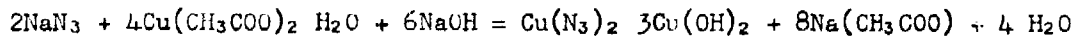
Yield 8.8 g. (theoretical on cupric acetate)

A summary of the tests carried out on these samples is given in the
Table.

/TABLE .....

TABLE

Examination of Normal and Basic Salts of Copper Azide

Compound	Analysis $Cu: N_3$		Ignition Temperature 5°/Min.	Electrostatic Sensitiveness Minimum Energy Ergs.	Action of Hydrazoic Acid Vapour	Hydrolysis (Copper Strip Test)
	Theory	Found				
CuN_3 Yellow Plates	1.512	1.506	192°C Very Violent	1 – 2 Completes	Converted to Black $Cu(N_3)_2$	Converted to $Cu(N_3)_2 \ Cu(OH)_2$ With No Liberation of HN_3
$Cu(N_3)_2$ Dark Green Needles	0.756	0.759	201°C Very Violent	1 – 2 Completes	No Effect	Converted rapidly to $Cu(N_3)_2 \ Cu(OH)_2$ With Liberation of HN_3
$Cu(N_3)_2 \ Cu(OH)_2$ Khaki Gel	1.542	1.512	207°C Violent	375 Completes and Partials	Converted to Black $Cu(N_3)_2$	No Apparent Effect
$Cu(N_3)_2 \ 2Cu(OH)_2$ Greenish Yellow Gel	2.258	2.273	199°C Less Violent	1300 Partials	Converted to Black $Cu(N_3)_2$	No Apparent Effect
$Cu(N_3)_2 \ 3Cu(OH)_2$ Sage Green Gel	3.024	3.363	201°C Mild	Not Done	Converted to Black $Cu(N_3)_2$	No Apparent Effect

Identification of Azide Corrosions

Corrosions on copper and brass discs were obtained by exposing the discs to an enclosed atmosphere of hydrazoic acid, generated by placing a small dish of a 1/5 solution of hydrazoic acid in the container. Scrapings of the corrosions were submitted for X-ray diffraction.

The copper disc corrosions consisted mainly of cuprous azide with some cupric azide.

The brass disc corrosions consisted of cupric azide with a little cuprous azide and an unidentified material (probably Mr. Lamnevik's "brass azide"!). Corrosions formed more readily on brass, at approximately double the rate.

Ignition of corrosions on the discs were studied using the approaching electrode apparatus. Most ignitions occurred with an energy of 1 - 2 ergs. The type of ignition and the energy required was related to the thickness of the azide film. With film thickness of up to 0.0001", partial ignition occurred (Figure 1).

Film thicknesses ≥ 0.0004" required higher ignition energies, unless the film was cracked and broken to allow a discharge path for the spark. In these circumstances, low energies, 1 - 2 ergs, were sufficient.

/ADDENDUM .....

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Studies on the sensitiveness of monobasic and dibasic cupric azides were in progress by E.R.D.E. Sensitiveness Section just prior to and during the Conference, and it is thought desirable to include the results though they were not presented.

	Monobasic Cupric Azide $Cu(N_3)_2 \, Cu(OH)_2$		Dibasic Cupric Azide $Cu(N_3)_2 \, 2Cu(OH)_2$	
	50%	S	50%	S
Impact	7.96 cm	0.170	11.04 cm	0.057
Friction	5.25 ft/sec	0.124	>10 ft/sec	-
Electrostatic discharge				
M/M Needle 520 $\mu\mu F$	375 ergs (completes and partials)		1300 ergs	
R/M Minimum capacitance	<11 $\mu\mu F$		~30 $\mu\mu F$	
Minimum energy	<30 ergs		700 ergs at 100 $\mu\mu F$	
	Complete ignition throughout except as stated		Partial ignitions throughout	

/Paper (C-4) .....

CORROSION OF COPPER DETONATOR TUBES IN THE PRESENCE OF LEAD AZIDE

L.E. Medlock

The problems of corrosion faced by the commercial manufacturer of detonators are similar to those encountered by Ordnance Factories, and differ chiefly in respect of life and storage conditions of the detonators. Commercial detonators are often used within a few months of manufacture so that adverse storage conditions will not normally effect the safe handling properties of the detonators. On the other hand, the scale of commercial manufacture is so high that even a 1 in 10^6 chance of appreciable copper azide formation could not be tolerated.

The most important protection of the initiating system is of course an effective seal, but if one postulates damage to the seal during storage, then the conditions under which copper azide may be formed are of importance.

A series of experiments was carried out in which copper tubes were suspended over lead azide in a constant humidity sealed atmosphere. The temperatures and humidities were chosen to correspond to normal and extreme storage conditions. At suitable intervals one tube was removed from the assembly and the azide content of the deposit measured. Figure 1 shows the variation of azide content (expressed as cuprous azide) with time.

The sample to sample variation does confuse the picture but the trend for all the samples of lead azide is the same in that the formation and retention of copper azide on the tubes is favoured by high humidity. High temperature on the other hand seems to reduce the quantity of copper azide retained on the tube, especially at the lower humidity. A possible explanation is that hydrolysis of the copper azide is favoured by high temperature to a greater degree than the hydrolysis of the lead azide.

(Note by Secretary

Mr. Medlock first referred to an incident occurring in 1914 in Austria, when an explosion took place after items had been stored for two years. Though there was some doubt about the mode of initiation, it was very likely to have involved copper azide.

Prolonged storage at a high humidity and high carbon dioxide content converts copper azides to insensitive products, containing copper carbonate and copper hydroxide).

/FIG. 1 .....
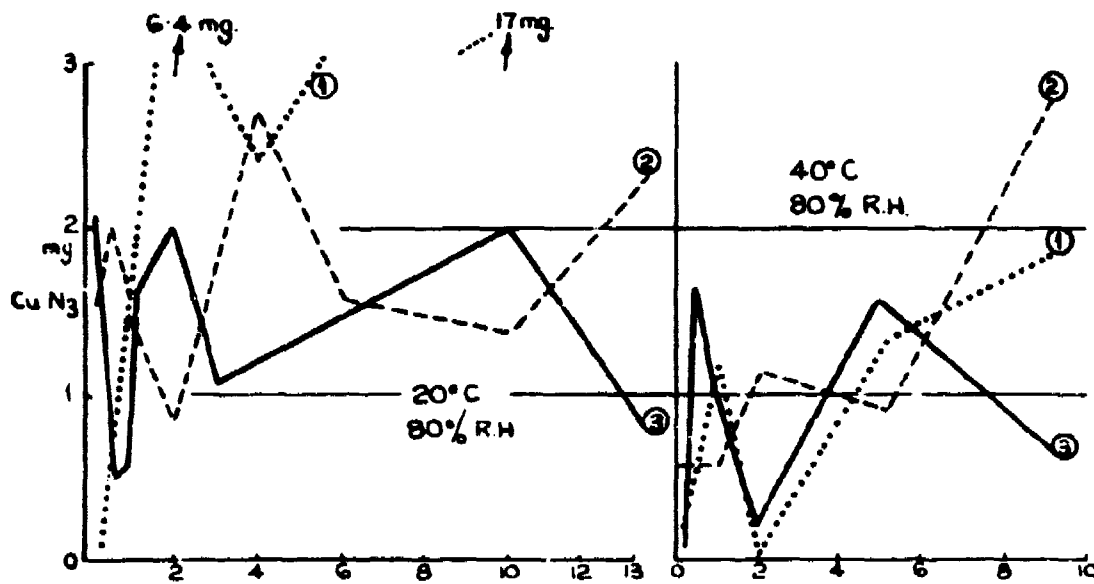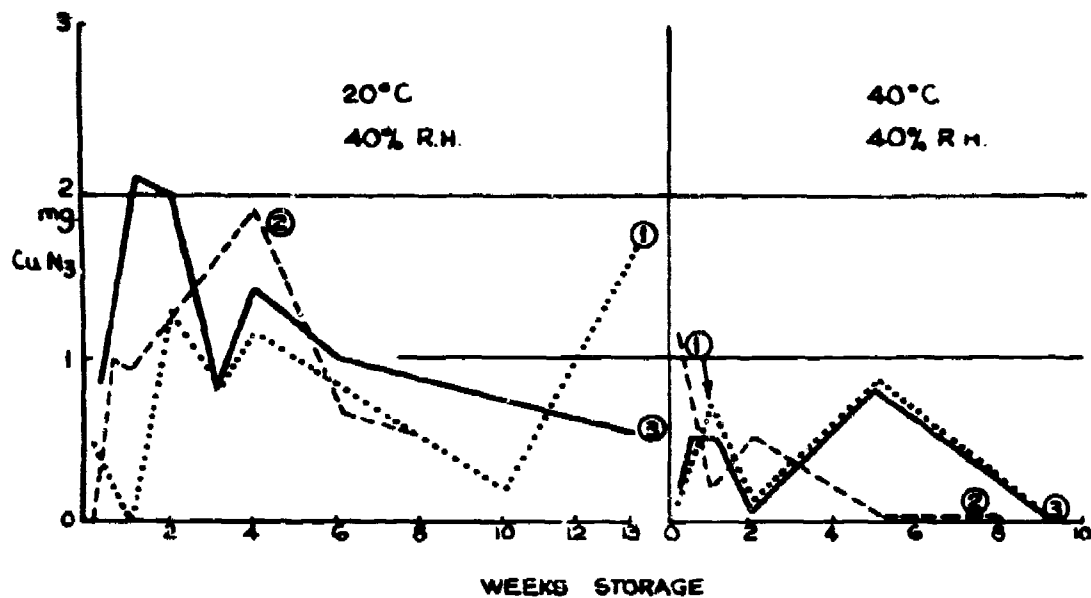
Legend 1 = Service Lead Azide to CS.2222

2 = I.C.I. Dextrinated Lead Azide

3 = I.C.I. Gelatin Lead Azide

FIG. 1

/As .....

- 85 -

As corrosion of copper cannot occur without decomposition of the
lead azide, the stability of the different types is of interest. Figure 2
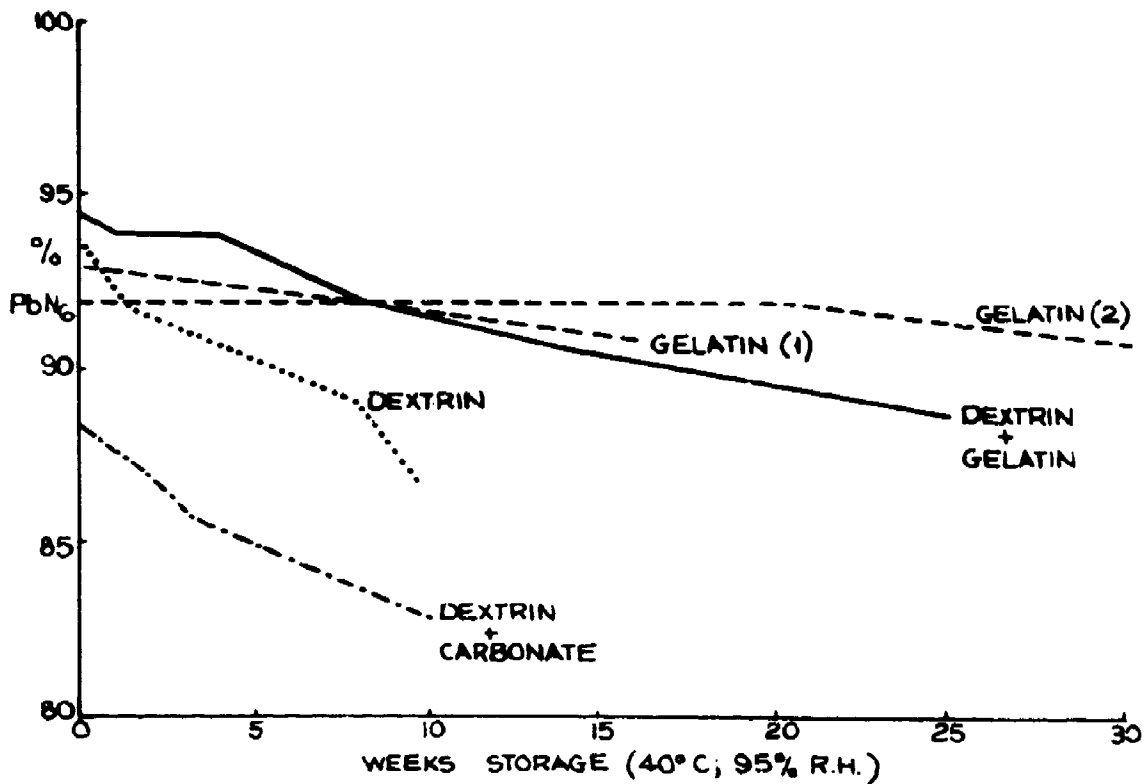illustrates the stability of five types of lead azide.

FIG. 2

The presence of gelatin in the lead azide seems to confer additional
stability under these conditions. The reason for this stability is not
clear but a form of protection of the lead azide molecule by the gelatin
is probable.

/Paper (C-5) .....

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THE CRYSTALLOGRAPHY OF COPPER AZIDES

J.R.C. Duke

Published X-ray data on cuprous azide have been available for a long time, but only incomplete results were available for the cupric compound. Cupric azide has now been re-examined and X-ray single crystal and powder data have been obtained.

Copper (I) azide

Copper (I) azide – CuN_3

Crystal system	:	Tetragonal
Space-group	:	$I4_1/a$
Unit cell dimensions:		

a	c	Ref
8.65(3) Å	5.59(4) Å	Wilsdorf (1)

X-ray powder data published by: Wilsdorf (1)

Copper (II) azide

Copper (II) azide – $Cu(N_3)_2$

Crystal system	:	Orthorhombic
Space-group	:	Pbnm or Pbn2$_1$
Unit cell dimensions:		

a	b	c	Ref
9.226 Å	13.225 Å	3.068 Å	Streumanis & Cirulis (2)
9.12	13.53	3.09	Duke (3)

Density (calculated) 2.57.   Density (observed) 2.58 ± 0.04

(X-ray powder data obtained by Duke)

The crystals are lath-shaped and strongly pleochroic, and appear to be brown-black when the electric vector is parallel to the length of the crystal.

/The .....

The data have been successfully applied in the identification of the corrosion products formed on copper and brass exposed to a moist atmosphere containing hydrazoic acid; both cuprous and cupric azides have been identified. It is generally difficult to crush cupric azide without causing an explosion, unless special precautions are taken, e.g. by immersion in a liquid and this places it in a class apart compared with the other substances we handle.

Preparations of basic cupric azide have also been examined by X-ray methods. A characteristic pattern has been obtained for a phase which analyses as $Cu(OH)N_3$ but the patterns from successive preparations do show some small variations, and work on this is not yet complete. This material has not proved suitable for single crystal examination. It has been found that moist cupric azide changes into this basic cupric azide when exposed to the atmosphere, although it appears to be stable when dry.

References

1. Wilsdorf, H., _Acta Cryst._, 1948, _1_, 115

2. Straumanis, M. and Cirulis, A., _Z. anorg. Allg. chem._, 1943, _251_, 315

3. Duke, J.R.C., (1966) Ministry of Aviation report (unpublished)

/Extract .....

by S. Johansson, S. Lamnevik and R. Söderquist

An extract from a literature survey dealing with crystal data and structures of metal azides, circulated during the session by Mr. Lamnevik, is reproduced below as being particularly relevant to Mr. Duke's paper.

CuN$_3$

The structure of copper (I) azide has been determined by Wilson[31] who showed that the crystals are tetragonal. The unit cell dimensions were determined from rotation and powder photographs:

$$a = b = 8.65_3 \pm 0.01 \text{ Å}, \quad c = 5.594 \pm 0.01 \text{ Å} \quad Z = 6$$

The space group is I4$_1$/a with

8 Cu at   8(d)

8 N$_I$ at   8(o)

16 N$_{II}$ at 16(f)   with x = 0.077,   y = 0.173,   z = 0.250

The interatomic distances are:

	equivalent neighbors	distance Å
Cu	4 Cu	3.36
	2 Cu	4.33
	2 Cu	5.15
	2 N(1)	2.795
	4 N(1)	3.36
	4 N(2)	2.23
	2 N(2)	3.28
	2 N(2)	3.56
N(1)	2 N(2)	1.17

/The .....

The structure is built from Cu^+ and linear N_3-groups, which form chains along the 111 diagonal. The N_3-group is linear according to this investigation. The co-ordination of copper and azide is the same. Each ion is surrounded by a cube consisting of 4 Cu^+ and 4 N_3^-. The azide group is here considered as a sphere.

$Cu(N_3)_2$

Only one X-ray investigation is published about copper (II) azide. Straumanis and Cirulis[32] found that the green-black crystals are orthohombic with Z = 4, with the following cell edges (rotation photographs):

$$a = 9.226 \text{ Å}, \quad b = 13.225 \text{ Å}, \quad c = 3.068 \text{ Å}$$

No attempts were made to determine the crystal structure.

$Cu(N_3)_2(NH_3)_2$

Recently Agrell[40] has refined her preliminary structure determination[41] of $Cu(N_3)_2(NH_3)_2$. The compound has orthorhombic symmetry and belongs to the space group P nma, the dimensions of the unit cell being:

$$a = 6.389 \pm 0.005 \text{ Å}, \quad b = 7.454 \pm 0.005 \text{ Å}, \quad c = 12.71 \pm 0.01 \text{ Å}$$

The co-ordination around the copper atom is distorted octahedral, there being four shorter and two longer copper-ligand bonds. The structure is built from chains of $Cu(NH_3)_2(N_3)_2$ octahedra running along the [100] direction, see Figure 8. The azide group is asymmetric with (two types)

N - N distances:

$$1.174 \pm 0.001 \text{ Å}$$
$$1.142 \pm 0.012 \text{ Å}$$
$$1.186 \pm 0.011 \text{ Å}$$
$$1.139 \pm 0.013 \text{ Å}$$

This is the first accurately determined azide structure and it clearly shows the asymmetry of the azide group.

/References .....

References

31. H. Wilsdorf, "Die Kristallstruktur des einwertigen Kupferazids, CuN_3"
    <u>Acta</u> <u>Cryst</u>., 1948, <u>1</u>, 115-118

32. M. Straumanis, A. Cirulis, "Das Kupfer (II)-azid. Darstellungsmethoden,
    Bildung und Eigenschaften", <u>Z</u>. <u>anorg</u>. <u>Chem</u>., 1943, <u>251</u>, 315-331

40. I. Agrell, "The Crystal Structure of $Cu(N_3)_2(NH_3)_2$", <u>Acta</u> <u>Chem</u>. <u>Scand</u>.,
    1966, <u>20</u>, 1281

41. C. Brosset and I. Agrell, "Structure of Azide Complexes, <u>Nature</u>,
    1964, <u>202</u>, 1210

/<u>Paper</u> <u>(C-6)</u> .....

PREVENTION OF COPPER AZIDE FORMATION IN AMMUNITION

S. Lamnevik

Abstract

As copper azides may be a substantial danger in ammunition containing lead azide, great efforts have been made to overcome this problem by appropriate design construction and chemically. Copper azides can always be found inside capsules made of copper or brass and loaded with lead azide. This is not considered to be dangerous, but copper azides situated on moving parts in a construction can be initiated by friction and fire the priming compositions in the neighbourhood causing an accident or bad function. In this paper the Swedish way of handling the practical problems and different ways to avoid copper azide formation are discussed.

Swedish Copper Azide Control of Ammunition

All ammunition containing lead azide is inspected for copper azide formation at regular intervals. To indicate azide corrosion droplets of a 30% ferric chloride solution is used. Examinations are made under the microscope. If a red colour is obtained (positive test for azide ions) with ferric chloride, the time necessary to decolorise the droplets is measured. This time is a rough estimate of the amount of azide present. It is reported as mg HN_3 per cm^2.

Results of the examinations are submitted to the Copper Azide Judgement Group where dangers of handling, storing and transportation of the ammunition parts are examined. Time of growth and amount of azide per cm^2 present at that time are used to make a forecast of the "critical year" when the corrosion layer will exceed 0.40 mg/cm^2. Layers thicker than that will propagate a detonation when initiated at one point.

Before the "critical year" is reached other tests are done, for instance, tests to determine whether the normal priming compounds in their capsules are liable to detonate if a copper azide detonation occurs. This does not necessarily happen. Other factors considered before destruction is ordered are the function of internal safety devices, mobilities of the various parts, etc.

Thanks to the Copper Azide Judgement Group's work much experience has been gathered and put into practice and much of the old fear of copper azide has vanished. The problem is now mainly an economical one, and is decreasing as new constructions are replacing older ones.

/Choice .....

Choice of Priming Explosives

One way to prevent copper azide formation is to use an alternative priming explosive to lead azide. This is a practical method because it allows old ammunition to be used after changing the priming capsules, and for new constructions it allows the use of brass which is the best machining material. At present the only useful, alternative primary explosive seems to be silver azide which, with water, gives a very low partial pressure of hydrazoic acid and has excellent priming properties.

Choice of Construction Materials

Materials not corroded, or corroded without formation of explosive products, by hydrazoic acid are plastics, glass, stainless steel, aluminium, lead, tin, titanium, silver, gold, zinc and magnesium.

Among these, aluminium and stainless steel are the only materials used in larger amounts in ammunition for economical and other reasons. They are not corroded by hydrazoic acid. Tin, zinc and silver are used as thin (ca. 50 micron) protective layers on brass and copper. Tin and silver do not react with hydrazoic acid; zinc reacts with formation of zinc oxide. When using tin and silver it is important to achieve a non-porous layer to avoid accelerated corrosion of the copper-bearing metal. Zinc coatings can be very thin (10 microns) and need not be perfectly impervious because of the metal's less noble character (electrochemical protection). However, zinc may react to form layers of non-explosive corrosion products which may cause problems on moving parts.

Special Constructions

There are two direct methods of reducing the partial pressure of hydrazoic acid in ammunition.

The first involves using an airtight construction with moisture- and carbon dioxide- absorbents inside. This technique has been used in some American artillery fuzes.

The other method is to use a construction which is ventilated, so that hydrazoic acid may escape. This will give no copper azide corrosion at all or, at worst, the least dangerous, basic copper (II) azides. This has been confirmed by experiments. The lead azide will be gradually destroyed, however.

/Use .....

Use of Hydrazoic Acid Destroying Agents

Zinc and magnesium react with gaseous hydrazoic acid forming oxides, nitrogen, ammonia, hydrazine and hydroxylamine (the last two in minor amounts). Zinc is used in Sweden in ammunition as discs, pierced with holes, and placed just above the lead azide containers. It is important that the discs have a large free area accessible to the hydrazoic acid vapour. Protection is satisfactory as long as the zinc is not passivated. Passivation is a problem; it is not understood why and how passivation occurs, but it might be due to contamination by oils or greases from previous machining operations. Although magnesium is better with respect to passivation, its effective lifetime is too short. Attempts to use palladium and platinum catalysts which decompose hydrazoic acid to ammonia and nitrogen have failed owing to catalyst poisoning and formation of highly explosive products on the catalysts.

Non-Metallic Protective Coatings

Most varnishes and lacquers are penetrated by hydrazoic acid in a short time when applied in normal thicknesses. The only protective finish acceptable according to our tests is a high molecular weight silicone resin normally used for electrical insulation of copper wires.

Chromate conversion coatings (IRIDITE-process) have been fairly successful on brass but not on copper.

Use of Inhibitors

At our Institute we have examined a number of inhibitors of copper corrosion to determine their suitability as inhibitors for copper azide corrosion. Excellent results were obtained with 1,2,3-benzotriazole. A very thin (5 micron) carrier film (polyvinyl acetate) with 1% benzotriazole prevented copper azide formation completely in tests of two months duration at 35°C and 100% relative humidity, and at a hydrazoic acid pressure of 0.1 mm Hg. Without inhibitor, corrosion occurred under the polyvinyl acetate film after eight hours.

One problem exists, however: 1,2,3-benzotriazole reacts with composition B at 90°C (and probably also at lower temperatures). We do not know whether this is dangerous and whether reaction occurs with other secondary explosives.

/Discussion .....

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Discussion on Session (C) Papers

Dr. Ball said he agreed in general with all that had been said on the properties of copper azide, but there was one aspect that had not been mentioned. This concerned the layer thickness and the rate of propagation in the layer, as these could be important factors in accidents. Measurements with 0.001 inch thick layers indicated a propagation velocity of 1400 metres/sec.

Mr. Taylor said that the statement made in the Annual Reports of the Society of Chemical Industry, that copper azide was spontaneously explosive, was incorrect; he would like this point placed on record (See Footnote).

Dr. Lovecy suggested that, as the term usually meant liable to explode without provocation, the statement was perhaps justified.

Both **Mr. Taylor** and **Dr. Ball** disagreed, and the former said that there was always some cause such as electrostatic charge or friction; otherwise it meant that almost every incident could be excused in this way.

The **Chairman** suggested that the statement in Annual Reports should in some way be clarified.

In answer to a question on the nature and disposition of the various layers formed on copper by hydrazoic acid, **Mr. Harris** and **Dr. Ball** agreed with the observations by **Mr. Lamnevik** that copper became covered with a layer of alpha cuprous azide, which in turn was covered by a thicker layer of the monobasic cupric azide. If the vapour pressure of hydrazoic acid was not high enough the dibasic or tribasic cupric azides were formed instead of the monobasic salt.

Mr. Taylor pointed out the risk of erroneous conclusions arising from the hydrolysis of copper azides and **Mr. Duke** mentioned a tendency for cuprous azide to convert readily to the cupric form.

Footnote:

Reports on the Progress of Applied Chemistry

1953, 38, 814, Steele, A.R.V.

Quotes "highly sensitive copper azides were formed which have been known to detonate spontaneously".

This is erroneous and should be corrected, as all known cases of accidental ignition of copper azide in ammunition have been associated with some movement. This correction was accepted by the author but he pointed out that there appeared to be no convenient means of correcting Annual Reports.

"Spontaneous" could be interpreted as occurring without any clear application of mechanical or thermal energy. Therefore this statement in the literature could be quoted by witnesses of courts of inquiry into accidents, thus obscuring the more relevant causes.

/Dr. Ball .....

Dr. Ball said that all the preventive methods, with the exception of the chemical inhibitors, had been tested at R.A.k.D.E. None was completely satisfactory. He stressed that with tin-plating it was essential that it should be non-porous. The sacrificial zinc method was no foolproof, since zinc tends to become passivated. Aluminium and stainless steel components, or the replacement of lead azide by another explosive, seemed to be the best solutions. It was generally agreed that, although it was desirable to remove the hydrazoic acid formed by hydrolysis of lead azide, this removal accelerated the degradation of lead azide, i.e., one obtained a measure of safety at the expense of the life of the store.

Mr. Blay pointed out that carbon dioxide absorbents were particularly undesirable, as they accelerated the breakdown of lead azide considerably. Varnishes were intended to prevent penetration of water into the initiatory materials.

Mr. Harris replying to Mr. Leslie, on the question of the action of shellac on lead azide, said that when dry the lac acids in shellac had no effect.

Mr. Taylor said that the use of hydrophobic surface-active agents gave a temporary suppression of hydrolysis, but this did not persist. Similarly, hydrophilic colloids gave a temporary protection, but this was lost on a long-term basis. He asked whether the cutting oil used in the manufacture of copper tubes accelerated the hydrolysis of azide.

Mr. Medlock replied that he had found no difference in the evolution of hydrazoic acid, as between normally handled tubes and specially cleaned ones.

Dr. Lovecy asked, in view of Mr. Medlock's results with gelatinised azide, whether the tests carried out by Mr. Blay had revealed similar effects.

Mr. Blay said that the tests were only short-term ones at present, but these showed gelatinised lead azide to be no better than Service lead azide.

Chairman: Mr. G.W.C. Taylor

Contributors: Mr. A.E. Hythes
                        Mr. A.T. Thomas
                        Mr. G.W.C. Taylor

Session Secretary: Mr. J.R. White

The session commenced forty minutes later than scheduled, but the <u>Chairman</u> said that no apologies were needed for the extra time taken by session C as the two fields of work were closely connected. He continued by saying that lead azide is a very sensitive primary explosive with a history recording many accidents. In spite of its sensitiveness, lead azide has a very good production record, probably because its history is well-known, and consequently full precautions are taken. This session was to be divided into three sections, the first dealing with precipitation and wet handling, the second with wet storage, transport, and drying, and the third with the use of the dry material, transport, and filling.

At this stage a short film was shown to illustrate the facilities available at E.R.D.E. Woolwich for the manufacture, drying, and sieving of initiators. This was followed by a slide showing a laboratory unit designed and made by E.R.D.E. Chemical Engineering Branch for the preparation of initiators up to 15 grams scale. The apparatus has a hydraulically controlled stirrer and a device for raising or lowering it, a control panel, and incorporates a heating unit capable of heating the contents of the reaction vessel to 100°C.

The <u>Chairman</u> then presented the first part of his paper 'Hazards in the Manufacture and Loading of Lead Azide' reminding the audience that where spontaneous explosion was referred to, he meant explosion occurring without any clear indication of mechanical, electrostatic, or heat energy being applied.

HAZARDS IN THE MANUFACTURE AND LOADING OF LEAD AZIDE (PART I)

G.W.C. Taylor

This paper is intended as a brief introduction to a discussion on this subject in which it is hoped that we may all benefit by contributions from the investigations of research workers and the long experience of production managers.

There is no doubt that the precipitation of lead azide by the interaction of sodium azide and soluble lead salts can give rise to conditions when spontaneous explosion can occur. This is especially related to the preparation of pure and near pure lead azide (absence of hydrophilic colloids as additives) and where mixing of solutions is poor and incomplete. Thus solutions mixed accidentally or by spillage (including that of mother liquor) are potential hazards. In support of the above, the incidence of accidental explosions during manufacture of British Service lead azide is about one in 6000, although recently there has been a long run without explosion during precipitation or washing of the product. There is no clear evidence of the cause of such ignitions despite many detailed enquiries, including one recently by D.C.I. Because of this low frequency and the fact that all evidence is lost, this problem is extremely difficult to solve by systematic research approach. Nevertheless the experiments conducted at E.R.D.E. have confirmed that spontaneous explosion of lead azide can be suppressed by the use of additives and there is an extensive record of freedom from explosion during manufacture of dextrinated lead azide and of R.D.1333 (R.D.1343) in which sodium carboxymethyl cellulose is the additive, and the degree of mixing of solutions is notably greater than that required for the preparation of Service lead azide.

ACCIDENTS IN THE MANUFACTURE OF
LEAD AZIDE (A SURVEY)

P.E. Wythes

This paper is based on a survey carried out by the late Mr. J. Dexter (Chemical Inspectorate) of Accident Reports since 1941 involving British Military Service type lead azide.

Incidents can be divided into two groups:

1. **In Manufacture of Lead Azide** (A batchwise procedure)

    10 explosions occurred in the pan and 5 occurred during sieving.

2. **During Filling**

    Over 140 incidents.

This report has been confined to the incidents during manufacture which are more likely to be chemical problems.

Explosions in the Pan

A common factor of explosions in the pan is that the explosion always occurs towards the end of the manufacturing process. Of the 10 incidents recorded:-

   3 occurred towards the end of the addition of sodium azide and lead acetate solutions;

   2 occurred at the end of the addition of the solutions;

   1 during the stirring prior to the addition of acetic acid (used to destroy any excess lead carbonate);

   2 during the addition of the acetic acid;

   1 during the stirring after the addition of acid;

   1 during the second washing stage;

From a chemical point of view the manufacturing process involves two aspects: quality of raw materials and process control.

/Quality .....

Quality of Raw Materials

The materials used are distilled water, sodium carbonate, lead acetate solution, sodium azide, acetic acid and methylated spirit.

The purity of all these materials is considered to be of the utmost importance by D.C.I. and there has never been any suggestion of materials of doubtful quality having been used.

The specification for lead acetate has been revised to include a carbonate limit. This was considered desirable so that the precise quantity of carbonate formed in the process for nucleation could be controlled. It may be desirable to check the pH of the solution before use (I understand E.R.D.E. do recommend this).

Whenever possible, efforts should continue to improve the standard of purity of raw materials.

Process Control

Process Control is at present purely mechanical and it is for consideration if any physico-chemical aids could be introduced.

At present temperature is recorded continuously and stirring speed intermittently. Rate of addition of solutions is controlled by means of jets and should not vary significantly if the solutions have been prepared correctly and are free from foreign matter. Provided, therefore, that the levels of the solutions in the aspirators are observed and recorded at intervals, the rate of addition of the solutions is under control.

Further Control

The possibility of microscopic examination of samples of crystals withdrawn during the process was considered. If significant variations in crystals were observed it might be necessary to stop the process and destroy the product. The suggestion was rejected for obvious reasons. The mechanics of introducing sampling equipment may in itself be a hazard and, in any case, crystals continue to grow from the time of their nucleation, and progressive changes will occur. Beta lead azide, thought to contribute to sensitivity, is known to be present in appreciable quantities half-way through the process.

The only useful thing that could possibly be achieved by microscopic examination is a more extensive examination of the final product; this may prove useful in investigating the occurrence of ignitions during subsequent handling and filling.

/The .....

The possibility of automatically recording the pH of the reaction during the run may be worth investigating. For this to be of any use there would have to be significant changes in pH with fluctuations in the proportions of the reactant solutions.

Explosions during Sieving

No evidence has been obtained that explosions occurring at this stage have been caused by "sensitive" azide and it would seem that accidents at this stage are a mechanical and/or human failure.

Summary

The manufacture of Service lead azide based on precise nucleation by 2½ per cent lead carbonate has been brought to a high degree of perfection.

Unfortunately, there is an occasional explosion during manufacture - I believe E.R.D.E. gives the incidence as about one in six thousand and the reason for this is at present unknown.

It is tempting to blame "sensitive" crystals which are "spontaneously" explosive and until all the properties of lead azide are fully understood this question will remain.

Meanwhile the only alternative seems to be to discourage the use of Service lead azide and change to phlegmatised types, overcoming the reduction in detonative power by redesign, particularly with regard to small detonators.

Discussion on Paper (D-2)

The Chairman thanked Mr. Wythes and invited questions from the floor.
Dr. Lovecy asked if there was a time factor or any particular condition
associated with the explosion of lead azide in the precipitating pan.

The Chairman replied that there was not, and added that since 1941
there had been a total of 19 explosions, although more than 6,000 batches
had been made since the last explosion. Mr. Whitbread asked if these
were all unexplained, and when told that they were, he asked if there was
a possibility that any of them had been caused by contamination with foreign
matter such as nuts and bolts. Mr. Robertson replied that this was most
unlikely as a very high standard of maintenance was observed in the R.O.F.'s.
Dr. Lovecy asked if there had ever been any explosions attributed to the
presence of other foreign matter, and was told that there was no direct
evidence that this was a cause.

The question was raised as to whether there had been any incidence of
explosion during the precipitation of lead azide on a small scale.

The Chairman replied that he thought there may have been one or two
when lead azide was first made, but he had no record of any such explosions
in recent years. He continued that there had been no injuries to operators
in any of the R.O.F. explosions, thus indicating that the design of building
and the operating regulations afforded adequate safety protection.

At this point Mr. A.T. Thomas should have presented his paper on
"Spontaneous Explosion during crystal growth of Lead Azide", but he was
indisposed and the Chairman gave it on his behalf. This was followed by
a film "Spontaneous Explosion of Lead Azide", made at E.R.D.E. Woolwich,
illustrating some of Mr. Thomas's work on his "Lead azide alarm clock"
using the master/slave manipulator. The Chairman said that copies of the
film were available for loan on request. Slides were also shown illustrating
the work done by Rogers & Harrison (1955) referred to in Mr. Thomas's paper.

SPONTANEOUS EXPLOSION DURING CRYSTAL GROWTH
OF LEAD AZIDE

A.T. Thomas

When lead azide is crystallising from cold aqueous solution it frequently happens that spontaneous explosions occur for no apparent reason. Explosions have been observed when crystallisation is carried out under a number of conditions and reproducibility of this phenomenon is somewhat erratic. Miles (1931) prepared beta lead azide crystals by the slow inter-diffusion of aqueous solutions of sodium azide and lead nitrate and frequently explosions occurred during the growth of the azide crystals. Rogers and Harrison (1955) made an attempt to determine the conditions necessary for explosion and carried out diffusion experiments using a barrier solution of sodium nitrate to keep the system hydrostatically stable. They found that a series of weak explosions can sometimes be detected in the system where a major explosion subsequently occurs. Further experiments carried out in an effort to repeat the conditions for micro-explosions were not always successful, probably due to the large number of variables involved and the likelihood that special conditions are required locally in the system.

Spontaneous explosions have been observed in this department during the following experiments.

1. Preparation of beta lead azide by the diffusion method described by Miles.

2. The slow absorption of hydrazoic acid vapour by aqueous lead salt solutions.

3. During the crystallization of lead azide from ammonium acetate solutions.

It is found that solutions of lead azide in ammonium acetate may be specified which will explode spontaneously and, by controlling concentration, temperature and conditions of cooling, the time to explosion may be predicted with reasonable accuracy. A critical experiment was carried out to show that spontaneous explosion is not associated with the large crystals of lead azide that are formed during crystal growth. In a solution containing 0.7 per cent lead azide, a number of large crystals had formed about 30 minutes before the predicted time of explosion. These crystals were filtered and the mother-liquor kept. At the predicted time of explosion the mother-liquor portion exploded while the large lead azide crystals remained intact. It is possible to suppress spontaneous explosion by the addition of small amounts of various additives such as dextrin, polyvinyl alcohol and other hydrophilic colloids.

/It is .....

It is suggested that spontaneous explosion may be associated with nucleating conditions and not with super-sensitivity due to the presence of internal strain and sudden release of stresses in large crystals.

TABLE 1

Spontaneous Explosion of Lead Azide

Lead azide (pure) dissolved in 50 ml. of 5 per cent
ammonium acetate solution at $70^{\circ}C$ and allowed
to cool to room temperature during two hours
without disturbance.

Lead azide per cent	Time to Explosion Min.
1.0	40 ± 2
1.0	50
0.9	75
0.9	65
0.8	80
0.8	85
0.7	210
0.7	220
0.6	225
0.6	255
0.5 — 10 Experiments	7 exploded overnight Large alpha crystals in intact containers.
0.4 — 4 Experiments	No explosion after four days standing. No crystals separated.

TABLE 2

Absorption of Hydrazoic Acid Vapour

Solution	Vol. cc.	Conc. per cent	Millimoles			No. of Experiments	No. of Explosions 48 hrs.	Crystals obtained
			Pb++	NaOH	HN3			
Lead acetate	4	20	2.10	nil	5	4	nil	Fragmented small
	4	10	1.05	"	5	4	1	Alpha
	4	5	0.57	"	5	4	nil	Lead azide crystals
	4	10	1.05	"	10	4	nil	
Lead nitrate	4	10	1.2	nil	5	8	nil	Elongated alpha lead azide crystals. 2 mm. long
Lead acetate	5		1.0	1.0	5	14	6	Large irregular
Sodium hydroxide	4		0.8	0.8	5	8	4	Alpha
	3		0.6	0.6	5	8	1	Lead azide crystals
	2		0.4	0.4	5	8	nil	3 mm. long
	3.8		0.8	0.8	5	Static 40	10	
	3.8		0.8	0.8	5	agitated 40	4	

Mr. R.C. Harris asked if observations were made up to the time of the spontaneous explosions. The Chairman said they were and went on to say that explosions which tend to occur during the diffusion process can be suppressed by the use of suitable additives, and to some extent by agitation.

Dr. Ball asked if the use of lead acetate in these experiments was a significant factor in causing explosions, but the Chairman said that this was not the case, as explosions had occurred when lead nitrate was used instead.

Dr. Lovecy asked if stagnation might be the cause of spontaneous explosion. The Chairman replied that there was nothing to indicate this as some explosions had occurred during agitation, and the suggestion had never been made at any court of inquiry. Dr. Todd asked if, in spite of stirring, local explosions might occur under stagnant conditions. He said that it has been shown that at high degrees of concentration crystallisation occurs layerwise, whereas at low concentrations crystals are formed by spiral growth leading to spiral dislocations, and when nucleation occurs, exothermal conditions prevail and local hot spots may cause explosion. The Chairman said he had discussed this possibility with Professor Frank, but not sufficient was known on the subject.

Dr. Kaufman asked if Mr. Thomas had examined his mother liquor after the crystals had been separated, by the Tyndall cone of light. The Chairman said this had not been done but was worth investigating; it was expected that nuclei would be present, and further work on the effect of temperature and supersaturation conditions would be undertaken.

Dr. Lovecy referred to the work done by Rogers and Harrison, and the Chairman stated that nuclei can form when crystals are present. Dr. Lovecy enquired if isothermal conditions were present during Rogers and Harrison's work; he thought that conditions under which nucleation can occur was a possible avenue to explore, but questioned if sufficient energy could be available to result in explosion.

Dr. Kaufman said he had done some calculations and enough energy to detonate lead azide could be released. Mr. Duke said that this had been confirmed by D.A. Young at Imperial College. Mr. Robertson asked if there was any risk of explosion during pouring from the precipitating pan. The Chairman replied that there had been no evidence of this, but mother liquor had exploded on cooling after being removed from the pan.

/Dr. Kaufman .....

Dr. Kaufman asked if any explosions were known to have occurred during the preparation of lead azide in which sodium carboxy methyl cellulose (C.M.C.) or dextrin had been used.

The Chairman replied that these additives tend to suppress spontaneous explosion and that probably more than 50,000 batches of lead azide containing C.M.C. have been made without incident. He added that in the R.D.1333 process vigorous stirring is employed, thus further reducing the probability of spontaneous explosion, whereas in the Service lead azide process there was a large space underneath the stirrer and a slower stirring rate was used. This was because, during early days of manufacture, there was some fear of mechanical attack by the stirrer on the lead azide crystals. Dextrin suppresses spontaneous explosion and formation of the beta polymorph. He had no record of any explosion occurring during preparations using dextrin, and this was confirmed by Mr. Medlock.

Dr. Kaufman asked if reduction of C.M.C. content in the R.D.1333 process might increase the possibility of spontaneous explosion.

The Chairman replied that this might be correct, but the effect could be investigated experimentally on a small scale.

Dr. Lovecy asked if the amount of C.M.C. used in the R.D.1333 process was related to the physical properties of the final product, rather than to its ability to suppress explosion.

The Chairman replied that it was related to the properties of the final product.

Dr. Lovecy referred to the work by Mr. Thomas and by Rogers and Harrison, and said it seemed that something curious could proceed during crystallisation experiments producing energy, which may either be able to discharge slowly or alternatively would accumulate and discharge catastrophically later.

Mr. Duke asked what would be the effect of agitation on the "alarm-clock" experiments. The Chairman said that experiments had shown that explosions could still occur, but were less frequent (Table 2 of Paper (D-3)).

Mr. Duke asked if phenomena such as "clicks", reported by Rogers and Harrison, had ever been experienced during large scale preparation. The Chairman said he had no record of any.

Mr. S. Lamnevik reported that in Sweden there is a factory which operates a process in which pure beta lead azide is prepared by precipitation without stirring. On storage under water the beta azide is converted into high purity alpha lead azide. The process has been operated for many years.

/Dr. Lovecy .....

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Dr. Lovecy said he thought it should be made clear that C.M.C. is present as the lead salt and that reduction in the amount of C.M.C. used might lead to a situation in which there was insufficient C.M.C. present to suppress spontaneous explosion. The Chairman said he thought that in the preparation described by Mr. Lamnevik he was working dangerously near to the limit where explosion was likely to take place.

Mr. Rask asked if there was any toxic hazard due to the liberation of hydrazoic acid during precipitation. The Chairman replied that there was, and that he would supply Mr. Rask with a copy of a report he had on the subject. Dr. Kaufman and Mr. Dubois asked if they could have copies too and this was agreed. The Chairman continued that there had been a minor accident in E.R.D.E. caused by a small pocket of hydrazoic acid exploding when distillation apparatus was being dismantled, and it was thought that pockets of hydrazoic acid could be responsible for the spontaneous explosions in lead azide preparation. Mr. Robertson asked if there was any evidence to indicate the presence of hydrazoic acid in sodium azide.

Mr. Leslie stated that if aged sodium azide solution was used in the preparation of lead azide, the resulting product could be particularly sensitive. The use of aged dextrin solution could also have the same effect. The solutions had been stored in glass bottles. Both Mr. Robertson and the Chairman had had no experience of this phenomenon.

Mr. Robertson asked if D.C.I. had any evidence of change of pH of sodium azide solution on storage. Mr. Sen said he had none.

The Chairman, introducing a discussion on the transport of lead azide, commented that in the U.K. there was a strong feeling that lead azide should be manufactured on the same site as it is used, rather than be transported in bulk to the filling factories. Samples of lead azide have been stored under aqueous industrial methylated spirit mixture, and Dr. Wyatt had carried out sensitiveness tests on them. Dr. Wyatt said that emery paper friction tests on Service lead azide and R.D.1333 showed no change before and after storage under a mixture of methylated spirit and water for 2 years, whereas R.D.134? and R.D.1352 showed a statistically significant decrease and increase respectively. It is doubtful whether these changes were significant with regard to practical hazard.

Dr. Kaufman asked at what temperature the samples had been stored and tested. Dr. Wyatt told him that storage had been at room temperature in glass containers. Dr. Todd asked if there had been any polymorphic change during the storage period. Dr. Wyatt said that Mr. Duke had examined the samples and found no change.

/Dr. Wyatt .....

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The **Chairman** then referred to the methods employed for drying lead azide. He said that the R.O.F.'s used cold dry CO_2-free air, but he knew that warm CO_2-free air was sometimes used; ordinary warm air was used by one manufacturere. There were no comments from the meeting on the subject of drying.

The next topic to be discussed, _viz._ the handling of lead azide, began with a film entitled "The Development of Electrostatic Charges during the Manufacture of Detonators", made by the Australian Government, and introduced by Mr. Clay. **Mr. Clay** said he was pleased to have the opportunity of showing the film, which he was seeing for the first time after final editing. The film showed the method used for filling detonators, and experiments carried out to determine the nature and size of electrostatic charges developed during pouring operations. Lead styphnate, lead azide, dextrinated lead azide and ASA composition were run down chutes of various materials after being tipped from an earthed brass measure. The charge developed on the chute was shared with a 0.001 μfd condenser and the resultant voltage measured on a Model 610A Keithly Electrometer. Temperature and humidity were not controlled but were about $75^{o}F$ and 60 per cent respectively. In general, lead azide generated a negative charge on the chute, whereas lead styphnate generated a positive charge. ASA usually generated a negative charge but occasionally gave positive charges. The highest charges developed were with lead azide and dextrinated lead azide on nickel chutes.

ASA composition was poured past an electrode at a potential of 1000 volts. High speed cine photography showed that some particles were attracted and others were repelled, but not to the extent expected under these conditions.

In many of the pouring experiments the voltages on the electrometer did not always come up slowly to a maximum but rose and fell, and came to a steady value only at the end of the pouring. Furthermore, a change in sign sometimes occurred. In order to study these phenomena more closely, a Tektronix C.R.O. was connected to the output of the electrometer and simultaneous cine records were made of the C.R.O. screen and of the pouring operation. This showed an immediate link between deflection and movement of the powder.

The **Chairman** thanked Mr. Clay and his colleagues in Australia for the opportunity of seeing the technique and results of their investigations. **Dr. Wyatt** said he liked the simultaneous obs   ations of potential movement and of powder movement. He agreed that lead azide and lead styphnate usually charged in opposite senses, but as regards magnitude he had always found lead styphnate to electrify much more than lead azide.

Dr. Lovecy asked what voltage was represented by each division on the oscilloscopic screen. **Dr. Wyatt** told him it was 0.03 volt. **Dr. Kaufman** asked if brass and stainless ste l, as used in the film, constituted the worst possible hazard. **Dr. Wyatt** said that, apart from nickel, brass was

/one .....

one of the worst metals with lead azide and ASA. Stainless steel was used
~~with lead styphnate in the experiments where simultaneous records were taken~~
of the C.R.O. screen and the pouring, as this combination gave the greatest
number of changes of sign.

Mr. Clay, in answer to a request by Dr. Wyatt for more information on
the nature of the incidents occurring with the filling of Australian
detonators No. 27, said there had been a number of explosions with ASA
occurring at various stages in the filling sequence. A number had taken
place when pouring from the graphited boat as well as from the brass measure.
Dr. Lovecy asked if there could be any mechanical reason for the explosions,
for example, the use of the Bowden cable. Mr. Clay said that the Bowden
cable was used only in the film to simulate normal procedure. The Chairman
asked Mr. Hedlock if he had any comments to make. Mr. Hedlock said he had
found the film of great interest, especially as he had previously done some
pouring experiments using P.E.T.N., with a different type of apparatus. He
commented that the energy involved when two charged particles of opposite
sign approached is dependent on the capacitance of the particles and is thus
extremely small. Consequently this was not a likely mechanism of ignition.
Dr. Lovecy then asked if 1000 volts was a generous estimate of the potential
of the charged particles, but Mr. Hedlock said he thought not.

Dr. Ball asked what types of lead styphnate and lead azide were used in
the film. Mr. Clay said that all the materials used were made at Maribyrnong,
the lead styphnate was R.D.1302, and the lead azide was changed halfway
through from Service to dextrinated.

The Chairman then presented the remainder of his paper "Hazards in the
Manufacture and Loading of Lead Azide", and said that the automatic transfer
equipment at R.O.F. Chorley referred to was now almost ready, and when
completed would be tested initially using an inert substitute for lead azide.

/Later (D-4) .....

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G. T. C. Taylor

The transfer of relatively large (and certainly fatal) quantities of
lead azide by an unshielded operator is common practice but the safety
records are very good. Because of the potential hazard there has been
progress in R.O.F. Chorley toward fully automatic transfer equipment for
lead azide production.

On the question of general handling and loading of lead azide it should
be emphasised that there are significant and large differences in both
mechanical and spark sensitiveness between relatively impure commerical lead
azide and the more efficient types used for military purposes. This is shown
especially in connection with the effect of the presence of grit which
dramatically sensitises the pure and near pure forms of lead azide to friction.
This can be verified easily by experiment and some types of added grit make
pure lead azide (and Service lead azide is pure on the outside of the crystals!)
extremely hazardous. Therefore there is a tendency to attribute ignitions
during loading operations to the sporadic intrusion of grit and one important
way of reducing the possibility of accidental ignitions is to operate in dust-
filtered conditions and to take other appropriate precautions to exclude
foreign matter.

It is important to note that certain other explosives such as RDX,
tetryl, and of course, tetracene, can act as sensitisers in this respect.

It is only comparatively recently that the threshold metal/metal
electrode spark sensitiveness of some types of lead azide has been determined
and it is significant that energies of the order of 2 ergs can cause ignition,
although this figure is nearer 20 ergs for lead azide in production. However,
metal/metal contacts are avoided in practice because of mechanical hazard and
there is little tendency to attribute accidental ignitions to this mechanism.

When asked for his comments Dr. Ball said a wide range of questions could be raised but he agreed with the substance of the paper. He was committed to using Service lead azide because it conformed with military requirements and performance, but there was no doubt that its handling presented greater hazards tnan did that of other types of lead azide, and tests had shown that C.M.C. and dextrinated types are less sensitive in the presence of aluminium, copper, and tinned copper. He would like to see Service lead azide replaced by these other types, as there would be a greater margin of safety in handling. In addition, the pelleting properties of the new types were better, with improved cohesion and less reassertion. He stressed the need to exclude grit and said he had raised the question of air conditioning with controlled humidity. It was possible to have long runs of the production of Service lead azide without incident because of the high standard of equipment maintenance and efficient training of personnel.

Dr. Wyatt agreed that attempts should be made to exclude grit. The sensitiveness to impact of Service lead azide is increased 3.2 fold when 5 per cent carborundum is added, and the sensitiveness to friction is increased more than 3 fold when an emery paper surface is substituted for mild steel. An azide less susceptible to grit than Service lead azide would obviously be an advantage. While on the subject of sensitisation, it should be remembered that many organic explosives, e.g., RDX, PETN and tetryl, and also sulphur will sensitise lead azide to impact.

He thought the air conditioning scheme in use in Australia should be adopted here, as the system in present use at R.O.F. Chorley tended to give pockets of different humidity. Two enquiries, one from Chorley on the advisability of continuing with the present minimum relative humidity over a range of temperatures, and one from Pakistan on the appropriate humidity to use at their high temperatures, had led to a series of experiments on electrification over a fairly wide range of relative humidity and temperature. The first part of the study was on the electrical resistance of fabrics, as this property had been shown elsewhere to be a useful guide to its electrification properties. Tests had been carried out by textile laboratories on the change in resistance when (a) the relative humidity was altered at one temperature and (b) when the temperature was altered at one value of relative humidity, but no systematic experiments had been carried out varying both over a fairly wide range. These had now been carried out for a variety of fabrics.

/Electrification .....

Electrification of powders on pouring had also been carried out over a similar range of temperature and humidity. The early experiments used a device with a pouring edge of about 1 inch width, but reproducible results were not obtained, possibly due to non-reproducible conditions of pouring. Some particles were leaving the metal pouring edge, while the remainder were rolling over other particles and did not touch the metal as they fell off. A twelve inch wide pouring device had been constructed, and, with care, reproducible results were obtained for lead azide, lead styphnate and L.D.N.R. Various metals had been used for this device in attempts to get a surface reproducibly clean for electrification experiments. The original equipment was made of brass, cleaned chemically with nitric acid. This was satisfactory for a time but was eventually abandoned. Another device was covered with platinum sheet, but this showed no great advantage. The presently favoured apparatus is chromium plated and is cleaned with distilled water only.

Both series of experiments, i.e., the fabric resistance and powder electrification tests, showed that the resistance or electrification obtained at a relative humidity of 65 per cent and a temperature of 20°C (68°F) can be obtained at higher humidities for lower temperatures or lower humidities for higher temperatures.

The Chairman remarked that Service lead azide contaminated with 5 per cent of a mixture of boiler grit, i.e., ash from chimneys, or "fly ash", and salt, may be super-sensitive; one increment exploded when the weight was put on it ready for the standard friction test. Sensitiveness tests carried out in the U.K. were usually on loose material in atmospheric conditions. In the U.S.A. it had been suggested that lead azide debris from filling machines (e.g. upstand fragments) was more sensitive than the unpressed lead azide. Tests carried out at E.R.D.E. on crushed pellets of lead azide and lead styphnate supported this conclusion both for friction sensitiveness and sensitiveness to electrostatic spark. However, pressed beta lead styphnate was slightly less sensitive.

Dr. Ball said that this was relevant to his earlier remarks, and that in the pressing of lead azide upstand can be the cause of trouble.

The Chairman then asked for final remarks.

/Mr. Van Patten .....

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Mr. Van Patten said he agreed with what had been said and that it all had a bearing on work done in U.S.A. **Mr. S.E. Harris** said he thought that good tooling and good supervision outweighed the problem of the sensitiveness of the material. All accidents of which he had experience were caused by man-handling, and not by poor tooling.

Dr. Lovecy said he thought that the differences in some of the electro-static test results were insignificant; the differences ought to be tenfold to mean anything.

Mr. Ferguson asked if ...R.D.E. had done any sensitiveness tests on Service lead azide of low bulk density, as Canadian experience indicated that it was more sensitive; in fact, there had been accidents with it during filling operations. He also asked if particle size could be linked with sensitiveness. The **Chairman** said U.K. experience showed that particle size had little effect on sensitiveness. **Dr. Wyatt** said he had not investigated low bulk density material, but he would not expect it to be more sensitive. **Mr. Ferguson** added that the most likely cause of the accidents he had mentioned was mechanical.

Dr. Ball remarked that the use of low bulk density material could lead to over-spill in filling, and this could be hazardous. The **Chairman** said we must know what is meant by "low bulk density"; it could be caused by the presence of branched and/or twinned crystals and this might lead to increased sensitivity. He continued that the minimum bulk density quoted in the original U.K. specification was 1.0 g/ml; this was later increased to 1.5 g/ml, and is now regarded as 1.8 g/ml. It is important to have a supply of material with constant bulk density, as any variation leads to filling problems. When asked for his comments **Mr. Rask** said that he had not had wide experience with lead azide. He had made dextrinated azide by the German method, and has since made Service lead azide, but had had no problems in manufacturing or mixing. He understood there had been some explosions in narrow grooves and that these had been caused by electrostatic discharge. **Mr. Leslie** said that though conditions at Ardeer were not ideal for making and handling lead azide, accident frequency had been reduced by substituting nylon punches for phosphor bronze punches, and he thought that some accidents were caused by the detonator tubes being slightly undersize.

The **Chairman** thanked all contributors to the papers and discussion and closed the session.

The Symposium Chairman (Dr. Dunstan) asked for a summary of each Session to be given by the chairman concerned.

Summary of Session A

Chairman: Mr. G.W.C. Taylor

In this session polymorphism was defined and the reasons given for its importance in the study and manufacture of lead azide. The crystallographic data in the literature and from recent Swedish and British work were reviewed, especially in connection with the more recently isolated gamma and delta polymorphs. The occurrence of a possible cubic form was described.

The present position on the preparation of pure beta normal lead azide and the gamma and delta polymorphs was given and the use of polyvinyl alcohol as a polymorph inducer was discussed.

The properties of the different polymorphs, especially with regard to sensitiveness, were next described. There are no very marked differences in sensitiveness between them. In particular, beta lead azide is not significantly more sensitive than alpha, as has sometimes been indicated in the past. Work was proceeding on sensitiveness of mixtures of polymorphs.

Basic lead azide was briefly reviewed. A simple well defined crystalline phase conforming to the empirical formula PbN_3OH has now been prepared and characterised.

/Summary .....

Summary of Session B

Chairman: Dr. I. Dunstan

Mr. Blay and Dr. Todd had considered in some detail the effects of water and carbon dioxide on lead azide, contrasting its high stability in dry air with the marked degree of breakdown under simulated storage conditions employing high humidity and carbon dioxide concentration. Dr. Todd had investigated sources of water and carbon dioxide in weapon assemblies. As indicated by Messrs. Blay and Sen, there had long been a diversity of opinion on analytical methods for azide, and certain differences between the U.K. and U.S. attitudes towards analysis of azide were discussed. A review of available methods had been given. The subject would clearly repay further study, and was in fact being pursued at E.R.D.E., particularly in relation to the gas volumetric method. It was also evident that attention must be given to the question of protecting lead azide from adverse environments, to removing sources of harmful chemical reaction and, in particular, to avoiding the presence of materials which tended to disturb the decomposition equilibrium by removing hydrazoic acid as it was formed. Mr. Lamnevik had outlined theoretical and practical approaches to the study of azide breakdown.

Summary of Session C

Chairman: Dr. R.M.H. Wyatt

Detailed accounts were presented of the formation and identification of six copper azides and one "brass azide". The six copper azides were cupric azide, alpha and beta cuprous azide, and monobasic, dibasic and tribasic cupric azides, this being the order of decreasing sensitiveness. Azide corrosion consists of a layer of alpha cuprous azide covered by a layer of monobasic cupric azide and the di- or tribasic salt (depending on the pressure of hydrazoic acid vapour). Friction and electrostatic discharge were likely causes for initiation of the corrosion product. however, each incident had to be considered in detail to see whether physical movement of corroded parts was a possibility, or whether there was a path for an electrostatic discharge. With regard to prevention, possible solutions involved choosing a less reactive explosive, the correct container for it, and suitable materials for other components in proximity. In cases where none of these solutions was practicable, it was possible to resort to non-porous metallic or organic protective coatings. There were special inhibitors such as 1,2,3-benzo-triazole, and sacrificial methods employing zinc. In all cases where hydrazoic acid was converted into something less objectionable, the effective azide content of the detonator was decreased, and it became less powerful.

/Summary .....

Chairman: Mr. G.W.C. Taylor

This session was concerned with the hazards involved in the manufacture and subsequent usage of lead azide. A study had been undertaken of the explosions which had occurred during the precipitation stages of manufacture of British Service lead azide. No cause had been discovered, but newer manufacturing processes appeared to have eliminated such occurrences, probably because of improved mixing conditions and the use of hydrophilic colloids and/or surface active agents. Experimental work on spontaneous explosions during crystallisation of lead azide was reported and discussed; such explosions were not associated with crystals growing to a critical size but were identified with nucleation conditions. The effect on sensitiveness of wet storage of lead azide was discussed and it was further reported that storage of certain solutions could give rise to more sensitive products. A film was shown illustrating a technique for measuring the electrostatic charge developed during the transfer of compositions containing lead azide. This was followed by a general discussion with many participants on the possible causes of accidental ignitions experienced during the loading of various types of lead azide. It was concluded that the sensitiveness of the lead azide to ignition by friction in the presence of grit, and the specific conditions of loading were important factors in a situation dominated by mechanical work being carried out on a very sensitive explosive.

CONCLUSIONS

The Symposium Chairman, Dr. Dunstan, in his concluding remarks, said that the papers and discussions had directed attention to several matters, viz:-

The importance of appropriate techniques of investigation, e.g. chemical analysis, mass spectrometry and X-ray crystallography.

The need for searching consideration by designers of the possible effects of components of weapons upon lead azide.

The need to establish well-defined experimental conditions to study these effects.

The need to study differences in behaviour of the various types of lead azide.

/Finally, ...

Finally, he thanked all those who had attended, especially the visitors
from overseas and all who had presented papers and contributed to the
discussions, and also those who had helped with such matters as secretarial
duties, projection of slides and films, and catering and transport arrange-
ments. He added that thanks were particularly due to Mr. Taylor, who had been
responsible for suggesting the Symposium and who had helped throughout with
its organisation, chaired two sessions and made two contributions.