X5604

AD640702

Copy 1

45

DEVELOPMENT DIVISION

COPY

M

PICATINNY ARSENAL

TECHNICAL GROUP

CHEMICAL DEPARTMENT

TECHNICAL REPORT

SERIAL NO. 1152

DATE February 21, 1942

1152

SUBJECT: STUDY OF THE ACTION OF LEAD AZIDE ON COPPER

FIRST AND FINAL REPORT

SYNOPSIS

It has generally been accepted that copper and brass can react with lead azide to form dangerously sensitive copper azide, and the use of copper alloys for detonators containing lead azide has been considered unsafe. Recently the British have authorized such use in military ammunition on the basis of tests which showed no reaction to occur. In view of these conflicting conclusions it was directed that a study be made to determine definitely if a reaction can occur.

It has been found that cupric azide is considerably more sensitive than lead azide and that, in the presence of moisture, the copper azide is formed when copper is in contact with either pure, crystalline lead azide or with the desensitized form covered by U.A. Army Specification No. 50-13-12. When moisture is absent, no reaction takes place; but, contrary to the widely held belief, the presence of carbon dioxide alone does not cause the reaction to take place.

As an extremely sensitive product can be formed by the reaction of copper and lead azide under conditions which are difficult to prevent, it is recommended that the use of copper alloys be prohibited in ammunition where such metal shall be in contact with lead azide.

No. 1152
Picatinny Arsenal, Dover, N.J.,
February 21, 1942.

TECHNICAL GROUP
CHEMICAL DEPARTMENT
CHEMICAL LABORATORIES DIVISION

Study of the Action of Lead Azide on Copper.

FIRST AND FINAL REPORT

INTRODUCTION:

1. Conflicting evidence has been obtained by various investigators in regard to reaction between metallic copper and lead azide. A recent letter (Ref. A) summarizes storage tests conducted by the British, the results of which indicated that no formation of copper azide or other extra-sensitive compounds took place during months of contact between copper and lead azide. Earlier investigators claimed to have observed the effects of a definite chemical reaction within lead azide-copper detonators, especially in mines, where carbon dioxide in the moist air acted on the lead azide so as to generate enough hydrazoic acid to form a sensitive copper salt on the capsule walls. The present policy of the British Services of loading lead azide in copper detonators has raised the question regarding the possible hazard involved in such a practice, and it was directed (Ref. A) that this Arsenal undertake a study of this reaction with the object of definitely settling the question as to whether or not copper azide is formed under certain conditions, and whether or not it is more sensitive than lead azide.

OBJECT:

2. To determine whether copper azide is formed upon storage at 50°C. of strips of polished copper in contact with commercial lead azide and with pure crystalline lead azide under the following conditions:

A. Dry.
B. Dry, in an atmosphere of carbon dioxide and air.
C. In a humidor containing air at 90 percent relative humidity.
D. In a humidor containing much carbon dioxide at 90 percent relative humidity.

RESULTS:

3. When polished copper strips in contact with crystalline lead azide complying with the requirements of British Specification L/8290/A, and copper strips in contact with lead azide complying with U.S. Army Specification No. 50-13-12 were subjected to storage under various conditions, periodic examinations gave the following data.

Humidity of Air	Carbon Dioxide	Effect on Polished Copper Strip After Contact for	
		Nine Days	Twenty Days
		Crystalline Lead Azide	
None	None	None	None
None	Present	None[a]	None[a]
90% R.H.	None	--	Explosive brown incrustation[b]
90% R.H.	Present	Explosive bluish-gray incrustation	Explosive bluish-gray incrustation[a]
		Commercial Lead Azide	
None	None	None	None
None	Present	None[a]	None[a]
90% R.H.	None	--	Explosive brown incrustation[c]
90% R.H.	Present	Explosive gray film	Explosive gray film[d]

[a] Where the surface of the copper was covered by the lead azide, it remained br[illegible] while the rest of the strip was tarnished green by the carbon dioxide present in the air.

[b] Minute flakes of the tough, tenacious incrustation obtained by scraping the surface with a steel spatula exploded sharply when touched with a flame. Bluish-green sparks accompanied the crackling noises, indicating the presence of considerable copper ion.

[c] The tough coating underlying the lead azide was found to detonate violently in contact with a flame, producing sounds very much louder than an equivalent amount of lead azide. Flashes were green in color.

[d] After rubbing with a cloth to remove any adhering lead azide, the gray film or deposit could be detonated by severe friction.

4. The above data indicate that there was no reaction between copper and either type of lead azide if no moisture was present; but that reaction took place in the presence of moisture, with the formation of a sensitive, [illegible] incrustation. In the presence of carbon dioxide, no reaction took place unless moisture also was present. Photograph M-120[illegible] (magnification 2X) shows the result of action of pure lead azide on copper in an atmosphere of carbon dioxide and moisture.

5. A sample of cupric azide was prepared and found to have the appearance shown by photomicrograph M-12102, attached. The material was black and was found to be considerably more sensitive to impact than commercial lead azide, these having Drop Test values of 24 and 69 centimeters, respectively.

DISCUSSION OF RESULTS:

6. When the thin incrustations formed by the reaction of the copper strip and the lead azide were detonated by the action of a flame, the resulting flashes were invariably blue in color. This was taken as evidence that copper was an actual chemical constituent of the sensitive material formed, since the blue flash could not be duplicated by subjecting a mechanical mixture of commercial lead azide and fine, pure copper shavings to the action of a flame. The sound produced by the latter mixture was so slight that it did not resemble the extremely sharp reports produced by copper azide. Copper azide explosions were easily differentiated from those of lead azide itself under similar conditions. This difference in sound effect was strikingly noticeable in Drop Tests of these materials.

7. The reaction between the lead azide and copper was not due to the presence of impurities or special characteristics of the samples of lead azide used, since they were analyzed and found free from reactive ions as shown by the following data:

	Pure Lead Azide	Commercial Lead Azide
Lead content, percent	71.12	69.60
	70.99	69.68
Average	71.06	69.64
Iron, aluminum, calcium, sodium, potassium	None	None
Nitrates, chlorides, acetates	None	None
Acidity	None	None

8. The sensitivity to impact of copper azide prepared is considerably greater than that of commercial lead azide, which is manufactured so as to be considerably desensitized. Regardless of any difference in sensitivity of copper and lead azides as such, the uncontrolled formation of either azide is highly objectionable since the sensitivity can vary very widely with the type of crystal formed.

CONCLUSIONS:

9. The results of the storage tests show a definite tendency of copper to form its azide as a result of prolonged contact with either commercial or pure lead azide when moisture is present. The presence of carbon dioxide alone has no distinct effect on this reaction.

RECOMMENDATIONS:

10. As the total exclusion of moisture from lead azide under the conditions of use is considered impracticable, it is recommended that the use of copper alloys in contact with lead azide in ammunition be prohibited.

EXPERIMENTAL PROCEDURE:

11. The crystalline lead azide was prepared by stirring mechanically 5.7 grams of lead nitrate in 200 cc. of water while adding slowly 2.2 grams of sodium azide in 200 cc. of water. After an additional minute of stirring, the mixture was filtered by suction and washed twice by stirring the residue on the filter with about 50 ml. of water. The white lead azide was further leached free of soluble salts by allowing the filter paper containing the product to stand in a funnel submerged in a beaker of water for 48 hours. The batch was allowed to air-dry before using.

12. The various storage conditions were obtained by charging two desiccators with calcium chloride, and two more with sulphuric acid, density 1.115. Dried carbon dioxide from a Kipp generator was passed into two of the desiccators for a few minutes, prior to inserting the numbered strips of cleaned copper, upon which was placed either commercial lead azide or some of the pure azide, as required. The desiccators were then placed in a chamber held at 50°C.

13. The copper azide was prepared by adding a solution of five grams of copper nitrate to a solution of two grams of sodium azide. The dark chocolate-colored precipitate which was immediately thrown down was filtered by suction, and given a water wash,

followed by alcohol and ether washes, to hasten drying of the product. The filter paper bearing the copper azide was removed from the Büchner funnel, and spread out on paper towelling to air-dry.

14. The sensitivity to impact tests were made with the Bureau of Mines Drop Test Machine, using a 500-gram weight. 0.02 gram of material was used for each test.

15. Determinations of the lead contents were made in accordance with the procedure prescribed in U.S. Army Specification No. 50-13-12. The procedure used in testing for acidity and the various metals and negative radicals were those prescribed in British Laboratory Method No. P.81.B.

REFERENCES:

A. O.O. 471.86/1197; P.A. 471.86/760; 1st Ind.

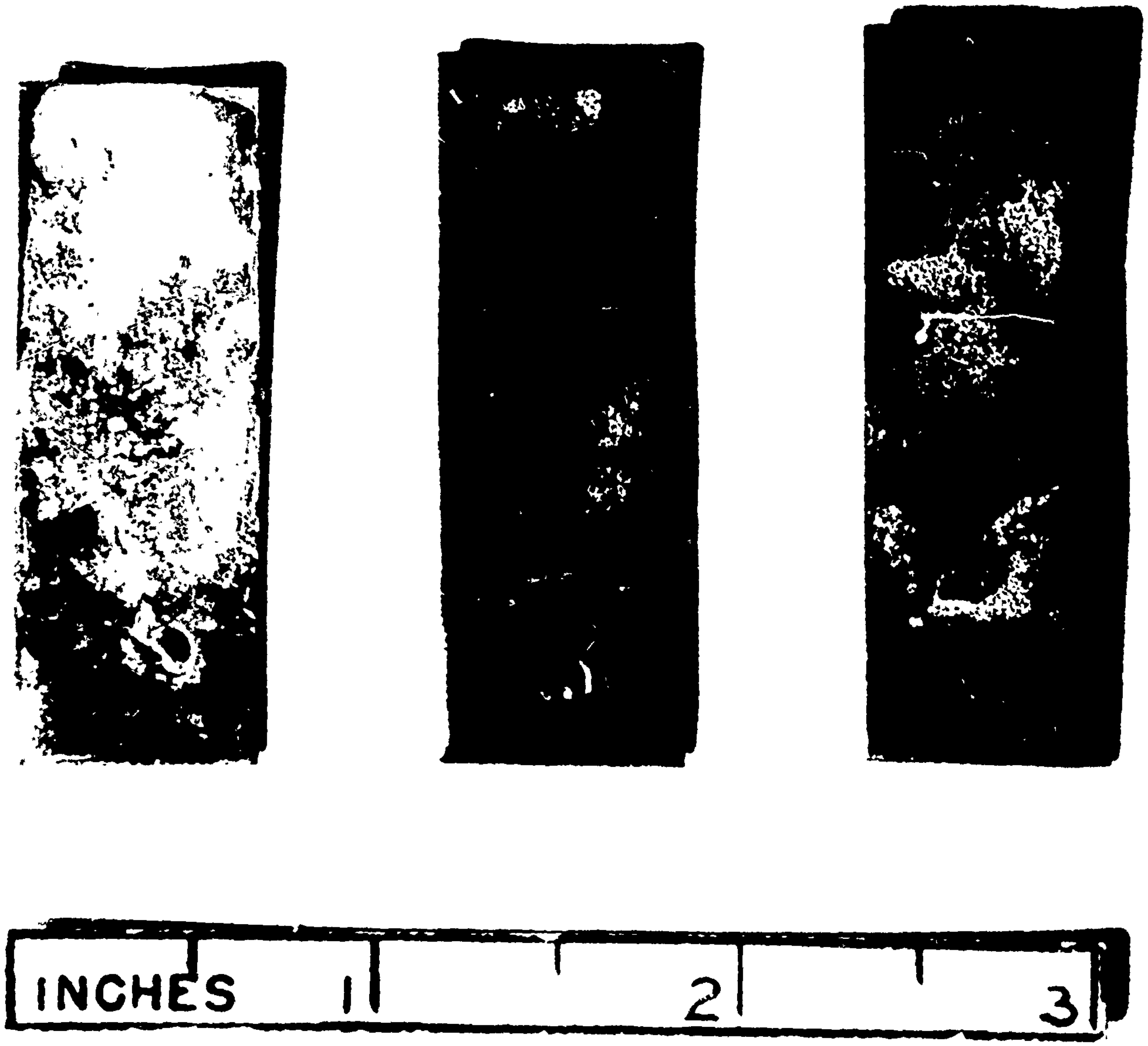
Submitted:
Wm. H. Rinkenbach,
Senior Chemist.

Prepared by: K. S. Warren
K. S. Warren,
Asst. Chemist.

Approved:
J. C. Hale,
Principal Chemist.

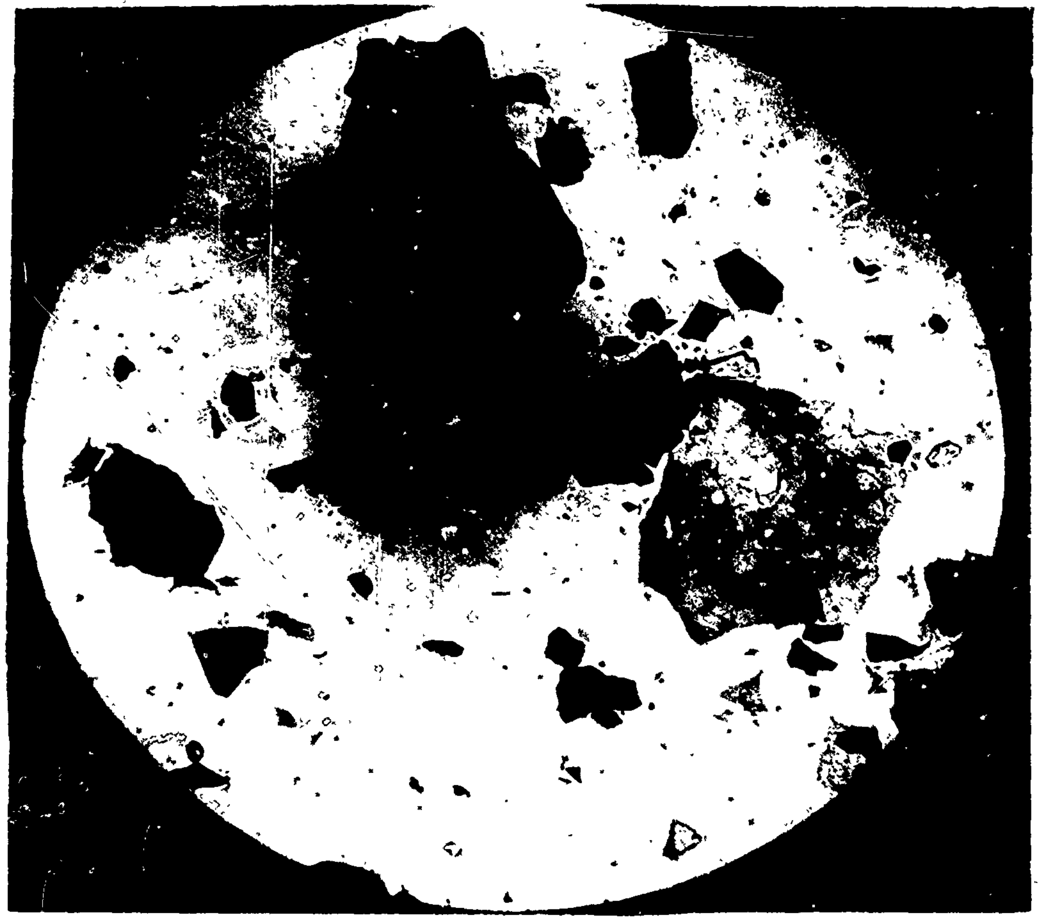
Reviewed:
D. D. Sager,
Chemist.

Approved:
J. W. Givens,
Capt., Ord.Dept.,
Chief, Chemical Dept.



M-12085 February, 1942 PICATINNY ARSENAL ORDNANCE DEPARTMENT

Copper strips after eleven days contact with lead azide.



M-12102 February, 1942 **PICATINNY ARSENAL** **ORDNANCE DEPARTMENT**

Copper azide prepared from copper nitrate and sodium azide

70x