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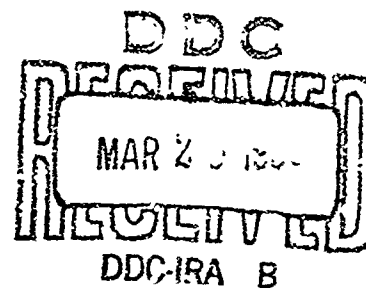


PICATINNY ARSENAL
TECHNICAL GROUP
CHEMICAL DEPARTMENT

TECHNICAL REPORT

SERIAL NO. 1302

DATE 28 June 1943



SUBJECT: STUDY PROPERTIES OF TETRAMINO CUPRIC NITRATE

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FIRST AND FINAL REPORT

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SYNOPSIS

In order to obtain information regarding the degree of hazard involved in the use of copper or copper alloys in equipment used for the manufacture of amatol, storage tests were made at 50°C. of copper foil in contact with ammonium nitrate, 80-20 and 50-50 amatols containing various percentages of moisture, in both open and closed containers.

It was found that in closed containers, a sensitive, purple tetramino cupric nitrate was formed very readily in the presence of ammonium nitrate, less readily in the presence of 80-20 amatol and to little or no extent with 50-50 amatol. In open containers under the same storage conditions, there was no formation of the sensitive purple salt. In all cases except those in which the minimum amount of moisture was present, there was corrosion of the copper strips with the formation of blue and green basic nitrates, and it was found that at normal temperatures, these basic nitrates would react with the copper metal to form the sensitive purple salt.

It is concluded that this work substantiates the requirement in specifications that no copper or copper alloys may be used in any part of the equipment which may come into contact with amatol, during its manufacture.

Initial number of samples contained of color -
2 samples of 80-20 amatol and 2 samples of 50-50 amatol until
the samples were exposed to the atmosphere and will be
initially of color and will be only.

No. 1302
Picatinny Arsenal, Dover, N.J.
28 June 1943

TECHNICAL GROUP
CHEMICAL DEPARTMENT
RESEARCH DIVISION

Study Properties of Tetramino Cupric Nitrate

FIRST AND FINAL REPORT

INTRODUCTION:

1. Specifications concerning mixing kettles and other equipment used in the loading of amatol, require that no copper or copper alloys be used in any part of the equipment that may come into contact with the amatol. This requirement was based on the assumption that ammonium nitrate might react with copper to form tetramino cupric nitrate. While no definite data relative to the sensitivity of this compound are available, it has been reported that the compound is explosive. (Mellor's Inorganic and Theoretical Chemistry 3,284: duPont Patent-B.P. 544,582).
2. Laboratory tests made in the past, relative to the corrosion products formed by the action of ammonium nitrate and sodium nitrate on copper, have shown these products to consist largely of basic copper nitrates. No evidence was obtained which indicated the presence of an explosive copper salt.
3. Since questions have arisen repeatedly regarding the possibility of using various copper alloys for the manufacture of tools and equipment for use in connection with ammonium nitrate and amatol, it was considered desirable to accumulate definite data on the significance of the reaction between ammonium nitrate and metallic copper.

OBJECT:

4. To prepare tetramino cupric nitrate and determine its sensitivity characteristics.
5. To determine the sensitivity to impact of 50-50 amatols, containing varying amounts of copper powder, cupric oxide and cupric nitrate present as impurities in the ammonium nitrate.
6. To investigate the action of ammonium nitrate containing varying amounts of moisture, when stored with metallic copper strips at 50°C.
7. To investigate the behavior of 80-20 amatol and 50-50 amatol containing varying amounts of moisture, when stored with metallic copper strips at 50°C.

RESULTS:

8. Tetramino cupric nitrate has a characteristic deep purple color which is entirely different from the blues and greens of the basic copper nitrates. Its appearance is shown in the photograph, M-15864.
9. It may be formed by the combined action of air, moisture and ammonia on metallic copper exposed above the surface of ammonium nitrate at an elevated temperature. or by the action of basic copper nitrates in the presence of air acting on metallic copper at normal temperatures.
10. The Drop Test on the nitrate was 19 cm. In comparison lead azide has a drop test of 16 cm. (Table I).
11. The explosive when compressed was not detonated or ignited by the spit of a black powder fuse but burned very slowly with a green flame when ignited in loose condition. Its Explosion Temperature Test value was 331°C. as compared with 335°C. for lead azide.
12. The Brisance value of the explosive as shown by the Sand Test was 17.2 grams of sand, when initiated by 0.24 grams of mercury fulminate and 0.19 grams of tetryl. In comparison lead azide has a brisance value of approximately 18 grams of sand.
13. The sensitivity of ammonium nitrate was not noticeably increased as the result of the addition of small amounts of copper salts. See Table II.
14. 50-50 amatols containing small amounts of copper salts as impurities, showed a very slight increase in sensitivity as compared with 50-50 amatol. See Table III.
15. Copper strips stored in contact with ammonium nitrate containing 1, 2, 5, 6, 8 and 16% of moisture, in closed containers at 50°C., developed no incrustation of sensitive tetramino cupric nitrate. Under the same storage conditions, copper strips in contact with ammonium nitrate containing 3 and 4% of moisture showed the development of the sensitive purple salt in 30 days. See Table IV. The sensitive purple salt was not formed on the metal in contact with moist ammonium nitrate at an elevated temperature, but only on the metal exposed above the surface of the ammonium nitrate.
16. A test specimen of ammonium nitrate containing 4% of moisture in a closed container, showed the development of the purple salt on a copper strip, after four days storage at 100°C.
17. Test specimens containing 2, 4 and 6% of moisture, stored in open test tubes and in open porcelain crucibles for four days at 100°C., showed no formation of the purple tetramino cupric nitrate.

18. Test specimens of 80-20 amatol containing varying amounts of moisture, in contact with copper strips, showed a slight development of the purple salt on the metal exposed above the surface of the amatol, in three months time. In open containers under the same conditions, there was no formation of the purple salt.

19. Test specimens of 50-50 amatol containing varying amounts of moisture, in contact with copper strips, showed no development of the purple salt in either open or closed containers, when stored at 50°C. for three months.

DISCUSSION OF RESULTS:

20. Drop tests on ammonium nitrate containing various amounts of copper salts as impurities, gave no indication that the sensitivity of the ammonium nitrate was increased as a result of this procedure. See Table II.

21. In order to determine how the sensitivity of 50-50 amatol is affected by the presence of copper containing impurities, a series of amatols were prepared from the above mentioned impure ammonium nitrates. They were then tested for their sensitivity to the impact of a 2 kilogram weight. The results which are appended in Table III show that the presence of cupric oxide has a greater effect on sensitivity than either copper powder or cupric nitrate, and that the presence of a very large amount of tetramino cupric nitrate results in only a slight increase in sensitivity.

22. The storage tests of copper strips in contact with moist ammonium nitrate in closed containers, showed that tetramino cupric nitrate is an end product of corrosion which is always accompanied by vari-colored basic nitrates of copper as well as cupric oxide.

23. The first sign of corrosion is the formation of a black layer of cupric oxide on the exposed portion of the copper strip above the ammonium nitrate. This is followed by the deposition of blue or green basic salts and finally the formation of purple tetramino cupric nitrate. On continued heating the blue and green salts dry out to a white powdery mass, while the purple salt is unaffected.

24. With regard to the behavior of the metal surrounded by and in contact with the moist ammonium nitrate, there is a formation of a slight amount of red cuprous oxide which is followed by the formation of blue and green corrosion patches and finally the metal is completely disintegrated. At the same time the ammonium nitrate is colored various shades of blue and green.

25. The sequence in the development of colors on the exposed portion of the copper strip, that is the portion which projects above the column of ammonium nitrate, is detailed in Table IV. Here it is shown that only in the samples containing 3 and 4% of moisture was there any formation of the sensitive purple salt. In each case the formation of black copper oxide

preceded the formation of the tetramino cupric nitrate, which is apparently formed by the simultaneous action of ammonia liberated from the nitrate and oxygen surrounding the exposed strip. A larger amount of the purple salt was formed in the presence of 4% than with 3% of moisture. The tests were continued for six months but are reported only to the end of the third month, there being no further change after the end of this period.

26. Since it has been postulated that the sensitive purple salt is formed by the simultaneous action of ammonia and oxygen on metallic copper, in the presence of a small amount of moisture, it appeared logical to conclude that if the ammonia was removed as fast as it was formed, the undesirable salt formation would be prevented. In other words, since the steam heated kettles used for ammonium nitrate and for amatol are open, the ammonia generated by the heating of ammonium nitrate should readily escape from the vessel and there would be no opportunity for its prolonged contact, in the presence of oxygen, with the walls of the vessel. In consequence there should be no formation of the purple, sensitive salt.

27. To test this concept, ammonium nitrate containing 2, 4 and 6% of moisture was placed in an open test tube surrounding a thin strip of copper foil, and exposed to a temperature of 100°C. for four days. The same procedure was followed with ammonium nitrate containing 2, 4 and 6% moisture surrounding copper strips in open porcelain crucibles. Examination of the copper strips after four days showed that the customary blackening of the metal above the surface of the ammonium nitrate, had not taken place and there was no indication of the formation of any purple colored salt. There was some oxidation of the metal surrounded by the ammonium nitrate, but the exposed metal tip while not bright, was clean.

28. This behavior is entirely different from that of a copper strip in a closed test tube surrounded by ammonium nitrate containing 4% of moisture, which was stored at 100°C. for four days. In this case the purple tetramino cupric nitrate formed a heavy deposit on the exposed tip of the metal.

29. These tests apparently indicated that the sensitive purple tetramino cupric nitrate is formed only when metallic copper is exposed to the combined action of ammonia, oxygen and moisture, at an elevated temperature. However it was later found that the salt may form under other conditions. When the crystals of tetramino cupric nitrate were heated at 100°C., there was a very slight blackening at the tips of the crystals but no other change took place. When the copper strips, heavily corroded with blue or green basic salts were heated, the basic salts were converted to a white crumbly powder. But when the blue-green corroded copper strips were allowed to stand exposed to air at room temperature for two weeks, the purple tetramino copper salt was formed under the blue-green corrosion product, in direct contact with the copper. There was a decrease in the amount of the blue-green basic nitrates and a gradual formation of the purple salt under the basic nitrates. Thus an elevated temperature or additional moisture is not required, simply the presence of basic nitrates in contact with copper and air at normal temperatures.

30. In order to observe the behavior of 50-50 and 80-20 amatols containing varying amounts of water, in contact with metallic copper, storage tests duplicating those made with ammonium nitrate were carried out with the two amatols, in both open and closed containers.

31. The formation of the purple salt was greatly decreased with 80-20 amatol as compared with ammonium nitrate, and with 50-50 amatol, there was little or none of it formed. As in the case of ammonium nitrate, the presence of 3-4% of moisture seemed to facilitate the formation of the salt to a greater degree than any other percentage of moisture. Even in the open containers, however, there was some corrosion of the copper strips buried in the amatol. This of course leads to the possibility of the formation of the sensitive salt on the metal, when exposed to air at normal temperatures.

SUMMARY AND CONCLUSIONS:

32. Tetramino cupric nitrate, a sensitive, purple copper salt may be formed by the combined action of ammonia, air and moisture on metallic copper, at an elevated temperature; or by the action of basic nitrates of copper on metallic copper at normal temperatures.

33. Its production takes place very readily in the presence of ammonium nitrate. 80-20 amatol is much less effective in producing the salt while 50-50 amatol has little or no action in its direct production. However, ammonium nitrate, 80-20 and 50-50 amatol in a moist condition readily corrode metallic copper with the production of basic nitrates and these nitrates readily react with metallic copper to produce the sensitive tetramino cupric nitrate.

34. It is concluded that the results of this work are in harmony with the requirements of specifications which specify that no copper or copper alloys be used in any part of the equipment that may come into contact with amatol.

EXPERIMENTAL PROCEDURE:

35. For the preparation of tetramino cupric nitrate - $\text{Cu}(\text{NO}_3)_2 \cdot 4 \text{NH}_3$ 10 grams of cupric nitrate. $6\text{H}_2\text{O}$ was dissolved in 8 cc. of water. To this was added 25 cc. of ammonium hydroxide (Sp.Gr. 0.9), the mixture well stirred and cooled to 5°C . A precipitate formed and the supernatant liquid was filtered on a Büchner funnel and the crystalline salt washed with alcohol, ether and air dried.

36. For the storage tests, one-half inch wide copper strips were placed in six inch test tubes and surrounded by 20 grams of ammonium nitrate containing various percentages of moisture. About one-half inch of metal projected above the surface of the ammonium nitrate.

37. The explosive properties of the purple tetramino cupric nitrate were determined by methods standard at this Arsenal.

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PA Tech.Rept. No. 1302
28 June 1943

Table I
Properties of Tetramino Cupric Nitrate

	<u>Tetramino Cupric Nitrate</u>	<u>Lead Azide</u>
I. <u>Drop Test, cm.</u> B.M. Machine	19	16
II. <u>Sensitivity to Flame:</u>	Burns slightly with a green flame.	-
III. <u>Sensitivity to spit of a black powder fuse:</u>	Not ignit. !	Ignited
IV. <u>Explosion Temperature Test, 5 seconds:</u> Degrees Centigrade	331	335
V. <u>Sand Test-200 gm. Bomb:</u> brisance, gm. sand	17.2	18
VI. <u>Minimum detonating chg.</u> Gm. mercury fulminate Gm. tetryl	0.24 0.19	

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Table II

Drop Tests on Ammonium Nitrate Containing
Copper Salts as Impurities.

Composition:

Ammonium nitrate, %	99.75 ^a	99.75 ^b	99.75 ^a	99.75 ^b	95	95	70
Copper powder, %	0.25	0.25					
Cupric oxide, %			0.25	0.25	5		30
Cupric nitrate, %						5	

a.-Mixed in the cold before melting.

b.-Ammonium nitrate melted before addition of copper salt.

Drop Test, 2 kg.wt.

Bu. of Mines, cm.

No detonation of any of the mixtures at 100 cm.

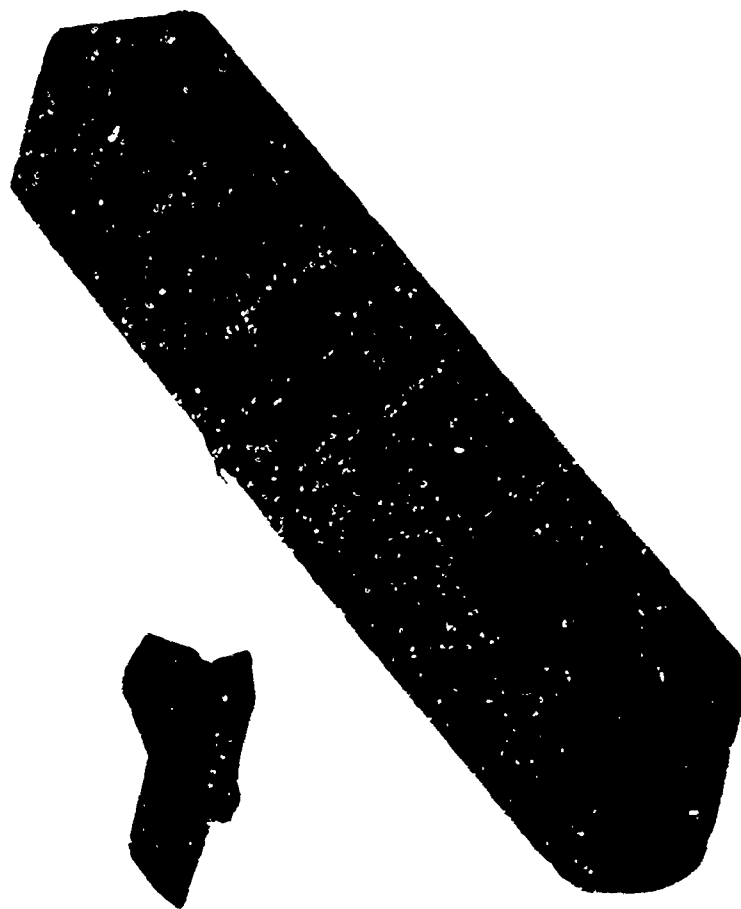
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Table III

Sensitivity of 50-50 Mixtures Made With
50% TNT and 50% of the Following Compositions.

<u>Compositions</u>	<u>Drop Test-inches. PA Machine</u>
1. NH_4NO_3 -99.75%-Copper powder 0.25% mixed cold, melted and ground	19
2. NH_4NO_3 -99.75%-cupric oxides 0.25% mixed cold, melted and ground	17
3. Copper powder-0.25% dissolved in molten NH_4NO_3	18
4. Cupric oxide-0.25% dissolved in molten NH_4NO_3	18
5. Cupric oxide-5% dissolved in molten NH_4NO_3	15
6. Cupric nitrate-5% dissolved in molten NH_4NO_3	16
7. Cupric oxide-30% dissolved in molten NH_4NO_3	16
8. Tetramino cupric nitrate	14

In comparison the Drop Test on 50-50 amatol was determined
as 19 inches.



M-15864

July, 1943

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(Tech. 13)

Tetrazine Cupric Nitrate - 3561