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MINOL IV, A NEW EXPLOSIVE COMPOSITION CONTAINING AMMONIUM NITRATE-POTASSIUM NITRATE SOLID SOLUTION. PART I

Carl Boyars, et al

Naval Ordnance Laboratory
White Oak, Maryland

29 March 1973

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By
Carl Boyars
James R. Holden
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29 MARCH 1973

NOL

NAVAL ORDNANCE LABORATORY, WHITE OAK, SILVER SPRING, MARYLAND

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MINOL IV, A NEW EXPLOSIVE COMPOSITION CONTAINING AMMONIUM NITRATE-POTASSIUM NITRATE SOLID SOLUTION, PART I

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ABSTRACT: Minol II (40% TNT, 40% ammonium nitrate, 20% aluminum) is useful as an explosive fill for bombs, because its use substitutes cheap, and abundant, ammonium nitrate (AN) for more expensive, and sometimes scarce, TNT. However, Minol II exhibits poor dimensional stability when exposed to temperature cycles during storage. It has been shown that growth of Minol II charges during temperature cycling is caused by the polymorphic phase transition which occurs in AN above 32°C. Review of the literature suggested that this phase transition could be prevented by substitution of a solid solution of potassium nitrate (KN) in AN for AN in explosive compositions. Some of the reported properties of such solid solutions (KN-AN-III or AN-KN) have been confirmed. Charges containing 40% TNT, 40% AN-KN and 20% aluminum (now designated Minol IV) showed better dimensional stability during temperature cycling than either TNT or TNT/aluminum (67/33).

ADVANCED CHEMISTRY DIVISION
CHEMISTRY RESEARCH DEPARTMENT
U. S. NAVAL ORDNANCE LABORATORY
White Oak, Silver Spring, Maryland 20910

NOLTR 73-49 29 March 1973

Minol IV, A New Explosive Composition Containing Ammonium Nitrate-Potassium Nitrate Solid Solution, Part I

This work was initiated as part of a joint Army, Navy, Air Force program to find alternate explosive fills for large-scale applications such as aircraft bombs. It has established the advantages of ammonium nitrate-potassium nitrate solid solution as an explosive component and Minol IV as an improved, low-cost explosive composition. The work is being supported by NOL Task 499/PA with funds from MIPR 2311-0033 originated by Picatinny Arsenal, Dover, New Jersey.

ROBERT WILLIAMSON II
Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

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1. INTRODUCTION

Ammonium nitrate (AN) has been used in explosives since the latter part of the 19th century (1). It came into use in military explosives during World War II largely as a replacement for part of the TNT in Tritonal (80% TNT, 20% aluminum) due to a shortage of TNT (2). These explosives, consisting of TNT, AN and aluminum were called Minols. Three compositions were developed: Minol I (48% TNT, 42% AN, 10% Al), Minol II (40% TNT, 40% AN, 20% Al) and Minol III (42% TNT, 38% AN, 20% Al).

More recently, during the Vietnam conflict, Minol II was investigated for large-scale applications such as GP bombs both due to another shortage of TNT and due to the lower cost of AN (2). However, problems were encountered in the preparation and use of Minol II. These appear to be due to the hygroscopicity of AN (3) and to the volume changes associated with transitions between its polymorphic phases.

One such difficulty which has been encountered in the field in the use of Minol is excessive growth of charges during storage. Such growth could be caused by gas producing reactions between AN and aluminum or between AN and TNT. However, since the difficulty is most frequently observed when Minol filled munitions are subjected to cycling temperatures in hot climates, a project was initiated to determine whether the polymorphic phase transition between form III and form IV AN was the primary cause of the excessive dimensional changes of Minol charges.

The IV to III phase transition of AN occurs under equilibrium conditions at 32.2°C and involves a density decrease of 3.8% (Figure 1 - double line for form V indicates uncertainty in this temperature region.) This temperature (89.8°F) is within the temperature range through which munitions might cycle between night and day when stored in a hot climate.

Numerous methods have been proposed to stabilize AN against the IV to III phase transition. A search of the patent literature shows quite an interest in this problem. British patents have claimed to reduce the density changes by the addition of from 10% to 25% potassium nitrate (KNO_3) or 5% to 10% magnesium nitrate ($Mg(NO_3)_2$) (4) or to move the 32° transition to 50°C by the addition of 30% by weight of the double salt $(NH_4)_3Mg(NO_3)_5$ or 18% of the double salt $(NH_4)Mg(NO_3)_3$ (5).

One U.S. patent (6) claims to stabilize the phase III crystals by mixing 8% powdered KNO_3 with AN (i.e., NH_4NO_3) and holding the mix between 32° and 100°C until stabilization against phase change is reached. Another patent claims to insure stability against phase change by the addition of 0.25 to 5.0% ammonium sulfate ($(NH_4)_2SO_4$) or ammonium phosphate ($(NH_4)_3PO_4$) to molten AN.

Methods reported in the literature for the stabilization of AN include the addition of potassium nitrate (8,9,10), magnesium nitrate (11), nucleating agents (12), and a mixture of boric acid, diammonium phosphate, and ammonium sulfate (13). Potassium nitrate (KN) is said to lower the 32°C transition about 6°C for each percent added (8), while magnesium nitrate raises the transition to 55°C and stabilizes it there. By the use of small quantities of a mixture of three ingredients, Brown, et al, (13) claim to have changed the 32°C transition temperature to 43 to 45°C.

Other additives which have been tried, despite claims to the contrary by the manufacturers, do not alter the transition temperature (14).

The primary objectives of this project have been: (1) to establish the polymorphic phase transitions of AN as the cause of excessive growth of AN containing charges, and (2) to develop a practical means of preventing these transitions.

2. PROCEDURE

Temperature cycling tests were performed to: (1) show that Minol II charges exhibit excessive growth during temperature cycling, (2) determine whether such growth is dependent upon the presence of AN, and (3) serve as references with which to compare the performance of experimental compositions.

To this end, four compositions were studied: (1) Minol II, (2) 67% TNT, 33% AN, (3) 67% TNT, 33% Al, and (4) TNT. Two types of charges were used: bare (or uncased) and cased. The bare charges were made by melt-casting the materials into one-inch molds, removing, cutting to two-inch lengths, and machining the ends smooth. The cased charges were cast directly into previously prepared one-inch ID pipes two inches long. The interiors of the pipes were painted with cavity paint conforming to JAN-P-450. After casting, the riser ends were machined smooth. All casting was performed by the NOL Casting House following normal procedures. Figure 2 shows typical charges used in these experiments.

Each thermal cycle consisted of approximately seven hours at 50°C followed by 17 hours at ambient (about 22°C). The lengths of all charges and the diameters of the bare charges were measured after each complete cycle. The moisture was controlled by conditioning the charges over desiccant for at least 48 hours prior to testing and by placing the charges in an empty desiccator during the test. Under these conditions, the charges were in relative humidity environments ranging from 38.5% to 49% during the temperature cycles.

Two bare and two cased charges of each of the four compositions were subjected to the temperature cycling test described. On the first heat cycle, the bare TNT/AN charges developed longitudinal cracks over their entire lengths. After two complete cycles, the charges were so badly cracked (Figure 3) that measurements were discontinued. The Minol II charges showed numerous surface cracks after the first heat phase and almost disintegrated upon further cycling (Figure 4). The physical appearance of the TNT and TNT/Al charges remained virtually unchanged during the test.

Cased charges of all four compositions were taken through six complete cycles. The dimensional instability of the explosives containing AN is well evidenced by longitudinal increases of 9% to 10% for the cased TNT/AN charges and 5.5% to 6% for the cased Minol II charges as compared to longitudinal increases of less than 3/4% for both the TNT and TNT/Al specimens. There was no significant difference in the growth of the TNT and TNT/Al. Comparisons of the growth of the explosives are shown in Figure 5.

The work to this point seemed to confirm the earlier hypothesis that the major problem in the growth of explosives containing AN is due to the 32°C phase transition (IV-III). This polymorphic transition from form IV to form III, which occurs above 32°C on heating, involves a density decrease of 3.8%. Obviously the reverse transition which occurs on cooling, involves a density increase of 3.8%. However, these phase transitions are reconstitutive; that is, they involve dissolution and regrowth of the crystals instead of rearrangement of the atoms within each crystal. Therefore, the AN crystals in any part of the TNT matrix of a Minol-type charge would not assume the same size and orientation during the transitions produced by successive temperature cycles.

In other words, when the charge was heated for the first time, a region containing AN would expand, pushing back the surrounding TNT matrix. However, on heating a second time, the AN would not generally expand in the proper shape to fill the existing void, but would push the TNT matrix in a different direction, producing a larger or second void. The results of our temperature cycling tests would indicate that this process continues until the TNT matrix crumbles or otherwise loses its dimensional integrity.

We attempted to study this behavior directly by means of scanning electron microscope (SEM) observations of the AN transition alone and within a TNT matrix. However, this was not possible because of the limitations of the technique. A change of structure on heating through 32°C was observed, but after a short time, holes appeared in the AN surface, probably due to vaporization of AN which has a vapor pressure over 1000 times the maximum pressure allowable for SEM operations.

3. REVIEW OF AMMONIUM NITRATE POLYMORPHIC SYSTEM

The AN polymorphic system has been the subject of numerous studies dating back to at least 1907 (15). Some have been undertaken because of the widespread use of AN both as a fertilizer and as an explosive (generally when mixed with fuel oil). Others have been performed because AN is a laboratory curiosity with five polymorphs with stability regions within a relatively narrow and accessible temperature range. Only a few studies whose results pertain directly to the Minol problem will be mentioned here.

At atmospheric pressure, the stability regions of forms I through V of AN are given (16, 17) as follows: I - 169.6°C (m.p.) to 125.2°C; II to 84.2°C; III to 32.2°C; IV to -17°C; V below -17°C.

Two of these phase transitions affect the preparation and use of Minol; the IV-III transition can occur during storage of loaded munitions and the III-II transition could occur during casting in molten TNT. The density of AN decreases 3.8% with the transition from IV to III (18) and increases 1.5% with the transition from III to II (19).

The temperature at which the IV to III transition actually occurs upon heating a sample of AN depends on its moisture content. At water contents greater than 0.1%, the transition occurs at 37°C (20). As the water content is lowered below 0.1% the transition temperature rises to a limiting value of 50 to 55°C. Below about 0.01% water, the transition is to form II (stable above 84.2°C) and not to form III. Under these conditions, the subsequent transition on cooling is directly to IV. The direct transition from IV to II is accompanied by a density decrease of about 1.7% (21).

At and above ambient temperatures, the ammonium cation in ammonium nitrate (AN) is reported to undergo free, or nearly free, rotation in the crystal lattice and thus have the properties of a single-atom cation with an effective radius of 1.48A (18). Nitrates of other monovalent cations form solid solutions with AN if their ionic radii are not too different from 1.48A (22). Thus the nitrates of potassium (ionic radius - 1.33A), rubidium (1.48A), cesium (1.65A), and thallium (1.50A) form solid solutions; but sodium (0.98A) does not. The effect which substitution of one of these cations for part of the ammonium cations in the crystal lattice has on the polymorphic transition temperatures of the resulting solid solution depends on the ionic radius of the cation introduced.

Cesium and thallium have ionic radii larger than ammonium. Substitution of these cations for ammonium in the AN crystal lattice has no effect on the IV-III transition temperature but lower the III-II transition temperature (22). The cesium radius (1.65A) differs more from ammonium (1.48A) than thallium (1.50A), and its effect on the transition temperature is greater.

Rubidium has the same ionic radius as ammonium (1.48A). Substitution of rubidium for ammonium in the AN crystal lattice has no effect on either the IV-III or III-II transition temperatures (22).

Potassium has a smaller ionic radius (1.33A) than ammonium (1.48A). Substitution of potassium for ammonium in the AN crystal lattice lowers the IV-III transition temperature and raises the III-II transition temperature (22). As the potassium content increases, the V-IV transition temperature rises slowly from -17°C for pure AN to -13°C for 6.2 weight percent KN. At larger KN contents, the V-IV transition is not observed and form III is reported to be the stable form (22). In a later study of the KN-AN system (23), it is reported that the III-II transition temperature rises with KN content from 84°C for pure AN to 120°C for 15 weight percent KN then declines. The authors of this study also report a different solid solution phase, AN dissolved in KN form III. This phase (AN-KN-III) is reported to form when the solid solution of KN in AN form III (KN-AN-III) is heated. The temperature, at which AN-KN-III starts to form on heating decreases with increasing KN content: 80 to 85°C at 10 weight percent; 70 to 75°C at 20 weight percent; and 50 to 55°C at 30 weight percent.

Solid solutions of KN in AN (KN-AN-III) can be produced either by melting the two salts together or by co-crystallizing them from water. The presence of potassium decreases the dimensions of the orthorhombic unit cell of the AN-III crystal from a=7.14, b=7.67, c=5.84A at 42°C for pure AN to a=7.06, b=7.60, c=5.79 at 20°C for KN-AN-III containing 19 weight percent KN (24).

In an equivalent manner, the presence of the larger ammonium ion in the KN-III crystal lattice expands and stabilizes its rhombohedral unit cell (pure KN-III is metastable at all temperatures). The equivalent hexagonal cell dimensions of an AN-KN-III solid solution with an AN/KN molecular ratio of 1/3 are a=5.52, c=9.09A; whereas those with a 1/1 molecular ratio are a=5.56, c=9.12A (24).

4. POSSIBLE WAYS TO AVOID AMMONIUM NITRATE PHASE TRANSITIONS IN MINOL

Stabilization of the form IV polymorph of AN would be the preferred way to prevent the IV-III transition, because IV has the higher density at ambient temperature. A recent study by Sjölin (20) indicates how this might be accomplished.

The IV-III transition involves dissolution and recrystallization of the AN crystals; therefore, its rate is very dependent upon the presence of a solvent (i.e., moisture). As the water content of AN falls below 0.2%, the observed transition temperature, upon heating, rises from 37°C to 50°C. At this temperature, the transition is no longer to form III but instead to form II (stable above 84°C). The IV-II transition takes place within the crystals and, therefore, is not dependent upon the presence of solvent. In studies of the effect of moisture on the transition temperature of AN, it was shown that the transition temperature changes as moisture content changes (24). At a very low water content, the IV-II transition is reversible; that is, on cooling form II transforms directly to form IV. The occurrence of form III is therefore eliminated. This is desirable, because the density change associated with the IV-II transition is only about 1.7% compared with the 3.8% density change associated with the IV-III transition.

Although excessive moisture in Minol creates a mixture that is extremely viscous (25), it would probably not be practical to maintain a sufficiently low moisture content in Minol-type charges in service use to eliminate the formation of form III in pure AN. However, Sjölin found that when additives such as magnesium nitrate or aluminum sulfate are dissolved in molten AN before it is solidified into prills, the additive is deposited in veins between the AN crystallites of the resulting prill. These additives form hydrates and take water away from the AN, making it unavailable as solvent for the IV-III transition. Prills, containing 1% to 2% magnesium nitrate, transform directly to form II on heating with overall water contents of up to about 1%. Furthermore, such prills have superior dimensional stability.

It might be possible to maintain water contents of below 1% in service charges; therefore, the use of AN prills containing magnesium nitrate in Minol-type compositions might be investigated. This solution to the growth problem has two possible disadvantages: (1) Munitions would have to be sealed sufficiently to prevent entry of even small amounts of water and (2) the AN would still undergo a phase transition on cooling, after casting in molten TNT. In addition, it has been shown that prills containing magnesium nitrate show a rapid physical breakdown when the moisture content exceeds 0.5% (13).

As was pointed out previously, solid solutions of potassium nitrate (KN) in form III AN can be produced by co-crystallization either from the melt or from water solution. Such KN-AN-III solid solutions, containing 5% to 10% KN by weight, have stability ranges extending from well below freezing to well above the temperature to which TNT is raised during casting operations. Therefore, substitution of a KN-AN-III solid solution for AN in a Minol-type composition should eliminate all problems caused by phase transitions of AN. KN is a relatively cheap and readily available compound which has been used in explosives. The cost of using KN-AN-III would be much higher than that of AN if the salts were purchased separately and reprocessed. However, a common last step in the commercial production of AN is melting the salt and spraying it into a prilling tower. If the KN were incorporated as part of this process, the additional cost should not be prohibitive. With this in mind, we have carried out a preliminary evaluation of KN-AN-III as a Minol component.

5. INVESTIGATION OF SOLID SOLUTIONS OF POTASSIUM NITRATE IN AMMONIUM NITRATE

Several experiments were carried out to check and supplement reported properties of KN-AN solid solutions in areas which pertain to the Minol problem.

Polymorph identifications were made by X-ray diffraction powder patterns obtained with a Norelco Wide Angle Diffractometer equipped with a scintillation counter and operating at a scan rate of 1° per minute. Copper radiation, filtered through nickel foil, was used. Reference patterns, obtained from commercial samples of KN and AN, checked within expected limits of error with the patterns distributed by the Americal Society for Testing and Materials (ASTM) for the forms stable at ambient temperature (i.e., KN-II and AN-IV). A sample of AN-IV was placed in a temperature controlled, X-ray diffractometer sample stage and heated at a rate of 0.14°C per minute. A phase transition occurred at 39°C, and a subsequent diffraction pattern checked with that given by ASTM for AN-III. Upon cooling, this sample reverted to AN-IV.

A saturated solution of AN in water at 70°C produced crystals of form IV when cooled to ambient (26°C). Fifty gram mixtures of KN and AN produced the following polymorphs, when dissolved in 20 ml of water by heating, and recrystallized by cooling to ambient: a 2.0 weight percent KN mixture produced form IV; 3.0% and 4.0% mixtures produced mixtures of form IV and form III; 5.0, 10.0, 20.0 and 30.0% mixtures produced form III. A 40.0% mixture produced a mixture of KN-AN-III and another phase identified as a solid solution of AN in form III KN (AN-KN-III) by comparison of its X-ray pattern with one given by Coates and Woodard (26). A 50.0% mixture produced a mixture of AN-KN-III and pure KN-II. A 70.0% mixture produced pure KN-II with a small amount of AN-KN-III. In this context, "pure KN-II" means a material whose X-ray diffraction pattern was not distinguishable from that of KN-II.

Unit cell dimensions were determined by indexing and fitting the diffraction angles of maxima in the X-ray powder patterns. Only those maxima were used which could be unambiguously indexed (identified as associated with a particular set of Miller indicies). All dimensions were adjusted to a least-squares fit between calculated and observed diffraction angles, the quantity actually measured by the diffractometer. This was accomplished by means of a FORTRAN code, written for a computer, which used a method of "steepest descents". Accurate diffraction angles were obtained by running the diffractometer at a scan speed of 1/4° per minute.

Since AN-III has an orthorhombic unit cell containing four molecules, the molecular volume in the crystal lattice is equal to one-fourth the product of the cell dimensions. Table 1 lists the cell dimensions and molecular volumes of the KN-AN-III solid solutions resulting from solution and recrystallization of 50 gram mixtures of the salts from 20 ml of water. The continuous decrease in the cell dimensions as the percentage of KN increases shows that a true series of KN-AN-III solid solutions is being formed. Data for other water volumes are included to illustrate that the composition of the solid solution also depends upon the concentration of the solution from which it was precipitated. It is interesting that some KN-AN-III solid solutions have molecular volumes significantly smaller than that of KN-II (i.e., 79.8A^3).

Potassium analyses were performed on the KN-AN compositions resulting from recrystallization 50-gram mixtures of the salts from 15 ml of water. Two analyses were performed on each sample, one on small aggregates and another on large aggregates. Each sample was dissolved in 100 ml of water containing approximately 1000 ppm sodium, and further diluted to a solution containing 2 to 5 ppm potassium. Standard potassium solutions were prepared using pure KN. The samples and the standard solutions were run in a Perkin-Elmer Model 303 atomic absorption spectrophotometer using optimum operating conditions as described in the Operations Manual (27). The results, calculated as weight percentage of KN are given in Table 2. Note that for initial salt mixtures of up to 20 weight percent KN, the resulting KN-AN-III solid solution contains about the same amount of KN as the original mixture and that its composition appears to be quite uniform.

Approximate III-II transition temperatures were determined for the solid solution samples whose analyses are described above by means of differential scanning calorimetry (DSC). Samples of approximately 5 mg were heated at a rate of 10°C per minute from ambient to 175°C. Observed transition temperatures and melting points are listed in Table 2. Duplicate runs were made for each composition. The shift in the phase transition temperatures is readily seen by comparing typical DSC curves of AN and 90-10 AN-KN (Figures 6 and 7).

6. TEST OF KN-AN-III (AN-KN) AS A SOLUTION TO THE GROWTH PROBLEM IN MINOL

As reported in Section 3, KN-AN-III solid solutions can be prepared by co-crystallization of KN and AN either from the melt or from water solution. For initial testing of this composition as a component of explosive charges, 1400 grams of KN-AN-III were prepared by crystallization from water. The material was a combination of several smaller batches, and the consistency of the product was monitored by determination of the molecular volume of each batch, as described in the previous section. The molecular volumes of the component batches ranged from 78.7 to 79.8A^3, indicating a KN content of about 10 weight percent.

Fisher laboratory reagent grade KN was used in this preparation. The AN used was from the same sample of prills used in the formulation of the charges described in section 2. These prills contain a clay-like anticaking agent which was removed during the recrystallization.

No difficulty had been experienced in casting the Minol II composition (40% AN, 40% TNT, 20% Aluminum) using the AN prills. However, this Minol composition was not castable using the smaller needle shaped crystals obtained from the KN-AN-III preparation. It was decided, therefore, to test the same TNT/AN composition previously tested (i.e., 67/33) but using charges made both with the co-crystallized material (charges now designated as TNT/AN-KN) and with AN recrystallized in a similar manner from water. Although different polymorphs are produced (IV of AN and III of KN-AN-III), the products are very similar in crystal size and shape.

Cased and uncased charges of both of these materials were thermally cycled between ambient and 50°C as previously described for the earlier charges. In addition, TNT and TNT/Al charges were subjected to the same treatment for comparison purposes.

After from six to nine cycles, the uncased TNT/AN charges had increased in length by about 5% to 6.5% and had longitudinal cracking to such an extent that measurements were no longer possible (Figure 8). In order to determine the effect of extended cycling and the linearity of growth during cycling, the cased charges were cycled through 50 complete cycles at which time they extended well beyond the ends of the cases (Figure 9). At this point they had increased in length by 13% to 20.5% (Figure 10).

The cased and uncased TNT/AN-KN charges, as well as those of TNT and TNT/Al were also cycled through 50 cycles. The increase in length of the uncased TNT/AN-KN charges was somewhat less than TNT (Figure 11). However, the cased TNT charges showed less growth than those of TNT/AN-KN (Figure 12). After cycling, the physical appearance of the TNT/AN-KN charges (Figure 13), as well as those of TNT and TNT/Al, was relatively unchanged.

In order to determine whether KN-AN-III eliminates excessive charge growth over a wider temperature range, a bare charge was cycled 50 times between ambient and -12°C; seven hours at -12, followed by 17 hours at ambient. The final volume increase for this charge was 0.87%. This should be compared to 2.43% for a charge of TNT/AN (made from recrystallized AN) similarly cycled. Another TNT/AN-KN charge was cycled 50 times between -12°C and 50°C; seven hours at -12, 15-1/2 hours at 50, and 1-1/2 hours at ambient. The final volume increase for this charge was 8.31%. Again, charge growth was not significantly larger than would be expected for charges not containing AN.

The promising early results obtained with TNT/AN-KN prompted us to look into possible ways to prill AN-KN so that Minol type compositions could be made. Several attempts at prilling were unsuccessful so the material was prepared as follows: a 90-10 AN-KN solid solution was made by blending AN and KN in a ball mill, melting the blended material, pouring onto a flat surface and breaking the solidified mass into pieces of various sizes. This material was then ground to conform to the particle size distribution requirements of Purchase Description PA-PD-3087A (Ammonium Nitrate, Grained). "Modified Minol II" (TNT/AN-KN/Al, 40/40/20) charges were made from this material. We designate this new explosive composition Minol IV.

Minol IV cast charges were cycled to determine whether improvement in dimensional stability would also be obtained for aluminum-containing compositions. After 50 cycles, cased charges increased in length by 2.04% compared to 2.51% for TNT (Figure 14) while uncased charges showed an increase in volume of 4.20% (Figure 15). This compared with 6.97% for TNT and 6.76% for TNT/Al.

These tests indicate that the dimensional stability of Minol IV during thermal cycling is as good or slightly better than TNT or TNT/Al. Ordnance loaded with Minol IV should be free of the problem of charge growth and exudation during storage which has been observed with Minol II (2).

7. CONCLUSIONS

This study has shown that:

a. Minol II charges exhibit excessive growth when subjected to cyclic temperature storage, ranging between 22°C and 50°C.

b. The primary cause of this growth is the polymorphic phase change of ammonium nitrate and not interaction of ammonium nitrate with TNT or aluminum.

c. The phase change, and thus the excessive growth, can be prevented by substitution of a solid solution of potassium nitrate in ammonium nitrate (AN-KN or KN-AN-III) for ammonium nitrate in Minol-type explosive compositions.

8. ACKNOWLEDGEMENT

The authors gratefully acknowledge the assistance of: Eleanore G. Kayser for differential scanning calorimetry, Ming Gon Lai for potassium analyses, Marriner Norr for survey of the literature, George Hoffman for his work in preparation of the charges, and Gaylon Ross of the National Bureau of Standards for his assistance in data reduction and plotting.

Table 1

CELL DIMENSIONS OF KN-AN-III SOLID SOLUTIONS

50 Gm Mixtures Recrystallized from Water

Weight % KN	Water ml	Cell Dimensions a	b	c	Molecular Volume Cubic Angstroms
5.0	20	7.136	7.678	5.836	80.0
10.0	20	7.107	7.664	5.818	79.3
20.0	20	7.075	7.652	5.768	78.1
30.0	20	7.026	7.629	5.747	77.0
40.0	20	7.023	7.620	5.730	76.7
10.0	15	7.118	7.664	5.818	79.4
15.0	15	7.093	7.655	5.781	78.5
30.0	15	7.057	7.642	5.758	77.7
10.0	10	7.147	7.678	5.822	79.9

Table 2

TRANSITION TEMPERATURES OF AN-KN SOLID SOLUTIONS

50 Gm Mixtures Recrystallized from 15 Mls of Water

Weight % KN in Mixture	Weight % KN in Product	III-II Trans.	II-I Trans.	Melting Point
5.0	4.9	101.0	125.0	161.2
	5.1	101.5	125.2	160.7
10.0	10.0	115.7	125.2	148.4
	9.9	114.3	124.4	149.0
20.0	21.4	99.5	-	153.5
	21.5	98.9	-	152.2
30.0	35.7	76.9	-	151.5
	36.1	77.0	-	150.9
40.0	39.4	71.0	143.5	155.4
	44.3	72.3	143.7	154.0

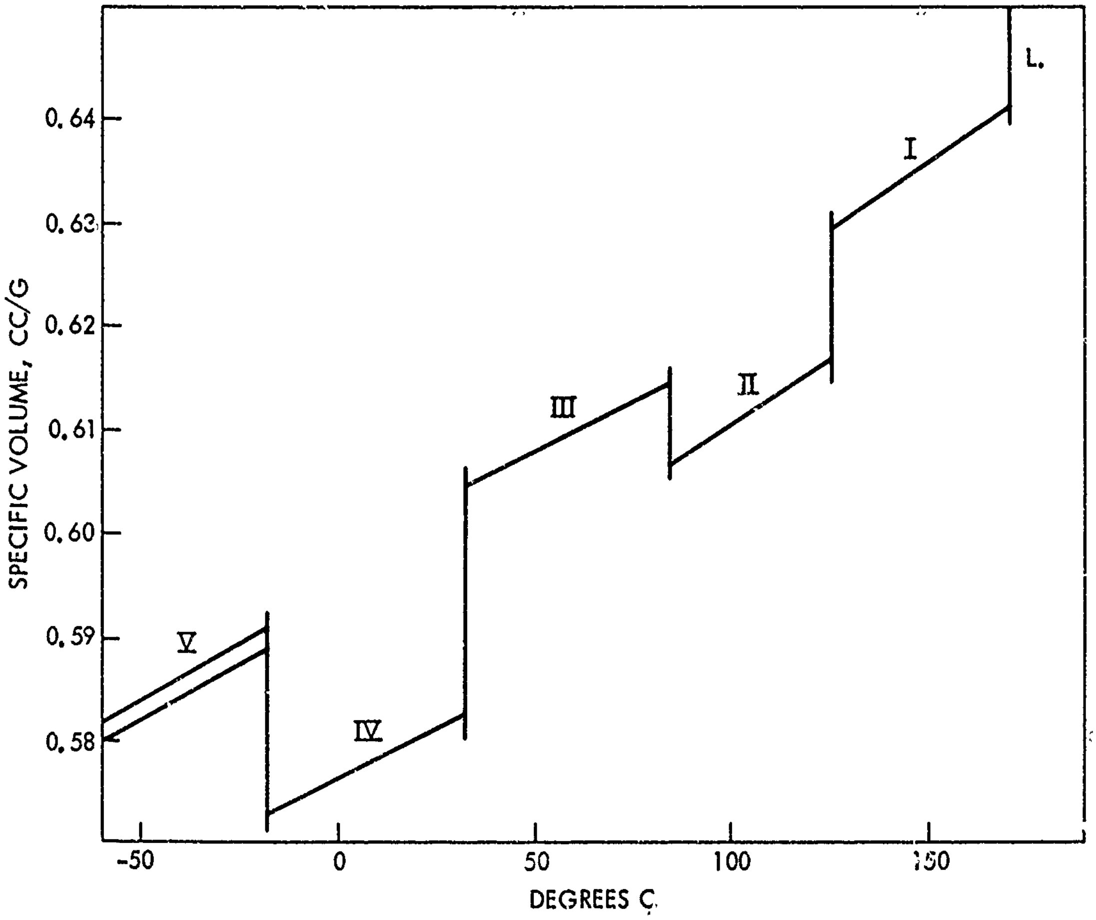

FIG. 1 (U) THE SPECIFIC VOLUME OF AMMONIUM NITRATE VS TEMPERATURE (U)

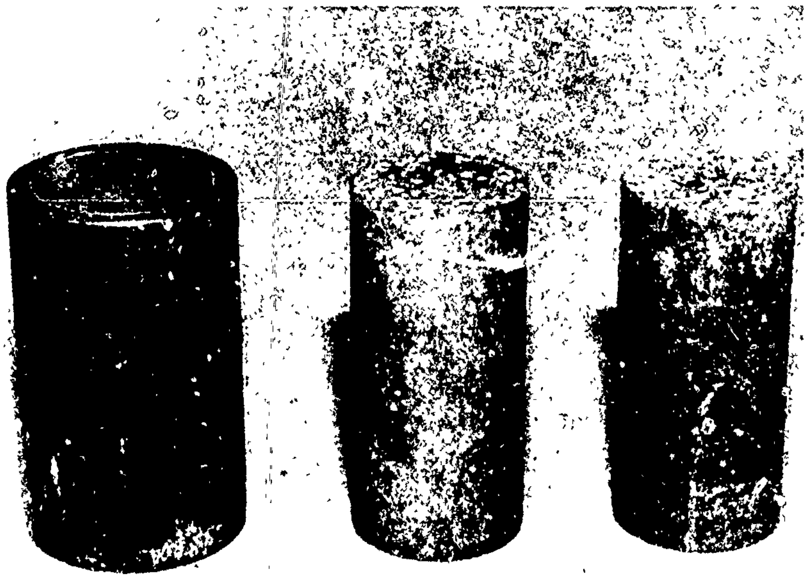

FIG. 2 (U) TYPICAL CHARGES USED IN CYCLING TESTS (U)

FIG. 3 (U) TNT/AN (67/33) CHARGES BEFORE AND AFTER THERMAL CYCLING (U)

FIG. 4 (U) MINOL II CHARGES BEFORE AND AFTER THERMAL CYCLING (U)

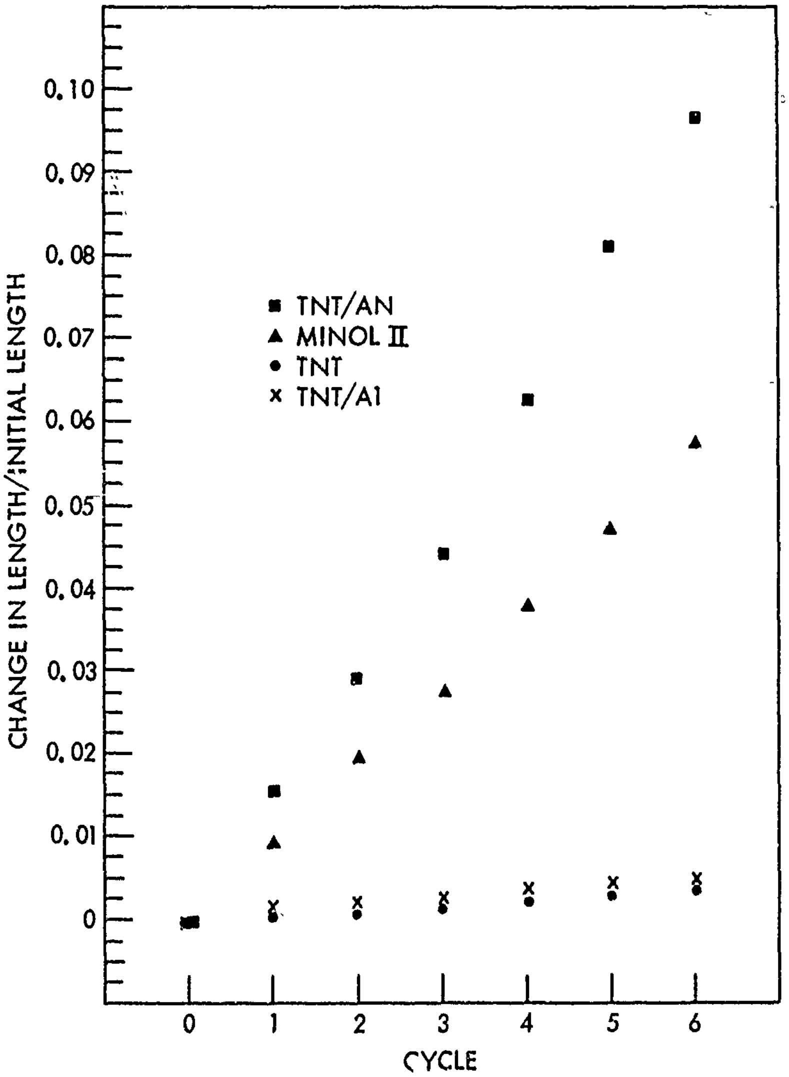

FIG. 5 (U) GROWTH OF EXPLOSIVE CHARGES DURING THERMAL CYCLING (U)

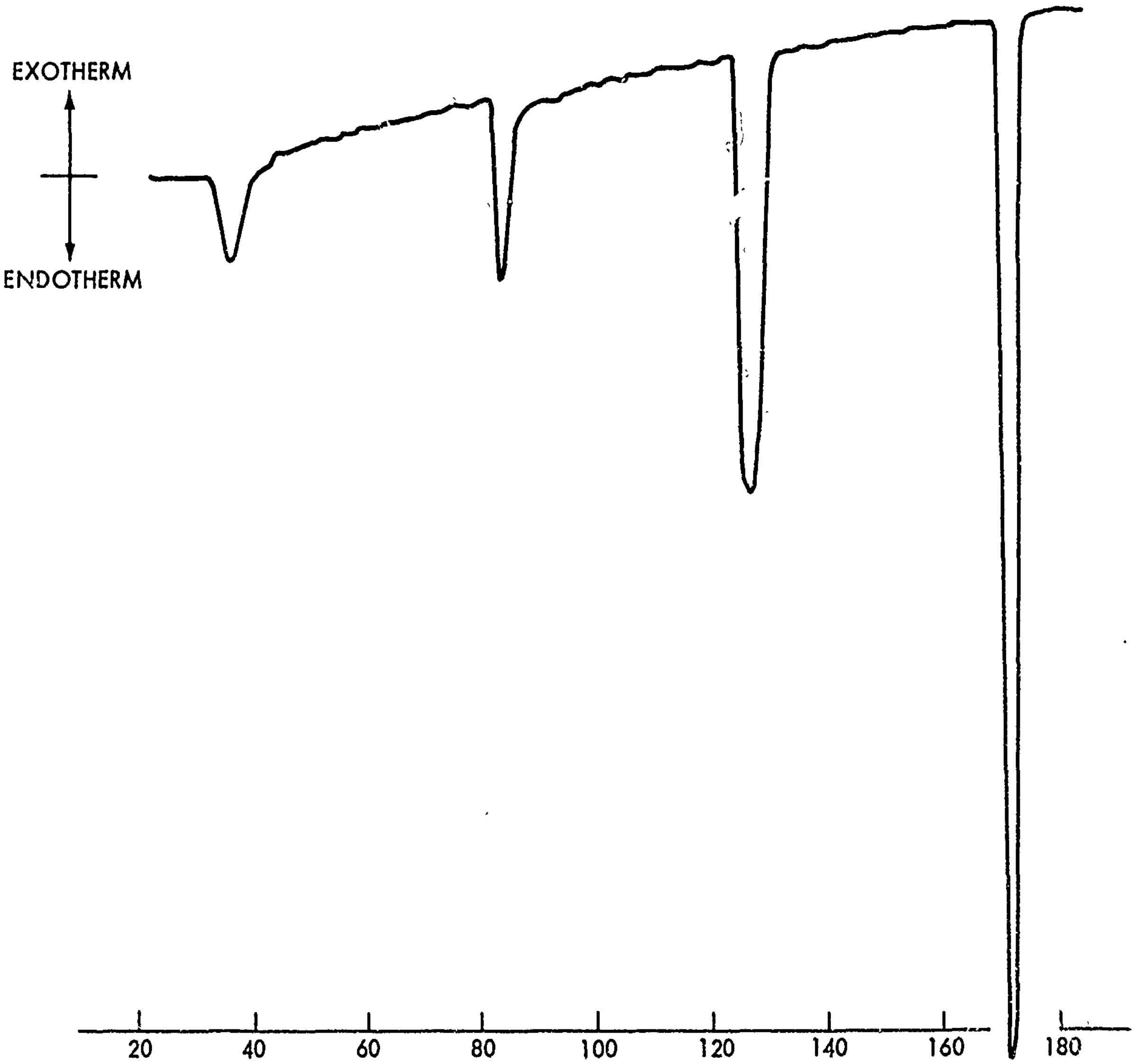

FIG. 6 (U) TYPICAL DSC CURVE OF AMMONIUM NITRATE (U)

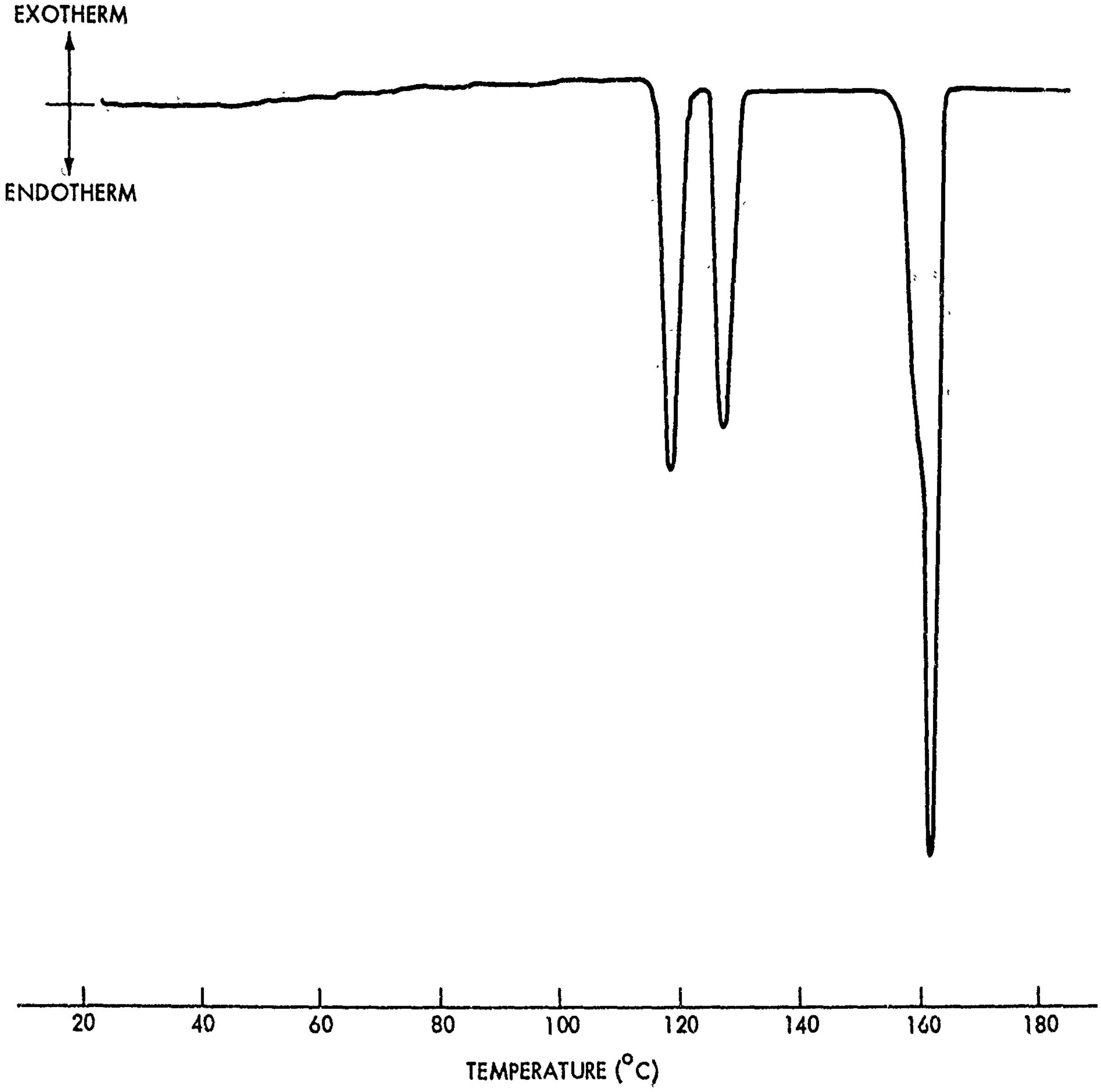

FIG. 7 (U) TYPICAL DSC CURVE OF 90-10 AMMONIUM NITRATE-POTASSIUM NITRATE SOLID SOLUTION (U)

FIG. 8 (U) TNT/AN (67/33) CHARGES (USING RECRYSTALLIZED AN) BEFORE AND AFTER THERMAL CYCLING (U)

FIG. 9 (U) CASED TNT/AN (67/33) CHARGES (USING RECRYSTALLIZED AN) BEFORE AND AFTER THERMAL CYCLING (U)

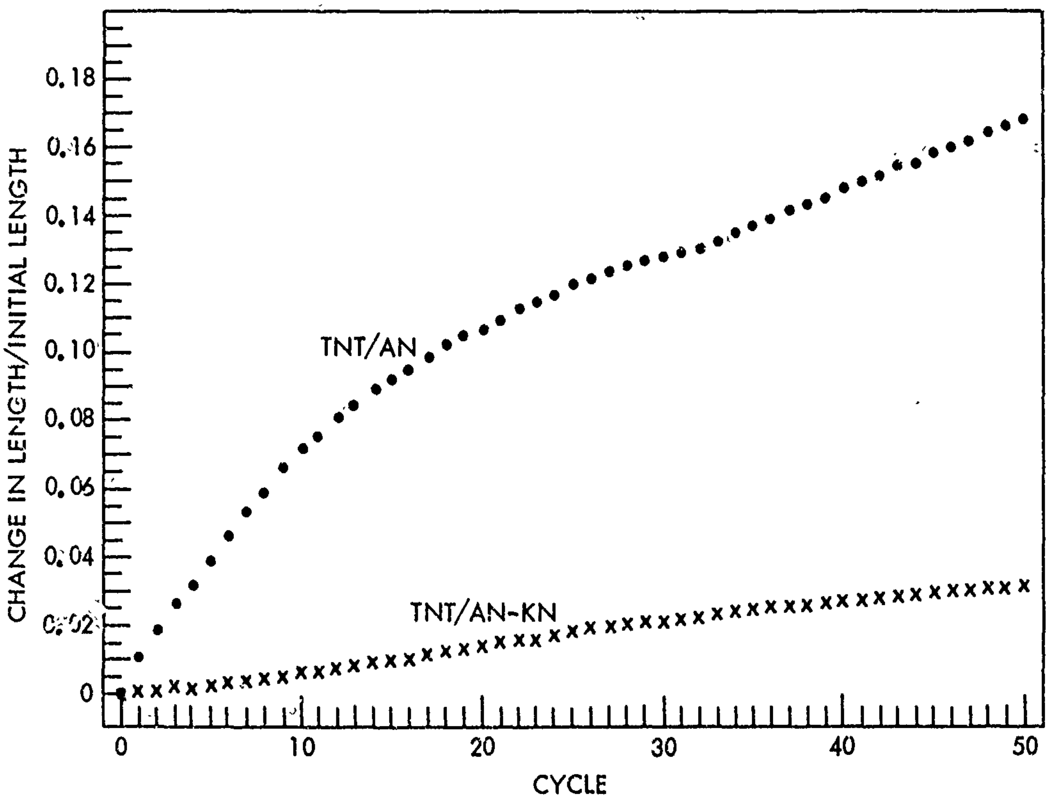

FIG. 10 (U) INCREASE IN LENGTH OF CASED TNT/AN (67/33) CHARGES (USING RECRYSTALLIZED AN) AND TNT/AN-KN CHARGES DURING THERMAL CYCLING (U)

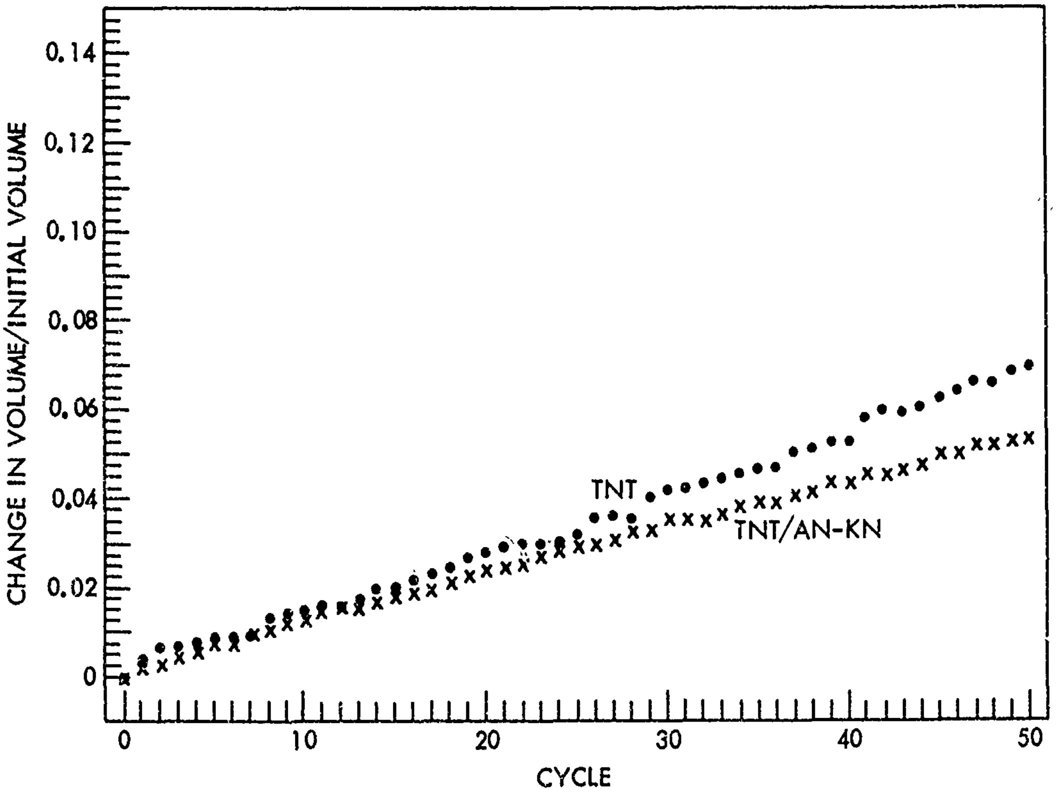

FIG. 11 (U) INCREASE IN VOLUME OF UNCASED TNT AND UNCASED TNT/AN-KN CHARGES DURING THERMAL CYCLING (U)

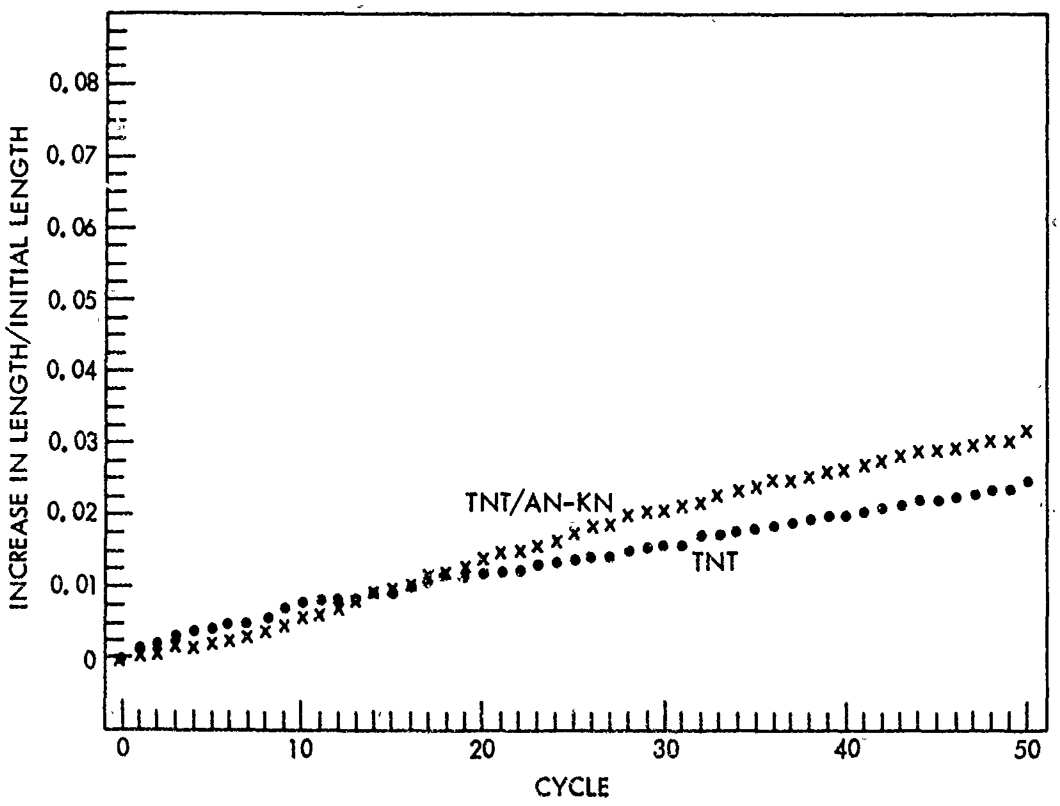

FIG. 12 (U) INCREASE IN LENGTH OF CASED TNT AND CASED TNT/AN-KN CHARGES DURING THERMAL CYCLING (U)

FIG. 13 (U) TNT/AN-KN CHARGES BEFORE AND AFTER THERMAL CYCLING (U)

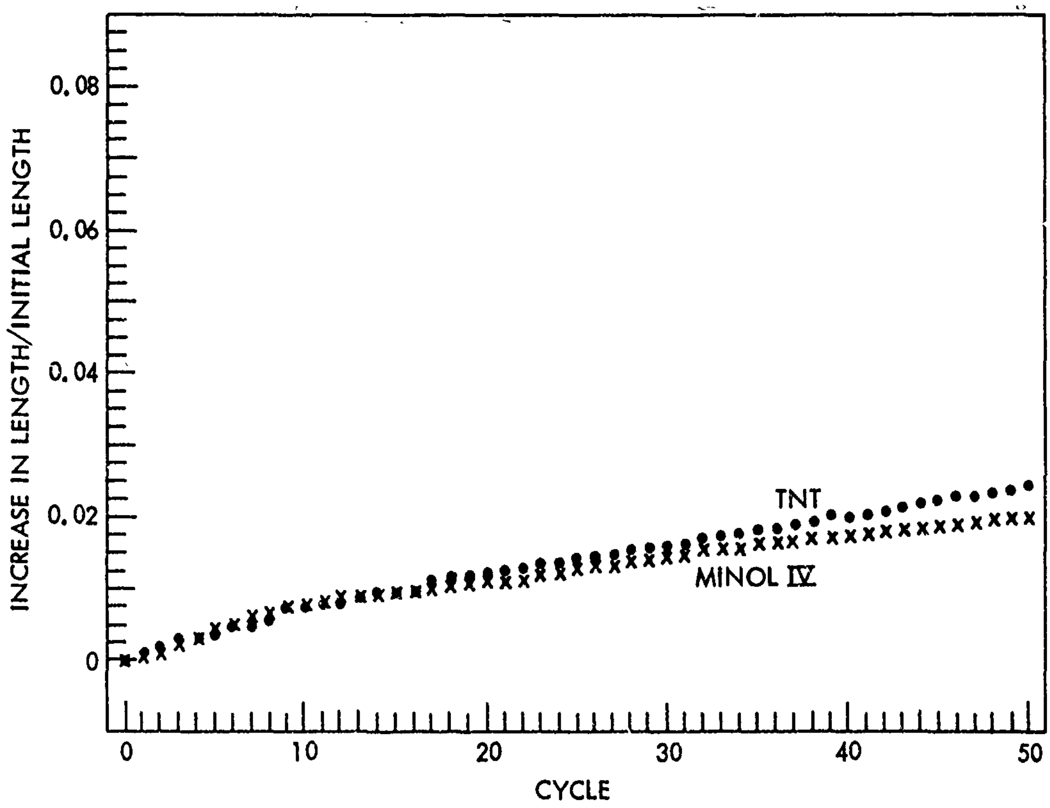

FIG. 14 (U) INCREASE IN LENGTH OF CASED MINOL IV AND CASED TNT CHARGES DURING THERMAL CYCLING (U)

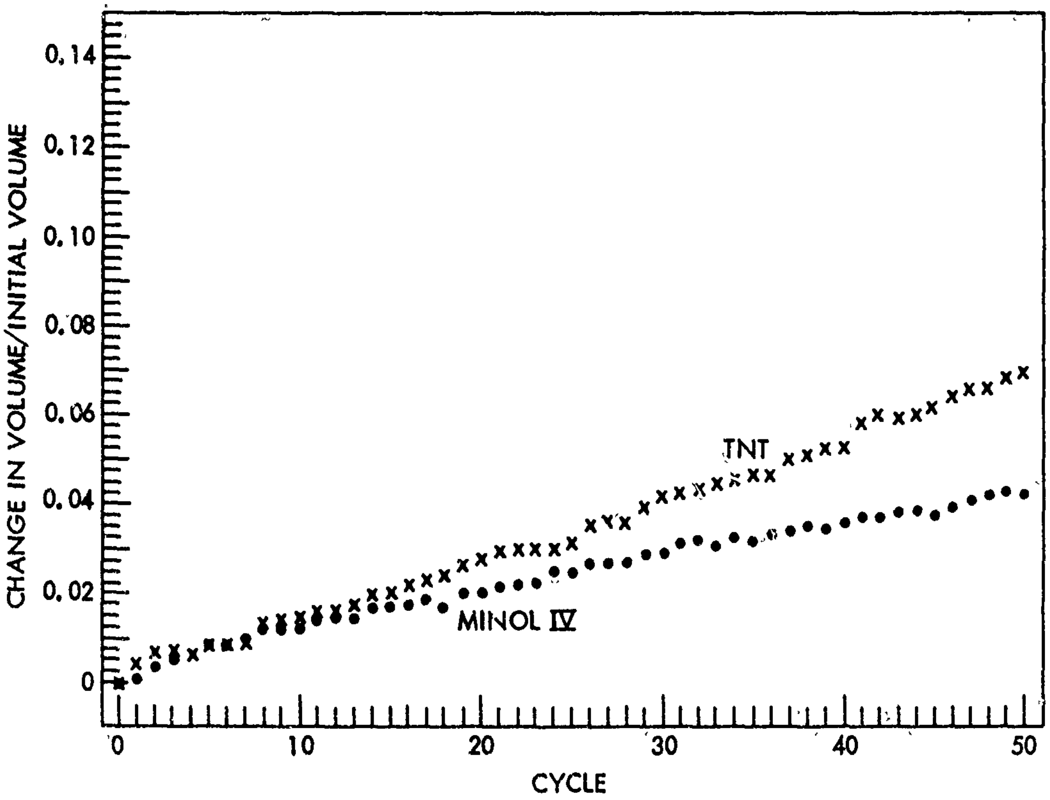

FIG. 15 (U) INCREASE IN VOLUME OF UNCASED MINOL IV AND UNCASED TNT CHARGES DURING THERMAL CYCLING (U)

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UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*
Naval Ordnance Laboratory
White Oak, Silver Spring, Maryland 20910

2a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

2b. GROUP

3. REPORT TITLE
Minol IV, A New Explosive Composition Containing Ammonium Nitrate-Potassium Nitrate Solid Solution. Part I

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

5. AUTHOR(S) *(First name, middle initial, last name)*
Carl Boyars, James R. Holden, and Albert L. Bertram

6. REPORT DATE
29 March 1973

7a. TOTAL NO. OF PAGES
~~29~~ 36

7b. NO. OF REFS
27

8a. CONTRACT OR GRANT NO.

b. PROJECT NO. PA MIPR 1311-0014

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
NOLTR 73-49

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. DISTRIBUTION STATEMENT

Approved for Public Release; Distribution Unlimited

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
Picatinny Arsenal
AMCPM-BR2
Dover, N. J. 07801

13. ABSTRACT

Minol II (40% TNT, 40% ammonium nitrate, 20% aluminum) is useful as an explosive fill for bombs, because its use substitutes cheap, and abundant, ammonium nitrate (AN) for more expensive, and sometimes scarce, TNT. However, Minol II exhibits poor dimensional stability when exposed to temperature cycles during storage. It has been shown that growth of Minol II charges during temperature cycling is caused by the polymorphic phase transition which occurs in AN above 32°C. Review of the literature suggested that this phase transition could be prevented by substitution of a solid solution of potassium nitrate (KN) in AN for AN in explosive compositions. Some of the reported properties of such solid solutions (KN-AN-III or AN-KN) have been confirmed. Charges containing 40% TNT, 40% AN-KN and 20% aluminum (now designated Minol IV) showed better dimensional stability during temperature cycling than either TNT or TNT/aluminum (67/33).

DD FORM 1 NOV 65 1473 (PAGE 1)
S/N 0101-807-6801

UNCLASSIFIED
Security Classification

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Minol Explosive Bomb Ammonium nitrate Potassium nitrate Solid solution Phase transition Phase change Explosive growth						

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(PAGE 2)

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