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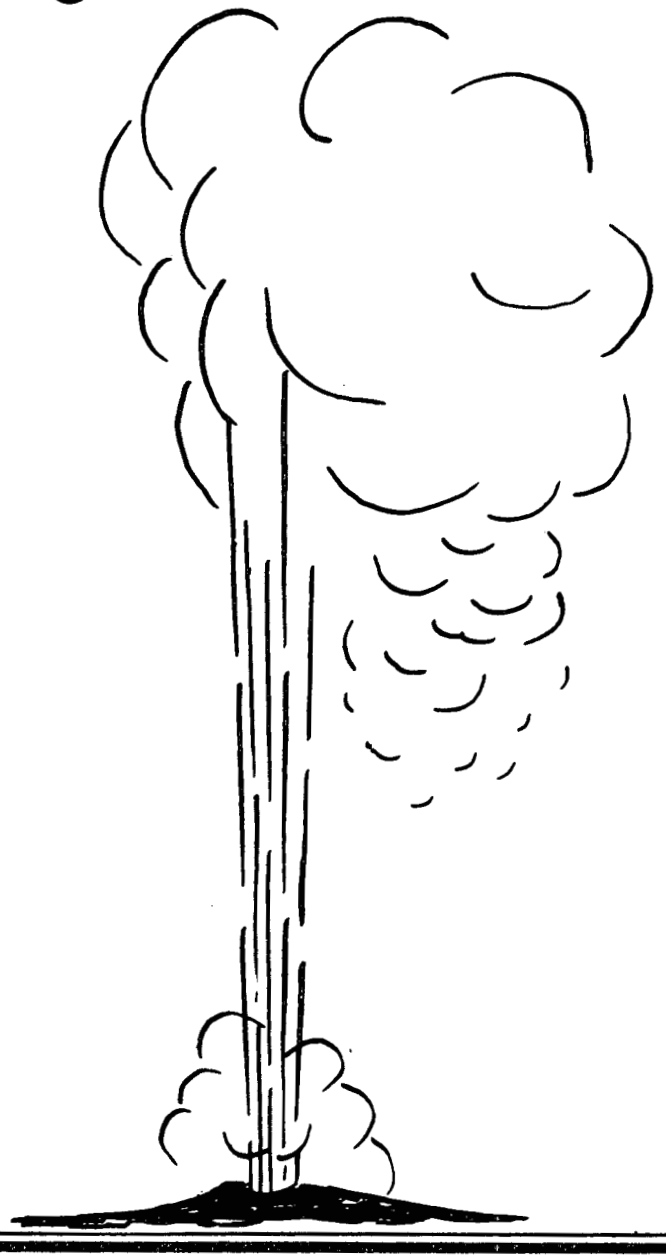

HIGH-TEMPERATURE EXPLOSIVE DEVELOPMENT FOR GEOTHERMAL WELL STIMULATION

Final Report

By
E. W. Schmidt
J. E. Mars
C. Wang

March 31, 1978

Work Performed Under Contract No. EY-76-C-06-2336

Rocket Research Company
A Division of ROCKCOR, Inc.
Redmond, Washington

U. S. DEPARTMENT OF ENERGY
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Final Report

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ABSTRACT

A two-component, temperature-resistant liquid explosive called HITEX has been developed which is capable of withstanding 561°K (550°F) for 24 hours in a geothermal environment. The explosive is intended for the stimulation of nonproducing or marginally producing geothermal (hot dry rock, vapor-dominated or hydrothermal) reservoirs by fracturing the strata in the vicinity of a borehole. The explosive is inherently safe because it is mixed below ground downhole from two nondetonable liquid components. Development and safety tests included differential scanning calorimetry, thermal stability, minerals compatibility, drop-weight sensitivity, adiabatic compression, electrostatic discharge sensitivity, friction sensitivity, detonation arrest capability, cook-off tests, detonability at ambient and elevated pressure, detonation velocity and thin film propagation in a wedge.

1.0 STATE-OF-THE-ART RELATED DEVELOPMENTS

It was the objective of the program described herein to develop a two-component liquid explosive capable of withstanding the high temperatures typically encountered in geothermal wells. The explosive is to be used in geothermal wells of marginal or nonexisting productivity to stimulate the flow of geothermal fluids by explosively fracturing the strata in the vicinity of the well bore. The increased permeability will allow steam or hot water to flow from the reservoir to the well at economical rates.

Geothermal energy constitutes a major energy resource of the United States. However, only a tiny fraction of the total geothermal energy potential is currently used for heating purposes or for producing power. Exploration and development of geothermal fields is more difficult than natural gas or oil fields because of the higher temperature and the more corrosive nature of geothermal well fluids. Likewise, stimulation techniques such as hydraulic fracturing or explosive fracturing cannot immediately be transferred from fossil fuel exploration to geothermal exploration. Explosive stimulation of oil and gas wells is now on the verge of commercial utilization, but currently used liquid explosives lack the thermal stability required for application in a geothermal environment.

Explosive stimulation of natural gas and oil wells has been conducted routinely since the early years of oil exploration (References S5, S6, O1, L3, H5, L4, H6, B5, E1). This was done mainly to "bring in" freshly drilled wells which may have suffered skin damage by becoming clogged with fines or drilling mud. One of the preferred liquid explosives for this application was so-called "desensitized" nitroglycerin. In spite of being designated "desensitized", this single-component liquid explosive was very dangerous to handle, and its use was abandoned when safer two-component explosives became available. Documents show that it was common practice to pour desensitized nitro by hand from a 5-gallon container down the hole (Reference B7). Obviously, this technique is not applicable to geothermal wells.

In the early 1960's, research in the area of explosives had advanced to the point where slurry formulations were being developed that could be pumped into the well in large quantities, and a new interest in explosive stimulation quickly developed within the industry. Major projects to develop explosive fracturing techniques were undertaken by organizations such as Dowell, Western, Pan American Oil Company (now AMOCO), Continental Oil, and others. The initial work centered around utilizing highly viscous slurries developed by such firms as Dow Chemical Company and Ireco Chemicals. Major problems were encountered in placing these viscous explosives in the well, and in developing formulations that could perform under the wide variety of pressures and temperatures encountered in wells. Further, these types of explosives were limited in that they could only be detonated in the wellbore. What was needed was a formulation that could be pumped back into the formation and detonated within the rock matrix itself, in small fractures within the rock, or within hydraulically-created fractures. For the past several years, three firms, Commercial Solvents, Talley, and Petroleum Technology Corporation are developing processes utilizing such

formulations. Regardless of the problems encountered with the slurries, sufficient tests were run throughout the industry to demonstrate that explosive stimulation, where relatively large quantities of explosives were used, is a viable process.

Table 1-1 contains published results for large-scale explosive stimulation treatments conducted in recent years. The Kentucky, Western and Dowell data gives the results of the borehole detonation process. The Talley data is for the fracture detonation process, where the explosives are pumped back into the formation through hydraulic fractures. One should note that the average production improvement ratio is on the order of 4 for gas wells and 3 for oil wells, but that the maximum production ratios are much higher. The general consensus is that as the industry gains additional experience, particularly in engineering the selection of the wells, the average improvement ratios should approach the maximum ratios observed.

Table 1-1
PUBLISHED RESULTS OF EXPLOSIVE STIMULATION TREATMENTS

Area or Company	No. of Wells	Average Production Before Shot	Average Production After Shot	Improvement Ratio Avg & Max
Kentucky	6,370	53 MCF/D	253 MCF/D	4.8 – 250
Western Co.	8	21 BBL/D	80.5 BBL/D	3.8 – 12
Dowell	4	Oil Wells		13.6 – 25
	6	Oil Wells		14.4 – 23
Talley	3	260 MCF/D	998 MCF/D	3.8 – 9
	4	11.6 BBL/D	30.3 BBL/D	2.6 – 14

Under ERDA contract E(34-1)-0001, Petroleum Technology Corporation (PTC), a division of ROCKCOR, Inc., has conducted chemical explosive field demonstrations in two noncommercial Oriskany gas wells owned by Hampshire Gas Company, and a Devonian shale gas well owned by Columbia Gas Systems (References P5 and L4).

Evaluation of the test results (Table 1-2) shows that the PTC system can be used to safely manufacture and inject a liquid chemical explosive into natural gas bearing formations. Although numerous stimulation treatments had previously been performed on the first two wells, the detonation in Hampshire No. 18 did improve the inflow (rate of pressure buildup) characteristics of

Table 1-2

USBM/ERDA CHEMICAL EXPLOSIVE FRACTURING OF GAS WELLS
SUMMARY OF RESULTS

Well Designation	Amount of Explosive Injected kg	lb	Well History	Results
Hampshire No. 10	9,149	20,170	Drilled 1964, acidized once,	No change. Hole diameter increased from 6 inches (15 cm) to 9–10 inches (22 to 25 cm)
Hampshire No. 18	10,333	22,780	Drilled 1968, acidized twice, no improvement as result of previous treatments	Inflow improved by factor of 1.66
Columbia No. 20117-T	13,753	30,320	Completed 1975, no previous stimulation attempts	Productivity increased. Well could not be cleaned out

Reference: P5

the well by a factor of 1.66. No improvement was seen in Hampshire No. 10. Marked improvement was seen in the producing characteristics of the third well, Columbia No. 20117-T, even though only one-fifth of the original open hole section could be cleaned out. The gas production rate was tripled to 43 MSCFD (thousand standard cubic feet per day) or 1,208 m^3/day (at 273°K and 1.01 bar). The formations capacity to produce ("kh factor") was increased tenfold. Nevertheless, none of the tests resulted in a commercial gas well. Only the last well, however, presented a real opportunity to obtain commercial production. Since a water leak caused by poor cementing precluded complete cleanout of this well, the results of this test were not considered conclusive. The wells which were made available to the test program were of no commercial value and had been utilized in extensive previous experimentation.

Additional gas well stimulation tests by PTC are currently in progress under ERDA contracts EY-76-C-08-0685 (jointly with Kentucky West Virginia Gas Company in Southeastern Kentucky, 3 wells), EY-76-C-08-0686 (jointly with Columbia Gas Systems in Franklin County, Virginia, 3 wells), and EY-76-C-08-0687 (jointly with Union Oil of California, in Canyon Sands in Southwest Texas, 2 wells) (Reference L5).

Under ERDA contract E(46-1)-8011, Physics International Company, a division of ROCKCOR, Inc., has conducted the development and field demonstration of an explosive fracturing method called DYNAFRAC (Reference M3). This method uses a narrow diameter cylindrical column of explosive placed in the center of the borehole and close-coupled to the formation by a coupling fluid (water, brine, oil, or other natural well fluids, Figure 1-1). The almost instantaneous borehole pressurization causes multiple vertical fractures to occur in the formation before stress relief can occur from the failure of the weakest plane of fracture. The program consisted of three principal tasks. The first task was to apply the DYNAFRAC process to at least five marginal stripper oil wells. The second task was to develop an augmented DYNAFRAC process, where an explosive pressure pulse is superimposed on a slow pre-pressurization profile generated by a solid propellant. The third task was to apply the augmented DYNAFRAC process to a gas-bearing reservoir, and compare the productivity improvement with that obtained by more conventional fracturing methods.

In principle, the DYNAFRAC method could be applied only to those geothermal wells which have a low enough permeability to hold a fluid for the required length of time. In the case of vapor-dominated reservoirs, the liquid (most likely water) would be pumped into the well from the surface, and the well must be kept under pressure to prevent the liquid in the well from flashing into steam. For water-dominated reservoirs, the borehole is generally already filled with water to start with. In the less developed dry hot rock reservoirs, a suitable coupling fluid would be pumped into the well prior to the test. None of the explosives used for DYNAFRAC, to date, would withstand the geothermal environment. An explosive such as the currently developed HITEX formulations would have to be substituted for nitromethane-based explosives.

It has been attempted (Reference A4) to encase TNT in Teflon shells to contain the molten explosive and protect it from the geothermal environment. Teflon was chosen because of its low thermal diffusivity, its compatibility with TNT, and its ability to withstand temperatures up to 710°K without decomposition. The Teflon containers were machined out of 44 mm (1.75-inch)

EXPLOSIVE CONFIGURATION FOR RAPID PRESSURIZATION OF BOREHOLE

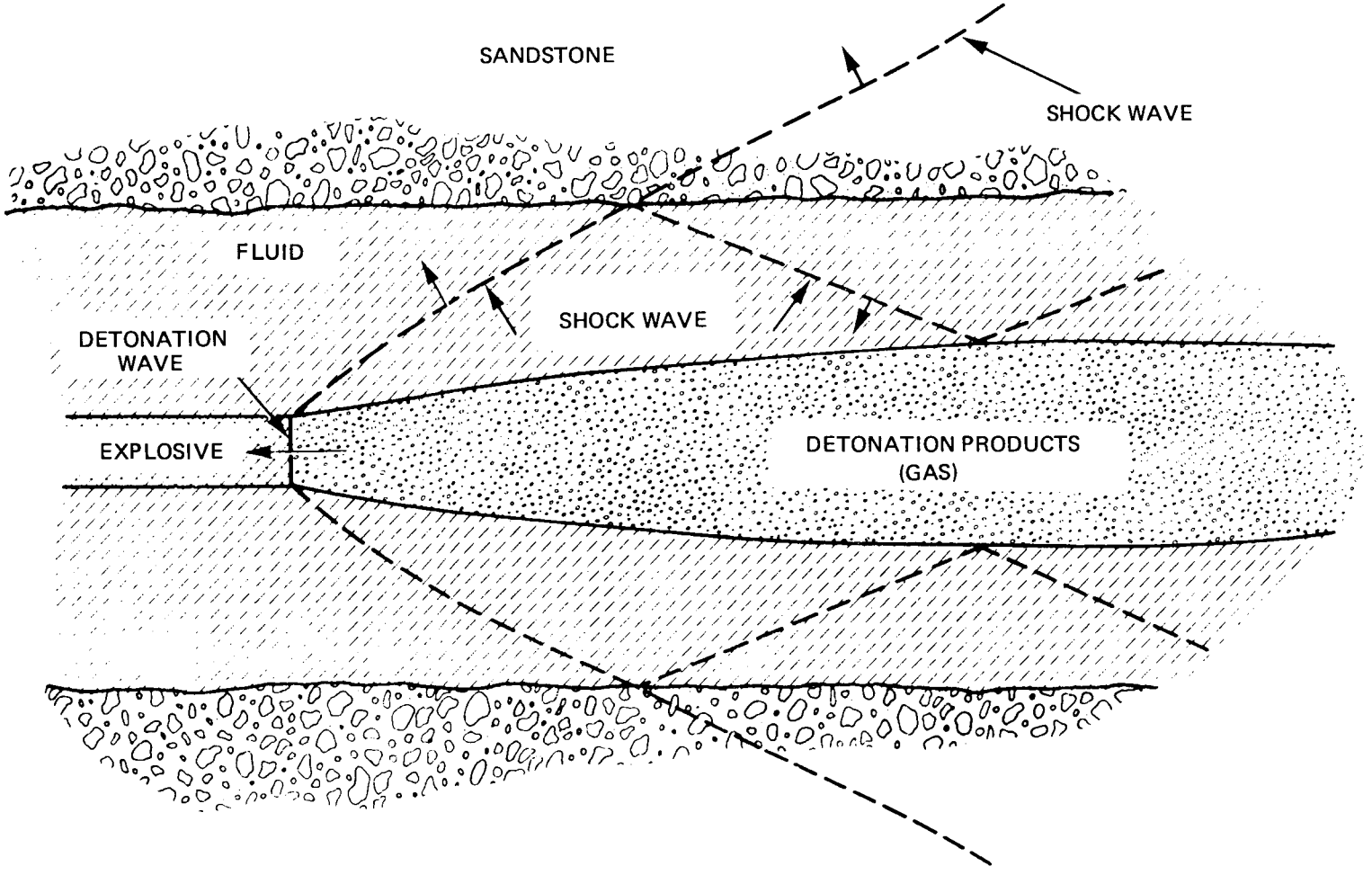


Figure 1-1

diameter solid stock material, producing wall thicknesses of 3.2, 6.3, 9.5, and 12.7 mm (0.125, 0.25, 0.375, and 0.50 inch, respectively). The cavities were filled with TNT to within 12 mm (0.5 inch) from the top, sealed with a 25 mm (1 inch) thick Teflon cap, and heated in an aluminum block furnace to 670°K. The experimental cookoff times were then compared to calculated data. Extrapolation to larger diameter charges indicates that a wall thickness of 6.3 mm Teflon (0.25 inch) would be sufficient to protect a 178 mm (7 inch) diameter charge for up to 30 minutes. Even longer times before cookoff would be possible by increasing the wall thickness. No actual geothermal well test results with the so encased explosive have been published up to this date.

In addition to stimulation of geothermal resources by chemical explosives, stimulation by nuclear explosives has been considered extensively (References B4 and R3). However, environmental concerns and political implications severely limit the applicability of nuclear devices to geothermal stimulation (Reference S7).

There has been increased interest in explosive fracturing of rocks for the in-situ recovery of oil shale (Reference M4) or in-situ processing of coal (References S8 and T3). Although explosive fracturing work so far has been done only in very shallow wells, future applications may require explosives capable of withstanding higher temperatures than the ones currently employed. Also, fracturing may have to be done in immediate vicinity to the formations which are artificially heated as the result of the recovery process.

As opposed to single-component explosives, two-component explosives can be safely handled in two separate nondetonable components above ground. The two components can be mixed remotely below ground to form a detonable liquid which can then be detonated on command. It is important to select components which do not autoignite upon mixing in the manner of hypergolic rocket propellants. Instead, the mixed liquid explosive can be pumped down the hole, and can be allowed to accumulate until the desired amount of explosive has been loaded. In the case of a geothermal well, the explosive would be exposed to the high temperature prevailing in the formation throughout the time from the beginning of the loading process until the charge can be detonated on command. Liquid explosives known prior to the start of the research program described herein, would inevitably have detonated prematurely or would have lost their explosive power by thermal degradation.

While there were no liquid explosives of satisfactory thermal stability available prior to the current work, a number of solid explosives has been described in the literature which might possibly survive long enough in a geothermal well to do limited fracturing work. However, none of these explosives is currently produced in tonnage quantities. Even if large-scale production should be commenced, the price of these special solid explosives would be prohibitive (see paragraph 1.2).

A general advantage of liquid explosives over solid explosives is that a larger amount of explosive can be loaded per unit length of bore hole because the walls are usually very irregularly shaped and the most narrow clearance dictates the outer diameter of a solid charge. If desired, the liquid explosive can be close-coupled to the formation, making the use of a coupling fluid unnecessary.

The liquid explosive can also be used as a proppant fluid by forcing it into the formation under high pressure immediately prior to detonation on command. In this fashion, hydraulic fracturing and explosive fracturing must not be regarded as competitive methods, but would nicely complement each other (Reference B5).

1.1 TWO-COMPONENT LIQUID EXPLOSIVES

Two-component liquid explosives have found widespread use for specialty demolition tasks. The inherent safety feature that two nondetonable components can be transported to the blasting site and mixed immediately prior to use, has made this a very attractive concept. However, an attempt to introduce hydrazine-based two-component explosives for commercial blasting in competition with water gel explosives was not successful for reasons of higher cost. However, if government regulations are tightened to further restrict the transporation of live explosives through populated areas, two-component explosives may find more widespread use than they do now.

One application which illustrates the logistic advantage of two-component explosives, and which would not have been possible with commercial solid explosives, was the salvaging of a partially grounded and sinking ore-carrying ship near Singapore. Nondetonable components were flown in by commercial carrier, and the more valuable engine section of the ship was severed from the cargo section by shaped charges and two-component explosives developed by RRC. The same operation with conventional explosives would have taken several weeks to carry out, and the ore carrier might have sunk by the time the explosives arrived by another ship. Other marine applications are in the North Sea oil field, where it is very undesirable to store live explosives on the drilling platforms (References F3 and F4).

Two-component explosives developed by RRC and its subsidiaries and sister companies include Astrolite-G, Astrolite-K, PTC-4, and EDA sensitized nitromethane. None of these explosives are capable of withstanding 394°K (250°F) in a downhole environment for more than a few hours. The PTC-4 explosive is currently field tested under ERDA (now DOE) contracts in demonstration shots using up to 13.6 Mg (30,000 lbs) of explosive (Reference P5).

1.2 HIGH-TEMPERATURE SOLID EXPLOSIVES

A survey of existing high temperature resistant solid explosives showed that only few explosives will withstand the geothermal environment without premature cook-off and, possibly, detonation.

There was no intention at the beginning of the program to use solid instead of liquid explosives for the stimulation of geothermal wells. Solid explosives cannot be handled as safely as liquid two-component explosives. The storage of large amounts of solid explosives at the wellhead would constitute a significant hazard potential.

Liquid explosives fill every recess in an unevenly drilled borehole. Thus, per foot of borehole depth, more explosive can be emplaced than with solid explosives.

A compromise between liquid and solid explosive would be to slurry the solid explosive in an inert liquid. A gelling agent would prevent the solid from settling after the slurry has been pumped down

the hole. However, this concept offers no advantages over either solid or liquid explosives. Another compromise would be to dissolve the temperature-resistant solid explosive in a liquid which, by itself, is not an explosive, but which may contribute to the exothermic reaction. However, many thermally stable solid explosives are less stable in solution or after they melt. Apparently, the stabilizing effect is tied to the arrangement of molecules in a crystal lattice. Once the integrity of the crystal lattice is lost, the thermal stability is markedly decreased.

Even though solid explosives are not useful as the main charge in the stimulation of geothermal wells, the development and application of liquid two-component explosives depends on the availability of temperature-resistant solid explosives for detonators and boosters. A literature and vendor survey has been conducted of high-temperature solid explosives in support of the liquid two-component explosive program.

While the temperature stability requirements to be met by the solid explosive are similar to those of the liquid explosive, the reliability and safety requirements exceed those of the liquid explosive. First of all, the material has to be handled above ground, although only at ambient temperature, in assembling and inserting the booster charge. The solid explosive is a vital link between the electric detonator and the main charge. If it should fail to fire on command or if it should detonate or deflagrate prematurely, the success of the entire stimulation effort would be in jeopardy.

A very thorough literature search on high-temperature explosives and detonators was conducted using the Lockheed Information Services DIALOG and the System Development Corporation ORBIT systems. Two literature searches were conducted for RRC by the Defense Documentation Center. The Chemical Propulsion Information Agency (CPIA) provided a bibliography on explosives (Reference C3). None of these sources nor the standard reference books revealed any information on a two-component liquid explosive suitable for use in geothermal wells. However, the search provided a number of useful references on temperature stability of solid explosives useful as primary explosives or boosters in geothermal applications.

A very useful survey of history leading to the development of high-temperature resistant solid explosives for navy applications is given in Reference K2, dated 1966. The problems encountered then with solid explosives will again have to be overcome for a liquid two-component explosive for geothermal applications. Initially, the Navy considered an explosive which developed less than 2 cm^3 gas after 48 hours at 373°K (212°F) in the vacuum stability test acceptable. Then, with the increasing aerodynamic heating of supersonic fighters and missiles, the temperature requirement was increased to 533°K (500°F). A gas evolution of less than 2 cm^3 after 48 hours at 533°K in the vacuum stability test is the new acceptance criterion for high-temperature solid explosives. The test is not directly applicable to liquid explosives because liquids generally have a higher vapor pressure to start with and may have to be confined under pressure at that temperature.

The heat-resistant explosives studied at NOL and other laboratories, which are of possible interest as boosters for liquid geothermal explosives are listed in Table 1-3.

Table 1-3
HIGH-TEMPERATURE SOLID EXPLOSIVES

Acronym	Chemical Name	Melting Point (^{o}K)
TATB	1, 3, 5 - Triamino - 2, 4, 6 - trinitrobenzene	>633
DATB	1, 3 - Diamino - 2, 4, 6 - trinitrobenzene	559
NONA	2, 2', 2", 4, 4', 4", 6, 6', 6" - Nonanitroterphenyl	>713
HNS	2, 2', 4, 4', 6, 6" - Hexanitrostilbene	589
DIPAM	3, 3' - Diamino - 2, 2', 4, 4', 6, 6' - hexanitrobiphenyl	579
TNN	1, 4, 5, 8 - Tetranitronaphthalene	613

Based on promising thermal stability of TATB and DATB, further synthetic effort at NOL was directed toward high-melting compounds with strong hydrogen-bonding possibilities. DATB has an unexpectedly low failure diameter in spite of low shock sensitivity. DATB sold for $4.00/lb in 1965 and has been used in the Sparrow III warhead.

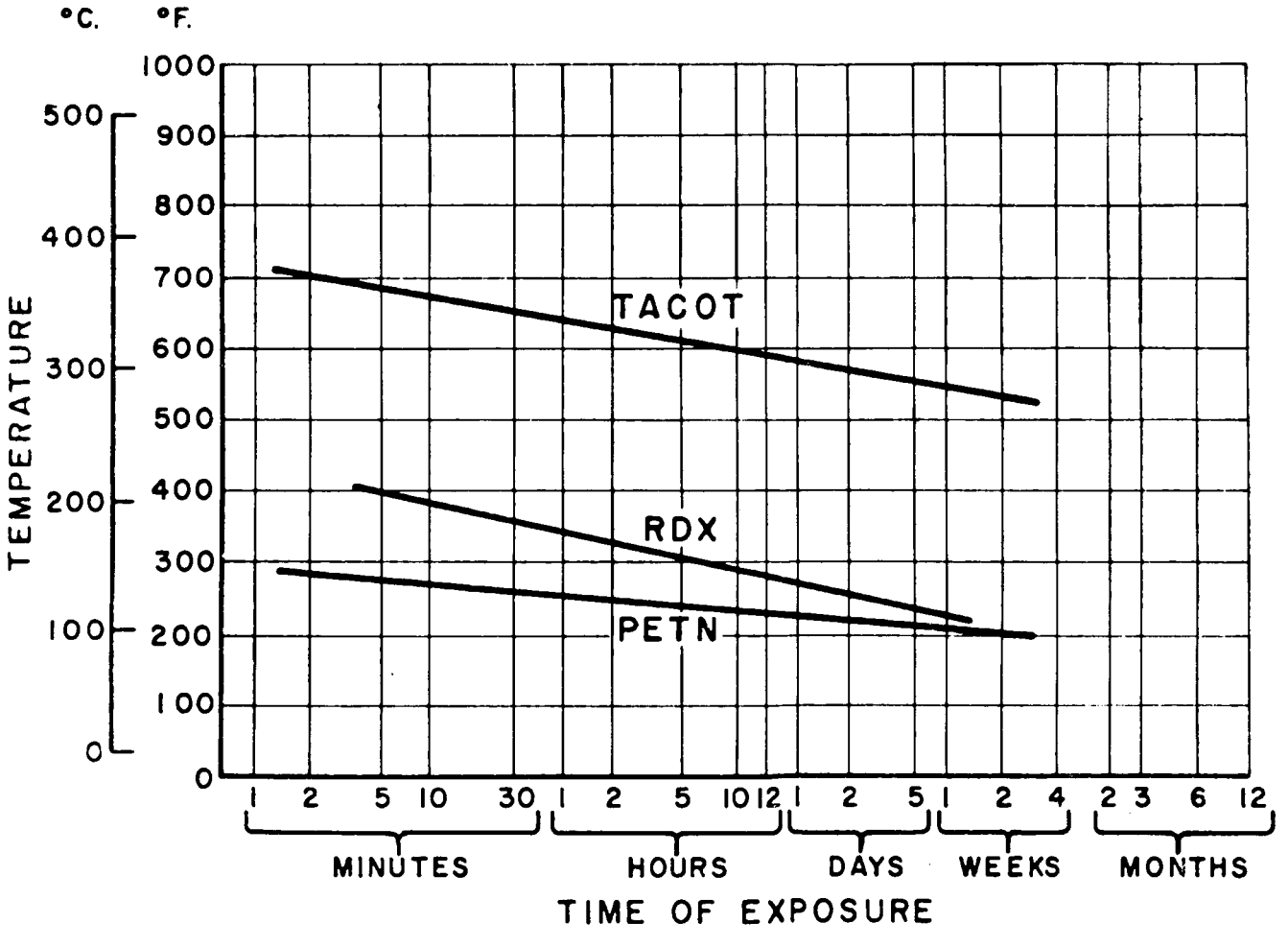
A high purity sample of TNN prepared at NOL melted at 613^{o}K and showed excellent thermal stability at 533, 553, and 573^{o}K, gas evolution at the highest temperature being less than was the case with NONA. TNN undergoes a phase transition which may not affect its usefulness when used as a solution or dispersion in an inert solvent.

In an effort to synthesize more stable unimolecular (oxidizer and fuel in the same molecule) solid explosives, weak "trigger linkages" have been identified which offer a point of attack in premature thermal decomposition of explosives. Systematically avoiding "trigger linkages" has resulted in the synthesis of some remarkably stable solid explosives. The same principle should be applied to the development of two-component high-temperature liquid explosives.

Du Pont offers a high-temperature resistant explosive called TACOT (Tetranitrodibenzo - 1, 3a, 4, 6a - tetraazapentalene). However, the compound is not sold in bulk, but only in manufactured products, such as detonators. Repeated attempts during the course of this contract to obtain either TACOT bulk explosive or pressed booster pellets were not successful. According to data provided by Du Pont (Figure 1-2), TACOT has excellent thermal stability.

In addition to detonators, booster explosives may be required to assure that the explosive main charge detonates at high order. A summary of candidate solid high explosives to be used as boosters

RELATIVE TEMPERATURE RESISTANCE OF TACOT AND OTHER EXPLOSIVES



Source: Du Pont Bulletin A-41655

Figure 1-2

in geothermal HITEX applications is presented in Table 1-4. In terms of vacuum stability at 473°K (Reference Table 1-5), HNS and TACOT appear to be superior to TATB, but TACOT is currently not commercially available in bulk because of a patent protection/sole source supply situation. TATB is a prime candidate because its explosive yield is much higher than that of either TACOT or HNS.

The objective of a castable explosive development program conducted by Hercules ABL (Reference H4) was to develop a solution cast explosive with a total underwater energy 25 percent greater than HMX, a critical diameter of less than 2.5 to 7.5 cm (1 to 3 inches), castable within a temperature range of 298 to 363°K, and lower cost than HMX using a nonexplosive sensitizer. The mixture was not supposed to lose constituents through volatilization at temperatures up to 348°K. While this upper operational temperature is far below that required for geothermal applications (505°K and up), some results obtained during that contract are of interest to the current program. The candidate explosives screened during that program had to satisfy a critical diameter requirement of less than 7.5 cm (3 inches), which may still be excessively high for explosives which have to detonate after displacement into the formation. It is possible to lower the critical diameter below 7.5 cm for an ordnance application by addition of RDX. However, this approach is not acceptable for a geothermal two-component explosive.

Another group of thermally stable explosives is based on fluoroaliphatic groups with nitro substitution. One such compound, DAPHNE, 1-fluoro-1,1-dinitroethane, showed only 3 percent weight loss after 8 hours in a sealed tube at 533°K (500°F). It is a liquid at ambient temperature which boils at 313°K/ 20 mm pressure. Fluoroaliphatic nitro compounds have higher heats of explosion than the aromatic nitro compounds, but are less stable. It is not expected that these liquid mono-explosives will be useful for the geothermal environment.

Another liquid explosive, NTN, developed by Lawrence Radiation Laboratory (Reference V3) does not have the thermal stability required for geothermal applications. It is not known if it is feasible to produce it in large quantities at economical cost.

It has been demonstrated repeatedly that thermal decomposition rates are 50 to 100 times faster in the melt or in solution than at corresponding temperatures in the solid state. The solid state immobilizes molecules and molecule groups which contribute to decomposition, making undesirable interaction impossible. In a melt or in solution, the active centers move about freely and will interact. This fundamental fact makes it more difficult to develop a pumpable liquid explosive than a solid explosive of equal thermal stability.

Comparing the rate of gas evolution at 533°K (500°F) of NONA and HNS, 5 mole-percent solutions in trinitrobenzene as a solvent (TNB itself is quite stable at 573°K), decomposed 5 to 7 times faster for NONA, and 70 times faster for HNS. This shows that NONA has more intrinsic thermal stability, whereas HNS owes its stability to the crystal structure of the solid.

Table 1-4

PROPERTIES OF EXPLOSIVES UNDER CONSIDERATION FOR GEOTHERMAL APPLICATION

Explosive	Density gm/cm^3	Melting Point ^oK	Current Thermal Application Range ^oK	Detonation Velocity m/sec	Detonation Pressure K bar	Impact(1) Sensitivity cm (solids)	Comments
Solids							
Z-TACOT	1.85	683	561–589	7,200	180	–	Commercially available. Sole source supply until patent expires
HNS	1.74	591	533–561	7,100	230	39	Commercially available
PYX	1.77	–	561–589	7,800	270	63	Developed by LASL, currently no commercial source
PATO	1.94	593	505–533	–	307	>320	Developed by LASL, currently no commercial source
DATB	1.84	562	505–533	7,700	282	>320	Used in military service, commercially available
TATB	1.94	(2)	533–561	7,970	313	>320	May be commercially available in near future. ERDA-controlled supply

Notes:

(1) Type 12 impact tool for solid explosives

(2) Does not melt prior to decomposition

Table 1-5

VACUUM STABILITY OF SOLID EXPLOSIVES AT 473°K
GAS EVOLVED (cm^3/g STP) VERSUS TIME (DAYS)

Compound	Days													
	2	7	14	21	28	35	42	49	56	63	70	77	84	90
TATB	0.3	0.9	2.1	4.1	7.2	11.1	15.8							
DATB	2.8	3.6	4.5	5.5	6.2	7.4	8.4	9.5	10.7	11.8	13.2	14.7	16.4	
PATO	1.0	1.9	2.8	3.4	4.0	4.6	5.2	5.6	6.1	6.5	7.2	7.7	8.7	10.7
PYX	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.4	0.4	0.4	0.5	0.6	0.6	0.7
Z-TACOT	0.4	0.6	0.7	0.8	1.0	4.1	4.9	7.1	8.6	10.8	11.2	11.4	11.5	11.5
HNS	0.4	0.7	1.0	1.2	1.4	1.6	1.7	1.8	2.0	2.3	2.5	2.6	2.8	3.0

1.3 HIGH-TEMPERATURE DETONATORS AND INITIATION BY SHAPED CHARGES

Commercially available detonators have marginal thermal stability for geothermal applications. Additional development is required to provide reliable means of initiating the high-temperature resistant explosive which has become available as the result of the work described in this report.

Under Task 15 – Supporting Studies, a preliminary evaluation of commercially available detonators has been conducted. The results of this effort are reported in paragraph 4.5.4.

Bubble-free liquid explosives are as hard to initiate as single crystals of solid explosives. In the absence of lattice defects, inclusions, cracks or bubbles, no hot spots can form which are generally assumed to promote initiation and propagation of detonation waves, in particular those at low velocity detonation (LVD).

In designing the initiating charge, the homogeneity of the liquid explosive sample has to be taken into consideration. Conceivably, an explosive sample might lose all bubbles which where entrained during the mixing process if it is left standing for a long time. A freshly mixed sample may be easier to initiate than an aged sample.

For almost all experimental testing and commercial as well as military explosive applications, the explosive is usually initiated with an electric bridgewire detonator or a percussion cap. The cap has to be in intimate contact with the explosive or booster to be initiated. If this is not possible because the cap does not withstand the temperature or pressure environment, different methods for initiation have to be sought. Shaped charges are a promising alternate means of initiation because they can penetrate heavy walls and can operate from a safe standoff distance. However, initiation of explosives by shaped charges is not a standard method, and very little information on this subject could be found in the open literature. Shaped charges have been used for the disposal of bombs or other ammunition. There is also some concern about the undesirable initiation of ammunition in a tank by the jet of a shaped charge which has penetrated the armor. It appears that the initiation of HITEX explosives by shaped charges should be further investigated.

In studying the initiation of cast pellets of RDX-TNT (60:40) by the jet of a copper-lined shaped charge, it was noted that the stagnation pressure of the jet particles required for initiation was much lower than the pressure required in the card gap test, 7.5 k bar compared to 17.5 k bar (Reference H3). It has been attempted to explain this by the shape of the shock front. The shape of the shock front from the card gap test can be approximated as triangular, while the shock wave from the impact of a shaped charge jet is rectangular.

2.0 EXPERIMENTAL TEST METHODS

The report on the technical effort is subdivided in two major sections: one describing the experimental methods used, and one describing the results when applying these test methods to a particular set of chemicals. The experimental methods are applicable to a wide range of explosives, not only the type of explosive developed here.

Wherever possible, standardized test methods i.e., those established by authoritative organizations such as the American Society for Testing of Materials (ASTM) or the U.S. Bureau of Mines (USBM) were used. However, the peculiarity of the explosive being a liquid rather than a solid, or the requirement to conduct the test at high temperatures, necessitated several changes to commonly established test procedures. It is desirable to adhere to standardized test procedures so that results obtained in this report may be compared to results reported by previous investigators on other explosives. However, in reviewing the literature, it became apparent that very little work had been done in measuring safety or performance of explosives at temperatures above 533°K (500°F). In many respects, the methods had to be developed here as part of the contract work. These methods may be useful for other explosive investigations, and are described here in sufficient detail to allow other investigators to adopt them to their test problems.

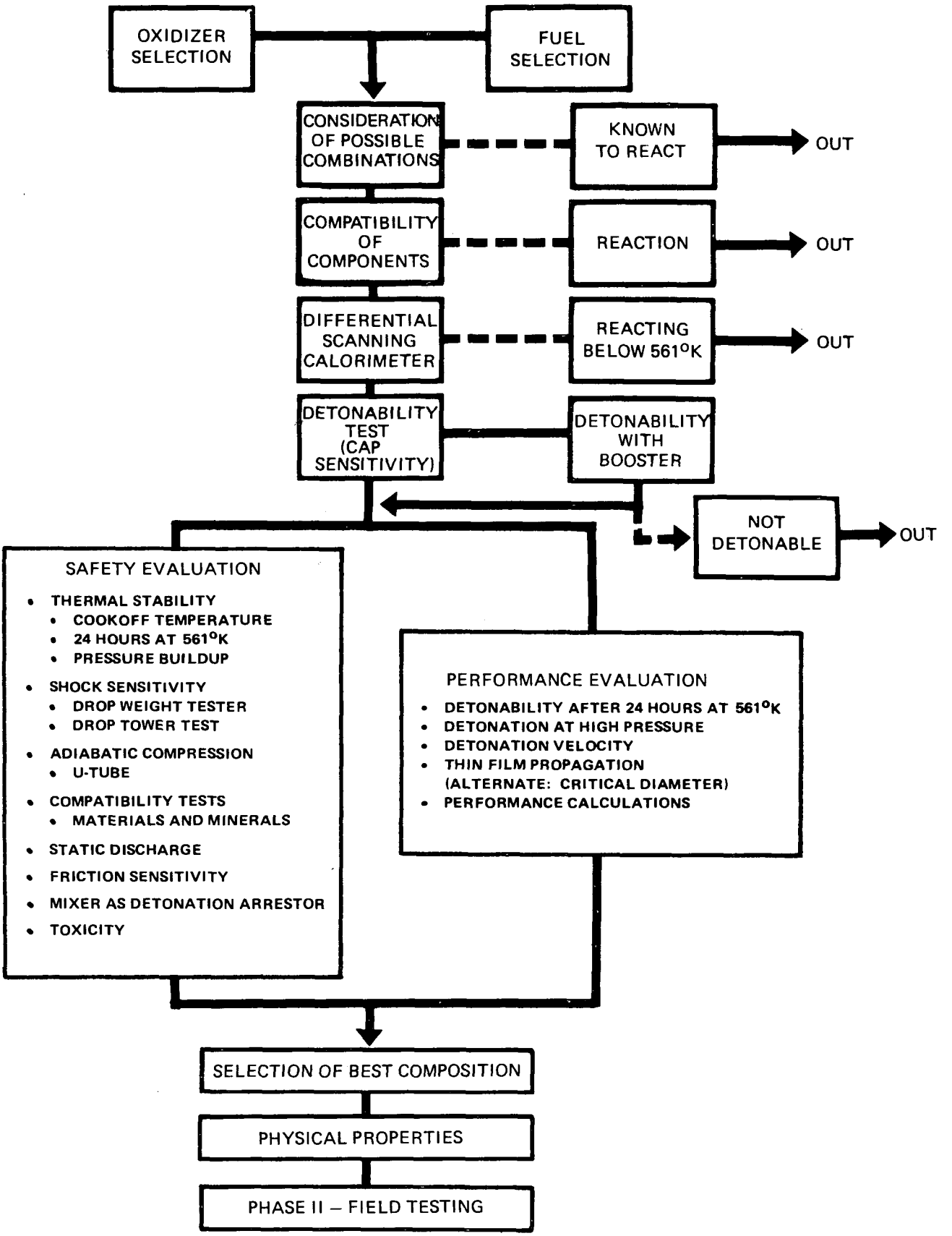
The rationale followed in selecting the type of tests and the sequence of events is illustrated in Figure 2-1.

Following the selection of candidate fuels and oxidizers, the compatibility of the two or more components was tested in laboratory screening tests. In addition to compatibility, also miscibility was observed at this time. Miscibility turned out to be an important selection criterion. Combinations which passed the screening test were then analyzed on the differential scanning calorimeter, which gives more quantitative answers to the question of thermal stability. Promising combinations were then subjected to detonability tests, preferably in open pipes if the vapor pressure of the ingredients was low enough to allow high-temperature testing without confinement. Those with higher vapor pressure had to be tested for detonability in sealed pipe bombs. Combinations which were not detonable with a cap detonator were usually retested with a 20-g booster of high explosive. Safety and performance evaluation tests would be carried out simultaneously because selection of the best composition depended equally on the safety and the performance of the explosive. Usually, there is a tradeoff between the two properties, because the most powerful explosives are not always the safest. An ultimately safe explosive may not have sufficient energy to be ranked among the best performing explosives. Separating the explosive into two nondetonable components significantly increases the handling safety of the explosive.

2.1 DEVELOPMENT TESTS

The objective of development tests was to prove or disprove theoretical considerations leading to selection of certain combinations of chemicals thought to make a useful high-temperature explosive.

LOGIC DIAGRAM – HIGH TEMPERATURE EXPLOSIVE



These tests had to be conducted on small quantities in the laboratory. The turnaround time of these tests had to be fast because a large number of tests had to be conducted. Frequently, screening tests result in premature ignition or explosion while the sample is being heated. For this reason, these tests had to be conducted with extreme precautions and with as small a sample as technically possible.

A more quantitative indication of thermal stability was obtained from thermograms using a differential scanning calorimeter. This very sensitive instrument would allow not only the measurement of the onset of an exotherm, but also the magnitude of an exotherm. It was able to operate with very small samples which were safe to handle in the laboratory. However, there is a relationship between sample size and critical temperature above which an explosive will autodetonate or autodeflagrate. The more promising combinations were, therefore, tested as 6-g samples in Pyrex® glass tubes, in flanged steel bomblets with a thermocouple inserted and a burst disc attached. The time and temperature at which an exotherm occurred and/or the burst disc ruptured could thus be recorded. The same tests were then repeated with minerals and other materials with which the explosive is likely to come into contact in the well.

2.1.1 Screening Tests

Screening tests were conducted to eliminate combinations of oxidizers and fuels which would react prematurely at 561°K (550°F) or below. The test would also identify fuels which decomposed (pyrolyzed) when heated by themselves or which autoignited when heated in air.

Because the explosive nature of any of the combinations under study was unknown at the beginning of the program, special precautions were necessary to conduct the screening tests. Because it was desirable to conduct the test in the laboratory (rather than remotely in a bunker) and to observe it from close up, only very small quantities of oxidizer and fuel were mixed. The testing was conducted in a well-drawing fume hood behind a portable safety shield made from 6.4-mm (0.25-inch) thick Plexiglass®, and the operator would wear heavy leather gloves and a face shield all the time. With those safety precautions enacted, it was considered safe to mix up to 0.5-g explosive in the laboratory.

2.1.1.1 Screening Tests in Open Test Tubes

Small Pyrex glass test tubes, 8-mm internal diameter by 75-mm length, were used for these tests.

The oxidizer and fuel were mixed in approximately equal weight proportions. No effort was made to mix the ingredients in exactly stoichiometric proportions (neither during the screening tests nor during the differential scanning calorimeter tests). It was not considered essential to have an exactly stoichiometric oxidizer: fuel ratio in these early tests and the results would be the same over a wide range of compositions. It would have been excessively time consuming to weigh milligram amounts of oxidizer and fuel in an effort to control the mixture ratio more accurately.

While mixing the ingredients, the operator was careful to keep the mixture behind the safety shield because some components were suspected of being able to react prematurely at ambient

temperature. The test tube was then inserted in a transparent heater made from two concentric lengths of Pyrex tubing. The transparent tube heater consisted of an outer shell of Pyrex tubing, 20 mm internal diameter by 100-mm long, into which was inserted an inner Pyrex tube 15-mm outer diameter by 100-mm long. The upper end of the inner tube was flared so that the flared portion rested on the rim of the outer glass tube. Nichrome resistance wire was wound in a spiral around the inner tube and connected to a variable AC power source to provide heating. A light bulb was placed behind the heater so the samples could be observed with transparent illumination. The heater was preheated and kept at constant temperature slightly above 561°K (550°F). A thermocouple in a thin wall glass sheath was inserted into the sample prior to lowering the test tube into the heater. The thermocouple output was recorded on a strip chart recorder, and observations were marked on the strip chart papers at the temperature at which the events occurred. The heating rate was approximately 0.8°K/s.

The temperature which could be reached in an open test tube was frequently limited by the boiling point of one of the constituents, usually the fuel. Tests with low boiling mixtures which did not show any premature reaction at the normal boiling point of their constituents had to be repeated with sealed test tubes as described in paragraph 2.1.1.2.

Visual observations made during the screening tests were miscibility, discoloration, gas evolution, boiling, charring, ignition of vapors in air, or explosion of the sample.

Initially, a sand bath was used to heat the samples. While this was a very safe approach from the standpoint of minimum confinement of the sample (higher confinement of explosive samples increases the hazard), any changes occurring in the mixture could not be observed. The same was true for an electrically heated ceramic heater with approximately the same dimensions as the test tube.

The majority of the tests were conducted in air. In some instances, interaction of the fuel alone was observed when the fuel was heated in air. Some tests were, therefore, repeated with a nitrogen purge.

2.1.1.2 Sealed Tube Screening Tests

Because many otherwise acceptable explosive combinations had boiling points below the operating temperature of a geothermal explosive, it was difficult to test these combinations in an open test tube at atmospheric pressure. Approximately 2 cm^3 of the more promising combinations were, therefore, sealed in 8-mm ID x 75-mm glass tubes and heated remotely in a sand bath to beyond 561°K at an average rate of 0.1°K/s. Because a larger quantity of explosive was involved in these tests, the tests were conducted in an explosives test bunker and not in the laboratory. Because initially some samples burst with overpressure without evidence of reaction, later tests were conducted with a heavier walled tube of 2.5-mm wall thickness instead of 1-mm wall thickness. The 1-mm wall tube was previously tested with water at 561°K and contained the vapor pressure (72 bar) without damage. However, it was difficult to reproducibly achieve a reliable seal on glass tubes free from stresses remaining in the solidified glass.

Thermocouples were attached to each individual test vial. If one of the tubes burst prior to completion of the test, the event could be observed on the strip chart record. The thermocouple would either be destroyed, resulting in an open circuit, or it would be displaced, indicating a different temperature than prior to the event. The several vials tested simultaneously in the sand bath were spaced at least 10 cm (4 inches) apart to avoid destruction by a neighboring explosion.

In the sealed tube tests, the size of the fragments was the only indication of the type of reaction. Some tubes simply broke in half (overpressure), while others were shattered into many small pieces. Samples which survived this test were carefully disposed of by breaking the vial in a bucket of water.

2.1.2 Differential Scanning Calorimeter Tests

A Perkin-Elmer DSC-1B differential scanning calorimeter (DSC) was used in these tests. The DSC provides more data than a plain differential thermal analysis (DTA) because it permits measurement of the magnitude of an exotherm or endotherm in addition to their location on the temperature scale. The instrument and its mode of operation is described in more detail in Reference P1.

The sample size used for DSC analysis is less than 10 mg, an amount which is safe to handle in the laboratory, even if the sample should explode during heatup. Because of the small sample size, and because larger batches of uncharacterized explosives should not be mixed in the laboratory, fuels and oxidizers were mixed in arbitrary, not stoichiometric proportions. This stemmed partly from the difficulty of weighing into sample pans such small quantities of hygroscopic chemicals and partly to enable the rapid testing of a large selection of samples. The results appeared to be fairly insensitive to mixture ratio. If there was any doubt, the test was usually repeated.

The temperature range of the DSC-1 is from 173 to 773°K (-148 to 932°F). The heating (or cooling) rate can be selected from a very slow 0.625°K/minute to a very fast 80°K/minute. A typical heating rate was 20°K/minute (0.66°K/second). Unless otherwise noted, this heating rate was used throughout this investigation. A few tests were conducted at 10°K/minute. The output recorded on a strip chart recorder was the extra current supplied or omitted from the sample pan to balance its temperature with that of an empty pan in the reference pan holder. The strip chart also carried pulse marks for every °K increase in temperature (every tenth mark omitted for ease of data reduction). The starting temperature had to be written in by hand to correlate the temperature scale with a temperature dial reading on the control unit.

The samples were sealed in 4.4-mm diameter aluminum cups with a crimped-on lid. In many cases, the sample cup did not contain the pressure developed by the more volatile fuels and would leak prematurely. Leakage showed up as excessive drift of the baseline on the recorder. Occasionally, the observation window would fog up from condensate. Sometimes one could see the sample cup move in the sample holder each time a high pressure jet was vented. Movement of the sample cup may also cause a step discontinuity in the trace on the strip chart recorder. The leakage at high pressure limited the number of compositions which would be successfully tested on the DSC to those with less volatile fuels.

The manufacturer of the instrument and other experienced users were consulted, but pressure-tight sample pans are not readily available.

A particular test problem was the corrosive attack of concentrated nitric acid on the aluminum pans at high temperature. All-gold pans were available, but their cost was prohibitive. It has been considered to gold plate the aluminum pans prior to use. A gold coating would not only protect the pan from corrosion, but would also result in a better crimp seal because gold is more malleable. Tests with nitric acid were abandoned before the gold plating of aluminum pans could be perfected.

2.1.3 Thermal Stability Tests

Thermal stability tests were conducted to identify any premature reactions between the oxidizer and the fuel which would preclude their joint use in a high-temperature explosive. In these tests, foreign materials were excluded from the mixture. However, by virtue of having to contain the sample in some kind of structural material, and having to immerse a thermocouple to measure the sample temperature, limited compatibility data with glass and stainless steel were already obtained at this stage of testing.

The thermal stability tests were essentially an extension of the screening tests, except that: 1) larger sample sizes were used, 2) the tests were conducted remotely, and 3) more quantitative data were obtained. In addition, the results from these tests would permit one to predict detonability in the 24-hour detonability tests. Also, the gas space above the explosive could be sampled and analyzed for decomposition products after the sample had cooled to ambient temperature.

The thermal stability testing was conducted in so-called "compatibility bomblets." A schematic drawing of the thermal stability test apparatus is shown in Figure 2-2. The apparatus consisted of an aluminum heating block into which up to five stainless steel bomblets could be inserted and heated simultaneously. The samples were contained in 22-mm diameter by 100-mm length open ended glass test tubes which were inserted into the steel bomblets and sealed with a flanged lid carrying a thermocouple and a burst disc. The air in the bomblets was replaced by a purge with nitrogen prior to sealing the bomblet. The stainless steel shielded thermocouple reached all the way into the sample. The burst discs (5 mil aluminum) were rated to burst at 75 to 96 bar (1100 to 1400 psig) at 561°K (550°F). Sample size in this setup was limited to 6 grams.

Until test number 36, samples were allowed to cool off in the heating block. Because the block was well insulated, it took more than 6 hours to cool to below 373°K (212°F). It was felt that the heating beyond the required 24 hours constituted an undue burden on the thermal stability test. In order to time the 24-hour exposure more accurately and in order to speed up testing, a remotely operated frame was added which held all five bomblets and lifted them simultaneously from the heating block after the 24-hour exposure.

The temperature traces sometimes exhibited exothermic temperature excursions of components which were obviously incompatible. These premature reactions were usually accompanied by rupture of the burst disc. Additional thermocouples were mounted near the vent hole of the burst disc, such that a separate trace on a multichannel recorder indicated the time at which a burst disc ruptured during a test.

COMPATIBILITY TESTING EQUIPMENT SET-UP

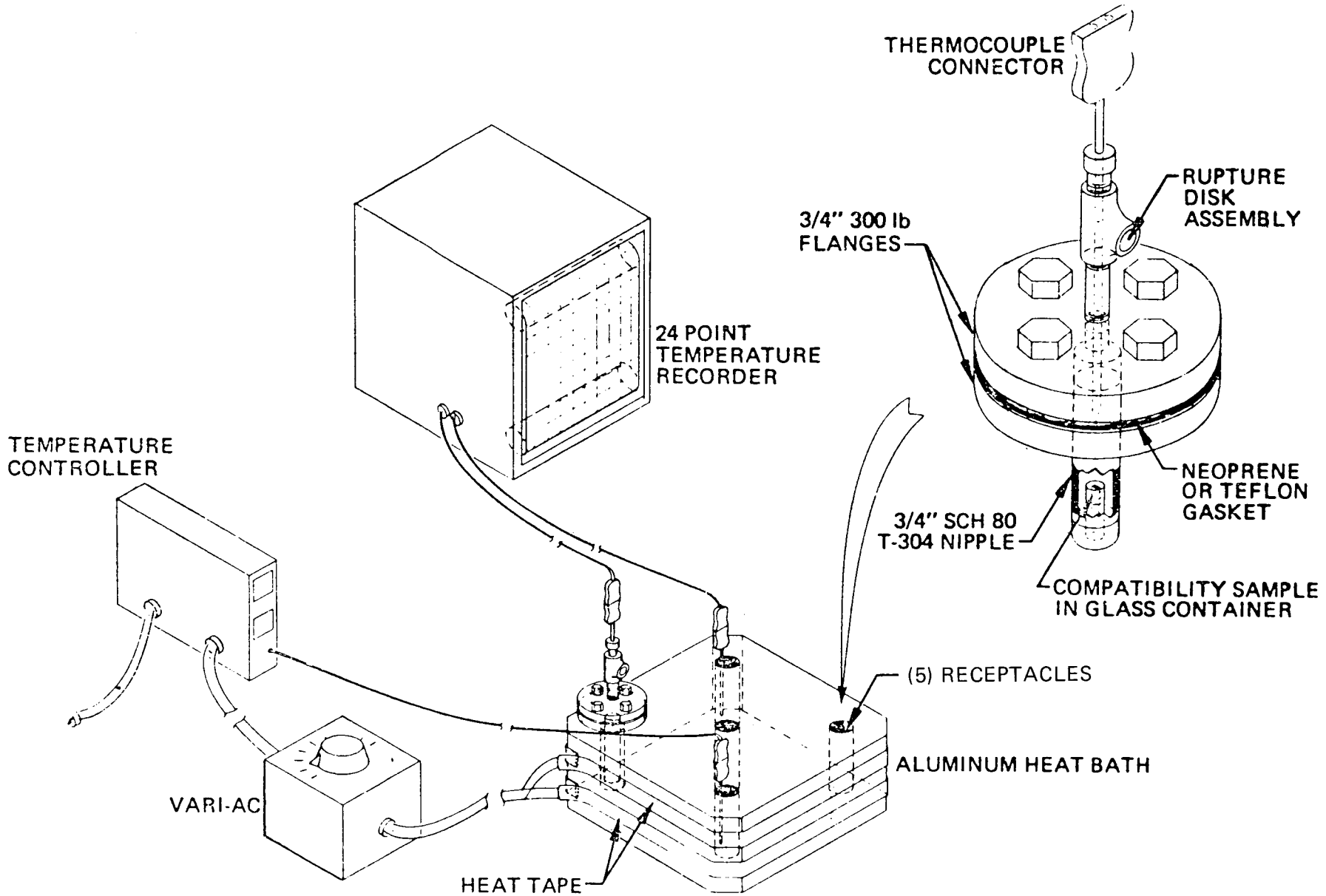


Figure 2-2

After cooling to ambient temperature, the bomblets were disassembled. Sometimes an overpressure could be noted when loosening the bolts which held the flanged lid. This was an indication of partial decomposition, and when an overpressure was noted, this observation was recorded in the test log. The test tube with the sample in it was then inspected visually and weighed. Even with the most stable combinations, a weight loss was commonly noted and had to be attributed to condensation and sublimation of more volatile constituents in other parts of the system and on the outside of the glass tube.

The residue was then dissolved in water, and if an all-nitrate oxidizer was used, the concentration of residual nitrate measured with an ion-selective electrode. Perchlorate would interfere with this analysis. Nitrite was analyzed using the Saltzman reagent (Reference S4).

Following test number 52, the T pieces at the top of the bomb lid were replaced by cross pieces, and a sample valve was added which would allow measurement of residual pressure and removal of gas samples for gas analysis.

2.1.4 Materials Compatibility Tests

Materials compatibility tests were conducted by the same method as the thermal stability tests, except foreign substances were added to the candidate oxidizer fuel mixture. The substances for compatibility tests with candidate explosives included such materials as mineral samples, various cements and drilling muds, iron casings, and fluids derived from the wells, etc. To prevent excessive dilution of the explosive mixture, the amount of foreign substances added was limited to less than 20 percent by weight of the explosive mixture. Typically, 0.5 g of the test substance was introduced to 4.1 g of the candidate explosive mixture.

2.2 SAFETY TESTS

The preeminent concern in the selection of explosives for construction, demolition or stimulation projects is the safety of the explosives used. It would be very dangerous to plan a large scale field demonstration test without having tested the safety properties of the mixed explosive and its unmixed ingredients. Safety tests have become a routine part of explosive development at RRC, and numerous explosives have been qualified for commercial sale using the same techniques now applied to HITEX.

2.2.1 Drop-Weight Sensitivity Tests

At least three drop-weight impact sensitivity test devices are commonly used in explosives characterization and hazards evaluation: the USBM impact apparatus, the Picatinny Arsenal drop-weight tester, and the JANNAF/ASTM/Olin/Technoproducts drop-weight tester. The USBM impact apparatus and the sample holder described in Reference M1 are primarily designed for solid samples. Two types of tools have been designed for this apparatus, the cup-and-plunger set and the type 12 tools. Selection of the method depends on the relative sensitivity of the sample. The method preferred for testing during this contract was the JANNAF/Olin Model T drop-weight tester in accordance with ASTM D 2540-66T (as far as liquid samples are concerned) and manufactured by Technoproducts at San Carlos, California.

It must be emphasized that, while testing of liquid samples is covered by an ASTM specification, there exists no standard drop-weight test for solid samples. Results obtained for solid samples with the three different machines mentioned above are not directly comparable, but a general trend and modest correlation between less sensitive and more sensitive substances is possible.

A very comprehensive survey on the different methods for drop-weight impact sensitivity testing of explosives and the history leading to the development of these methods was published recently by Boyars and Levine (Reference B1). However, no standard test method for drop-weight testing at elevated temperatures has been described up to this time. Several mechanisms have been proposed for the initiation of explosives by impact. In the case of liquid explosives, the adiabatic compression of small bubbles in the liquid is a likely mode of initiation. For solids, friction is likely to create hot spots, and initiation becomes generally easier if a hard grit material is mixed with the test sample. Wenograd (Reference W1) showed a correlation between impact sensitivity and the temperature at which pure high explosive explodes within 250 μ when subjected to rapid temperature rise. This thermal theory would also lead to the conclusion that a thermally stable solid explosive will be less impact sensitive at ambient temperature than common solid explosives. This has been confirmed by the results described in paragraph 4.2.1.

A problem common with all drop-weight tests is how to diagnose a positive test. Generally, one can rely on an audible report or a visible flash if a test is positive. However, the noise of the weight impacting on the hammer makes it very difficult to discern between mechanically and chemically generated noise. The test apparatus cannot always be placed in a dark room, and a flash may be hard to see in a laboratory with average artificial or daylight lighting.

Various sensing methods have been proposed to give a more definite and less subjective indication of a positive test, including an ionization probe (Reference S2), infrared probe (References R1 and S1), or measurement of the amount of gas evolved (Reference W2). However, none of these methods was available with the existing setup.

The drop-weight tester, as illustrated in Figure 2-3, consisted of a triangular weight holder riding on three vertical guide rods. The empty holder weighed 1 kg. The weight would be increased in increments of 50 g up to a total of 6 kg by adding metal discs. Alternatively, a fixed weight, i.e. 3 kg, could be used and the weight holder and weights portion could be raised or lowered to give different levels of impact. The tester had to be mounted on concrete floor or on a large concrete block. It was important that it was always aligned vertically to minimize friction losses along the guide rods.

The solid sample holder consisted of a sliding plunger and an anvil. Both were manufactured from hardened steel. The surfaces between which the solid sample was held had to be repolished occasionally because strongly positive tests would erode the metal and generate a star-shaped coarse pattern. While some drop-weight test machines prescribe a coarse surface like that of a tool file, for the sake of reproducibility it was preferred that the surfaces of the firing tool remain smooth.

DROP-WEIGHT TESTER

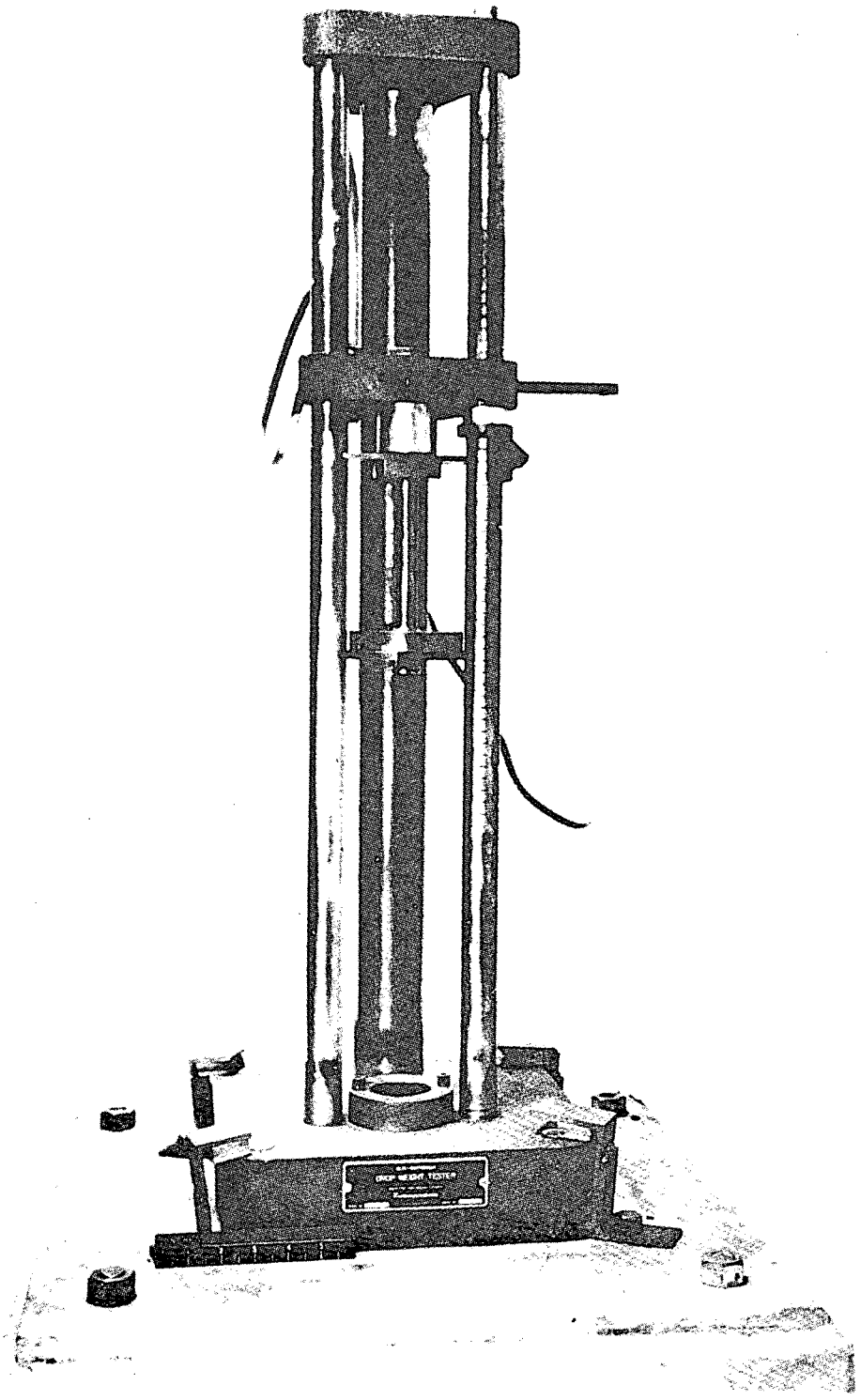


Figure 2-3

Technoproducts, the manufacturer of the Olin drop-weight tester, also provides brass cups to fit the plunger. It was found that the use of brass cups introduces more scatter in the testing of dry samples. Therefore, it was preferred to place the solid samples (approximately 20 mg) directly on the bare anvil and gently lower the plunger onto it.

The liquid sample holder, illustrated in Figures 2-4 and 2-5, contained a 0.03 ml sample in a 9.3-mm diameter cup between an O-ring which served as a spacer. The liquid sample filled the space only partially, leaving a ~50 percent ullage between the liquid surface and the seal. The sample was sealed by a 0.4-mm (16-mil) thick stainless steel diaphragm which was held down by a piston with an exit hole. In case of a positive test, the diaphragm ruptured and showed a hole. The system could be calibrated with water as liquid, causing hydraulic rupture of the diaphragm.

Because the explosive would have to be handled and pumped in the hot geothermal environment, it was thought desirable to measure its impact sensitivity in the drop-weight tester at elevated temperatures. The existing impact apparatus was not designed for high sample temperatures and, therefore, had to be modified by attaching a heating jacket. Because all explosives would be liquids or completely molten at the test temperature, only the liquid sample holder had to be modified by attaching a 400-W nozzle heater to the body of the sample cup assembly.

Two thin (3-mm) aluminum sleeves were inserted between the heater and the body to provide better heat transfer. Since the nozzle heater covered the horizontal gas vent holes in the upper portion of the body, small holes were drilled vertically from the shoulder of the body to intersect with the existing holes, thus providing unobstructed venting ports. The outer diameter of the cap of the sample cup assembly was reduced by a few millimeters to allow free rotation of the cap when it had to be tightened or loosened.

For development tests, it was sufficient to conduct repetitive tests with fresh samples. Occassionally, the weight was dropped repetitively without replacing the sample. However, this is not a standard procedure and data from such a test do not bear any statistical weight.

The initiation of explosives by impact is a statistical process and the boundary between safe and unsafe is not very sharply defined. Therefore, it is common practice to determine the point at which exactly 50 percent of all experiments result in ignition. The exact 50 percent point is thus bracketed by an "up and down method." This 50 percent point is determined by conducting a large number of tests in the vicinity of the 50 percent point and interpolating to the sensitivity number E50. This number is commonly reported in kg cm, which is the product formed by multiplying the mass of the weight times the height from which it dropped.

2.2.2 Drop Tower Test

The drop tower test was based on a military specification for rocket motors (Military Specification MIL-R-22713 (WEP) Amendment 1). The specification called for dropping of the loaded rocket motor three times, head first, tail first, and horizontally onto a 3-inch-thick steel plate (Brinell hardness of at least 207) from a 40-foot height.

SAMPLE CUP ASSEMBLY, EXPLODED VIEW

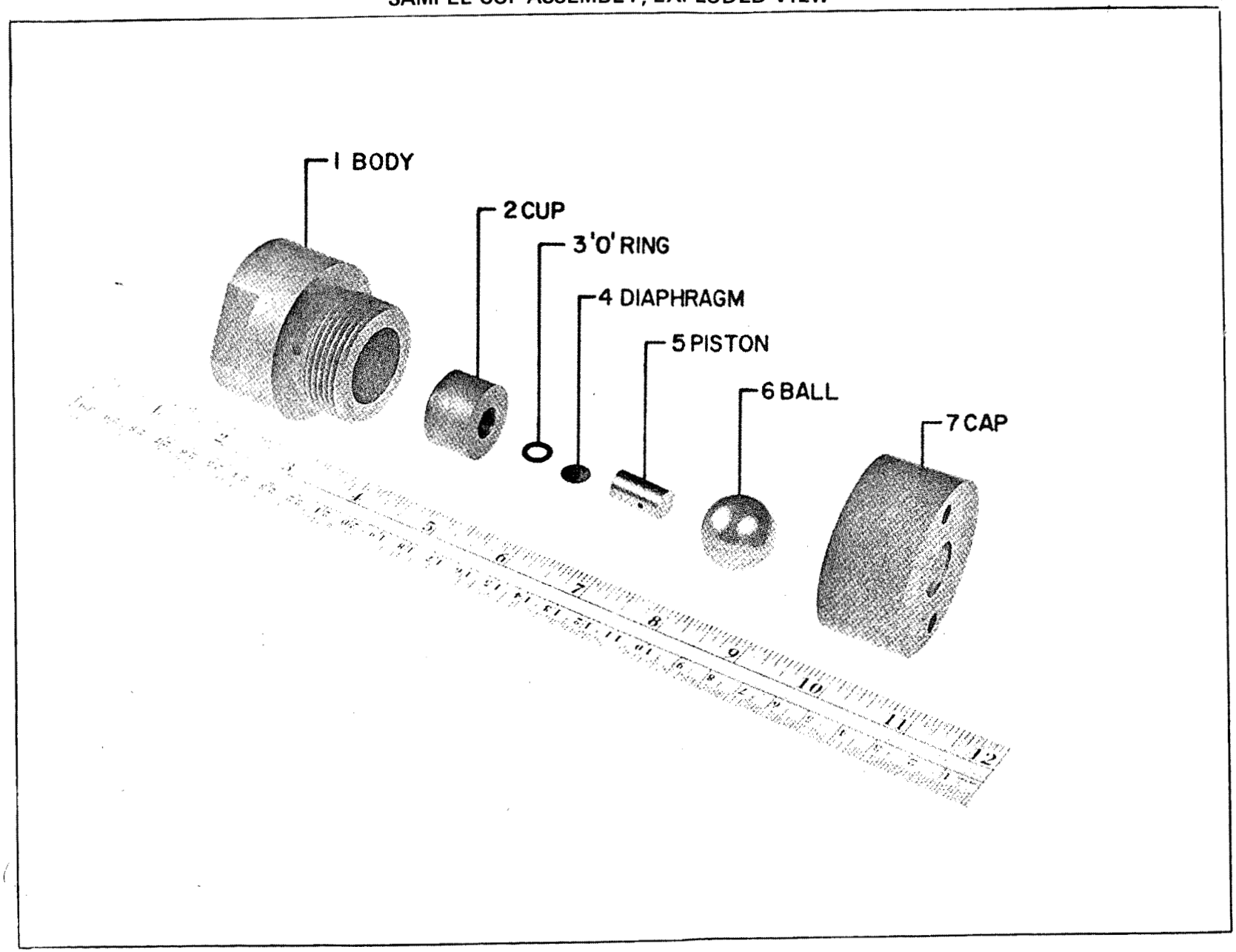
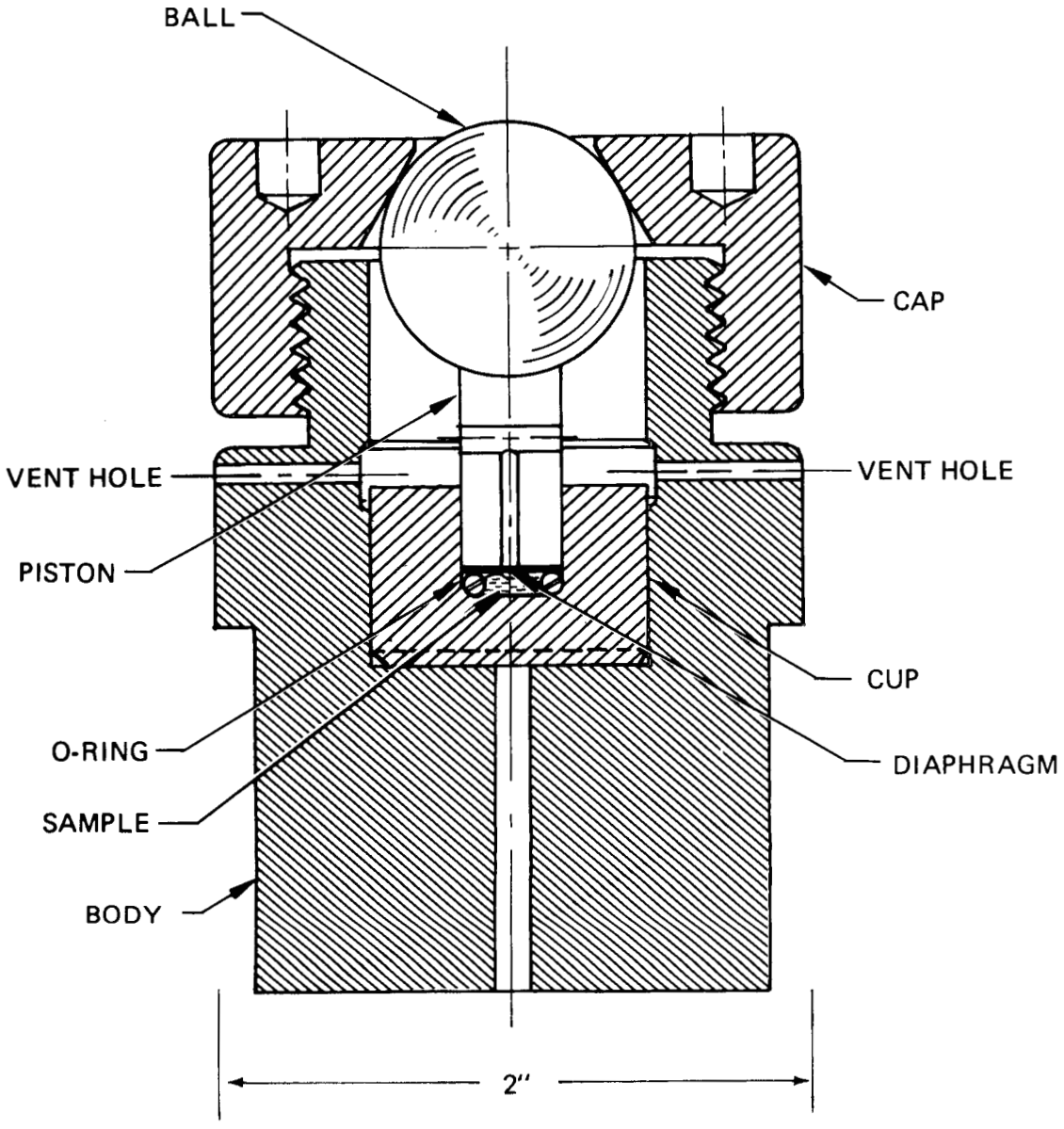


Figure 2-4

SAMPLE CUP ASSEMBLY



In actual field applications of the present two-component explosive, the oxidizer and the fuel will be handled separately above ground. The components are then mixed underground to form the explosive. It is, therefore, not expected that containers loaded with explosives will have to be transported. Nevertheless, this test provided additional data about the sensitivity of explosive to impact.

To perform this test, a metal beam was attached to the rear of a pick-up truck. The truck was positioned near the edge of a cliff so that the beam extended out from the cliff and suspended over a steel plate over 40 feet below. The bomb assembly as shown in Figure 2-6, containing 200 g of the fused candidate explosive, was tied to a nylon rope and hooked up to the end of the metal beam. The power line going out to the bomb along the beam for heating and temperature recording could be easily disconnected by simply lowering the bomb slightly (connections were made so that they easily separated) at the desired temperature, and the bomb was permitted to drop freely onto the steel plate below. In the event no detonation occurred, it could be retrieved by pulling it up with the nylon rope, and the drop repeated.

2.2.3 Adiabatic Compression Test

Adiabatic compression tests are frequently conducted with candidate liquid monopropellants or explosives (Reference R4). The adiabatic compression sensitivity test developed by Aerojet-General Corporation (Reference J1) and recommended by JANNAF has since been withdrawn. Instead, it was decided to use a U-tube adiabatic compression test also developed by Aerojet and since used in characterizing numerous liquid rocket propellants at high temperatures (Reference V2).

The same method was employed here with only a few modifications. Instead of heating the sample with a hot metal bath, an electric heating tape was wrapped directly around the sample tube. The stainless steel sample tube had the dimensions 6.4 mm (0.25 inch) OD by 546 mm (21.5 inch) length and a wall thickness of 0.7 mm (0.028 inch). The sample temperature was monitored using a thermocouple attached on the outside of the tube at the base of the U-shaped sample tube where the sample was located. Figure 2-7 shows a photograph of the test setup with the sample tube (covered with white ceramic wool insulation) attached at the bottom. When the desired temperature was reached, the cylinder at the top of the setup was pressurized and a valve was opened remotely, allowing the nitrogen gas to rupture a burst disc located directly above one end of the sample tube, sending the 2,000 psi of nitrogen gas into the sample tube.

2.2.4 Spark (ESD) Sensitivity Tests

The sensitivity of hot, molten explosive to electrostatic discharge (ESD) was determined using the Allegany Ballistics Laboratory test apparatus. The test was accomplished with a fixed voltage (5,000 volts) variable capacitance apparatus with a point to plane electrode configuration. The wiring diagram of the apparatus is shown in Figure 2-8.

The explosive sample was contained in a thin layer on a flat metal pan which could be heated to 477°K (400°F). The entire assembly was contained in a plexiglass enclosure to protect the operator

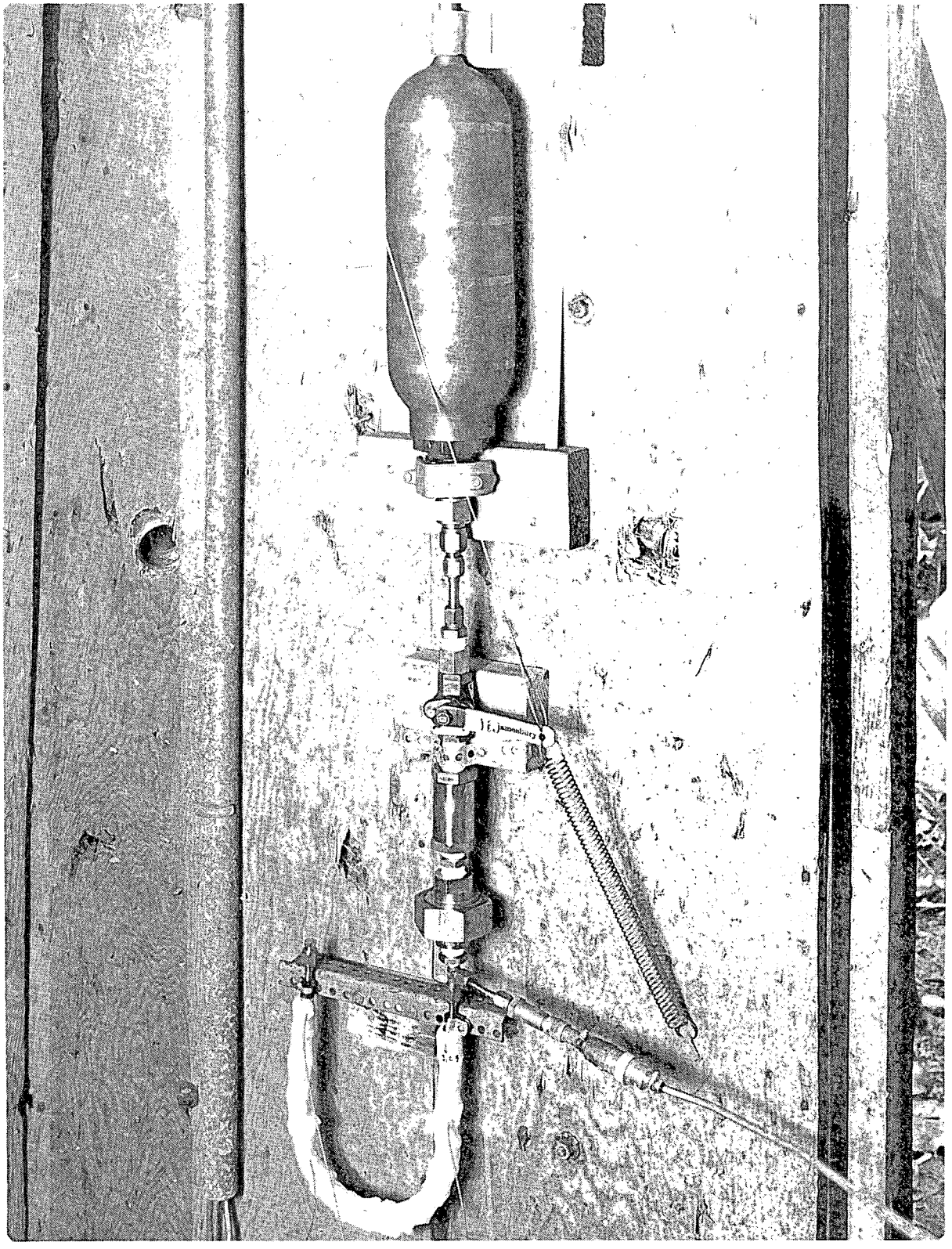
BOMB ASSEMBLY FOR 40-FOOT DROP TOWER TEST

11111-87

2-15

Figure 2-6

ADIABATIC COMPRESSION TEST APPARATUS



ABL ELECTROSTATIC DISCHARGE TEST MACHINE

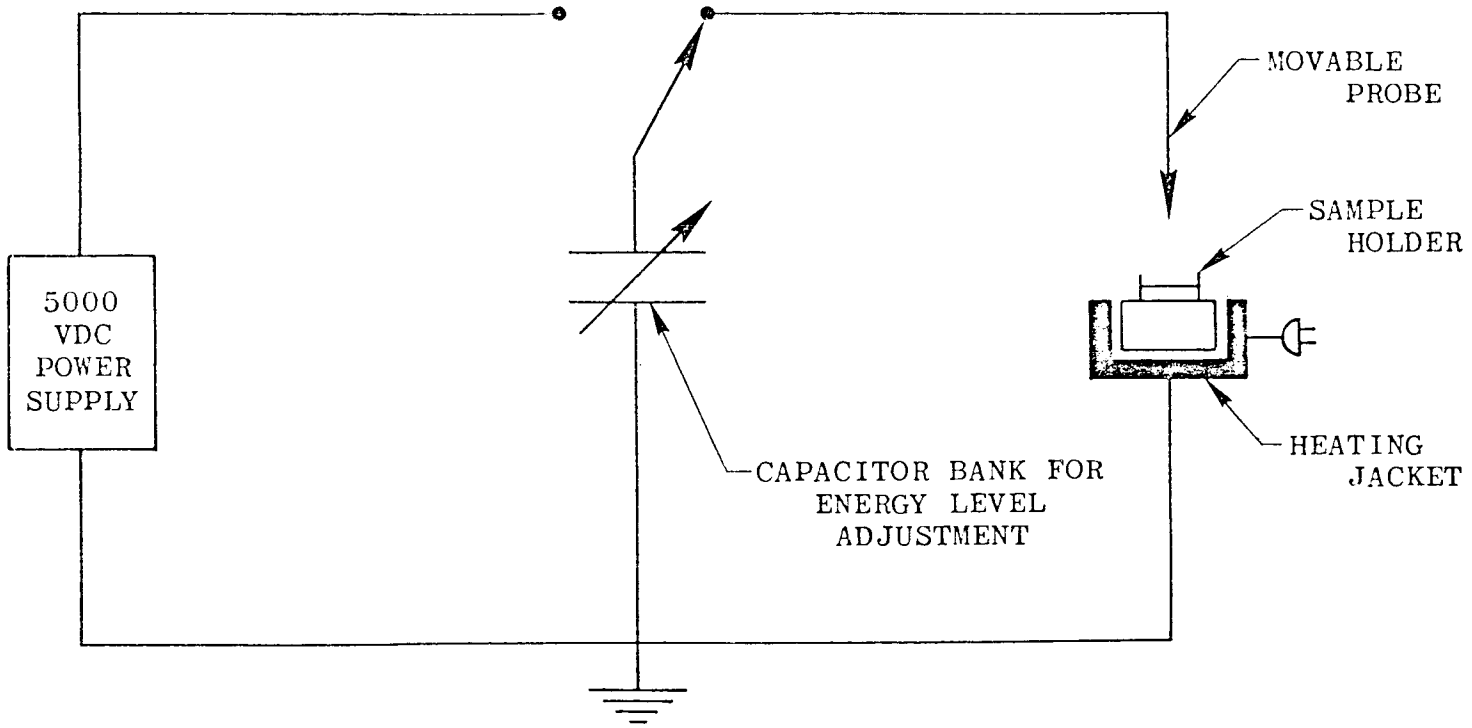


Figure 2-8

in case of a positive test. The sample was in air at ambient pressure during the test. The pin electrode was lowered manually until arcing occurred. This method has certain shortcomings over a constant gap width method because the distance from which arcing occurs and the arc shape depend on the dielectric constant of the explosive under test.

2.2.5 Friction Sensitivity Tests

Friction testing was performed on the Allegany Ballistics Laboratory Mod 1 friction test machine (Figure 2-9). The machine consisted of a stationary wheel in contact with a movable anvil. The sample was placed on the anvil and was subjected to the friction between the wheel and anvil under known contact pressures and velocities. The plate could be moved at varying speeds, while the inertia of the wheel caused a sliding and differential speed between the two bodies.

The machine is similar to the U.S. Bureau of Mines pendulum machine (Reference M1), except it occupies less space and is easily housed indoors.

2.2.6 Detonation Arrest Test

The purpose of the detonation arrest test was to demonstrate the ability of the mixer section of an explosive well stimulation assembly to arrest a detonation occurring down-well from the mixer. Ideally, the detonation should not propagate past the mixer (the mixer being placed somewhere below the surface in the actual operation), nor proceed to the surface.

A true scale model was employed to simulate such an event above ground. The model assembly consisted of a 0.6-m (24-inch) long section of 75-mm (3-inch) diameter pipe containing the mixed explosive. One end of the pipe was sealed by having a 0.5-mm (20-mil) thick piece of stainless steel shim stock welded to the bottom. This donor section was placed directly over a 0.9-m (36-inch) long acceptor section of 75-mm diameter pipe, which contained a coaxial 36-mm diameter pipe of the same length. In the acceptor section, the center was filled with just the fuel, and the oxidizer was filled in the annulus surrounding the fuel. Figure 2-10 is a photograph showing the interface of the two sections. In order to prevent an air gap in the assembly which would have attenuated the detonation wave traveling down from the donor section, the acceptor section was filled completely full. Two overflow drainage tubes (one each for oxidizer and fuel in the acceptor section) were built in to permit overflows when the components expanded upon heating. The completed fixture, prior to loading, is shown in Figure 2-11. The thin dip tube extending from the top of the donor section was connected to a nitrogen gas cylinder to stir the explosive mixture prior to detonating it. After the fixture was loaded and the desired temperature was reached, the donor section was detonated with a number eight cap surrounded by 20 g of C-4.

2.2.7 Cook-Off Tests

Cook-off tests were conducted to approximate the maximum tolerable temperature of the explosive composition before it ignited or autodetonated. This test was essentially a large scale DTA/DSC test, except that endotherms or weak exotherms were not detected. Strong exotherms will immediately lead to ignition or explosion of the sample.

FRICTION TEST MACHINE

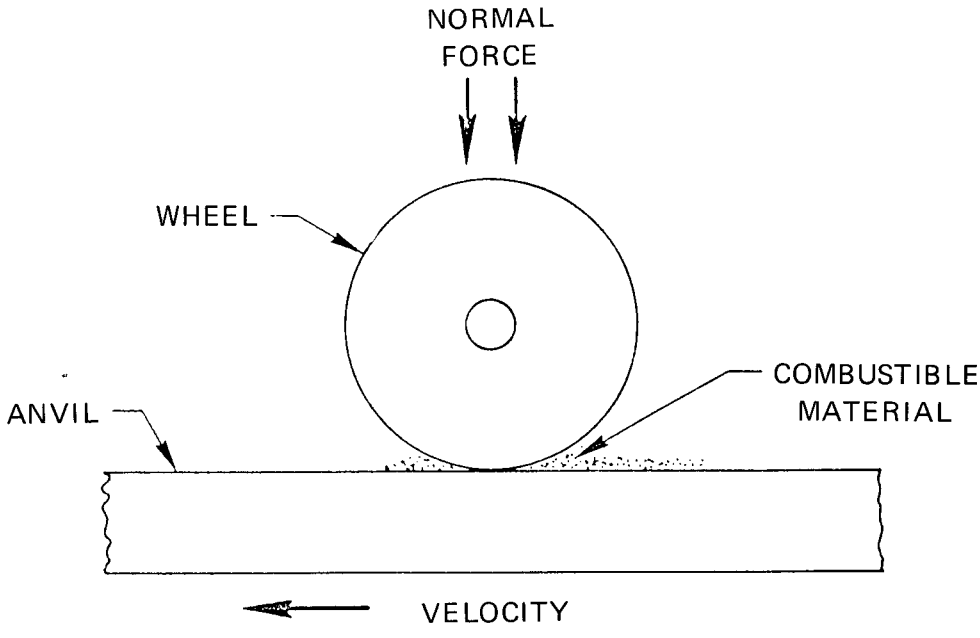


Figure 2-9

CROSS SECTION OF DETONATION ARREST TEST FIXTURE AT DONOR ACCEPTOR INTERFACE

DETONATION ARREST TEST FIXTURE

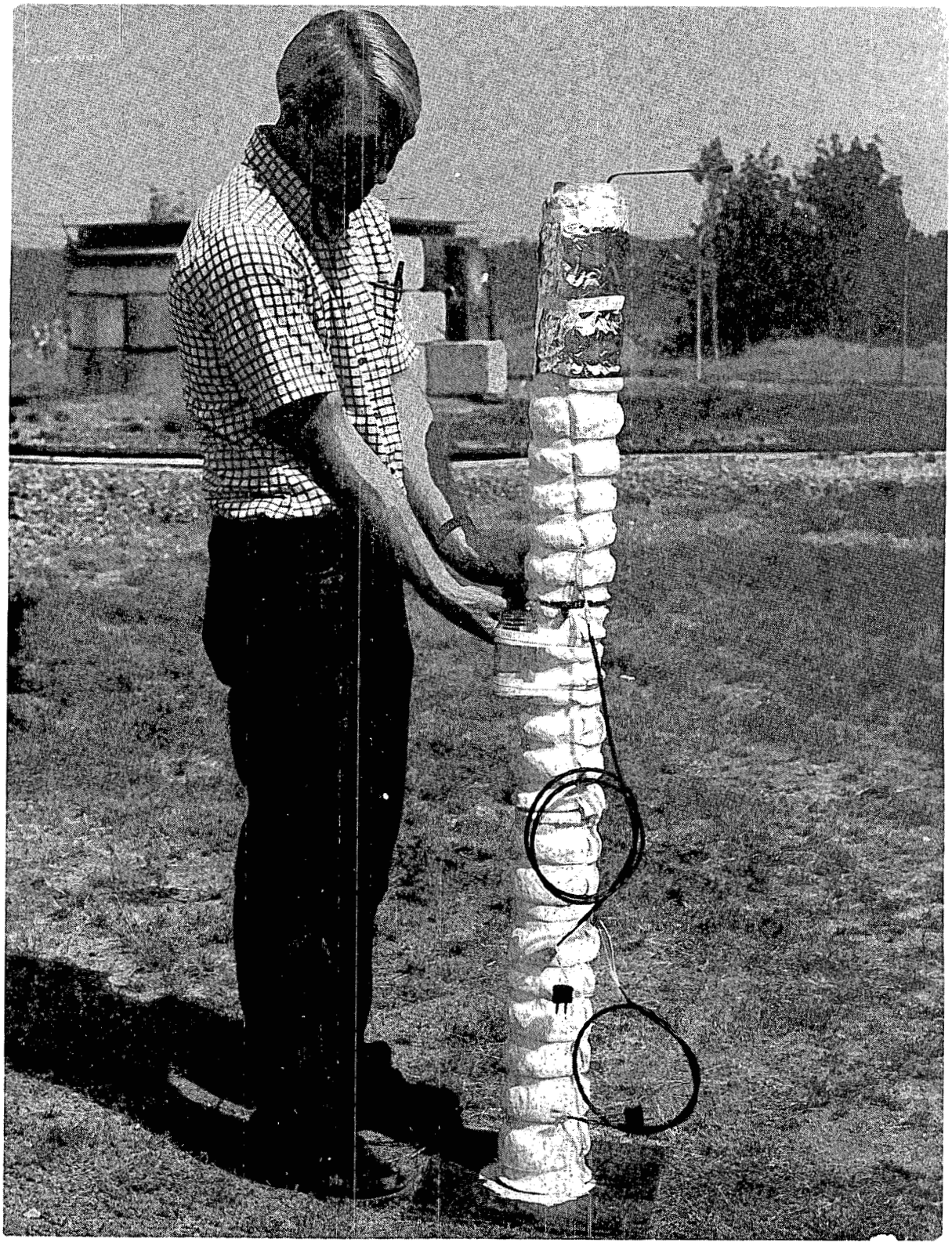


Figure 2-11

Four-cm diameter by 15-cm length steel pipes served as the container for this test. Either a 150-g or a 175-g sample mixture was hermetically sealed in the pipe container and heated by means of electric heating tape wrapped around the outside. To promote uniform mixing of the components in the container, the latter was mounted on a shaking apparatus, Figure 2-12, which tilted the container over a 90-degree angle. The container was shaken for 5 minutes after the components were melted. In the case of nonmiscible components, Cab-o-sil® (fumed silicon dioxide) was added to help stabilize the emulsion. All cook-off tests went as planned. If a sample did not burst the pipe, the shaped charge was attached to it after cooldown to cut it open and dispose of it safely.

2.2.8 Open Burning Test (Ignition Test)

It is often desirable to determine if an explosive mixture can be ignited to burn, and if so, whether or not the process of burning undergoes a transition from deflagration to detonation.

This test was conducted with over a pound of the candidate explosive mixture contained in a 4-cm diameter by 30-cm length pipe. After the mixture was heated to the desired temperature, an igniter was fired just below the upper surface of the explosive mixture. This was done similarly to the remote insertion of a blasting cap. The igniter consisted of a M-100 electric match surrounded by a mixture of 1.1 g IP-10 powder (23.7 B/70.7 KNO_3) and 16.4 g B/KNO_3 (2R-type pellets), all wrapped in 0.025-mm thick aluminum foil. The heat of reaction of B/KNO_3 pellets is 6,270 J/g (1500 cal/g). This should have been sufficient in determining the ignitability of the candidate explosive. An additional test, the bonfire test which exposes the explosive to a prolonged burning period, would be a helpful safety test to complement this test.

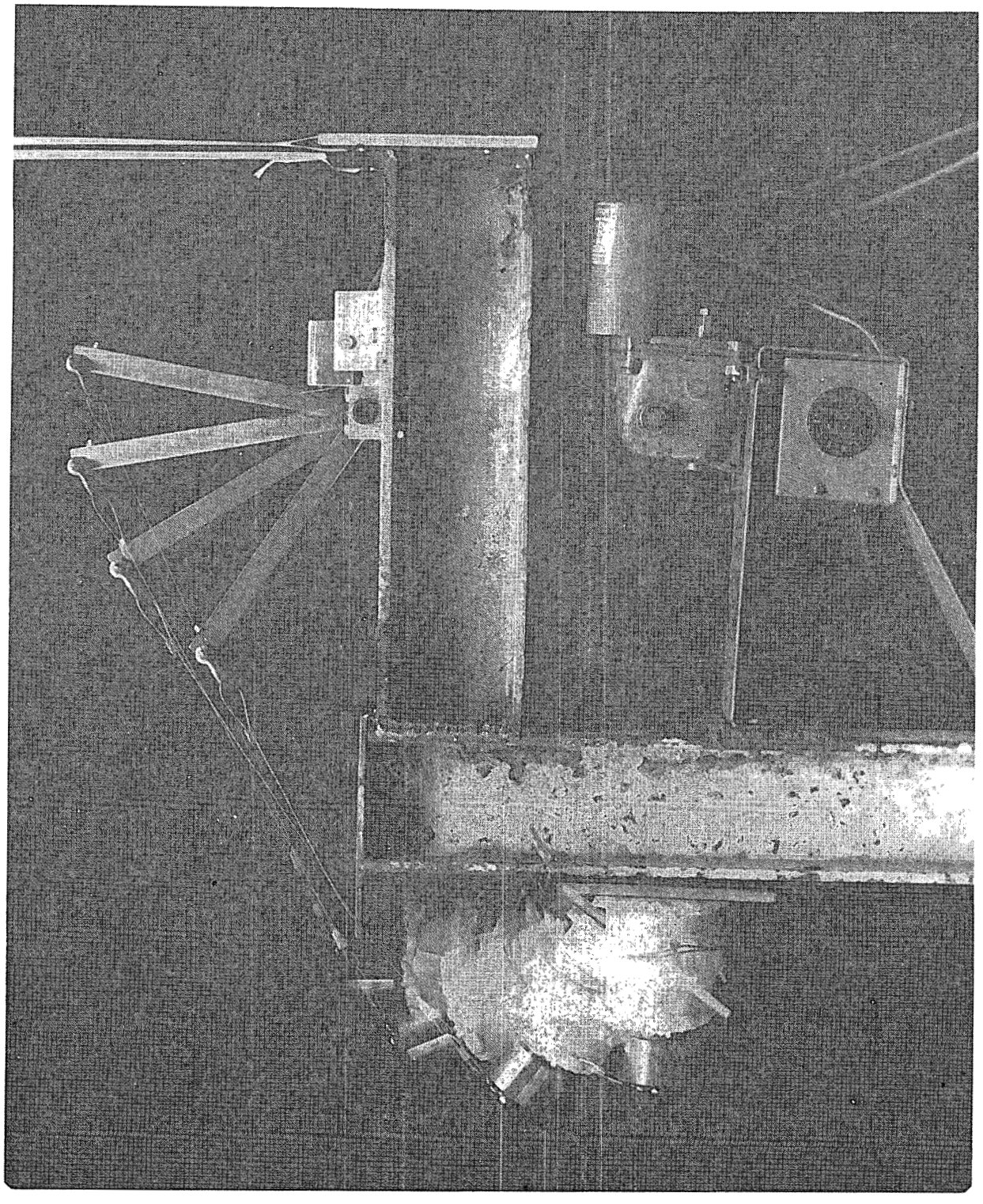
2.3 PERFORMANCE TESTS

It is very difficult to measure the power and characteristics of explosives because the entire event of detonation takes place in a matter of microseconds. The instrumentation necessary for detonation rate measurements is, therefore, much more complicated than instrumentation for the burning rate measurement of solid rocket propellants. An approximate indication of the explosive power of an explosive can be obtained from a plate denting (perforating) test and from studying the fragment size. This was done in ambient pressure and high pressure detonability tests. In addition, several ambient pressure detonability tests were conducted after heating the explosive to 477 to 560°K (400 to 550°F) for 24 hours and then detonating it on command. The detonation velocity is an important criterion in the evaluation of candidate explosives. It was determined in three repetitive tests on the ultimate candidate formulation. All explosives fail to propagate a detonation wave if the sample diameter or thickness drops below dimenions where excessive amounts of shock wave energy are lost to the confining walls. This dimension has been determined in a wedge test, starting with a gap width known to be above the critical thickness of the explosive and converging to a gap width presumed to be beyond the high-order propagation capabilities of the explosive. The results from this test were of importance to assess the capability of the explosive to detonate or deflagrate in narrow crevices in the geothermal formation to be fractured.

2.3.1 Detonability Tests

It was the objective to test the explosives using well-established standardized tests recommended by such authorities as the American Society for Testing of Materials (ASTM), the Joint Army Navy

STROBOSCOPIC ILLUMINATION PHOTOGRAPH OF SAMPLE SHAKER



11111-84 1946-6

Figure 2-12

NASA Air Force Committee on Propellants (JANNAF), or the U.S. Bureau of Mines (USBM). It would be desirable to use a standardized test so that the results may be compared to the wealth of already existing data. However, none of the established test methods was directly applicable to the testing of liquid explosives at high temperature without requiring some modification.

The method used here is remotely related to the cap sensitivity test described on page 19 of USBM IC 8541 (Reference M1). However, that method is suitable for solid explosives only because the sample is contained in a cardboard tube.

A plate-denting test developed at the Bruceton Explosives Research Laboratory (USBM), and widely used at the Los Alamos Scientific Laboratory (Reference S9), used 152- by 152-mm (6- by 6-inch) plates of 52-mm (2-inch) thick cold rolled 1018 steel. This test showed good correlation with experimentally determined detonation pressures of a large number of explosives tested. It would have provided more quantitative data than the plate-dent measurements made during this contract, which used thinner plates which were easily perforated. However, the effect of heat diffusing from the sample into the target plate on the depth of the indentation is unknown.

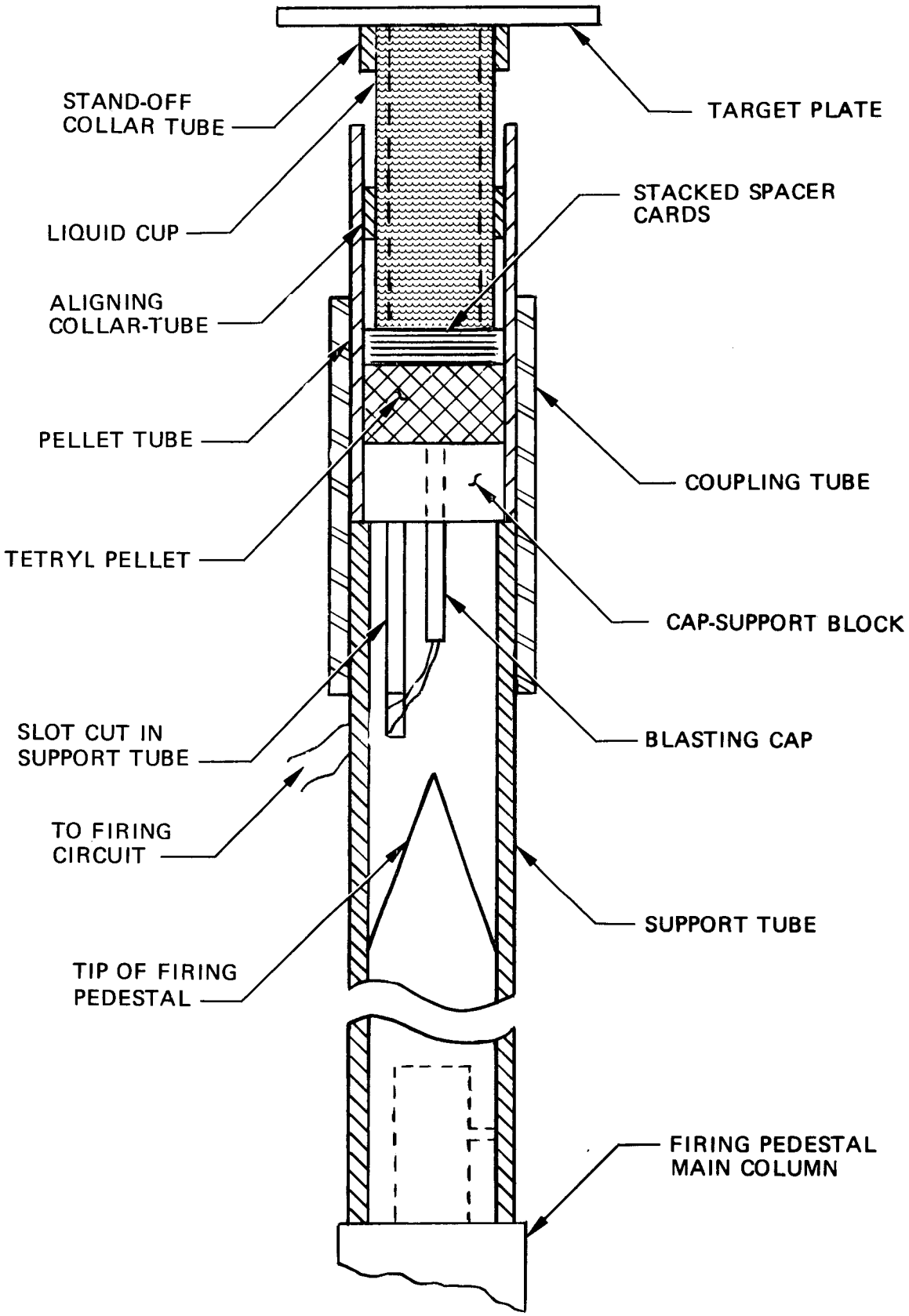
The detonability test used here for the screening of candidate explosive formulations is a modification of the Naval Ordnance Laboratory (NOL) card gap test originally developed to test the detonability of liquid monopropellants. The test is described in References A5, J1, and W3. Additional experimental data can be obtained if a pressure gauge and a continuous detonation rate probe are added (References M1 and R2). However, the witness plate indentation and the pipe fragmentation was sufficient indication for the detonation behavior of the samples under test.

The NOL card gap test which is illustrated in Figure 2-13 uses a donor charge of 50-g tetryl with upward propagation. An increasing number of plastic cards can be placed between the donor charge and the acceptor test sample to attenuate the shock until the sample no longer detonates. The upward propagation makes it difficult to retain and locate the target plate after a positive test. For this reason and a number of other reasons, downward propagation was preferred for the high-temperature explosive development. The existing ASTM-NOL card gap test apparatus did not lend itself to testing under high pressure or at elevated temperature. Also, some of the samples had to be mixed until immediately prior to initiation, which is easier to achieve with an open pipe standing upright.

A close coupling between the heated sample and the detonator and the booster during the entire heat up period prior to firing was not possible for the high temperature tests. None of the commercially available boosters and only few detonators are able to withstand the 561°K temperature environment without detonating prematurely ("volunteering") or failing when fired on command ("duds").

Likewise, the card gap sensitivity of the explosive was not yet determined because the cellulose triacetate sheet prescribed by the specification does not withstand temperatures above 450°K (350°F). The shock attenuation characteristics of alternate plastics capable of withstanding higher temperatures are not known.

CARD GAP TEST ASSEMBLY



The witness plate material and dimensions used in the detonability tests at RRC were in accordance with ASTM-D2539-66T. The specification prescribed a cold-rolled mild steel plate, 4 by 4 by 3/8 inch (10 by 10 by 0.95 cm). The material used during this program was ASTM-A36 (SAE 1010-30) grade steel. Two different lots of witness plates were used during the contract. In order to assure uniformity of the two separate shipments, one plate each was tested with the Rockwell hardness tester using a 1/16-inch (1.59-mm) ball. The Rockwell B hardness was 70 on the old lot and 75 to 80 on the new lot. Within the accuracy of the method and expected plate-to-plate variations (which could only be eliminated by measuring a statistically significant number of plates), the two types of plates were considered identical. A Rockwell B hardness of 75 corresponds to a tensile strength of approximately $4.48 \cdot 10^8$ N/m^2 (65,000 lb/in.^{2}).

Another frequently used detonability test is the small-scale gap test developed by the Naval Ordnance Laboratory (Reference A1). That test uses an acceptor column of 25-mm (1-inch) diameter by 190-mm (7-1/2-inch) length. A cylindrical steel block 76-mm (3-inch) OD, 38-mm (1.5-inch) thick is used as a witness plate. Indentations on this block are much smaller than on the ASTM-size plate and are generally measured in thousands of an inch. A correlation between dent depth and hardness of the material was established to allow for correction if a different hardness material is used. The 1018-1020 steel used by NOL had a Rockwell B hardness of 78. The original work was done with the Rockwell B scale, but its range was too limited. The DPH (Diamond Pyramid Hardness) was used by NOL for later correlations.

The correlation equation is:

$$d_C = d_O + 2/3\ (H - 83)$$

where:

d_C = corrected dent

d_O = observed dent

H = Rockwell B hardness.

A corresponding correction formula for the ASTM-size square witness plates does not yet exist.

NOL also conducted some small-scale gap tests at elevated temperatures. It was desirable not to change the temperature of the witness block and its strength. Instead, the explosive sample was placed in a Teflon insulation jacket and temperature conditioned in a separate chamber. It was then transferred to the gap test setup and fired as soon as possible, within 30 seconds. The authors estimated that the temperature of the acceptor would have changed no more than "10 to 15 degrees" (presumably ^{o}F) from the soak temperature. The NOL small-scale gap test has also been considered for the high-temperature explosive program. However, it was considered more difficult to convert to higher temperature operation than the ASTM-type setup.

One question relating to the depth of indentations on the witness plates is the question of the loss of tensile strength because part of the plate is heated too close to the temperature of the explosive.

However, the pipe section with the 0.02-inch (0.5-mm) stainless steel shim silver soldered to the bottom, rested only loosely on the witness plate. There was some heat transfer to the witness plate which, in turn, rested on dry sand. The temperature profile in the witness plate was not uniform, resulting in both vertical and horizontal temperature gradients. Assuming an AISI 4130-type mild steel, yield strength at 561°K (550°F) is approximately 80 percent of that at ambient temperature and ultimate strength is approximately 90 percent of that at ambient temperature. The temperature dependence of material strength has to be kept in mind when comparing results obtained at different temperatures. However, within the temperature band of 505 to 561°K (450 to 550°F), strength changes only by a few percent. This is within the scatter of data of the indentation measurement on repetitive tests, and a temperature correction of the data listed in Table 4-22 is not required.

The ASTM methods prescribed a 0.08- (0.003-inch) polytetrafluoroethylene (PTFE) or a 0.05-mm (0.002-inch) polyethylene membrane to seal the bottom of a pipe section and contain the liquid sample with a minimum of attenuation from the donor to the acceptor. The illustration in Reference A5 also showed a brass shim soldered to a zinc-galvanized pipe, but there is no reference to this mode of sample containment in the text.

For the same reason of avoiding attenuation of an initiating explosive shock, the thickness of any containment material between the sample and the witness plate had to be minimized. Because the entire assembly had to be able to withstand 561°K, PTFE or polyethylene were not suitable to achieve a seal at the bottom of the pipe. Brass was not compatible with some of the oxidizers under test. In this program, a stainless steel shim, 0.5-mm (0.02-inch) thick, has been silver-soldered to the bottom of all pipes. This arrangement withstood the higher temperatures well, and the attenuation by the stainless steel shim was minimal. In a few cases where not a strong detonation had occurred, the steel disc was found explosively clad to the witness plate after the test. A 0.5-mm thick shim had to be used because it was found difficult to attach thinner material without warpage.

It was undesirable to weld the container directly to the witness plate because the heating may cause annealing and softening of the steel in the witness plate. However, it was difficult to stabilize tall (>15-cm) sample tubes standing on the witness plate without providing some attachment to the witness plate.

The ASTM procedure prescribed a 2.54-cm (1-inch) internal diameter by 7.62-cm (3-inch) length "standard steel pipe." The wall thickness was not specified. During the program described here, 3.81-cm (1.5-inch) ID by 14.0-cm (5.5-inch) pipe, with a wall thickness of 4.76 mm (0.187 inch) was used instead, as illustrated in Figure 2-14, left. The wider tube was preferred because some candidate explosives may be hard to detonate in small samples in a 1-inch diameter tube. It was the intent to make full use of the 100-g explosive limitation placed on the York Center test bunker by using wider and longer samples than the ASTM test. An explosive with a density of 1.0 g/cm^3 would fill the pipe to a height of 8.8 cm (3.47 inches). Because the density of the samples varied from test to test, and because the material expanded upon heating, a pipe length of 14 cm was deemed sufficient to account for most sample sizes. The sample size was always 100 grams, but

DETONABILITY TEST SAMPLE HOLDERS

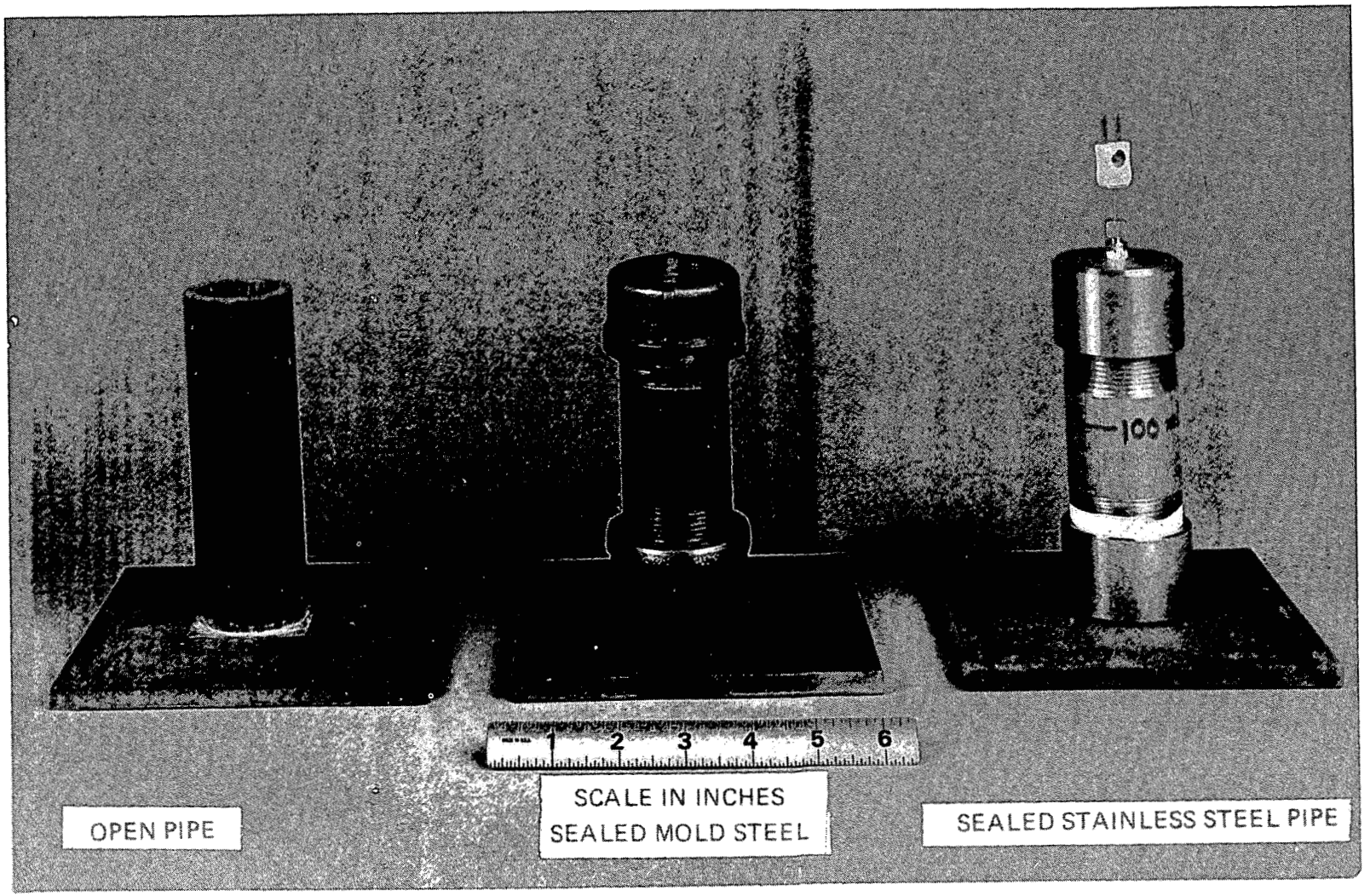


Figure 2-14

because the density varied, the liquid level may have been different with each test. For testing of this kind, a length-to-diameter ratio of at least three should be maintained.

As mentioned before, the ASTM method does not prescribe the pipe wall thickness. The confinement of the sample is known to be of importance and affect detonability as well as detonation velocity. A wall thickness of 4.76-mm steel is deemed sufficient confinement in a 38-mm internal diameter pipe, although not equivalent to downhole conditions. In addition to the indentation on the witness plate, also the pipe fragmentation served as an indication of the explosive force of the sample under test.

It was elected not to coat the inside of the pipe with PTFE as recommended in the ASTM procedure, because any explosive which undergoes premature reaction with rust commonly found on ordinary steel pipes would have to be eliminated for the geothermal well stimulation application. It would be impractical to have to coat all tubing and other components in the well with PTFE to make it compatible with the explosive. By not coating the pipe with PTFE, the detonability test results serve as a data point for compatibility evaluation at the same time.

The samples were heated by an electrical heating tape wrapped around the outside of the pipe in a spiral. Because the heating tape was lost during each test, only the lowest quality, expendable heating tape with fiberglass insulation was used for most of the tests. Because the low quality heating tape was not suitable for use on electrically conductive surfaces, and in order to avoid hot spots, a single layer of 0.8-mm (0.03-inch) thick asbestos paper was wrapped around the steel pipe prior to winding the heating tape around it. After a few months, the use of asbestos paper was abandoned because there was concern about asbestos fibers remaining suspended in the air in and near the bunker after a positive test. Asbestos fibers have been identified by OSHA as a carcinogen, and the industrial use of asbestos is currently being curtailed. In looking for a replacement for asbestos, it was very difficult to find an electric insulator which has sufficient thermal conductivity, but no electric conductivity, because the two properties go usually in parallel. After the use of asbestos was abandoned, the pipes were coated with a thin layer of two-component silicone rubber RTV 630 (or 8111) instead. In order to minimize heat loss to the environment, the outside of the heating tape was wrapped with a layer of 12.7-mm (0.5-inch) thick ceramic wool (Kaowool) insulation, which was held in place by a fiberglass tape with self-adhesive backing.

Two thermocouples were generally used to monitor the temperature of the test: one bare thermocouple would dip into the explosive sample, and the other thermocouple was inserted between the asbestos paper and the pipe, or between the heating tape and the silicon coating. The thermocouple wire lead to an ice junction behind a blast shield, from where a multi-conductor cable conducted the signal to the Energetic Material Development Laboratory (EMDL) building approximately 100 feet away, where the temperatures were recorded on strip chart recorders. The power to the heating tape was controlled from the same location with a Variac transformer. Generally, it took 30 to 40 minutes for the sample to reach 505°K (450°F), and an additional 10 to 20 minutes to reach 561°K (550°F).

The thermocouple, which dipped into the sample, had to be mounted such that it would not be caught by the mixer and wrap itself around the mixer shaft, making temperature readings impossible and impeding the rotation of the mixer. There was also some concern that the conductive salt melt would shorten out the thermoelectric voltage received from the hot junction if the thermocouple wire had only spun fiberglass insulation. However, the conductivity of the melt seemed to be low, and the current through the thermocouple was so low that no interference occurred. The other concern was that a thermocouple made of dissimilar metals, dipping into an electrolyte such as molten salt, might generate a galvanic electromotive force which would interfere with the thermoelectric signal. No such interference was observed.

The depth to which the detonator was dipped into the sample was chosen such that at least the lower 2/3 of the cap were immersed in the liquid. There is an optimum position of the cap in relation to the liquid surface. If the cap sticks out too high, insufficient energy is transferred to the sample to achieve initiation. If the cap is submerged too deeply, all explosive above the cap is wasted because it does not contribute to the indentation on the witness plate. Generally, the cap was inserted to the proper depth, and a microswitch on the cap insertion apparatus would turn on an indicator light, confirming that the cap was remotely lowered and properly positioned in the sample. In a few instances, the light did not come on, but the sample had to be disposed of by firing the detonator anyway. A few tests gave dubious results in spite of the fact that the light indicated proper insertion. Following January 3, 1977, the cap was lowered 25 mm (1 inch) lower than usual and reproducible initiations were obtained since.

Various methods for mixing the oxidizer and fuel ingredients were used during the program. Because it was considered too dangerous to mix 100 g of an unknown explosive by hand, all mixing operations were conducted remotely.

Initially, oxidizer and fuel were filled into the pipe separately, one layered on top of the other. After several tests in an arbitrary filling sequence, the fuel was always placed at the bottom and the oxidizer at the top. Since the fuel is usually less dense than the oxidizer, it was hoped that mixing would occur as the mixture melted. Additional mixing might be provided by convection currents after the mixture was completely molten. In some cases, the mixtures were heated close to the boiling point of one of the ingredients or water of crystalization would be lost from the oxidizer. Thus, bubble formation would also have aided the mixing process.

After 43 tests without a mechanical mixer, it was obvious that mixing by convection and density gradients was insufficient and it was suspected that oxidizer and fuel were stratified, thus preventing complete reaction.

Subsequently, five different mixing methods were tested and actually used. For open pipe tests, these were a propeller mixer, a spiral mixer, a high-shear counterrotating mixer, and a nitrogen purge. Sealed pipe test mixing techniques will be discussed later.

The first mechanical mixer (Figure 2-15, left) used a standard laboratory mixer blade and a variable speed motor. It was later found that the torque developed by this motor was insufficient to achieve

MECHANICAL MIXERS USED FOR HITEX TESTS (SCALE IN INCHES)

Figure 2-15

good mixing of viscous mixtures, such as those including gelling agents. The mixer motor was mounted on a remotely operated mixer stand, which would allow to lower and raise the motor and the blade to any elevation between 1 and 60 cm above the witness plate. The test was started with the mixer in the sample. After all material was molten, and after the test temperature was attained, the mixer was turned on for 0.5 to 2 minutes, then turned off and raised to a position where the motor and the blade were protected from the effects of the blast. A microswitch would indicate when the motor had reached the fully elevated position. The same switch could also be used to trigger the remote cap insertion device which would lower the cap into the explosive sample.

More viscous mixtures were not properly mixed by a single propeller blade mounted at the end of a shaft. In order to achieve better mixing, a metal ribbon was twisted to a spiral and attached to a shaft (Figure 2-15, center). This vertical mixer blade would draw the mixture downward in the center and assure uniform mixing throughout the entire sample column. A scaled-up version of this mixer was also used for the larger diameter open-pipe tests (see Figure 2-19).

The laboratory-type variable-speed mixer motor was later replaced by a drill motor which provided more torque.

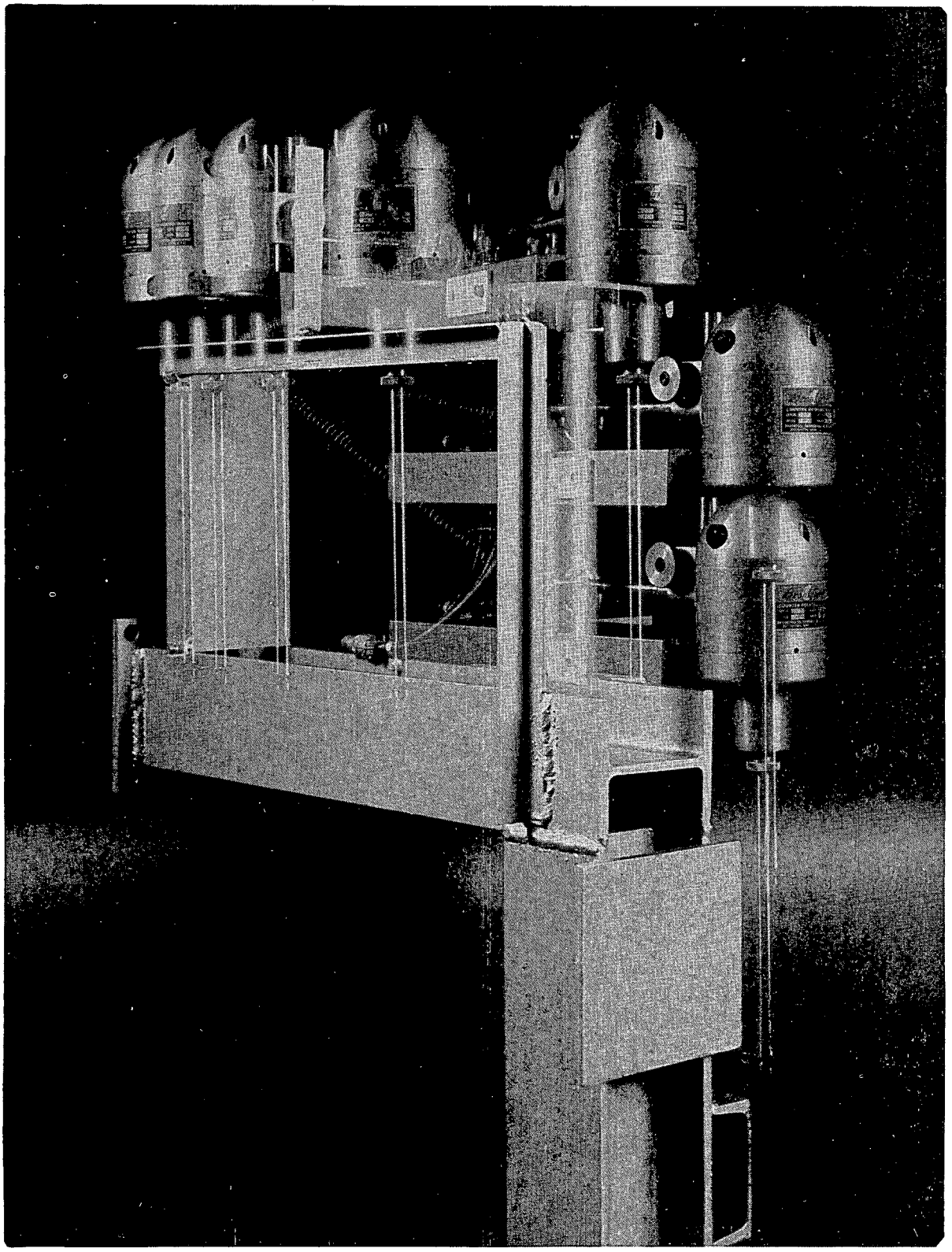
While the spiral mixer worked satisfactorily for miscible combinations, it was felt imperative that extremely fine droplet atomization of a milk-type emulsion was required for nonmiscible combinations. The detonation properties of heterogeneous liquid-liquid explosives was expected to depend heavily on the droplet size. This effect had been previously observed with two-component liquid gun propellants (Reference A3). The best mechanical mixer for preparing emulsions is a counterrotating two-blade high-shear mixer such as the one shown in the right of Figure 2-15. Another remotely operated mixer stand was built to lower and raise this motor to move it to a safe position before firing the detonator. Figure 2-16 shows the mixer in the mixing and in the retracted position prior to installation in the test bunker.

The use of static in-line mixers for continuous flow processes such as field demonstration tests has been considered. However, such mixers are not easily scaled down for small-scale batch tests such as the ones conducted here.

Some explosives which did not undergo detonation with a No. 8 blasting cap were subsequently tested with a booster of 20 g C-4 high explosive wrapped in a glass test tube around the No. 8 cap. C-4 is a plastic-bonded explosive of putty-like consistency, containing 91 percent RDX and 9 percent plasticizer and binder. The explosive force of the booster alone was tested with a pipe filled with 100 g water instead of explosive. As illustrated in Figure 2-17, the destructive force of the booster alone was significant, and it became difficult to differentiate between effects caused by the booster alone and eventual augmentation by the explosive under test when judging the pipe fragment size only. However, witness plate indentations were distinctly different for samples which were considered positive and those which were not.

The open-pipe test method could only be used for ambient temperature tests or tests with fuels which boil far above 505°K (450°F). It was very undesirable to heat the sample close to the boiling

STROBOSCOPIC ILLUMINATION PHOTOGRAPH
OF HIGH-SHEAR MIXER IN INSERTED AND RETRACTED POSITION



WITNESS PLATE INDENTATION/PERFORATION AND PIPE FRAGMENTS OF NEGATIVE AND POSITIVE TEST WITH 20g C-4 BOOSTER

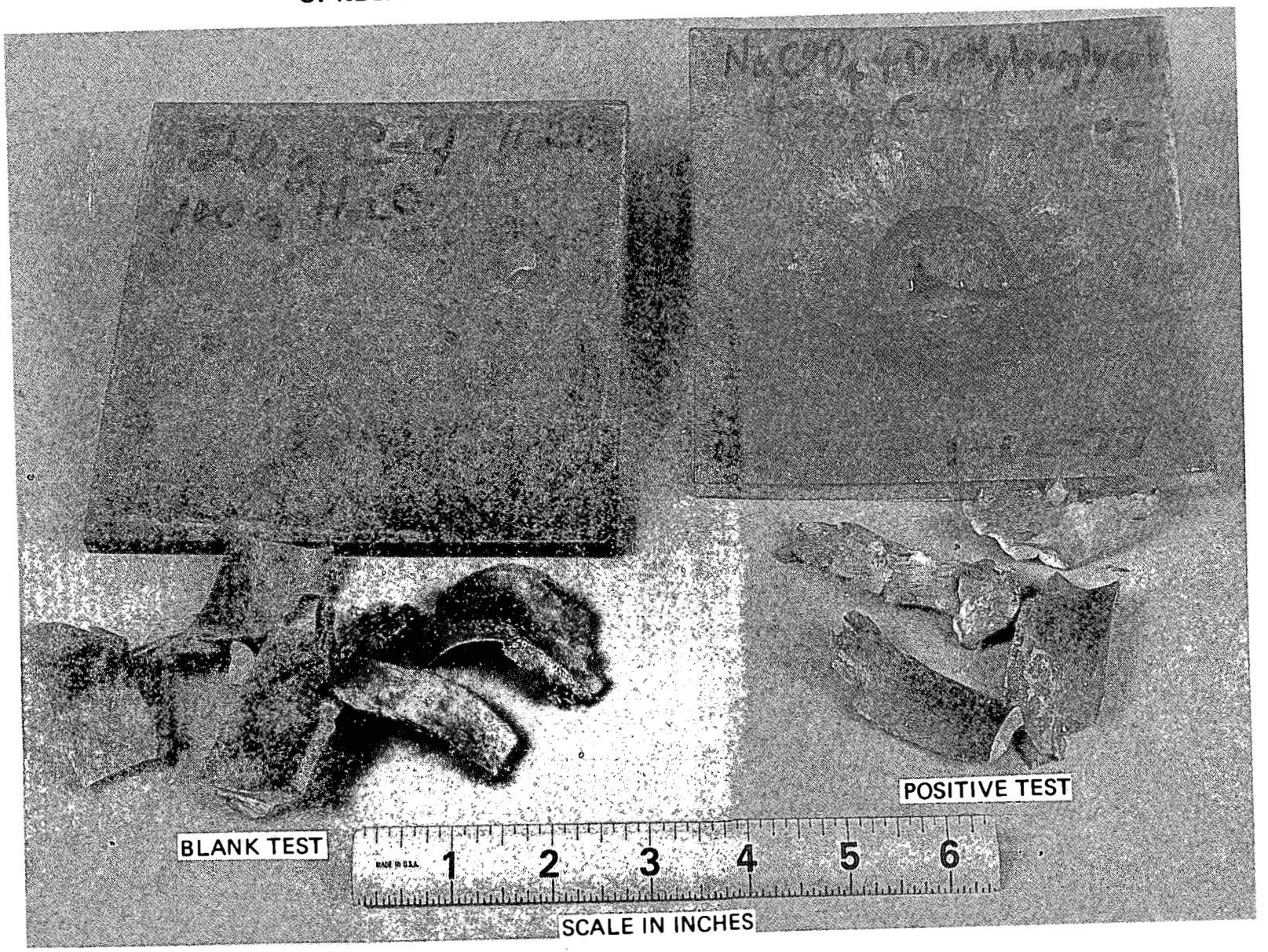


Figure 2-17

point of the fuel because the oxidizer : fuel ratio would change by evaporation, and the mixture might boil over and ignite when it comes into contact with the heating tape. The more volatile mixtures were, therefore, tested in sealed pipe bombs with threaded end caps. The internal diameter and length were close to the open pipe geometry. Sealing the explosive sample in a closed bomb for detonability tests was not a standard test method.

Detonability tests in closed pipe bombs created the following new problems not previously encountered with the open-pipe tests:

1. The handling of an explosive mixture in a closed-pipe bomb constituted a higher hazard potential than mixing of two constituents in an open pipe at ambient temperature.
2. It was very difficult to mix nonmiscible ingredients intimately in a closed pipe without having a mechanical feedthrough for a rotating or oscillating shaft.
3. The detonator could no longer be in intimate contact with the explosive sample unless it was enclosed in the bomb along with the sample. Because only few commercially available detonators could withstand that environment for several hours, an alternate means of initiating the sample had to be sought.
4. The threaded caps on the end of the pipe would attenuate the shock before it impinged on the witness plate, such that open pipe and sealed pipe witness plate indentations were no longer comparable.
5. If a sample failed to detonate on command, the safe disposal of the undetonated remains had to be conducted with extreme caution.
6. It was more difficult to obtain a thermocouple reading of the sample temperature.

The following discussion addresses itself to the problems in this order and corrective action which was taken to solve each problem.

Figure 2-14 shows the three different types of detonability sample holders used during this program. The open-pipe test, shown in the left part of the picture, was limited to combinations with low vapor pressure or temperatures sufficiently below the boiling point. More volatile compounds had to be tested in one of the sealed pipe bombs shown in the center and right. The cast iron pipe bombs were hard to use because the caps were not flat and would not stand level on the witness plate. Also, the cast iron caps were hard to seal by silver soldering or use of Teflon tape. It was, therefore, preferred to use the stainless steel bombs, shown in the right part of the photo, even for noncorrosive samples.

In order to avoid the hazard of handling a live pipe bomb while clamping it in a vise and putting on the threaded cap with a pipe wrench, it was attempted to take advantage of the two-component nature of the explosives under test. The pipe bombs were filled with the oxidizer salt (the more bulky of the two constituents) first, and the fuel was heat sealed in a polyethylene bag placed separately on top of the oxidizer. The polyethylene provided a safety barrier between the oxidizer and the fuel until the sample was heated and the polyethylene would melt. The likelihood of a premature reaction and explosion of the pipe bomb while it was being installed in the shaker was

virtually eliminated by this precaution. In a separate safety test series, polyethylene foil and polyethylene powder were tested with all solid oxidizers in the differential scanning calorimeter, but no exotherms were observed below 570°K (567°F), the upper temperature limit of the instrument. As a result of this test, it may be concluded that polyethylene and oxidizers will not contribute to a premature reaction while the pipe bomb is assembled and heated. This practice of sealing the fuel in a polyethylene bag was later abandoned as a better understanding of the requirements for detonating these mixtures developed, i.e., poorly mixed nitrates and fuel generally presented no hazard. Besides, it was not always certain if the polyethylene bag always ruptured to release the fuel. The threads of the pipe and cap were carefully cleaned of eventually spilled oxidizer and fuel so as not to cause an ignition hazard by friction while the pipe was being closed.

The assembled pipe bombs with heater tape and thermocouples attached were then mounted on the remotely operated shaker apparatus shown in Figure 2-12. A multiple exposure was taken of the apparatus in action to show the shaking/tilting motion of the pipe which was vigorous enough to achieve good mixing of all miscible mixtures. A microswitch was attached to the rocker arm, which operated a signal light to indicate that the pipe bomb was in the upright position prior to firing the shaped charge.

It has been attempted to improve the mixing efficiency of the device during tryouts with water/oil mixtures by including a steel ball in the pipe with the mixture. However, the steel ball had a tendency to hang up in the groove formed by the wider diameter lid which did not screw down all the way to the lip of the pipe. No inside mixing device was used in these sealed pipe tests.

The only commercially available high-temperature detonators, the Du Pont X-637 or X-321 K are not designed to withstand 561°K (550°F) for 24 hours. The caps are only guaranteed for 100 percent fire after 1 hour at 533°K (500°F). It was not known how compatible the materials of the cap are with the various oxidizers and fuels to be tested. The expense of the special blasting caps was prohibitive to the carrying out of an extended compatibility program to verify that the cap can safely be included in the pipe bomb for the entire duration of a 24-hour test. An alternate means of initiating the samples was sought, in which the detonator was not exposed to the high temperature for the same duration as the sample, or not exposed to high temperature at all.

Consideration has been given to installation of a detonator well in the top cap into which the detonator could be inserted remotely immediately prior to firing. However, it may be very difficult to align the well and the cap insertion apparatus. The wall of the well would have to be very thick, otherwise the well might collapse under internal pressure from the sample. The strong wall might attenuate the shock from the cap to a point where reliable high-order initiation cannot be achieved. An alternate mode of initiation had to be sought which would also allow the disposal of samples which failed to detonate.

The preferred alternate approach was the use of shaped charges such as the ones used by the petroleum industry to perforate well casings after a well has been "brought in." Model 17-3204-5, 43-mm (1-11/16-inch) diameter shaped charges containing 13 grams of RDX with a copper cone encased in a glassy shell were obtained from Gearhart-Owen Industries of Fort Worth, Texas.

Normally, they are strung from a long wire and are interconnected by a length of 80 grain/foot Primacord which is used to detonate them. For the purpose of this program, they were used individually. Instead of using Primacord, a dab of approximately 2 g C-4 was placed into the notch provided for the Primacord and a standard No. 8 cap was positioned lengthwise adjacent to it.

A series of initial tests was conducted with the shaped charges in order to obtain a better understanding of their initiating and penetrating power. In one test, three witness plates were stacked on top of each other for a total thickness of 2.9 cm (9/8 inch), and the shaped charge fired from a distance of 1.3 cm. As illustrated in Figure 2-18, the jet penetrated all three plates. Two schedule 40 stainless steel bombs were filled with 100 g water and shaped charges were fired at the pipes both horizontally just beneath the water level and vertically. As illustrated in Figure 2-18, the jet not only penetrated horizontally leaving an entrance and a slightly wider exit hole, but also penetrated vertically through the top lid, 100 g of water, the bottom lid and the 0.95-cm (3/8-inch) witness plate. The horizontal test was also repeated with a mild steel schedule 40 pipe bomb filled with 100 g water. The results were identical to those obtained with the stainless steel bomb.

While it was comparatively easy to measure the temperature of an explosive sample in an open pipe, the measurement of the sample temperature in a closed pipe bomb at high pressure (vapor pressure of fuel and oxidizer) was more difficult. A shielded thermocouple with a stainless steel shield had to be inserted through a pressure-tight Conax fitting into the sample, as illustrated on the right hand of Figure 2-14. The outside thermocouple was attached directly to the pipe in an area where the silicone had been scraped off, and then covered with fiberglass tape.

In those cases where no detonation was observed in the 38-mm (1.5-inch) diameter open pipe in spite of boosting, and where other (theoretical) data indicated that a powerful explosive should be expected, additional testing was conducted in larger diameter (76 mm = 3-inch and 102 mm = 4-inch ID) open pipes made from schedule 40 mild steel pipe. Tests in larger diameter pipes were expected to eliminate the critical diameter problem which may exist with some explosive compositions in the narrower pipe. Because only a small number of large diameter tests was to be conducted, no attempt was made to protect and recover the mixer motor. Instead, a conventional hand drill motor was mounted vertically approximately 30 cm (1 foot) above the pipe (Figure 2-19). The motor was wrapped in a plastic bag to avoid ignition of fuel vapors by the sparks in the motor which was not explosion proof.

The 76-mm ID schedule 40 pipe had a wall thickness of 5 mm. The pipe sections were 0.38 m tall and were directly welded onto a witness plate of the same dimensions as before. A typical test in a large pipe would require ~2,300 g (~5 lbs) of explosive which would fill the pipe to within 5 cm (2 inches) from the rim.

The 24-hour detonation tests incorporated both the examinations of thermal stability and detonability. For reporting coherency, the 24-hour test procedure was included with detonation test procedures/results under the performance tests/performance results section rather than the safety test section.

EFFECTS OF GEARHART-OWEN 17-3204-5 SHAPED CHARGES ON SEALED SAMPLE PIPES AND WITNESS PLATES

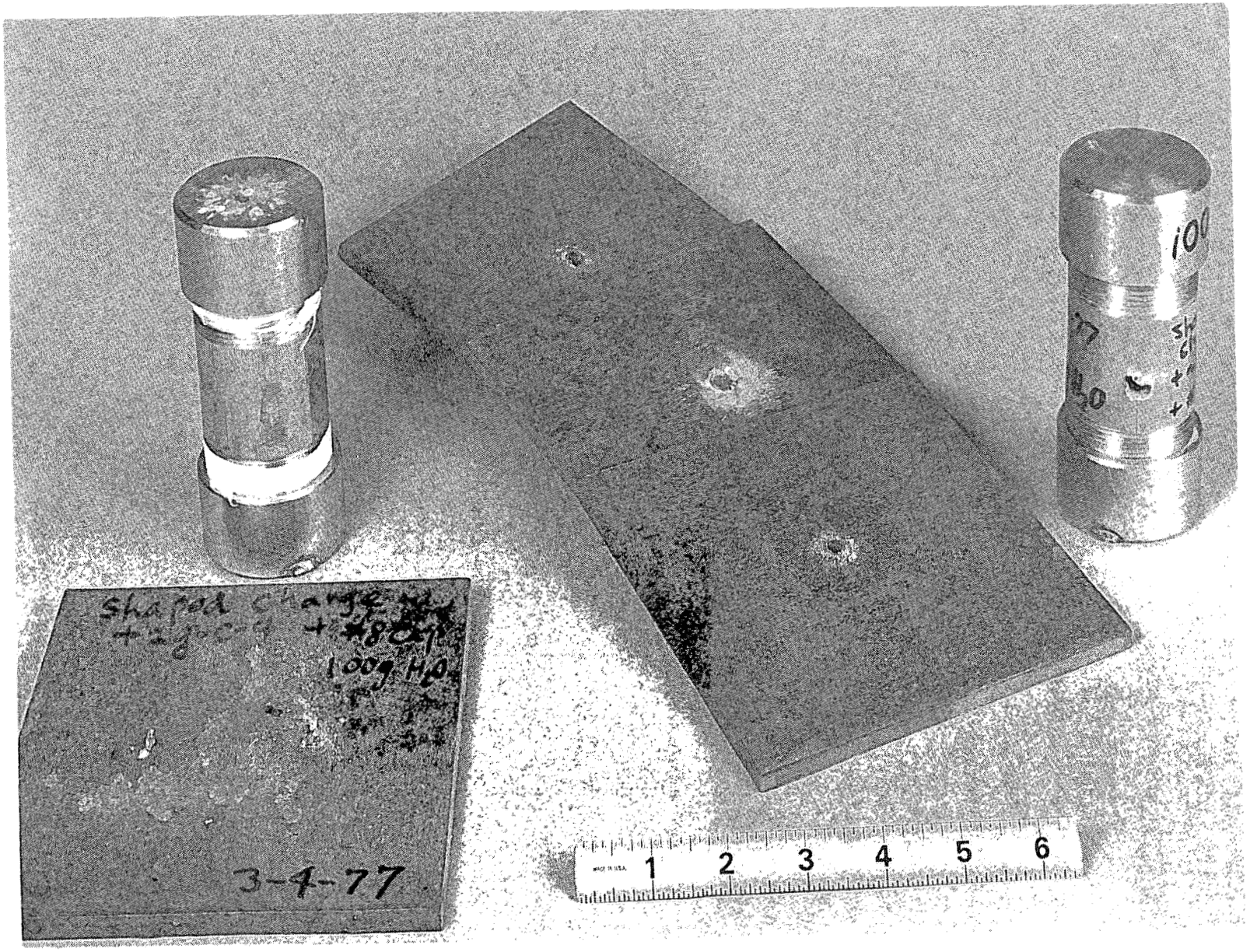


Figure 2-18

76mm DIAMETER DETONABILITY TESTS BEFORE AND AFTER DETONATION

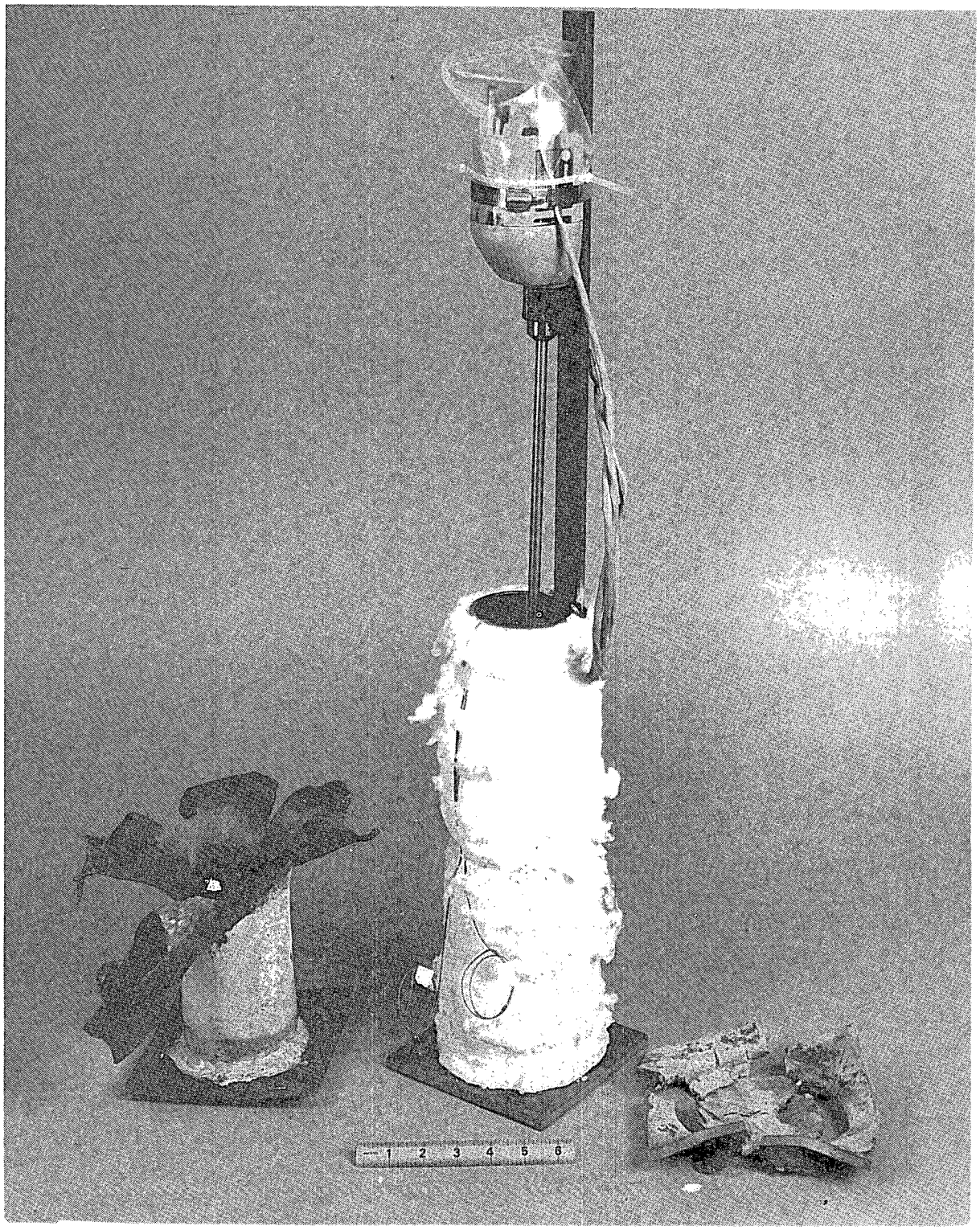


Figure 2-19

The 24-hour detonation tests were designed to find out if the potential candidate explosives remained detonable after being heated for 24 hours at elevated temperature. These tests were probably too severe. In actual field applications, the explosive mixture probably will not be exposed to high temperatures for more than one third of this test period. (Loading a well and detonating the explosive normally should be completed in 4 to 6 hours.)

The method of testing utilized a modification of the sealed-pipe detonation tests. A sealed pipe bomb assembly containing the explosive mixture was again shaken by the mechanical shaker used earlier to promote mixing. The attachment of a shaped charge used for initiation to the setup had to be modified to make sure that the shaped charge could survive for 24 hours without absorbing too much heat from the bomb to be detonated. For this purpose, two rods were attached to the witness plate at a standoff distance from the body of the bomb. The shaped charge could then be taped to the rods, leaving an approximately 5 mm air gap between the shaped charge and the insulation on the body of the bomb. The shake-mixing period was set at 5 minutes during every 30 minutes interval to permit ample mixing, and yet prevent excessive wear and breakage of the shaker. At the end of the 24-hour period, the bomb was brought to the upright position and fired.

2.3.2 High Pressure Detonability Test

The high pressure detonability test was designed to simulate the condition encountered by explosives at the bottom of a well. Typically, in the operation of Petroleum Technology Company with its PTC-4 explosive, the latter initially may experience an applied pressure of approximately 69 bar (1,000 psi). As the explosive fills the well, the explosive at the bottom also experiences hydrostatic pressure in the amount of about 230 bar (3,400 psi) (assumed for 1 mile down and an average density of 1.5 g/cm^3). Thus, a total of 300 bar (4,400 psi) could be exerted on the explosive. PTC's experiences have been a lowering of detonation velocity with increasing pressure. There are cases where explosives become nondetonable when placed under pressure.

The high-pressure detonability test bomb consisted of a flanged cylindrical pressure vessel made from steel (Figures 2-20 and 2-21). The 51-mm ID by 1250-mm length sample volume was able to hold 420 g (lb) of explosive. The flanged lid carried a thermocouple, a pressurization port and a vent port. At the bottom of the vessel there was a nitrogen inlet secured by a check valve, through which nitrogen could be introduced to stir the mixture. The stainless steel tubing which fed the nitrogen from the compressed gas supply/regulator past a blast wall to the test site was secured to the ground every two meters to prevent whiplash effects when the pressure is released by blasting open one end. The high-pressure vessel could be heated externally by an electric heating tape.

At the beginning of the test, 420 g (0.93 lb) of pre-fused explosive was loaded at ambient pressure by repeatedly melting and adding material through one of the gas ports until the desired amount of explosive was contained in the bomb. After connecting it to the nitrogen system at the test site, the explosive was melted remotely and stirred by bubbling nitrogen through the bottom of the tube at a slow rate. After the desired test temperature was attained, the sample was slowly pressurized to 345 bar (5,000 psi) with nitrogen through the top inlet, causing the check valve at the bottom to close. Immediately after reaching the desired pressure, the sample was detonated on command. The short

HIGH PRESSURE DETONABILITY TEST
BOMB DRAWING

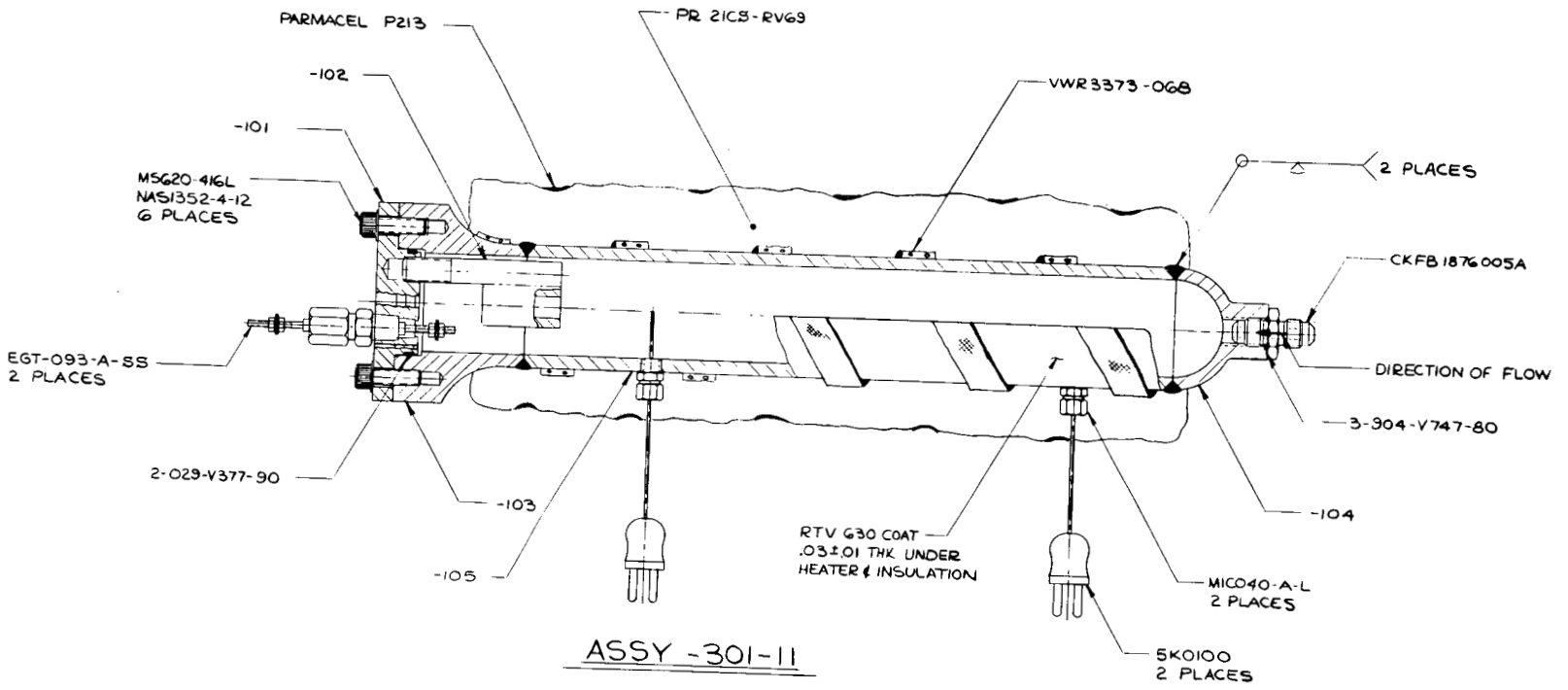


Figure 2-20

HIGH PRESSURE DETONABILITY TEST BOMB

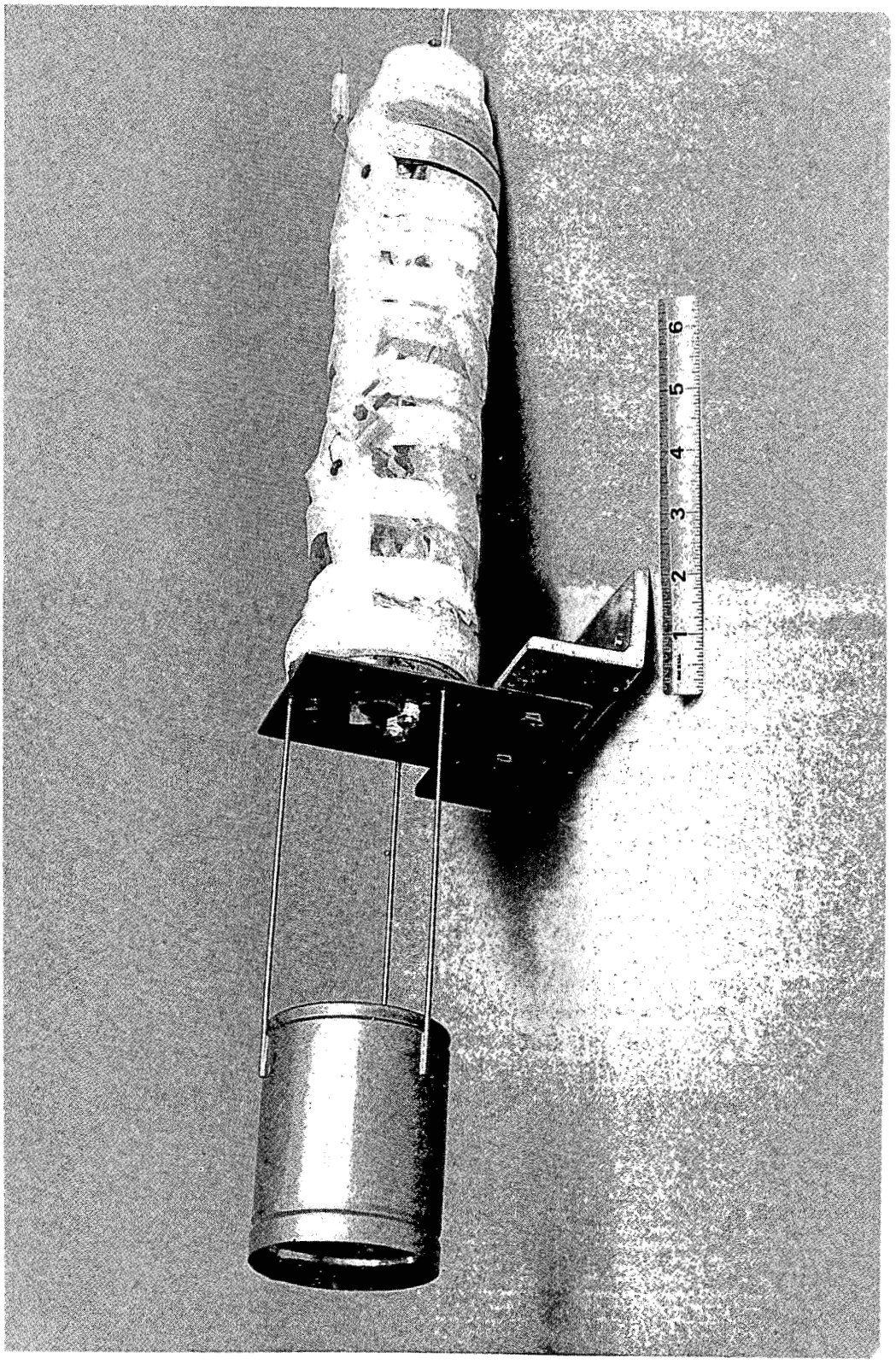


Figure 2-21

interval would not have been sufficient to achieve saturation of the explosive with nitrogen gas. There was concern that saturating the explosive with pressurant gas might alter the results. It was initially considered to pressurize the explosive via a sliding piston separating the explosive from the pressurant gas or hydraulic fluid. However, the combination of temperature and pressure made it very difficult to design a leak-free system. Also, no O-ring material was identified yet which was known to be compatible with the explosive.

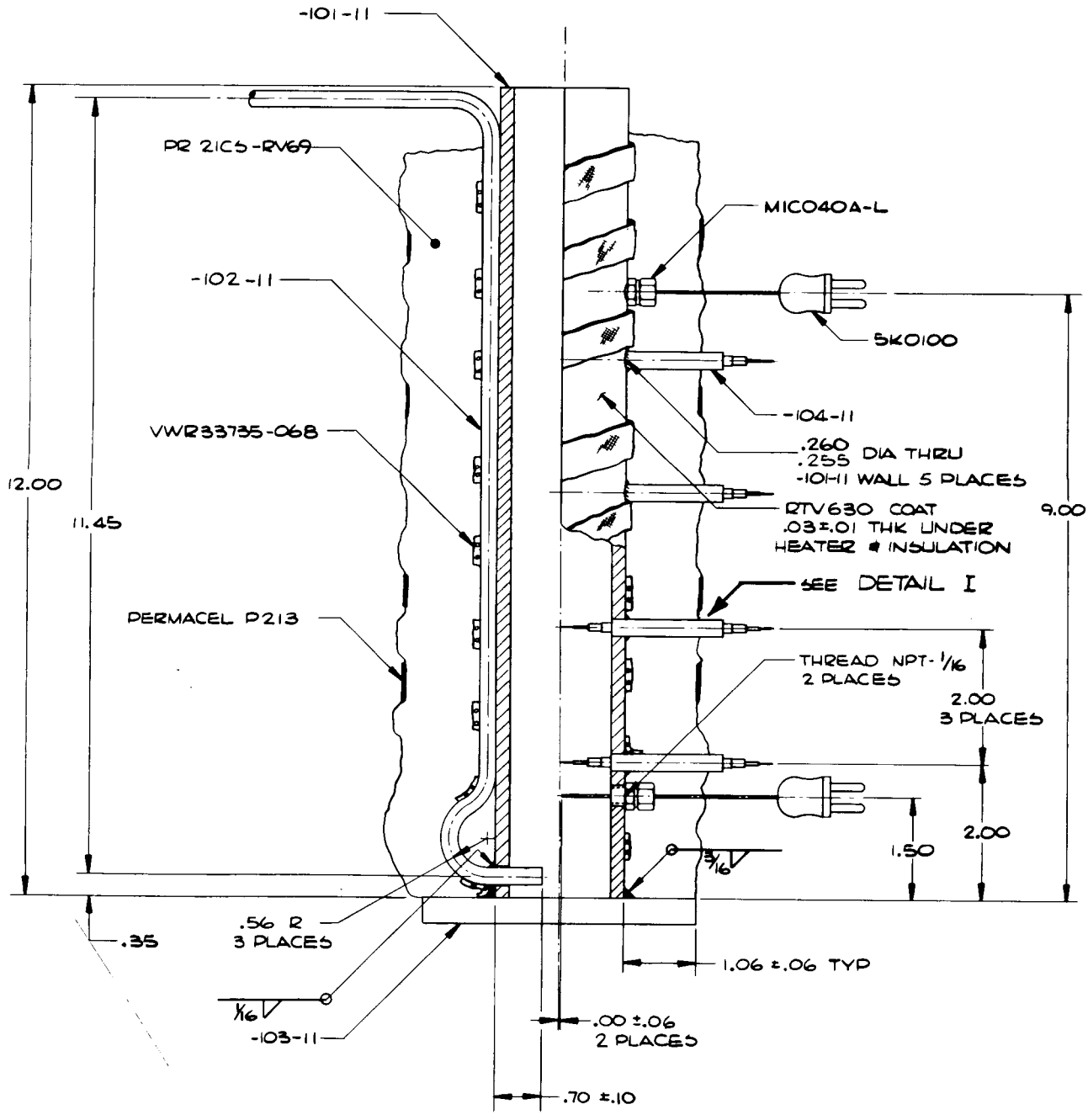
For initiation of the explosive, it was initially planned to use a booster pellet of a high-temperature resistant solid explosive inside the vessel, initiated by a high-temperature blasting cap. However, available high-temperature blasting caps (Du Pont X-321-K and X-637) were not rated for high pressure. Available high-pressure blasting caps (Du Pont E-96 or E-98) were not rated for exposure to high temperatures. The problem was compounded by the inability to obtain TACOT high explosive in bulk or in the manufactured shape of booster pellets. In looking for alternate high explosives, HNS was considered marginal. TATB was selected because it had better temperature resistance, and a sample of TATB was provided by ERDA. However, upon closer examination, it became apparent that the critical diameter of TATB was above the dimensions of the high-pressure test bomb. Therefore, it would have been very difficult to achieve reliable initiation of the sample under test. The problems of internal initiation were unsurmountable within the given time and budget, and it was decided to resort to external initiation which was successfully used in sealed bomb tests at lower pressures.

The 13-g RDX perforating gun-shaped charges were considered too weak to penetrate the high-pressure shell and deposit sufficient energy in the explosive to achieve a high-order ignition. A scaled-up version of a larger shaped charge was made from a 50-mm diameter shaped charge with a copper-lined cone. The charge was filled with 450 g of C-4 and placed at a standoff distance of approximately 100 mm from the top of the bomb. A prior test with an identical shaped charge and a similar steel pipe bomb filled with water had shown that no fragmentation of the pipe occurred, and that the jet was well developed and pointed so that it only left two holes in the top and bottom caps. Any pipe fragmentation which would eventually occur with the explosive test sample must therefore be caused by the detonation of the explosive.

2.3.3 Detonation Velocity Determination Test

The detonation velocity of selected explosives was determined using a detonation velocity test fixture shown in Figures 2-22 and 2-23. The test fixture consisted of a 0.3 m (12 inch) long steel pipe, 37 mm (1.5 inch) inside diameter, 4.75 mm (0.187 inch) wall which was welded to a 9.5 mm thick mild steel witness plate which was 229 by 229 mm. The outer surface of the pipe was electrically insulated with a thin layer of RTV-630 silicone rubber. An electrical heating tape was wrapped around the pipe and was thermally insulated by a layer of Kaowool insulation. Thermocouples were placed at the top and bottom of the pipe with the probes penetrating the wall so the temperature of the explosive could be monitored. Four ionization pins were inserted through the pipe wall at intervals of 76 mm (3 inches). The pins were electrically insulated at the tip by a thin layer (approximately 0.05 mm = 0.002 inch) of RTV-630 silicone rubber. A small diameter tube attached to the outside of the pipe and penetrating the pipe at its base was used to provide a

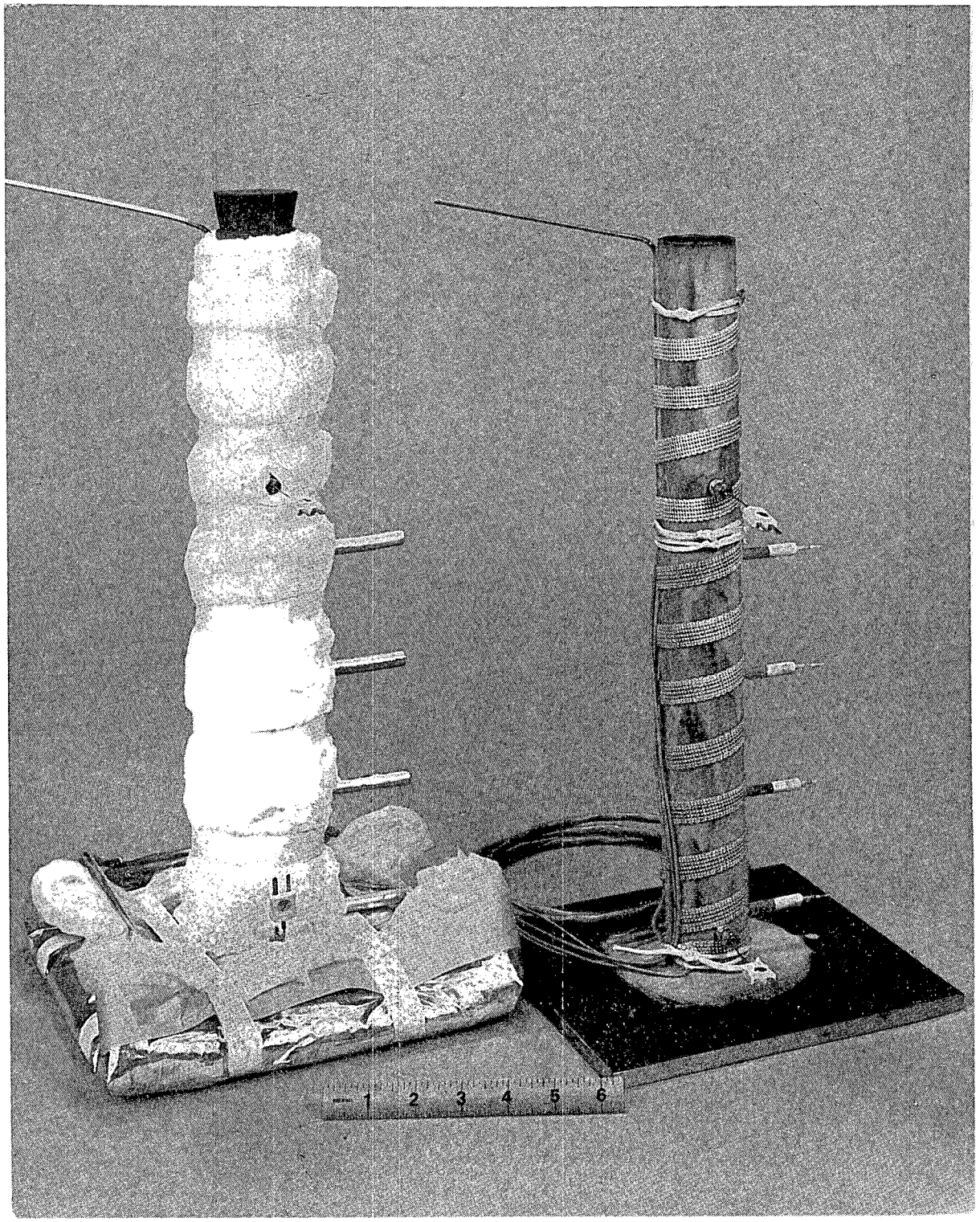
DETONATION VELOCITY TEST FIXTURE DRAWING



—ASSY - 301-11—

Figure 2-22

DETONATION VELOCITY TEST FIXTURES DURING ASSEMBLY



stream of nitrogen gas which mixed the explosive after it was liquified. The pipes were loaded with the solid explosive ingredients, which were then melted to provide maximum packing density as trapped air in the solids was expelled when liquefaction occurred. This operation, done remotely, was carried out a week before the testing took place. Although the explosives tested were detonable after they were melted, they were not detonable when solidified so they were able to be handled directly once they had cooled to room temperature. During the test operation, the solid explosive was melted by means of the heating tape, and then gaseous nitrogen was bubbled through the explosive to ensure that the liquified explosive was thoroughly mixed. The explosive was initiated by remotely inserting a detonator when the proper temperature had been reached. The detonator consisted of 20 grams of C-4 explosive, contained in a 19-mm (0.75-inch) diameter glass test tube, which was initiated by an RP-80 electric detonator.

The detonation velocity was measured by measuring the time it took for the detonation wave to pass between the pins. The ionization pins used to measure the detonations velocity were insulated with RTV-630 silicone rubber. They were connected to electrical capacitors in the control room. Thirty seconds prior to detonating the explosive, the capacitors were charged. They were connected to an electronic time interval meter and a group of raster oscilloscopes to give redundant data. As the conductive plasma of the detonation wave passed each pin, it vaporized the silicone rubber insulation, allowing the capacitor to discharge. The discharge of the capacitor was then recorded by the time interval meter and the raster oscilloscopes (having accuracy of $\pm 0.1\ \mu$ sec and $\pm\ 0.2\ \mu$ sec, respectively). From the data of pin spacing and time interval, the detonation velocity was readily determined. In some tests, the silicone rubber insulation on a pin failed prematurely, and since the molten explosive was quite conductive, it was impossible to charge the capacitor. However, sufficient data points were obtained to provide the detonation velocity of all samples. The test results are discussed in detail in a following section.

Some modification of the ionization pins was found to be necessary after preliminary testing of the first pins made showed them to be too unreliable. Initially, the use of an insulative coating of silicone rubber (Sil Grip SR-573) or of Ryton® polyphenylene sulfide resin was proposed since initial tests showed them to be capable of withstanding both the high temperature and the corrosive effects of the liquified explosive. However, no way was found to apply a thin uniform coating (about 2 mils thick) for either material. Additionally, it was found that the Ryton coating frequently failed to bond where it touched the Teflon insulating layer in the pins; also, there seemed to be more failure to insulate adequately with the Ryton coating. Since RTV-630 silicone rubber had been used previously with good success in insulating other test apparatus exposed to high temperatures, it was tested and found acceptable for electrically insulating the pins after the pins were modified. As shown in the drawing (Figure 2-22), the end of the pins were cut back in successive layers to expose the bare inner wire and then expose each successive insulating and shielding layer. This was found to be unacceptable for applying an insulating coat that would adhere. It was also determined that upon heating the pins, the Teflon layer would expand. Therefore, the following revised process was used to electrically insulate the ionization pins.

First, the pins were cut to the approximate length. Then they were heated at 300°F for 30 minutes to make the Teflon layer expand. Next, one end of the pin was ground flat on a grinding wheel and

the sharp edges were rounded with Emery paper, leaving a slight (1 to 2 mil) protuberance of the inner wire. The outer copper sheath was then sanded with fine Emery paper until all of the varnish and dirt was removed, leaving a clean surface (which was not touched until the silicone rubber was applied). RTV-630 silicone rubber was prepared and diluted 50:50 (by volume) with toluene. The diluted silicone rubber was applied one drop at a time with continuous rotation of the pin to keep a uniform coat. The pin was rotated in a current of warm air supplied from an electric hot air gun to rapidly remove the toluene. After sufficient RTV-630 rubber had been applied, the pins were placed in a 110°C oven for 10 minutes to accelerate the cure of the rubber. The pins were tested to verify the integrity of the coating. One problem was noted, however. The pins did show conductivity sometimes after they had been installed in a test fixture which was subsequently loaded with explosive ingredients (as solids) which were then liquified by heating, then allowed to resolidify. However, in no case did more than one or two pins fail, so measurements were made in all tests.

2.3.4 Thin Film Propagation Test

The critical dimensions below which a detonation of a given explosive no longer propagates at high order can be determined either in circular (cylindrical) or rectangular sample cross sections. In either case, the diameter or the gap width is reduced gradually until the sample ceases to detonate. This can be done in a sequence of several tests with constant diameters (width) or, better yet, in a single test with conical or tapered (wedge-shaped) sample geometries. The stepwise transition between a "self-donor" section above the critical dimension and a test section close to the critical dimension as described in ASTM 2541-66T (Reference A6) is not recommended because reflections from the shoulder may cause a nonuniform shock wave which would aid propagation in the more narrow tube. Likewise, a continuous gradual transition in a wedge is preferred over a stepwise narrowing of gap width.

Several wedge test techniques have been described in the literature (References M1, W4, and R5), but none was directly applicable to the high-temperature explosive. The use of an open tray would have caused excessive losses by evaporation. On the other hand, it was desired to obtain more quantitative data than those obtainable with polished brass wedge walls as witness plates (Reference S10). Therefore, a highly instrumented wedge test was designed which would allow measurement of the detonation velocity as a function of gap width.

The wedge test fixture was designed to determine the detonation velocity of an explosive at high temperature (505°K, 450°F) and ambient pressure in a tapering section of explosive of constantly decreasing width, thereby determining the "critical diameter" which actually was a "critical width" due to the geometry of the device. "Critical" dimensions are those diameters or widths of explosive samples below which an explosive will not sustain high velocity detonation, i.e., the detonation velocity falls below 4,000 m/sec.

Since no reference to previous wedge testing of explosives done at temperatures of 505°K or more could be found, the test fixture was based initially on previous fixtures used to test explosives at ambient temperature and pressure such as those used by Petroleum Technology Corporation. The final test fixture configuration was developed by RRC with some assistance from personnel at

Physics International, another ROCKCOR subsidiary, at whose explosives test site the test was conducted. The design of the wedge test fixture was based on the following requirements and constraints.

In order to determine the critical dimension of any two-component explosives at 505°K or above, it was necessary to provide fairly rapid, uniform heating, and when the explosive was melted, it had to be mixed remotely in such a manner that the mixing device did not interfere with the testing, i.e., if a mechanical stirrer were used it could not be left in the explosive since it could cause distortion of the detonation wave. Also, it was imperative to initiate the explosive with a planar detonation wave so that the resulting detonation wave in the explosive was initiated uniformly, otherwise the data would have limited or little value. That meant that new technology would have to be developed for high temperature initiation if an internally placed detonator were used, or else a stand-off device would have to be fabricated which could be positioned against the wedge fixture remotely just at the moment initiation was desired, so that the conventional explosive used in the detonator would not be heated to its detonation point and cause premature initiation of the detonator. The actual measurement of the detonation wave was to be conducted in the same manner as described in the preceding section on detonation velocity, i.e., ionization pins placed in the sides of the wedge test fixture would be connected to capacitors which would be charged 30 seconds prior to initiation of the explosive. The capacitors would be connected to an electronic time interval meter and a group of raster oscilloscopes which would measure the time at which the capacitor discharged; that would occur when the detonation wave removed the insulation from the ends of the ionization pins.

The wedge test fixture which finally evolved, consisted of a thin, long wedge of steel (containing the explosive) which was mounted on a holding fixture so that the wedge could be elevated before heating of the explosive commenced, and then remotely lowered to a horizontal position after the explosive was liquified and mixed (Figure 2-24). The explosive was initiated by use of an externally mounted initiator-booster charge contained in a remotely actuated sliding device (Drawing SK-6012, Figure 2-25).

The wedge containing the explosive tapered from 40 mm (1.6 inch) to 5 mm (0.2 inch) over a length of 1.219 m (48 inches). Heating was provided by electrical heaters, as shown in Figure 2-24, which also shows the positions and spacings of the ionization pins used to measure the passage of the detonation wave. The wedge was insulated with a layer of Kaowool insulation. Thermocouples were used to remotely monitor the temperature of the explosive. Mixing of the explosive was done remotely by means of an electric drill motor with an attached mixing blade. The trigger on the drill motor was taped in the "on" position so that stirring could be accomplished by supplying power, when desired, from a control room.

The sliding device (Figure 2-25) contained a wedge-shaped booster charge of 230 grams of C-4 explosive which was shaped on the bottom of the wedge to conform to the contour of the wide end of the wedge (the end of the wedge enclosed by a piece of 5-mil shim stock – see Figure 2-24). An RP-80 detonator was inserted at the top of the C-4 charge and used to initiate the explosive. These rather elaborate initiation conditions were necessary in order to ensure that a uniform plane wave initiation occurred so that accurate detonation velocity measurements could be obtained.

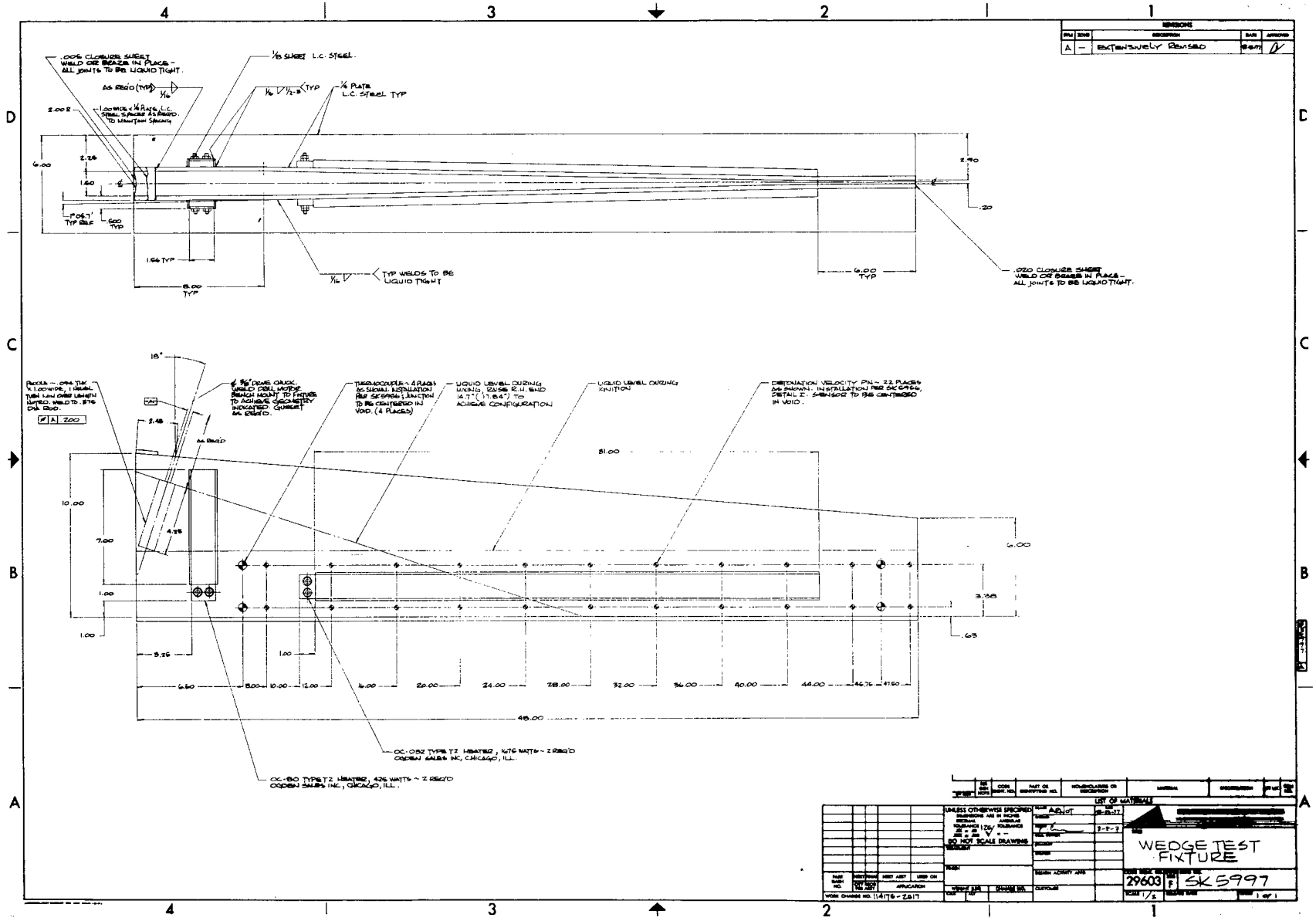

WEDGE TEST FIXTURE
SK5997
29603
.020 CLOSURE SHEET WELD OR BRAZE IN PLACE – ALL JOINTS TO BE LIQUID TIGHT.
1/8 SHEET L.C. STEEL.
1/4 PLATE L.C. STEEL TYP
TYP WELDS TO BE LIQUID TIGHT
.094 PLATE
OC-80 TYPE T2 HEATER, 425 WATTS ~ 2 REQ'D OGDEN SALES INC, CHICAGO, ILL.
OC-082 TYPE T2 HEATED, 475 WATTS ~ 2 REQ'D OGDEN SALES INC, CHICAGO, ILL.
LIQUID LEVEL DURING IGNITION
DETONATION VELOCITY PIN ~ 22 PLACES AS SHOWN. INSTALLATION PER DRAWING, DETAIL E. SENSOR TO BE CENTERED IN VOID.
81.00
48.00

Figure 2-24

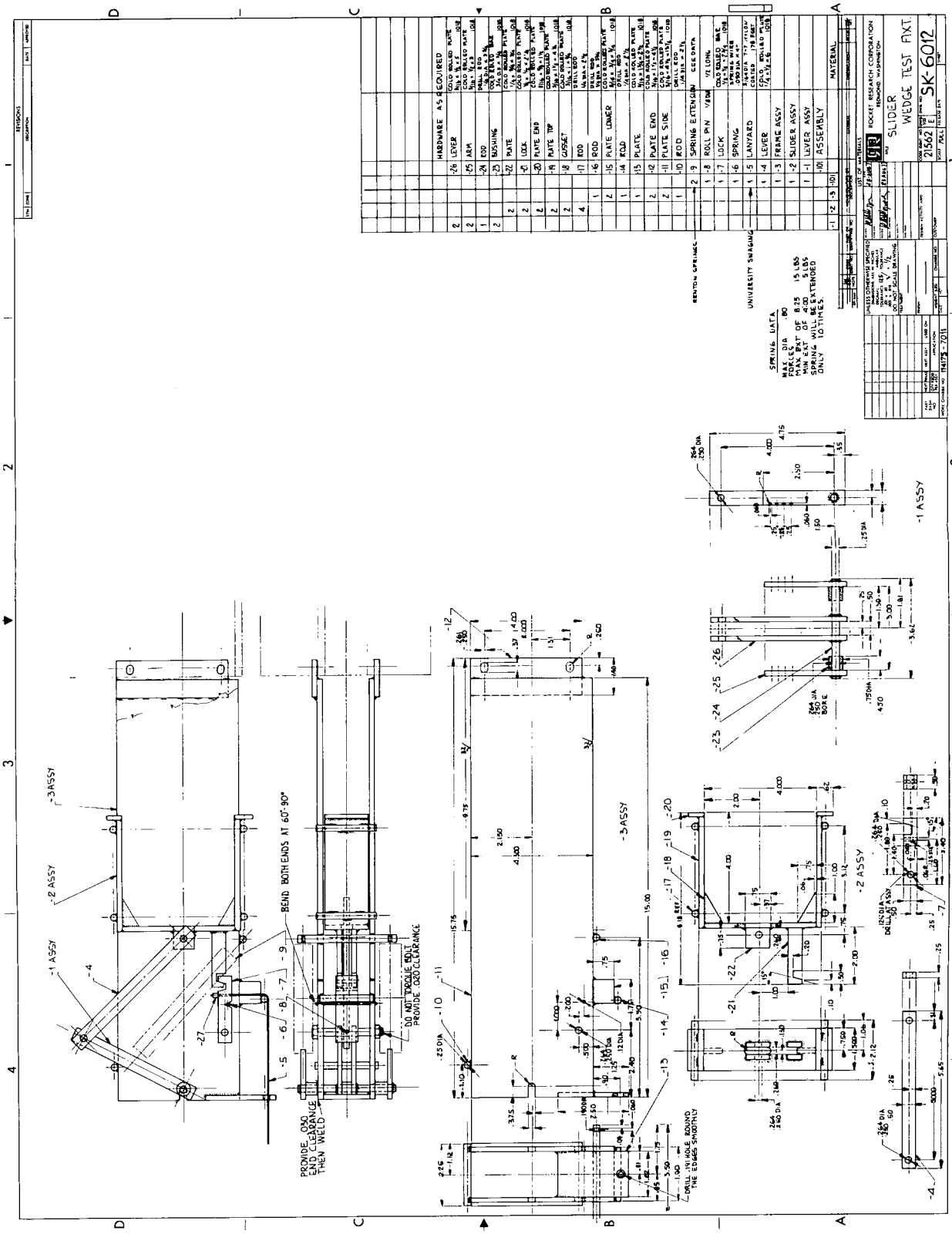

SLIDER
WEDGE TEST FIXT.
SK-6012
ROCKET RESEARCH CORPORATION
REDMOND WASHINGTON
21562
UNIVERSITY SWAGING
BEND BOTH ENDS AT 60°-90°
PROVIDE .030 END CLEARANCE THEN WELD
DO NOT WELD HERE PROVIDE .060 CLEARANCE
DRILL HOLE ROUND THE EDGES SMOOTHLY
-1 ASSY
-2 ASSY
-3 ASSY

Figure 2-25

Initially, an internally positioned high-temperature detonator using TATB (1, 3, 5-triamino-2,4,6-trinitrobenzene) was proposed, since TATB can withstand the temperature the explosive was to be subjected to. However, further consultation with persons familiar with the use of TATB and the obtaining of several documents describing the use of TATB as an initiator made it seem unlikely that its use was warranted without full-scale evaluation. This was not possible, due to financial and schedule restrictions, so the use of C-4 positioned externally was decided upon.

The ionization pins were fabricated as described in the preceding section covering the detonation velocity testing.

The wedge test fixture was supported by a bracket (see Figure 2-26). The fixture was loaded with explosive before testing by melting the two components and allowing them to solidify in the fixture with it in the elevated position (done remotely). Since the solidified explosive is not readily detonable, if at all detonable, in the solid state at room temperature, it was safe to manually handle the wedge test fixture already loaded. The solidified explosive had been tested previously at ambient temperature, using a number eight blasting cap as initiator with a 20 g booster charge of C-4 and the results were negative. The wedge test fixture was raised to a tilted position prior to testing with the stirrer in place so that when the explosive liquified, it could be mixed remotely by applying power to the drill motor used to turn the mixing blade. By having the wedge fixture in a raised position, the liquid explosive was contained at the wide end of the wedge at a depth of about 8 inches, so it could be readily mixed. After mixing of the explosive, the wedge fixture was lowered to a horizontal position remotely by means of a solenoid switch which released a pin holding the positioning rod. This allowed the weight of the fixture to drop it into the horizontal position. Two standard automotive shock absorber units were used to control the rate of descent of the fixture. When the wedge fixture was in the horizontal position, the explosive level was below the tip of the stirring blade, which eliminated any interference of the blade with the detonation wave.

The ionization pins were connected in a similar manner as those in the detonation velocity test described previously, i.e., they were connected to capacitors which were charged 30 seconds prior to initiation of the detonation. The capacitors were connected to an electronic time interval meter and a group of raster oscilloscopes which simultaneously recorded the discharge of the capacitors (caused by the passage of the detonation wave which stripped the insulation from the ionization pins).

2.4 PHYSICAL PROPERTIES DETERMINATION METHODS

In order to better characterize the candidate explosive and its oxidizer and fuel components, a number of physical properties were determined. These included melting point, solubility, viscosity, density, vapor pressure, and electrical conductivity. While the oxidizer and fuel components were fairly safe to handle, their combined explosive mixture had to be treated with caution. As the obtaining of physical properties usually requires close handling of the test substance, it was often difficult to develop a safe method to make the necessary measurements. Attempts were made to scale down to the minimal amount of materials needed for each determination. Also, whenever possible, the determinations were conducted behind a barrier. In one instance, an instrument was

WEDGE TEST FIXTURE DURING ASSEMBLY

Figure 2-26

constructed (for conductivity measurement) to accommodate the small size of the test sample. In some cases, accuracy was sacrificed for the sake of safety. For example, the accuracy of both density and conductivity measurements could probably be improved if larger samples were used. The physical properties measured to date are only preliminary data.

2.4.1 Melting Point Determinations

Melting point determinations were performed using the same setup as that for screening tests. The test sample was heated in a 10-mm by 75-mm test tube by a transparent furnace (described earlier). The melting temperatures were obtained using a stainless steel sheathed thermocouple probe inserted into the sample, which also served to agitate the sample.

2.4.2 Solubility Determinations

The solubilities in water were measured between ambient temperature and 333°K (60°C). For the candidate explosive mixture, separate components totaling 50 g were placed together in a beaker. Distilled water was added through a buret. Stirring was achieved with a magnetic stirring bar. Usually three runs of the same substance were made to obtain the final results.

2.4.3 Viscosity Determinations

The usual Ostwald viscometer for liquids is awkward for the present task. Considerable difficulties would be encountered in attempting to transfer melts into capillary size openings at temperatures above 406°K. The most convenient method appeared to be using the Brookfield viscometer, which measures viscosity according to the spinning rate of a spindle immersed in the sample. This was the method of choice here.

Both the oxidizer and the fuel component of the candidate explosive have low viscosities (close to water) at the temperature range of interest. This required the use of the largest spindle for the instrument, which, in turn, necessitated the use of large test samples, in the order of 300 g to 500 g. As the operation of the Brookfield viscometer requires direct handling of the switches on the instrument, it was deemed potentially too hazardous to measure one pound of the mixed explosive with it unless a remote control could be developed. An alternative method was not available at the time of this work. It is hoped, instead, that a qualitative estimate of its viscosity can be derived from observing the viscosity values of its components, assuming additive behavior.

2.4.4 Density Determinations

Density determinations of the candidate explosive and its components were carried out in graduated test rubes made from buret sections. The graduated test tube containing the sample was heated in the same transparent tube furnace used for screening tests. Temperatures of the melt were taken with a stainless steel sheathed thermocouple probe. It was raised from the melt prior to reading the volume of the sample. The calibration of the buret scale was not corrected for the increase in temperature.

2.4.5 Vapor Pressure Determinations

It was difficult to determine the vapor pressure of the mixed explosive or its fuel components at temperatures beyond 505°K (450°F) because of incipient decomposition. An experiment was carried out by heating a sample mixture of the candidate explosive in a bomblet. The pressure rise was monitored by a Bourdon gauge attached to the bomblet. The mixture was heated to 561°K (550°F) at an average rate of 1.2 °K/min. The pressure change or decomposition rate was relatively slow, up to 505°K (450°F), but became quite rapid afterwards. Results of this test will be discussed in paragraph 4.4.5.

When a sample of the explosive ingredients is melted down in a test tube for the first time, one can usually see gassing or bubbling beginning at about 472°K (390°F). However, no color change is associated with this gassing. This gassing may be due to the moisture present, as two of the ingredients of the explosive $(NaKCa)NO_3$ and acetamide, are known to be quite hygroscopic. Absorption of water is inevitable during normal handling.

If one were to disregard for a moment the decomposition and the interference by absorbed moisture, it is possible to estimate the minimal vapor pressure of the explosive mixture, $P_{mixture}$, by adding partial pressures of the ingredients:

$$P_{mixture} = P_{(NaKCa)NO_3} + P_{GuNO_3} + P_{acNH_2} \text{ where } P_x = \text{partial pressure of x}$$

At temperatures up to 505°K (450°F), it is reasonable to assume that $P_{(NaKCa)NO_3}$ and P_{GuNO_3} are much less than P_{AcNH_2}. Therefore,

$$P_{mixture} \cong P_{AcNH_2} \cong \frac{n_{AcNH_2}}{n_{NaNo_3} + n_{KNO_3} + n_{Ca(NO_3)_2} + n_{GuNO_3} + n_{AcNH_2}} P^o_{AcNH_2}$$

where:

n_x = number of moles of x

P_x^o = vapor pressure of pure x.

2.4.6 Conductivity Determinations

In keeping with using small samples for physical properties determination, conductivity measurements were obtained with 2 g samples in 10 mm by 75 mm test tubes. Again the transparent heater was used to melt the solids.

A conductivity cell had to be constructed to fit in the 10 mm by 75 mm test tube. Two pieces of nickel wire about 12 cm long each were gold plated at one end, covering approximately 2 cm. The wires were then inserted through capillary glass tubes (the ones used for capillary melting point determinations, but with both ends open) so that only 1 to 2 mm of the gold plated ends were exposed. The air space between the wires and the capillary tubes was filled with RTV-630 rubber so as to hold the wires stationary. The two sheathed wires were then taped parallel together, but

keeping the gold plated ends approximately 1 cm apart. Finally, another piece of glass tubing was fitted over the two sheathed wires to protect the gold plated ends. Platinum black was then deposited on the exposed gold plated ends. The completed conductivity cell was used in conjuction with the YSI Model 31 Conductivity Bridge Meter. The cell constant was determined at 1 kHz using potassium chloride solutions with known conductivity.

3.0 CANDIDATE EXPLOSIVE SELECTION

3.1 OXIDIZER SELECTION

The following criteria were applied to the selection of oxidizers for the high-temperature explosive:

- High useful oxygen content
- Not friction sensitive in mixture with organic compounds
- Good thermal stability
- Low melting point
- Low vapor pressure
- Readily available/low cost
- High density
- Noncorrosive
- Low toxicity

Except for the first two criteria, the same criteria also apply to the selection of fuels discussed in the subsequent chapter. The useful oxygen content of oxidizers differs from the total oxygen content by the amount of oxygen which is needed to satisfy the oxygen demand of the cation, carbon or hydrogen in forming a metal oxide, carbon monoxide, carbon dioxide, or water. For instance, the total oxygen content of sodium nitrate is 56.4% by weight, but the useful oxygen content is only 47.1% by weight. A major decision in the selection of oxidizers is the question of whether or not inorganic or organic oxidizers shall be used.

Special care must be taken to avoid oxidizers which would decompose prematurely under geothermal downhole conditions. Compounds with positive heats of formation such as tetranitromethane or hexanitroethane are automatically suspect of exothermic decomposition, possibly explosive decomposition. While it is very desirable to have an explosive mixture downhole with a very high heat of explosion, the handling above ground of large quantities of oxidizer with a positive heat of formation constitutes an unnecessary risk.

There are only few organic compounds such as tetranitromethane (TNM) or hexanitroethane which have an oxygen balance of greater than one; i.e., they have excess oxygen beyond that required to oxidize all carbon to carbon dioxide. Theoretically, these oxidizers together with fuels could be used as two-component explosives, and there are several patents proposing such mixtures as explosives or propellants (References T2, L1, F1). However, these compounds are not thermally stable and may detonate by themselves. Mixtures of TNM with organic fuels are very shock sensitive (Reference T1). No further work has been conducted with organic oxidizers, and all oxidizer evaluation was subsequently concentrated on inorganic oxidizers.

Several of the more exotic oxidizers which were considered in the proposal, such as the fluorinated compounds and perchloric acid, were eliminated already early in the program for reasons of

practicality. While a marginal heat release can be expected from the interaction of weakly oxidizing materials such as ammonium sulfate, ammonium borate, ammonium phosphate or ammonium tetrafluoroborate with the strongly reducing compound hydrazine, these combinations were not pursued any further because hydrazine is not thermally sufficiently stable to satisfy the geothermal temperature requirements.

Chlorates have been eliminated from further consideration because their mixtures with organic compounds are very friction and shock sensitive. Nitrites are generally inferior to nitrates because they have a lower useful oxygen content. However, they are useful additives in lowering the melting point of nitrates without introducing new elements. Furthermore, the presence of nitrites must always be expected after nitrates have been heated to elevated temperatures for longer times.

After evaluating a wide range of oxidizers, inorganic nitrites, nitrates and perchlorates evolved as the most promising candidates for the high temperature explosive. A summary of physical properties of nitrites, nitrates and perchlorates has been compiled in Table 3-1 in the order of decreasing useful oxygen content at ambient temperature. In addition to the useful oxygen content based on unit weight, the useful oxygen content per unit volume is important. It is listed at ambient as well as higher temperatures for the solid and molten salts. It affects the density, detonation pressure, and detonation velocity of the formulated explosives. Some of the salts form well-defined hydrates with water of crystallization. Water will dilute the explosive and is generally undesirable, but may be useful in lowering the melting point of the mixture.

Several oxidizers were tested as their hydrates rather than the anhydrous salt. This was done because the oxidizer was more readily available as the hydrate and because some oxidizers may decompose and hydrolyze while attempting to remove the last molecules of water.

If a single compound oxidizer cannot be found which has the desirable chemical and physical properties, the next step is to look for mixtures of oxidizers. The most important physical property of binary or ternary mixtures of oxidizers is the melting point. The melting point of mixtures is always lower than that of the lowest melting pure constituent. The lowest melting mixture is called a eutectic mixture. The point in a phase diagram where the melting point is at a minimum is called a eutectic point. In search for low melting oxidizers, a significant amount of study was required on eutectic mixtures and phase diagrams.

Inorganic nitrates and perchlorates are likely candidates for oxidizers in a two-component high temperature explosive. Preliminary testing had indicated good compatibility with some of the candidate fuels. The ternary sodium nitrate/sodium nitrite/potassium nitrate eutectic had been chosen initially because it was readily available (heat transfer salt) and its melting point was known. However, the composition of this ternary mixture was not selected by the companies now selling it with an explosive application in mind.

Table 3-1
PHYSICAL PROPERTIES OF INORGANIC OXIDIZERS

Compound	Formula	Molecular Weight	Melting Point °K	Temp. for Density °K	Density g/cm³	Useful Oxygen % by Wt.	Useful Oxygen g/cm³	Heat of Formation at 298°K	
								kcal/mol	kJ/mol
Nitric acid (100%)	HNO_3	63.013	231	298	L* 1.5027	63.48	0.954	-41.40	-173.2
Lithium nitrate	$LiNO_3$	68.944	537	293 631.6 882.5	S* 2.388 L 1.723 1.586	58.02	1.385 1.000 0.920	-115.3	-482.4
Lithium perchlorate	$LiClO_4$	106.390	509	293	S 2.428	60.15	1.460	-90.89	-380.3
Calcium perchlorate	$Ca(ClO_4)_2$	238.98	543	293	S 2.651	53.56	1.420	-178.0	-744.0
Sodium perchlorate	$NaClO_4$	122.44	755 (d)	298	S 2.536	52.27	1.326	-91.48	-382.7
Calcium nitrate	$Ca(NO_3)_2$	164.09	834	291	S 2.651	53.56	1.420	-178.0	-744.0
Sodium nitrate	$NaNO_3$	84.995	580	293 594.6 1011.4	S 2.261 L 1.900 L 1.620	47.06	1.064 0.894 0.762	-101.5	-424.7
Nitric acid (68%)	$HNO_3 \cdot H_2O$			293	L 1.41	43.17	0.609	–	–
Potassium perchlorate	$KClO_4$	138.55	883	283	S 2.55	40.42	1.018	-103.6	-433.0
Potassium nitrate	KNO_3	101.11	607	293 653.1 1044.7	S 2.10 L 1.837 1.537	39.6	0.832 0.727 0.609	-117.7	-492.0
Sodium nitrite	$NaNO_2$	68.995	544	273	S 2.168	34.78		-85.9	-359.4
Calcium nitrate tetrahydrate	$Ca(NO_3)_2 \cdot 4H_2O$	236.15	315.8	293	S 1.896	33.87	0.642	-509.37	-2131
Ammonium perchlorate	NH_4ClO_4	117.49	dec.	293	S 1.95	34.04	0.664	-70.74	-296.0
Ammonium nitrate	NH_4NO_3	80.043	442.8	298	S 1.725	19.99	0.345	-87.93	-367.9

* L = Liquid S = Solid

3.1.1 Nitrate Oxidizers

Although most inorganic nitrates, in particular those of the alkali metals, have satisfactory thermal stability, it must not be overlooked that many nitrates when heated beyond their melting points will decompose according to:

$$M\,NO_3 \longrightarrow MNO_2 + 1/2\,O_2$$

This is an endothermic process and is reversible; i.e., nitrite melts may autoxidize when exposed to air for very long times; however, this condition would not occur during use of nitrites as a high-temperature explosive ingredient. For long-term use, such as in heat treatment vats for metallurgical applications, use of an equilibrium mixture of nitrates and nitrites is preferred. Such mixtures, such as the ternary eutectic of 40% sodium nitrite, 7% sodium nitrate and 53% potassium nitrate are widely used under the designation "heat treatment salt" (HTS). The salt mixture is available from du Pont under the trade name Hitec® and from Croton Chemicals under the trade name U-Tec-Tic®.

In discussing nitrate oxidizers, hydrogen nitrate (i.e., nitric acid) is discussed first in accordance with the organization scheme derived from the periodic table of the elements. The fact that nitric acid is dicussed first does not necessarily imply that is is considered first candidate among the many oxidizers to be discussed. The sequence in this part of the report does not necessarily constitute a ranking. Oxidizers and explosive combinations therewith will not be ranked until paragraph 3.5 later in this report.

3.1.1.1 Discussion of Individual Inorganic Nitrates

The vapor pressure of nitric acid can be lowered by dissolving nitrates in it. Many nitrates form well-defined solvates with nitric acid as the solvate. Binary and ternary systems with nitric acid will be discussed in paragraph 3.1.1.2.

Physical properties of candidate nitrates have already been listed in Table 3-1. Lithium nitrate has the highest useful oxygen content of all nitrate oxidizers under evaluation. However, lithium minerals are not in abundant supply, and the price of lithium nitrate will remain very high. The second and third best nitrate oxidizers are calcium and sodium nitrate with very similar useful oxygen concentrations. Both nitrates are readily available, with sodium nitrate being a naturally occurring mineral (Chile saltpeter). Both nitrates are widely used as fertilizer. Typical Chilean recrystallized sodium nitrate is 98.5% pure with major contaminants being sodium chloride, sodium sulfate, potassium nitrate, and magnesium nitrate. None of these contaminants is expected to interfere with the use of Chile grade sodium nitrate for HITEX applications.

To select an explosive combination with maxium thermal stability, the reactions which cause premature decomposition of the mixture, as well as those leading to the decomposition of the ingredients by themselves, must be known. Numerous publications have been devoted to the decomposition of nitrates or perchlorates. A few references could also be found which dealt with the decomposition of mixtures of nitrates and perchlorates.

The decomposition of Chile saltpeter (mostly sodium nitrate) in the presence of ferric oxide has at one time been investigated as a source of nitric oxide for the production of nitric acid. While the decomposition of sodium nitrate for that application may be quite desirable, it is very unwanted for high-temperature explosive applications.

A thermogravimetric study of the decomposition of sodium nitrate by CASES (Reference C1) using a heating rate of 2.5°/minute in an argon or nitrogen atmosphere showed that the sample began to lose weight at 800°K, and decomposition was complete at 1,173°K. This temperature is well above the upper operating temperature of a geothermal explosive. If sodium nitrate was heated to 973°K, the weight loss was much faster in an argon atmosphere than in oxygen. The presence of oxygen retards the decomposition of sodium nitrate, but does not completely prevent it. Sodium nitrite is formed as an intermediate product, but ultimately it decomposes also.

A similar test with sodium nitrite showed that under argon gas, the decomposition began at 870°K and was complete at 1,170°K, approximately 1.5 hours after reaching the temperature maximum. Sodium nitrate is formed as an intermediate initially, but disappears again as the decomposition progresses. The ultimate product of decomposition is sodium oxide. If the test is repeated under oxygen, nitrite begins to become oxidized at 970°K, but there is an induction time of several hours before oxidation begins.

If ferric oxide is added to sodium nitrate, the gaseous products are predominantly nitrogen oxides instead of nitrogen and oxygen; and decomposition commences at 670°K instead of 870°K (Reference C2). Aluminum oxide also lowered the threshold of decomposition to below 670°K. Ferric oxide and aluminum oxide contamination in HITEX combinations must therefore be avoided because they may lead to premature decomposition.

Calcium nitrate is usually supplied as the tetrahydrate which melts at 315.8°K with partial loss of water. Heating the melt to 420°K for 3 hours will give the anhydrous calcium nitrate, melting at 834°K. Partial decomposition by hydrolysis was suspected during drying. However, no nitric acid could be detected in the vapor space above the salt with a moist pH paper. The anhydrous calcium nitrate is very hygroscopic and has to be stored in a tightly sealed container until used. Calcium nitrate is the most hygroscopic nitrate in the group of sodium, potassium and calcium nitrate and imparts this property also to ternary eutectic nitrates made therefrom.

Ammonium nitrate contamination in fertilizer grade calcium nitrate severely reduced the usefulness of this otherwise very attractive oxidizer. Commercial fertilizer grade calcium nitrate contains 15.5% total nitrogen, 1.05% of which is contained as ammonium ion. This composition corresponds to 78.5% calcium nitrate and 6.0% ammonium nitrate. One sample (Norsk Hydro A.S.) was also analyzed for metal contamination and was found to contain less than 0.5 ppm iron, cobalt, nickel, chromium or manganese (below detectability limit) which might catalyze decomposition of ammonium nitrate if present in detectable amounts. On the DSC, the fertilizer grade calcium nitrate showed endotherms at 364°K and 524°K and an exotherm at 472°K, which is attributed to the decomposition of ammonium nitrate.

Ammonium salts such as ammonium nitrate and ammonium perchlorate have been included in Table 3-1, and some limited testing has been conducted with these oxidizers. Ammonium salts are of interest as oxidizers because they are readily available, are widely used in current explosives (PTC-4, ANFO) and do not leave solid oxide residues. However, most ammonium salts decompose prematurely at the temperatures encountered in geothermal wells. There were some references in the literature that ammonium perchlorate can be stabilized by certain additives (Reference M2). However, the stabilization is only marginal and not sufficient to raise the useful regime for this oxidizer to the geothermal temperature niveau. Salts of hydroxylamine, hydrazine, nitrosyl or nitronium (nitryl) have also been considered as oxidizers, but are generally too unstable to be of any use in the higher temperature environment.

Ammonium nitrate would be a very attractive high-temperature explosive ingredient because it is readily available at low cost in large quantities, and it is already extensively used in explosives with fuel oil (ANFO). However, pure or prilled ammonium nitrate decomposes at temperatures below the lower useful limit of geothermal explosives (477°K = 400°F). Its rate of decomposition may be accelerated by the presence of fuel constituents in the explosive mixture and by minerals and structural materials (rust) most likely encountered in downhole environments.

In the temperature range 443 to 533°K, the principal products are nitrous oxide and water:

$$NH_4NO_3 \longrightarrow N_2O + 2\,H_2O$$

Some nitrogen and free acid may also form according to equation:

$$5\,NH_4NO_3 \longrightarrow 4\,N_2 + 9\,H_2O + 2\,HNO_3$$

Nitramide NH_2NO_2 has at one time been suggested as an intermediate. Isotope labeling has shown that one of the nitrogens in N_2O comes from the ammonium, and the other one comes from the nitrate ion. Nitric acid catalyzes the reaction while ammonia or water inhibit it. A mechanism involving nitronium ions $NO_2^{\oplus}$ was proposed (Reference B2). Even in dilution with other inorganic nitrates of the alkali and alkali earth metals, the rate of decomposition of ammonium nitrate at 477°K (400°F) will be too high to result in a thermally stable explosive for geothermal applications. Only few binary or ternary eutectics involving ammonium nitrate were therefore included in the oxidizer evaluation.

3.1.1.2 Binary Nitrates

It is desirable that the oxidizer has a low melting point and high oxygen content. A low melting point facilitates above-ground handling and avoids plugging of equipment if the explosive mixture cools on its way to the bottom of the hole. There is a trade-off between melting point and oxygen content in that the lowest melting nitrates or perchlorates do not always have the highest oxygen content.

A literature survey has been conducted in an effort to identify low melting nitrates or perchlorates with favorable oxidizer properties. The survey included binary as well as ternary mixtures of

nitrates or perchlorates. Insufficient information could be found on mixtures of nitrates with perchlorates which should receive additional consideration.

The majority of data was found in Reference V4. Figures 3-1 through 3-12 were plotted in a uniform format to facilitate comparison of the various systems. The authors listed on these graphs identify the set of data used when more than one set of data was listed in Reference V4. The melting temperature and melt composition at the eutectic point are listed for each of the eutectics.

Of the systems with lithium nitrate (Figures 3-1 and 3-2), the lowest melting binary eutectic is formed with 66% potassium nitrate at 402°K. Systems with lithium nitrate may not be very practical because lithium salts are very expensive ($2.80/kg). A more economical nitrate mixture can be obtained with sodium nitrate and potassium nitrate, with a melting point of 495°K (Figure 3-3).

Calcium nitrate is a very attractive oxidizer because its useful oxygen content is slightly higher than that of sodium nitrate, but calcium is more readily available than lithium. Melting point curves of calcium nitrate mixtures with sodium nitrate and potassium nitrate are illustrated in Figures 3-4 and 3-5 respectively. In spite of the high melting point of anhydrous calcium nitrate (834°K), low melting eutectics can be obtained with sodium or potassium nitrate. The eutectic composition with 54.2% postassium nitrate melts at 419°K.

Ammonium nitrate (AN) by itself or in mixture with fuels does not have the thermal stability to survive a geothermal environment without decomposition. It is hoped that dilution with other nitrates may retard the decomposition of AN. Both eutectics with sodium (Figure 3-6) or calcium nitrate (Figure 3-7) melt only a few degrees above the boiling point of water. This temperature is easily maintained, and the freezing of oxidizer is prevented by steam tracing the oxidizer feed lines leading from the oxidizer tank to the downhole mixer.

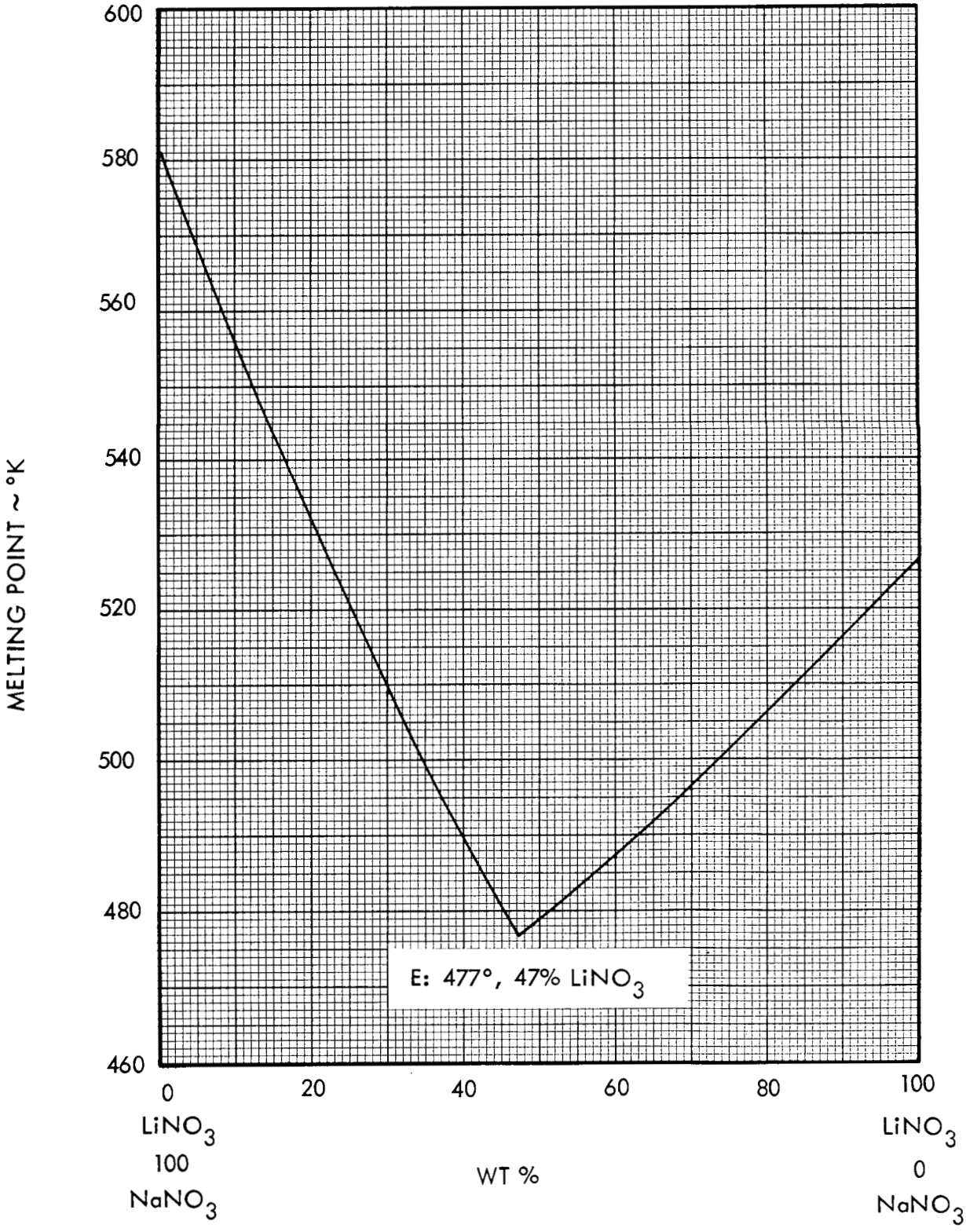
The melting point of nitrates and the vapor pressure of nitric acid can be lowered by using solutions of nitrates in nitric acid. Many nitrates form solvates with nitric acid which sometimes crytallize as well-defined compounds. The primary interest is again on solutions of alkali metal nitrates in nitric acid, but also ammonium nitrate or tetraalkylammonium nitrate solutions in nitric acid have been considered.

Potassium nitrate forms a 1:2 solvate with nitric acid which melts at 293°K (Reference P2). A 1:1 solvate melting between 295 and 301°K is not as well characterized. The area between this compound and the pure potassium nitrate in Figure 3-8 had to be extrapolated as indicated by the dashed line.

Addition of 34.8% by weight of potassium nitrate to nitric acid decreases the vapor pressure at 288°K from 46 mbar to 20 mbar (35.5 to 14.9 mmHg). Vapor pressure measurements at higher temperature were not reported, but it may be assumed that the vapor pressure will be reduced by a factor of 0.4 up to temperatures close to the normal boiling point. This would make the nitric acid easier to handle as an oxidizer.

MELTING POINT DIAGRAM OF THE BINARY SYSTEM

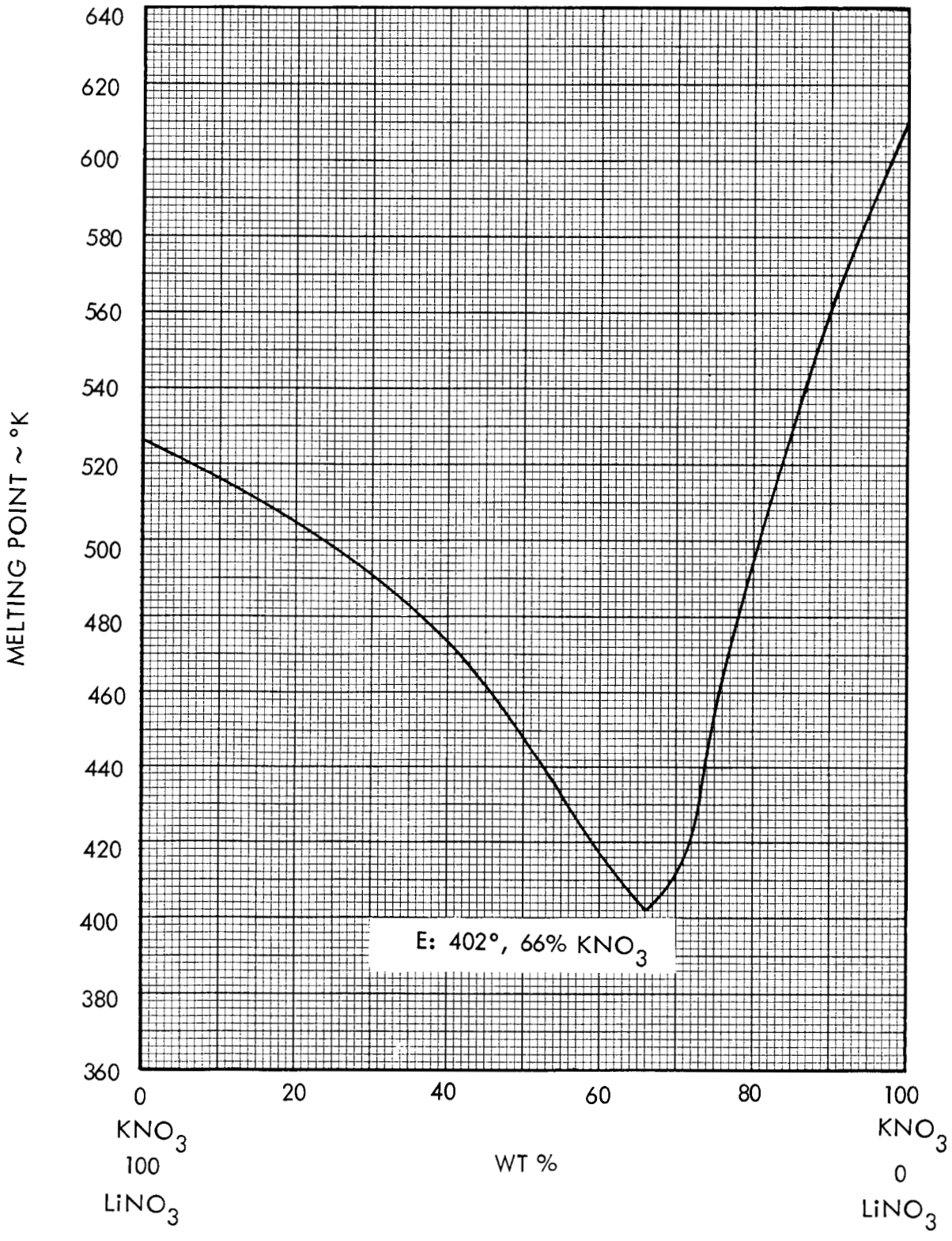
LITHIUM NITRATE/SODIUM NITRATE



CARVETH, H.R. (1898)

Figure 3-1

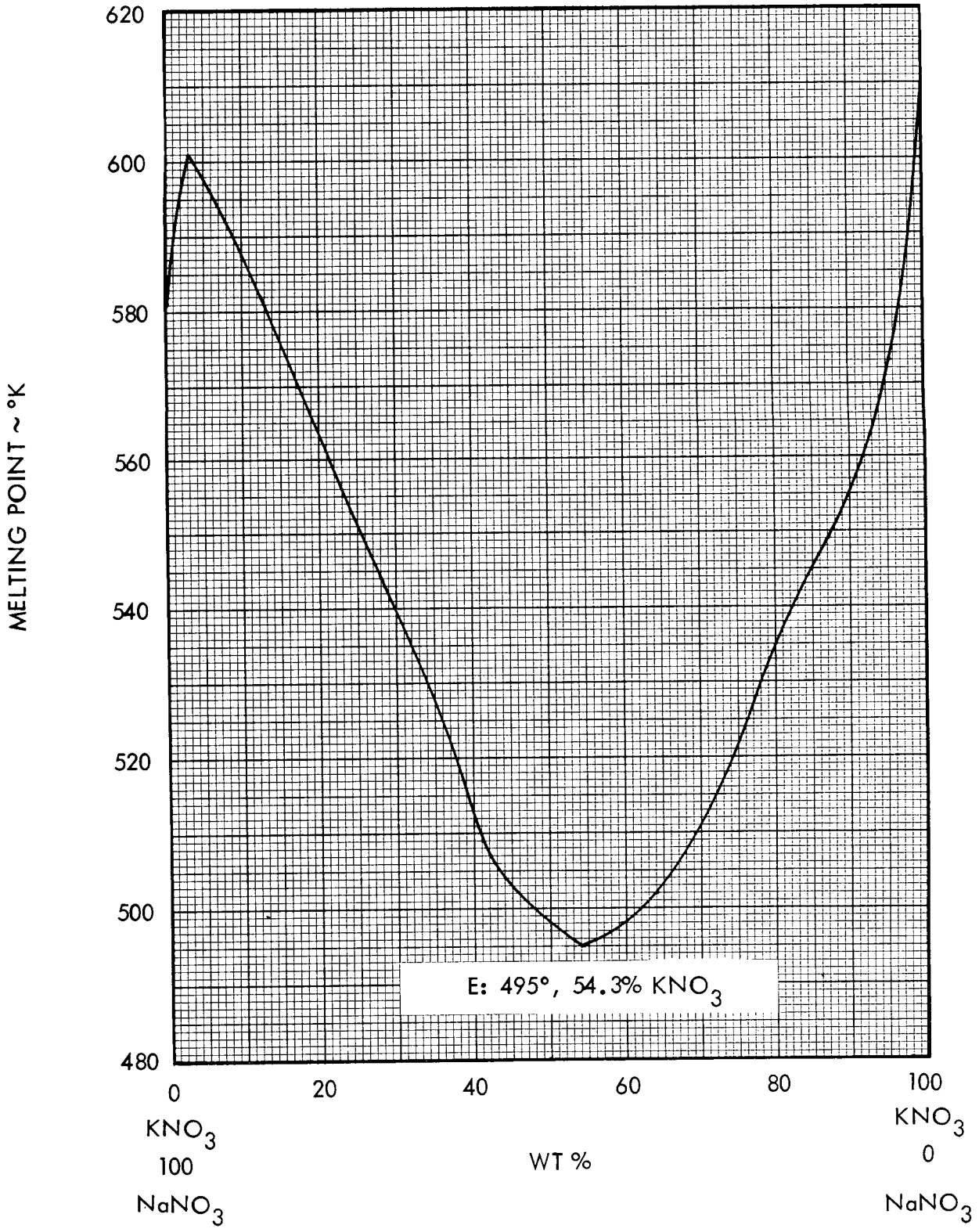
MELTING POINT DIAGRAM OF THE BINARY SYSTEM
LITHIUM NITRATE/POTASSIUM NITRATE



CARVETH, H.R. (1898)

Figure 3-2

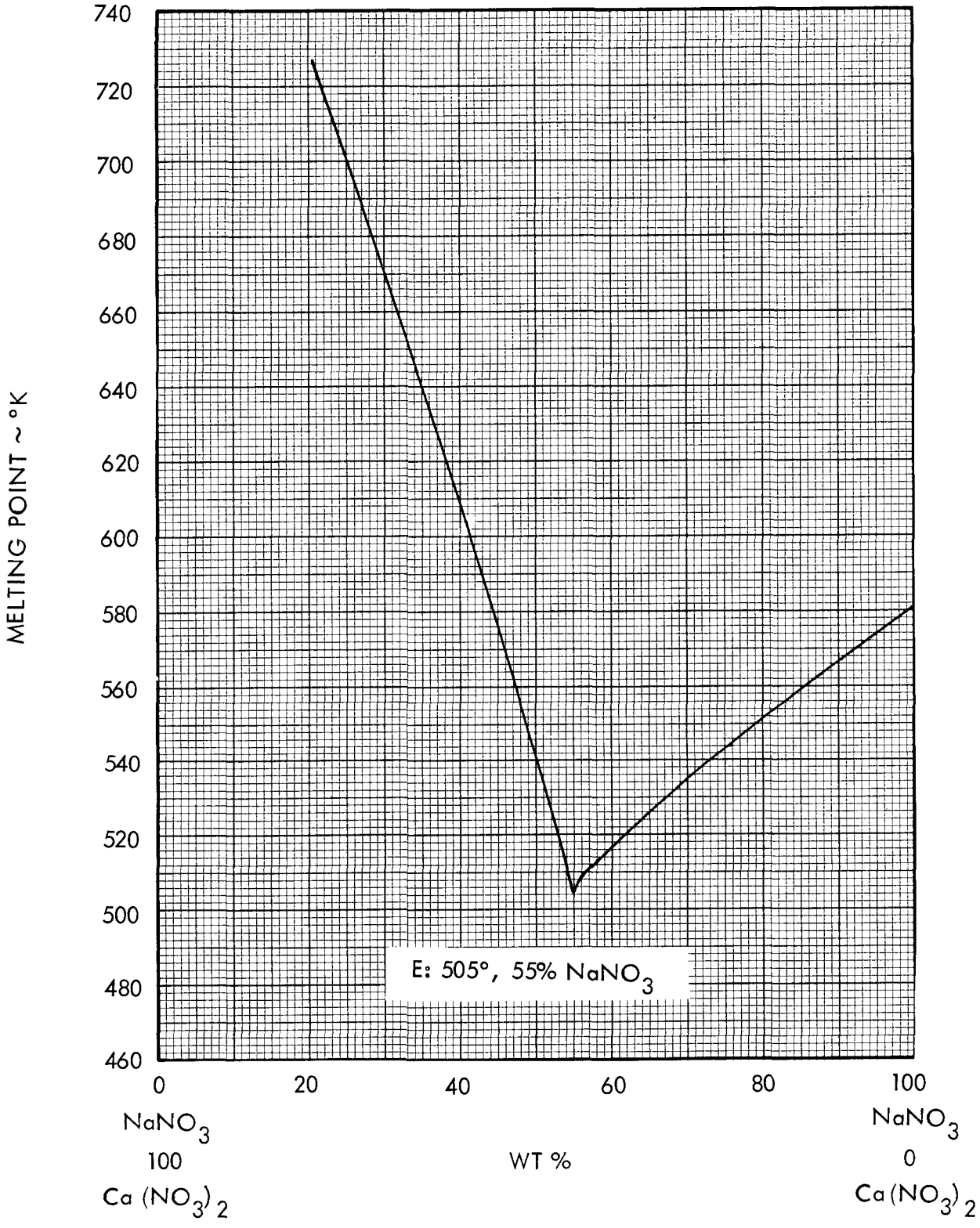
MELTING POINT DIAGRAM OF THE BINARY SYSTEM SODIUM NITRATE/POTASSIUM NITRATE



PROTSENKO, P.I. AND BERGMAN, A.G. (1950)

Figure 3-3

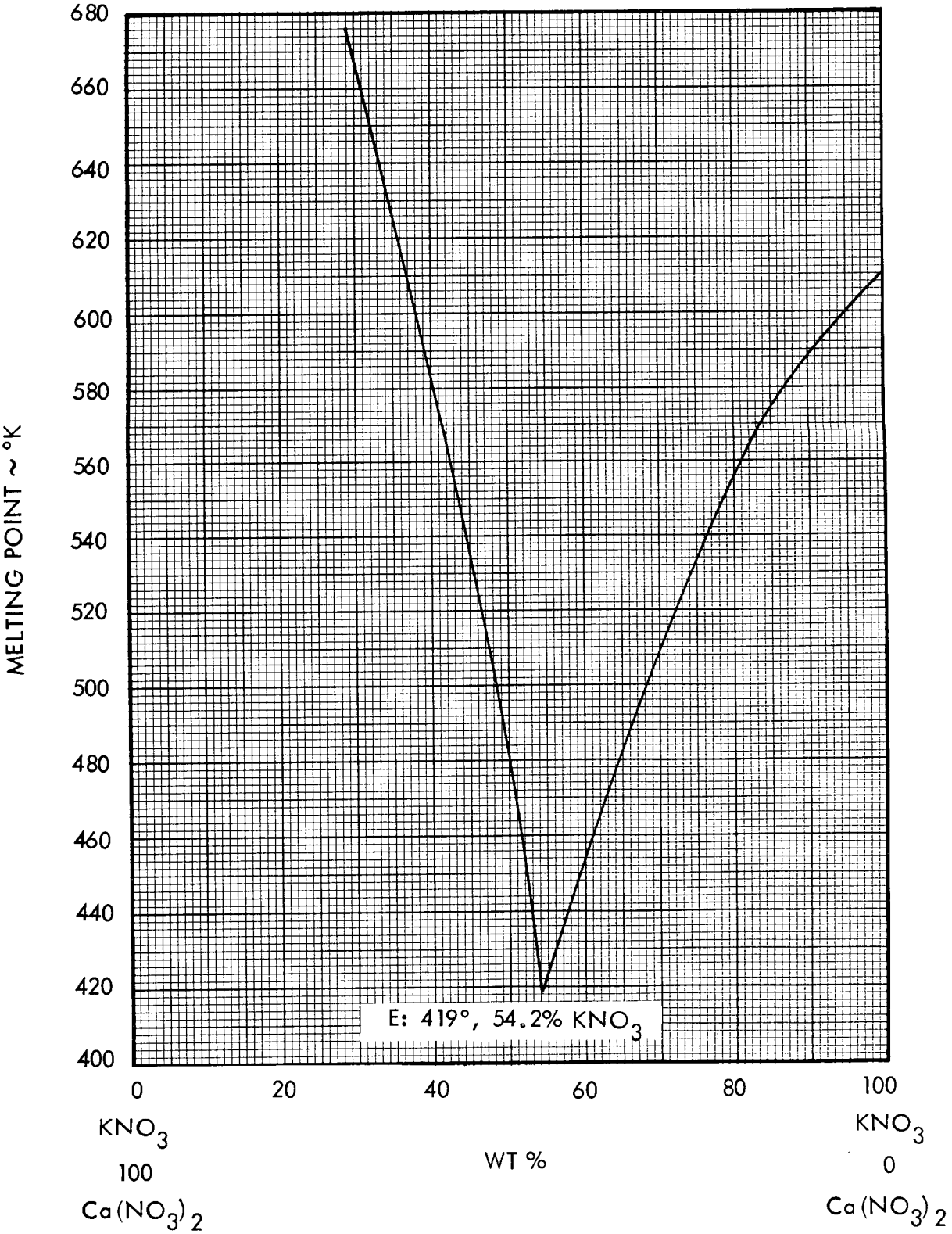
MELTING POINT DIAGRAM OF THE BINARY SYSTEM SODIUM NITRATE/CALCIUM NITRATE



BERGMAN, A.G. (1943)

Figure 3-4

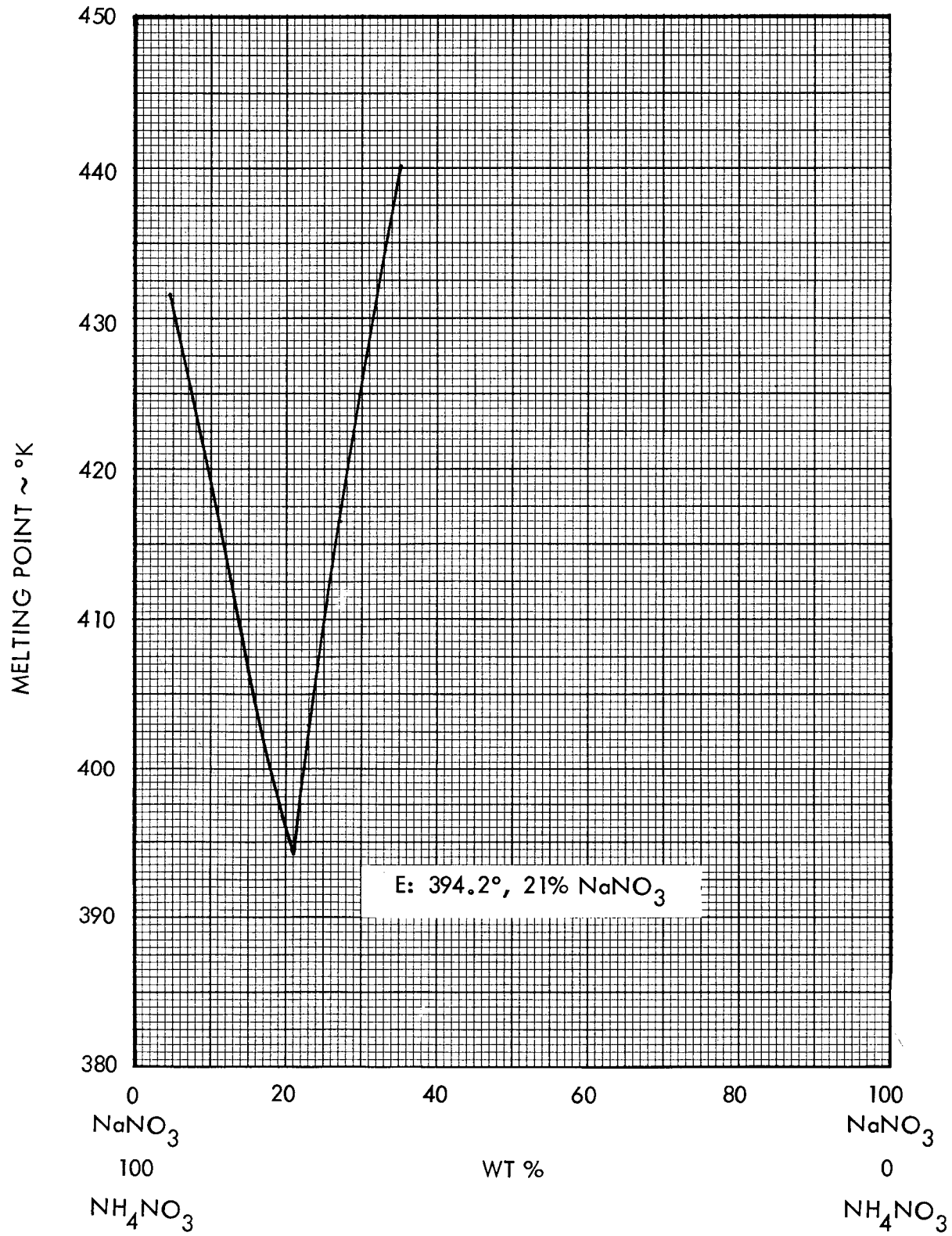
MELTING POINT DIAGRAM OF THE BINARY SYSTEM POTASSIUM NITRATE/CALCIUM NITRATE



PROTSENKO, P.I. AND BERGMAN, A.G. (1943)

Figure 3-5

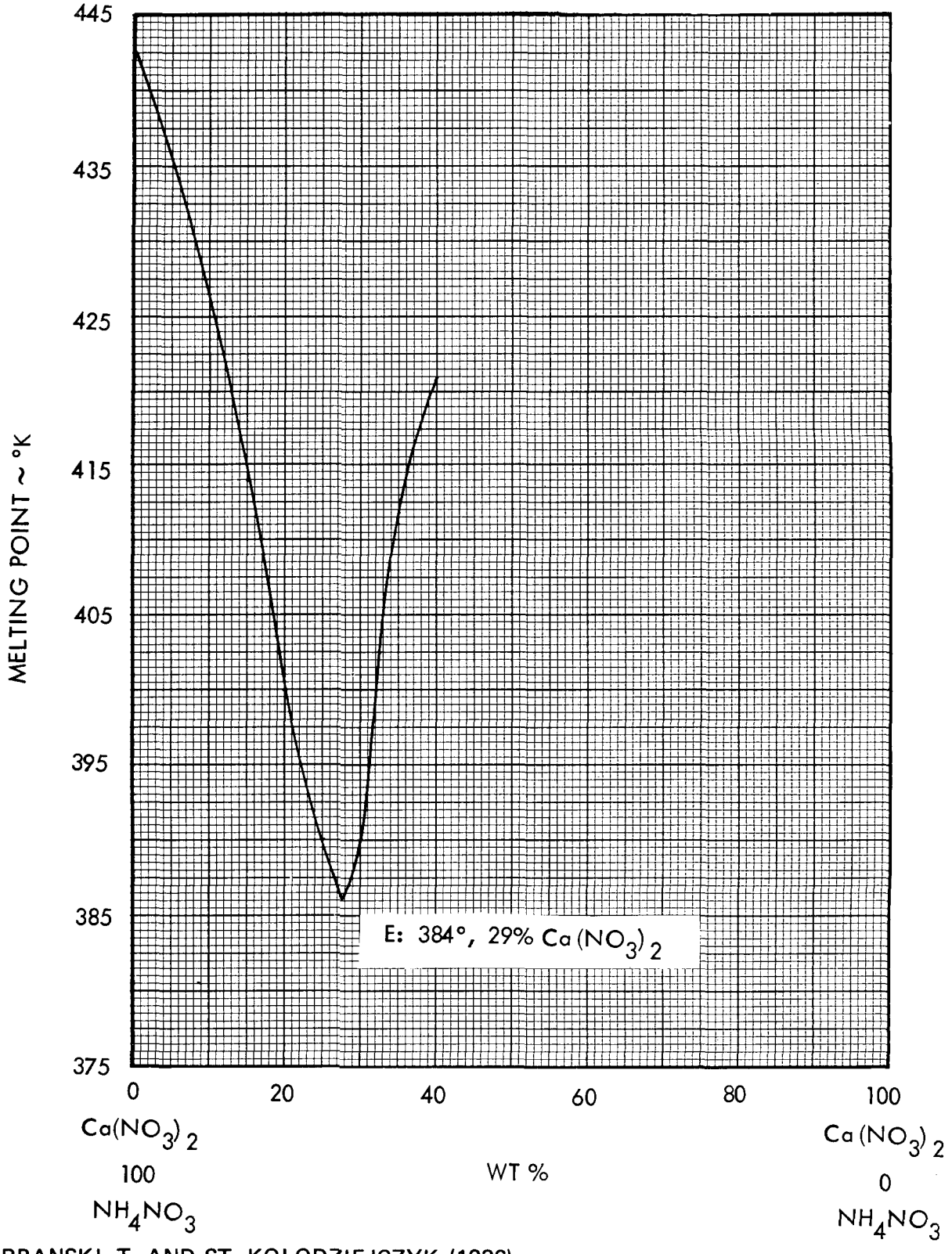
MELTING POINT DIAGRAM OF THE BINARY SYSTEM SODIUM NITRATE/AMMONIUM NITRATE



HOLMES, E.O. AND REVINSON, J.D. (1944)

Figure 3-6

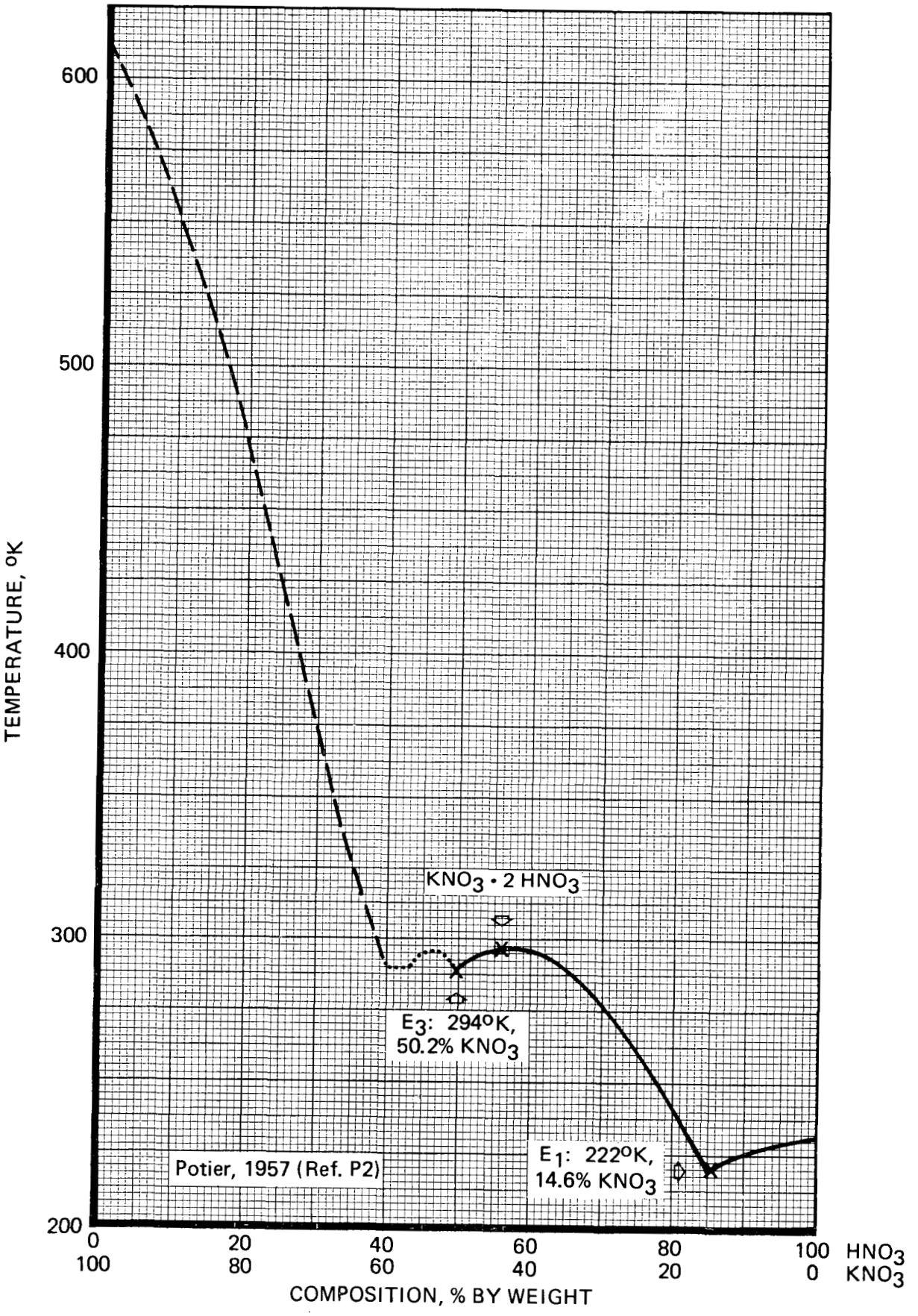
MELTING POINT DIAGRAM OF THE BINARY SYSTEM CALCIUM NITRATE/AMMONIUM NITRATE



URBANSKI, T. AND ST. KOLODZIEJCZYK (1936)

Figure 3-7

MELTING POINT DIAGRAM OF THE BINARY SYSTEM NITRIC ACID/POTASSIUM NITRATE



11111-90

Figure 3-8

Ammonium nitrate has been previously eliminated from further consideration because of insufficient thermal stability. The thermal stability problem cannot be avoided by forming binary or ternary nitrate mixtures. Generally, compounds decompose faster in melt or in solution than in the crystalline state. In the case of ammonium nitrate, most oxidizer additives accelerate rather than retard the decomposition. Only few systematic studies have been conducted on this subject.

Solutions of ammonium nitrate in nitric acid lower the vapor pressure of nitric acid. It is not known if the mixture is thermally less stable or more stable than its ingredients. Ammonium nitrate forms a di-solvate with nitric acid, $NH_4NO_3 \cdot 2\ HNO_3$, which melts at 303°K. There are two eutectics in the system – a nitric acid-rich at 10.4% by weight, NH_4NO_3 which melts at 225°K, and another one at 55% NH_4NO_3 which melts at 289°K (Reference P3). The phase diagram of the system looks very similar to that of HNO_3/KNO_3.

Unlike potassium nitrate solutions in nitric acid, the ammonium nitrate solutions may become detonable with increasing ammonium nitrate content. This would be very dangerous for an oxidizer which has to be handled in large quantities above ground. An alternate approach would be to feed three constituents (nitric acid, ammonium nitrate solid, and fuel) and premix the two oxidizer components below ground before adding the fuel.

Guanidine is quite unique as an organic compound because it is the strongest organic base. The thermal stability of its salts exceeds that of ammonium salts. However, guanidinium nitrate has no available oxygen and thus has to be classified as a fuel rather than an oxidizer. It will be discussed in more detail in the chapter on fuel selection. As an admixture to alkali metal nitrates, guanidinium nitrate lowers melting points just like any other inorganic nitrate. The system lithium nitrate/guanidinium nitrate based on RRC data is illustrated in Figure 3-9. Also, a few combinations of guanidinium nitrate and sodium nitrate were prepared for melting point determination. The eutectic point for these nitrates appears to lie in the region of 2:8 by weight and 3:7 by weight sodium nitrate-guanidinium nitrate. The 2:8 mixture melts at 435° to 490°K. Beyond a certain concentration of guanidinium nitrate additive, these oxidizers would become detonable by themselves. This would violate the design concept of the envisioned explosive stimulation system. The safe concentration of guanidinium nitrate additive would have to be determined by experiment.

3.1.1.3 Ternary Nitrates

Ternary mixtures allow melting points which are below those of the best binary eutectics at the expense of increased complexity if three ingredients have to be mixed in the proper proportions. However, this mixing can be done at the factory and would not complicate logistics of mixing explosive in the field.

The overall objective of this study was to find low-melting oxidizers with high oxygen content. Binary mixtures would be preferred from the standpoint of simplicity in preparation and quality control. However, still lower melting points or higher oxygen contents may be realized using ternary instead of binary systems. Ternary nitrates/nitrites are used in heat transfer salts and a large amount of data exists on these systems.

MELTING POINT DIAGRAM OF THE SYSTEM LITHIUM NITRATE/GUANIDINIUM NITRATE

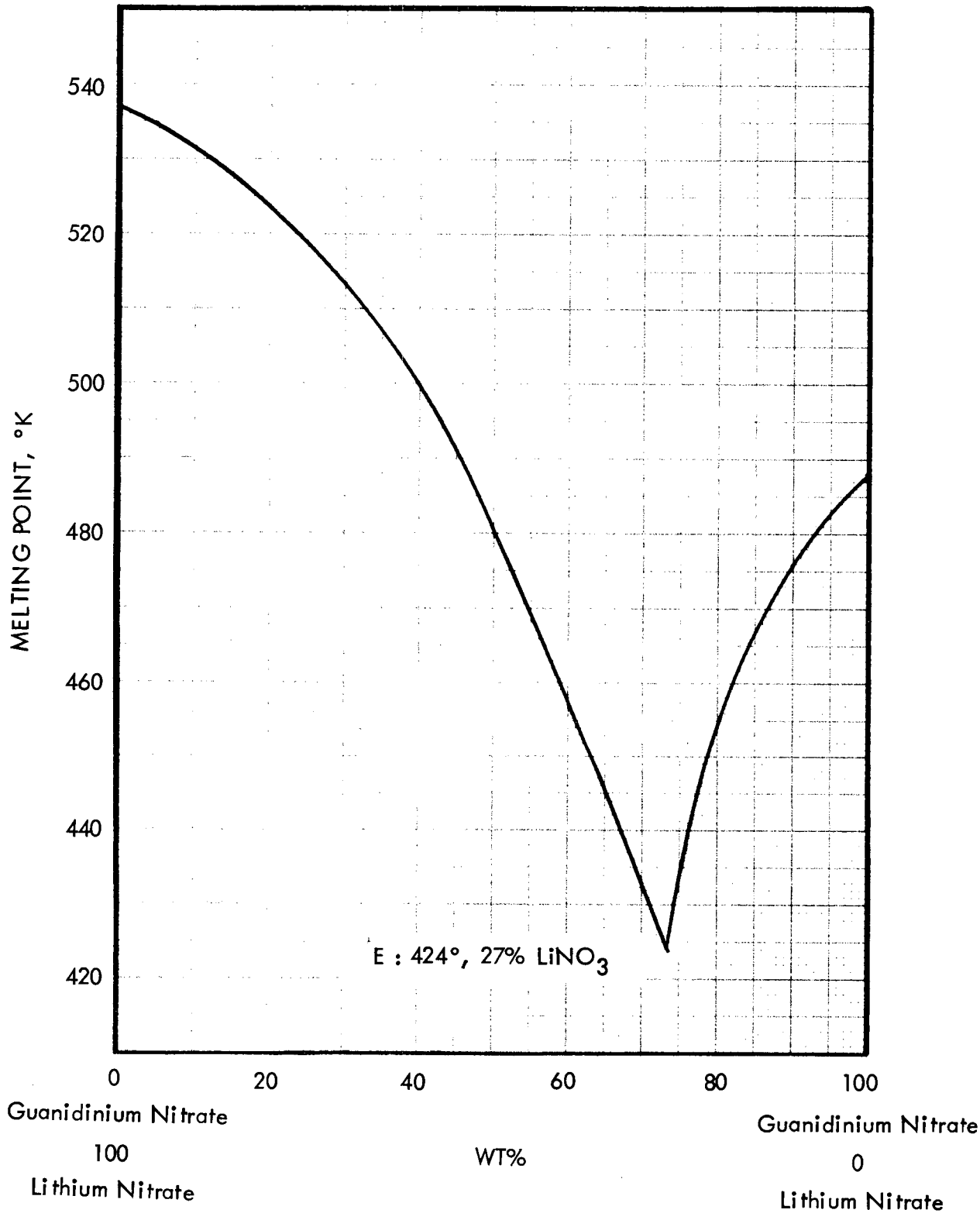


Figure 3-9

In the ternary phase diagrams, Figures 3-10 through 3-13, many of the previously discussed binary systems recur as the sides of the triangle which represent binary systems where the concentration of a third possible ingredient is zero. Similar to the binary eutectics marked on the sides of the graphs, there exists a ternary eutectic which represents the lowest melting mixture in the system. The ternary eutectic always melts lower than any of the binary eutectics. It is surrounded by melting point isotherms. Translated to a topographic map-type representation, the ternary eutectic is the lowest spot in the triangle. The isotherms are elevation lines, and the bold lines connecting the three binary eutectics with the ternary eutectic are the "valleys".

In a ternary diagram, the corners generally represent the pure compound and percentages of all constituents should add up to 100. However, in order to show more detail in one corner of the triangle, an expanded scale may occasionally be used, resulting in a truncated or distorted triangle.

The ternary system lithium nitrate/sodium nitrate/potassium nitrate is one of the most easily interpreted ternary nitrate systems (Figure 3-10). Some of the other systems were more difficult to plot because of various solid-solid solution phases occurring or because of insufficient data to cover the entire range of compositions. The lithium nitrate/sodium nitrate/potassium nitrate ternary eutectic melts at 392°K. In view of the 100-degree drop in melting point from the sodium/potassium binary, the addition of 30% lithium nitrate appears to be quite worthwhile.

In the system sodium nitrate/potassium nitrate/calcium nitrate (Figure 3-11), the ternary eutectic is extremely close to that of the potassium nitrate/calcium nitrate binary, and only a 13-degree drop can be achieved by going from a binary to a ternary mixture. Nevertheless, this ternary eutectic nitrate oxidizer has been identified as the most promising oxidizer, and the majority of the explosive development tests have been conducted with this oxidizer. The nominal composition is 11.2% sodium nitrate, 44.3% potassium nitrate and 44.5% anhydrous calcium nitrate. The melting point of the eutectic is 406°K (133°C = 271°F). This temperature is low enough that freezing of the melt in the lines can be avoided by steam tracing. The steam jacket pressure to maintain 410°K (279°F) is only 3.3 bar (48 psia). This ternary nitrate, called NaKCa (pronounced **Nacka**) nitrate, is an extremely favorable compromise between oxygen content, melting point, and cost. All ingredients are readily available at prices below 10 cents per pound. The oxidizer is not as corrosive as nitric acid, and it is not detonable by itself. NaKCa nitrate is thermally stable at the temperatures considered here. On the differential scanning calorimeter, endotherms were observed at 608 and 683°K, indicating incipient decomposition.

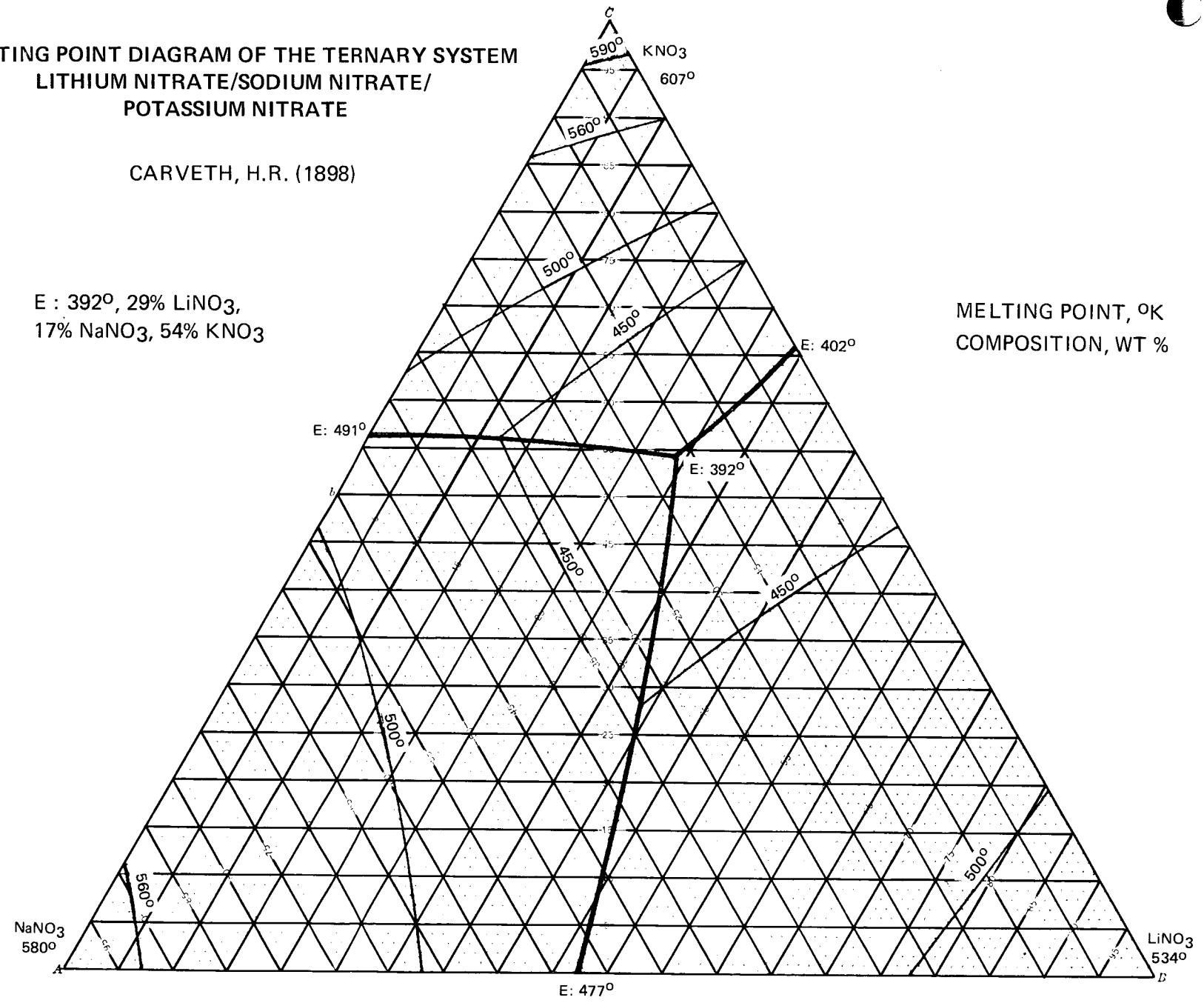
Eutectics in ternary systems with ammonium nitrate (Figures 3-12 and 3-13) occur at very high ammonium nitrate concentrations, 66 to 69% ammonium nitrate. It is not expected that these mixtures are thermally stable at 561°K (550°F). Mixtures with lower ammonium nitrate concentrations might be stable enough and deserve additional study.

The melting point of binary or ternary nitrate mixtures may be lowered by adding small quantities (less than 10%) of water or nitric acid. The hot mixture would have to be kept under pressure to prevent loss of the volatile liquid.

MELTING POINT DIAGRAM OF THE TERNARY SYSTEM
LITHIUM NITRATE/SODIUM NITRATE/
POTASSIUM NITRATE

CARVETH, H.R. (1898)

E : 392°, 29% $LiNO_3$,
17% $NaNO_3$, 54% KNO_3



MELTING POINT, °K
COMPOSITION, WT %

Figure 3-10

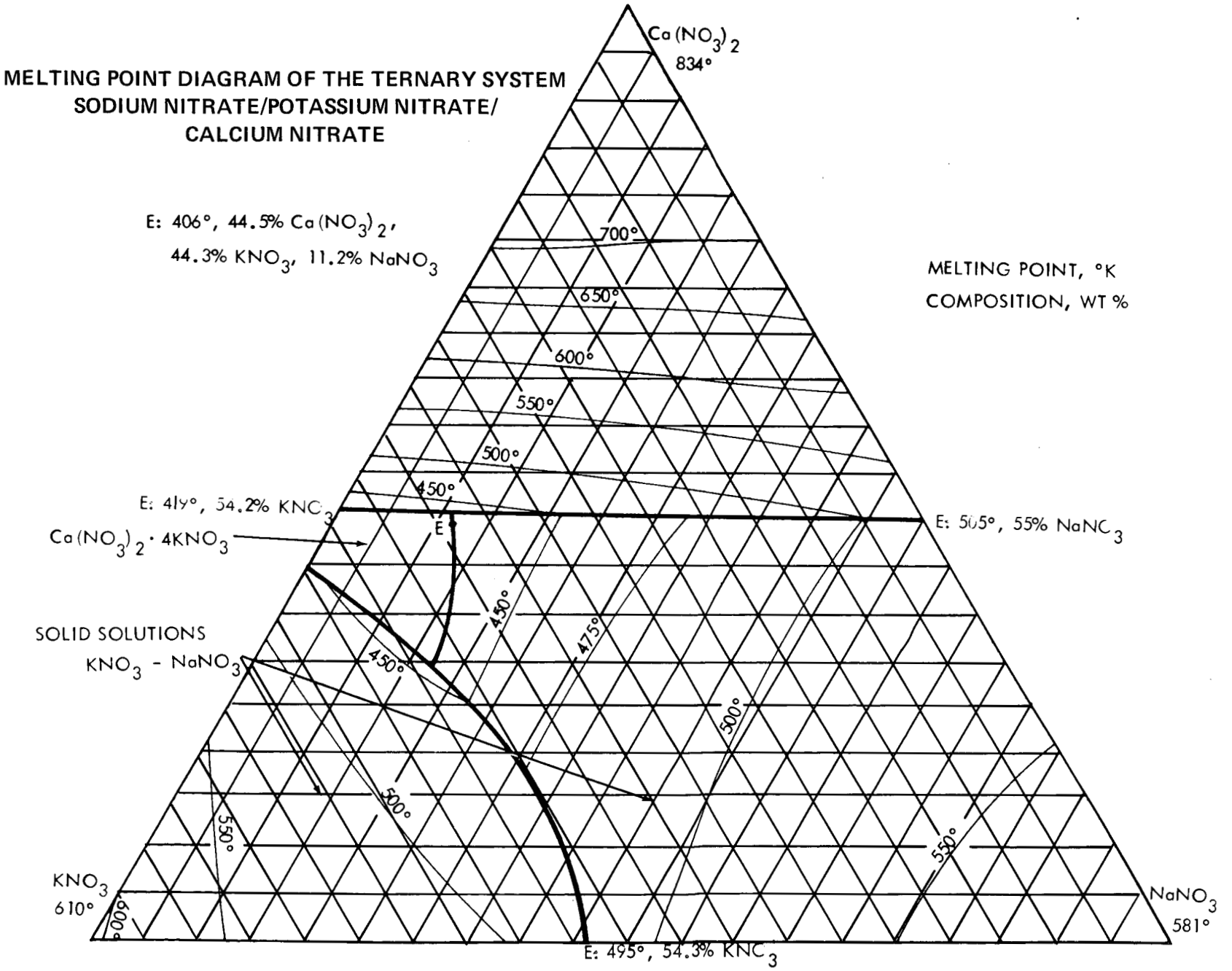

MELTING POINT DIAGRAM OF THE TERNARY SYSTEM
SODIUM NITRATE/POTASSIUM NITRATE/
CALCIUM NITRATE
E: 406°, 44.5% Ca(NO3)2,
44.3% KNO3, 11.2% NaNO3
Ca(NO3)2
834°
MELTING POINT, °K
COMPOSITION, WT %
700°
650°
600°
550°
500°
450°
E: 419°, 54.2% KNC3
Ca(NO3)2 · 4KNO3
E
E: 505°, 55% NaNC3
SOLID SOLUTIONS
KNO3 - NaNO3
450°
475°
500°
550°
KNO3
610°
NaNO3
581°
E: 495°, 54.3% KNC3

Figure 3-11

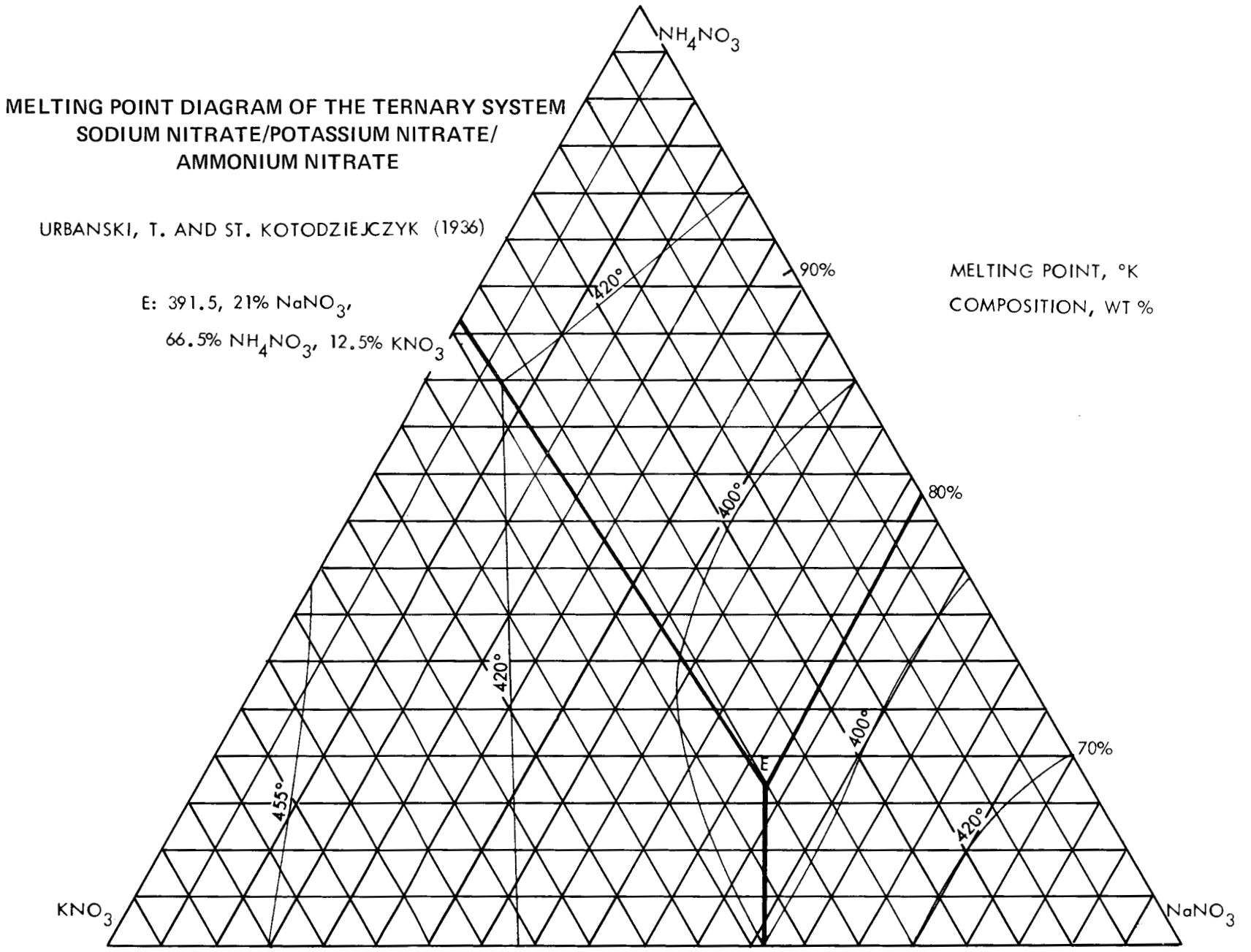

MELTING POINT DIAGRAM OF THE TERNARY SYSTEM
SODIUM NITRATE/POTASSIUM NITRATE/
AMMONIUM NITRATE
URBANSKI, T. AND ST. KOTODZIEJCZYK (1936)
E: 391.5, 21% $NaNO_3$,
66.5% NH_4NO_3, 12.5% KNO_3
MELTING POINT, °K
COMPOSITION, WT %
NH_4NO_3
KNO_3
$NaNO_3$
90%
80%
70%
420°
400°
420°
400°
455°
420°
E

Figure 3-12

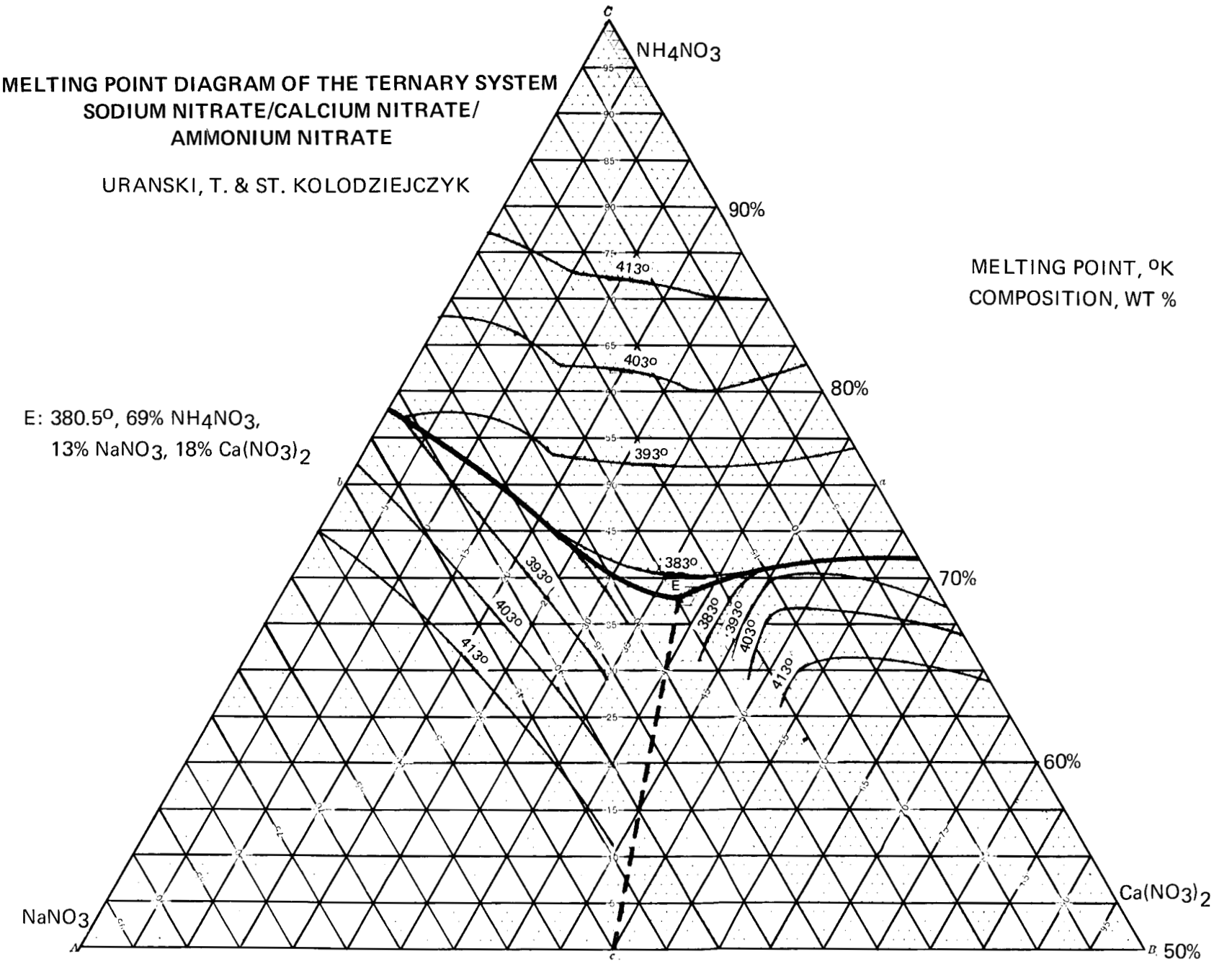

MELTING POINT DIAGRAM OF THE TERNARY SYSTEM
SODIUM NITRATE/CALCIUM NITRATE/
AMMONIUM NITRATE
URANSKI, T. & ST. KOLODZIEJCZYK
E: 380.5°, 69% NH4NO3,
13% NaNO3, 18% Ca(NO3)2
MELTING POINT, °K
COMPOSITION, WT %
NH4NO3
NaNO3
Ca(NO3)2
90%
80%
70%
60%
50%
413°
403°
393°
383°
E

Figure 3-13

Complete solution and clear melts may not always be necessary, but are preferred. The current PTC system pumps a slurry of oxidizer with 15% solids suspended in hot saturated aqueous solution. A similar approach is possible for the geothermal explosive. Insufficient melting point data were found in the literature on mixtures of nitrates with low concentrations of water or nitric acid. Melting points will have to be determined in a series of laboratory experiments if the melting point of the selected oxidizer has to be lowered further.

The melting point of NaKCa nitrate could be lowered further by addition of guanidinium nitrate, one of the selected fuel ingredients. However, beyond a certain guanidinium nitrate content in the oxidizer, the mixture may become detonable. The melting point of NaKCa nitrate is already low enough that further melting point depressing additives are no longer required.

Ternary nitrate mixtures with nitric acid have not yet been described. The ternary diagrams of the systems (H, Na) NO_3/H_2O, (H, K) NO_3/H_2O and (H, Na, K) NO_3 had to be intuitively extrapolated from the experimental data on binary mixtures plotted along the sides of the triangle.

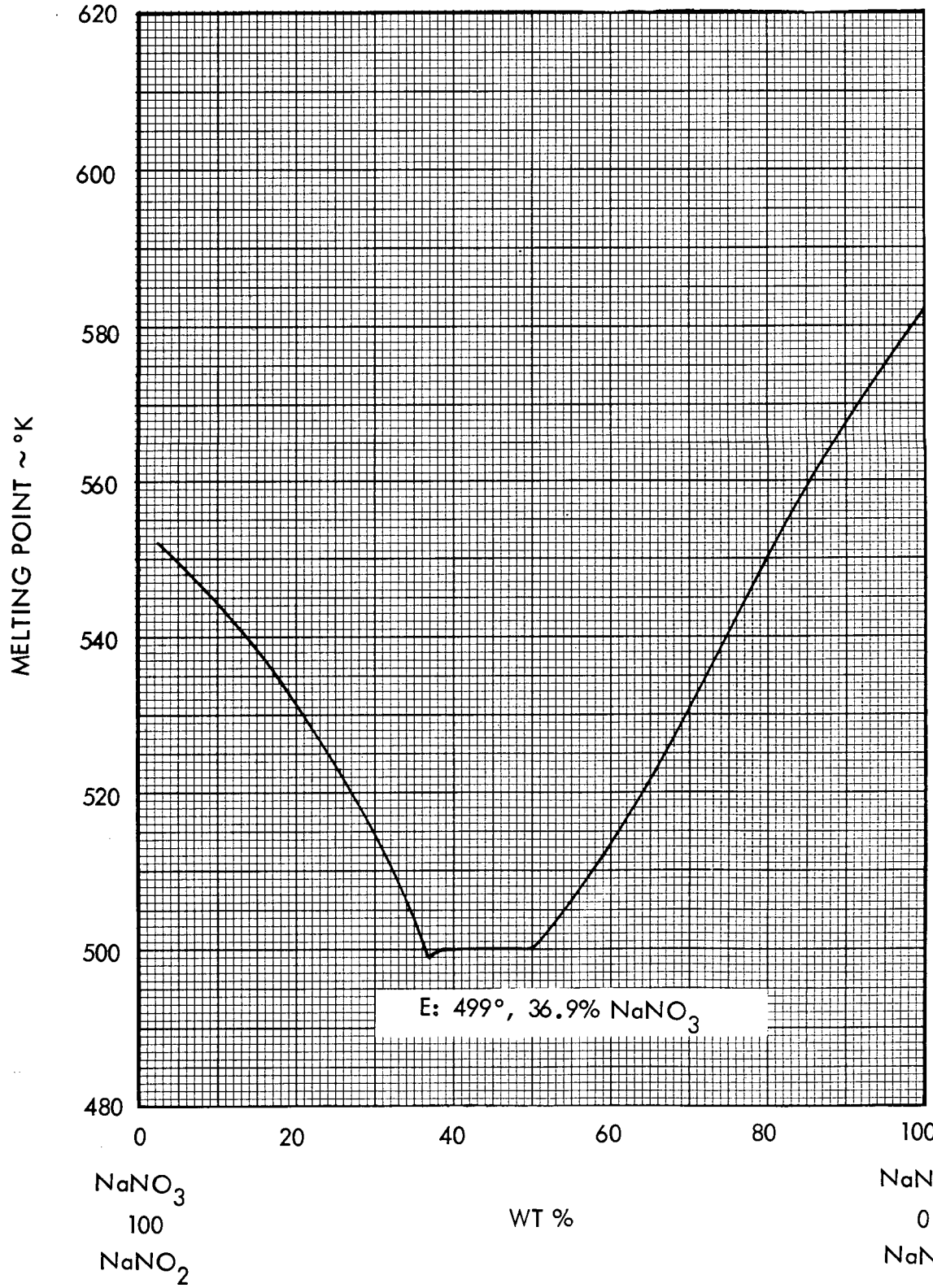
For the water-containing systems, it would be desirable to stay as far away from the water corner as possible. However, addition of some water is very useful in lowering the melting point of some of the mixtures. From a standpoint of maximum useful oxygen content, it would be desirable to stay close to the nitric acid corner. A compromise will have to be sought which should also include vapor pressure data, which are not available at this time.

3.1.1.4 Nitrate Eutectics with Other Anions

In the area of binary salt systems with different anions, the system sodium nitrite/sodium nitrate was studied as illustrated in Figure 3-14 (see also Reference K3). However, the addition of sodium nitrite is undesirable because it lowers the oxygen content of the oxidizer. The melting point diagrams of the quaternary systems Li, Na/NO_2, NO_3 (Reference S11), Li, K/NO_2, NO_3 (Reference P6) and Ca, Na/NO_2, NO_3 (Reference P7) have been reviewed in search of low-melting formulations. None of these systems offer any advantages over NaKCa nitrate. Among other anions to be considered, perchlorates would be more desirable additives. However, no data on nitrate/perchlorate binary, ternary or quaternary systems could be found. Perchlorates are desirable oxidizers because of their high oxygen content. Chlorates also have a good oxygen content but have to be eliminated for safety reasons (friction sensitivity).

Insufficient data were found in the literature on melting point curves of binary oxidizer mixtures of nitrates and perchlorates with common or different cations. Melting point data were therefore determined as part of the oxidizer study under this contract. The results in Figures 3-15 and 3-16 show that all mixtures melt above 500°K. In search of a low-melting oxidizer, the nitrate mixtures discussed in the preceding paragraph appear to be more convenient to handle in the molten state because of their lower melting point. No distinct melting point minimum could be observed in the system potassium nitrate/potassium perchlorate.

MELTING POINT DIAGRAM OF THE BINARY SYSTEM SODIUM NITRATE/SODIUM NITRITE



BERGMAN, A.G., BERUL', S.I., & NIKONOVA, I.N. (1953)

Figure 3-14

MELTING POINT DIAGRAM OF THE SYSTEM
SODIUM NITRATE/SODIUM PERCHLORATE

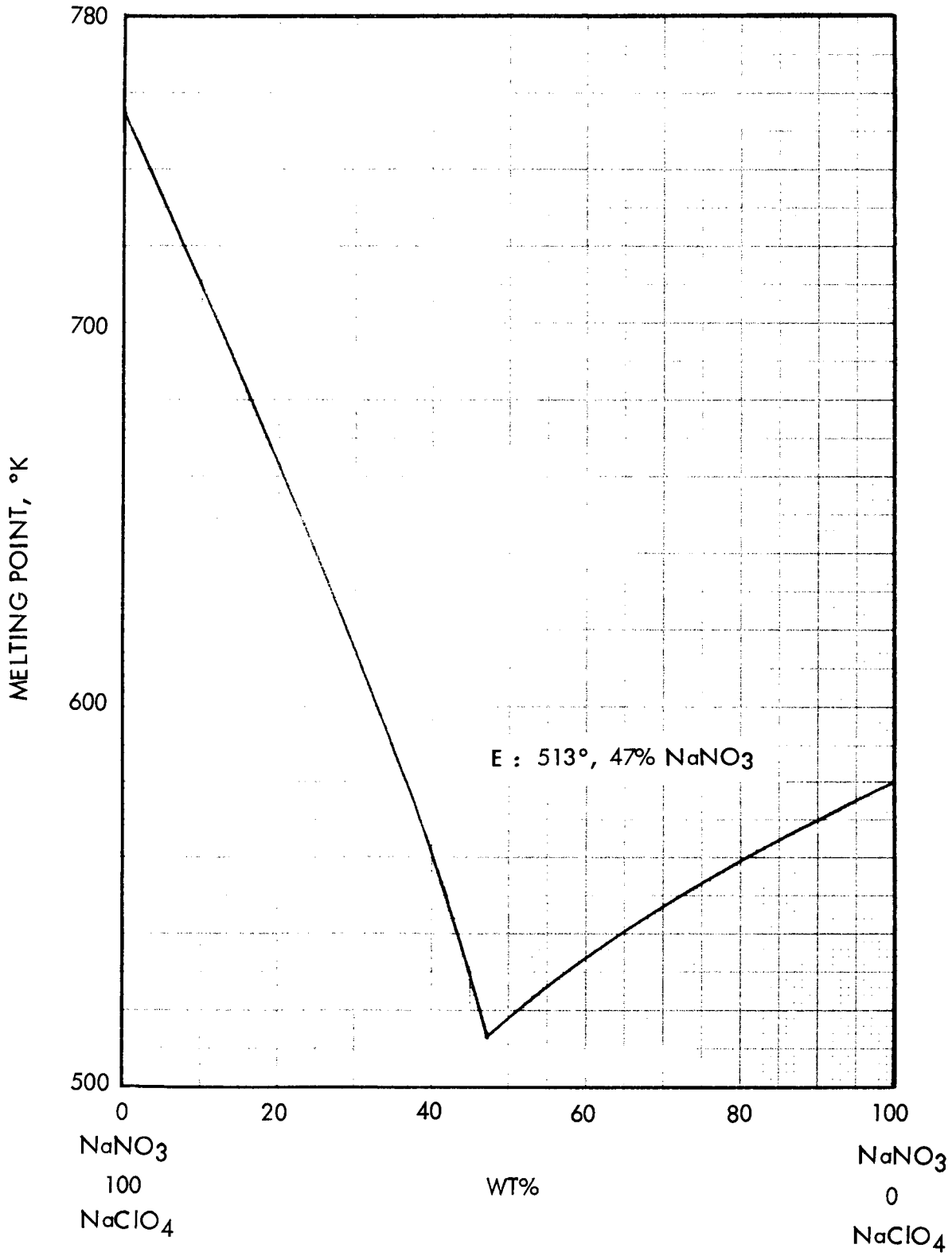


Figure 3-15

MELTING POINT DIAGRAM OF THE SYSTEM
POTASSIUM NITRATE/SODIUM PERCHLORATE

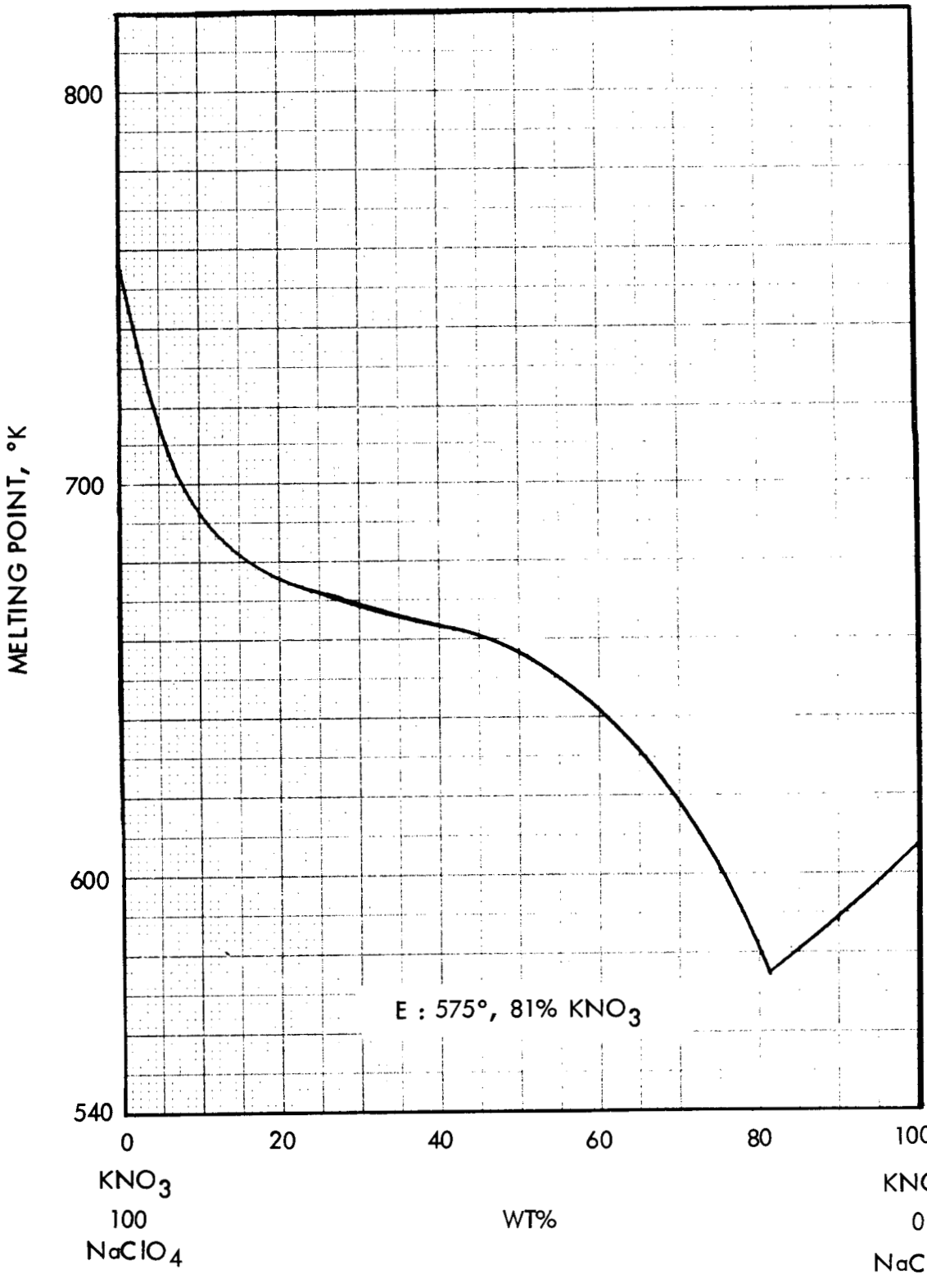


Figure 3-16

When assessing the thermodynamics of oxidizers and oxidizer constituents, it was surprising to learn that the disproportionation of sodium nitrite according to the equation

$$5\ NaNO_2\ (S) \longrightarrow Na_2O\ (S) + 3\ NaNO_3\ (S) + N_2\ (G)$$

is actually slightly exothermic with $\Delta H^r = -5.02$ kcal/mole under standard conditions. The question arose if such a reaction is possible and if yes, does it constitute a hazard?

The other question was if it is safe to mix a powerful oxidizer such as sodium perchlorate with an oxidizable compound such as sodium nitrite. Under standard conditions the reaction

$$4\ NaNO_2 + NaCl\ O_4 \longrightarrow 4\ NaNO_3 + NaCl$$

is exothermic with $(\Delta H)^{298} = -68.6$ kcal/mol $NaCl\ O_4 = -287$ kJ/mol $NaCl\ O_4$.

Subsequently, the two oxidizers were heated together in the DSC, but no exotherm could be noted. The effect of contaminants with possible catalytic action would have to be investigated if one wanted to spike nitrites with perchlorates.

3.1.2 Perchlorate Oxidizer

Perchlorates are generally superior to nitrates because they have a higher useful oxygen content. However, all perchlorates melt higher than the corresponding nitrates and begin to decompose at temperatures little beyond their melting point (References P8 and S12). This makes it more difficult to handle oxidizer melts on the surface prior to mixing with the fuel. Perchlorates also are generally less soluble in candidate fuels than the corresponding nitrates.

Perchlorates are more expensive than nitrates, and the supply depends very much on other uses which make it worthwhile for chemical industry to produce perchlorates in large quantities. Because there is only a limited market for perchlorates, a tendency to a single source supplier situation had developed several years ago. This situation had to be corrected by federal court action under the antitrust (anticartel) law. It would be very undesirable if the supply of HITEX ingredients depended on such a market situation.

Perchlorates will decompose either to form the chloride and oxygen or to form the oxide and a mixture of chlorine and oxygen:

$$M\ ClO_4 \longrightarrow M\ Cl + 2\ O_2$$

$$M\ ClO_4 \longrightarrow 1/2\ M_2O + 1/2\ Cl_2 + 7/4\ O_2$$

Hydrated salts will also decompose by either of the above equations, but in the latter case, the hydroxide and free perchloric acid may be formed. In general, decomposition to the chloride is observed for the alkali metal perchlorates and for the alkaline earth perchlorates, except for

magnesium and calcium which simultaneously form the oxide. Only lithium perchlorate has a melting point well below the temperature at which decomposition commences. Reported literature melting points for the other perchlorates vary significantly depending on how much decomposition had occurred before the melting point temperature reading could be taken. The kinetics of perchlorate decomposition and the effects of catalysts have been extensively investigated. The chloride formed in the reaction may act autocatalytic, progressively accelerating the decomposition of more perchlorate. Basic salts such as lithium carbonate retard the decomposition of perchlorates.

Lithium perchlorate is unique in that it not only melts much lower than the other perchlorates, but it is also quite soluble in water and organic solvents (Table 3-2). Mixtures of $LiClO_4$ and organic solvents have been patented as monopropellants (Reference F2). Even though the mixtures are described as nondetonable, it may be assumed that with different stoichiometry and by use of a booster, they can be made to detonate. Lithium perchlorate-based high temperature explosives would be quite attractive, but the high cost of the oxidizer may prevent large-scale utilization.

Table 3-2
SOLUBILITY OF LITHIUM AND SODIUM PERCHLORATE IN ORGANIC SOLVENTS

Solvent	Solubility, g/100g Solvent	
	$LiClO_4$	$NaClO_4$
Methanol	182.3	51.4
Ethanol	151.8	14.7
n-Propanol	105.8	4.0
2-Propanone	136.5	51.7

Eutectics in the systems lithium perchlorate/sodium perchlorate (Figure 3-17) and lithium perchlorate/potassium perchlorate (Figure 3-18) melt in the neighborhood of 400°K and occur at the lithium-rich end of the system.

In addition to the combinations graphed here, fused salt mixtures of $NaClO_4$ and $KClO_4$ at various ratios were looked at. All have melting temperatures exceeding 543°K. No specific data were obtained for these. Review of eutectic perchlorates excluding lithium perchlorate has not revealed any mixture of oxidizers with melting points below 475°K (References M9, K5, K6).

MELTING POINT DIAGRAM OF THE SYSTEM
LITHIUM PERCHLORATE/SODIUM PERCHLORATE

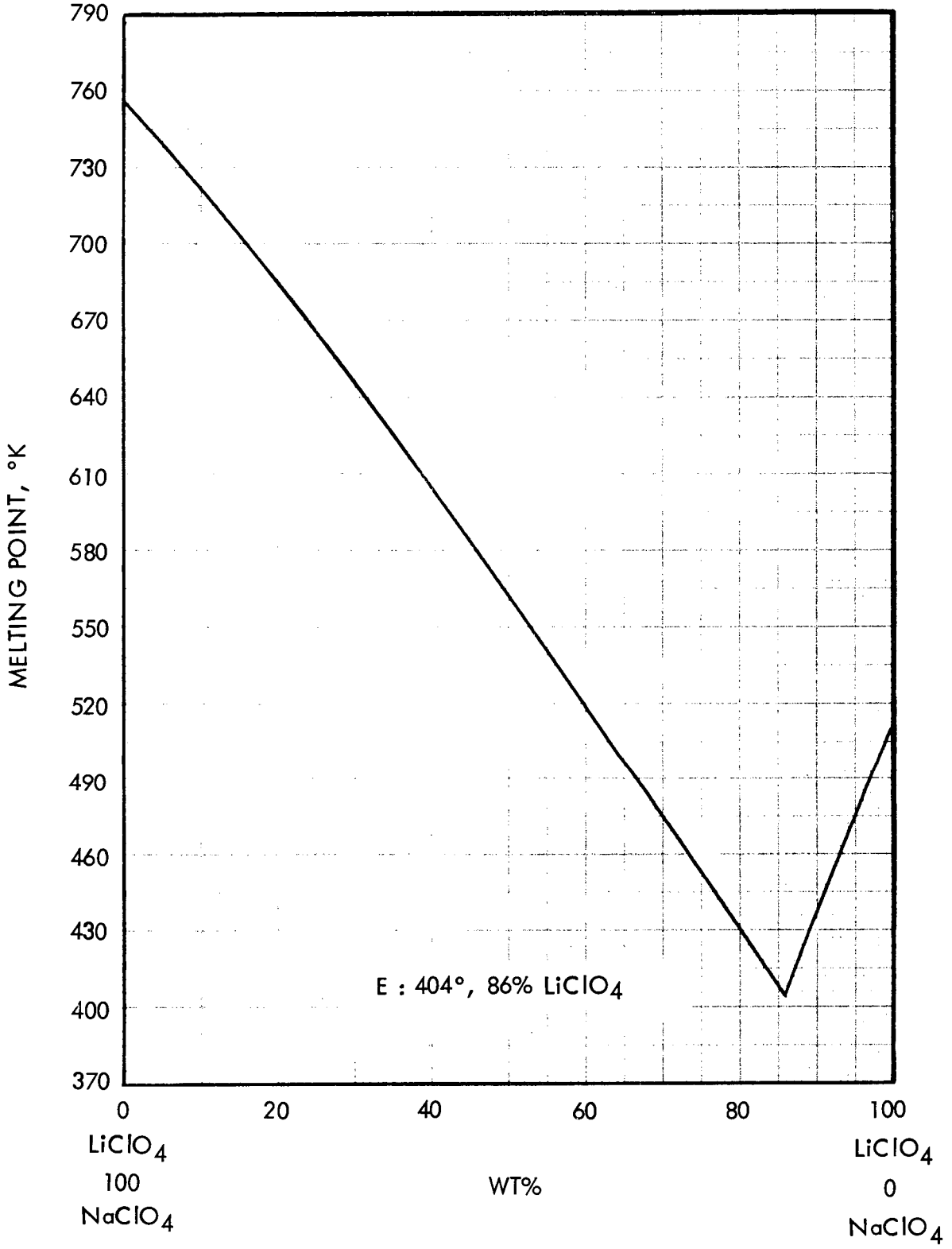


Figure 3-17

MELTING POINT DIAGRAM OF THE SYSTEM
LITHIUM PERCHLORATE/POTASSIUM PERCHLORATE

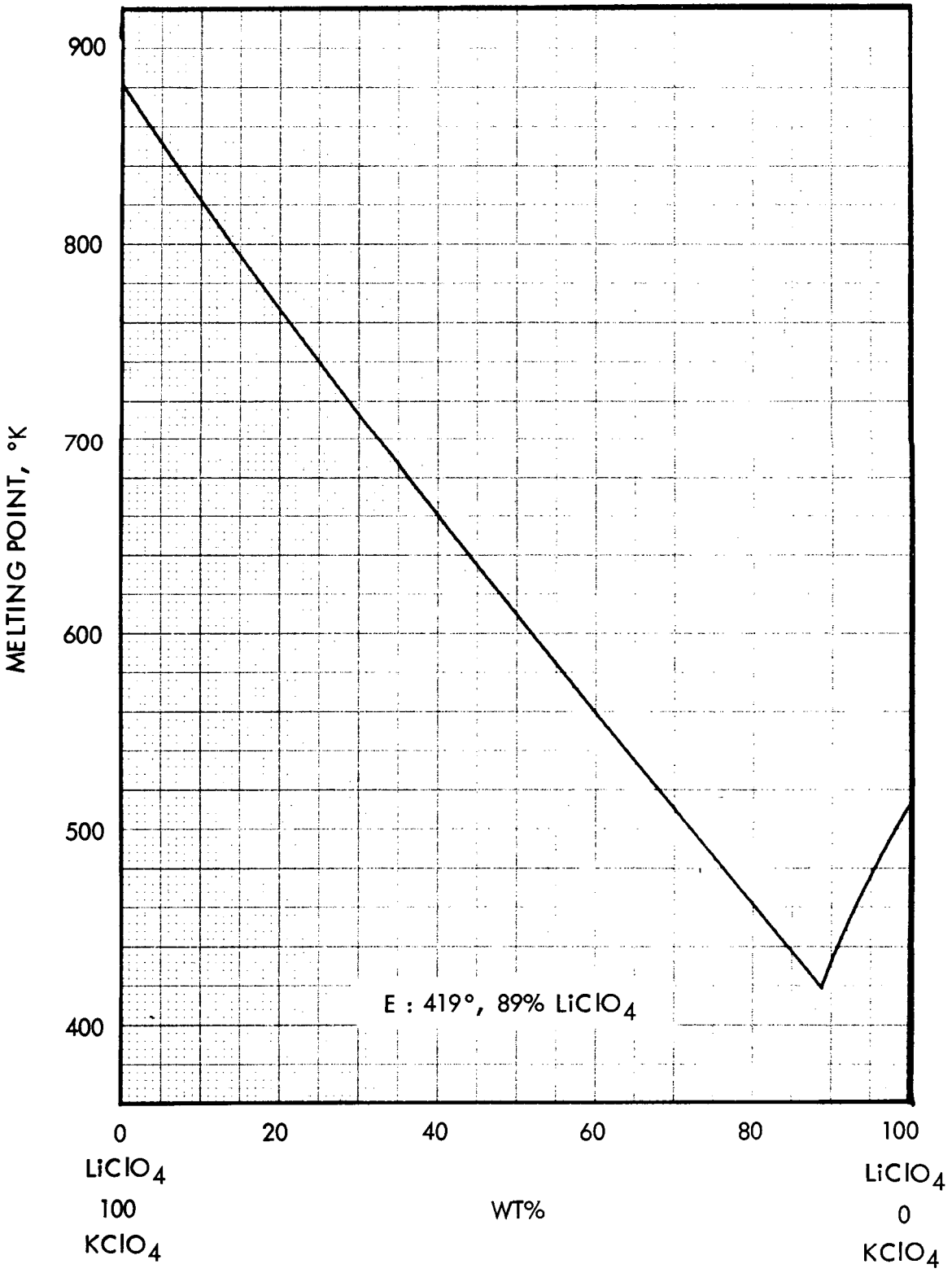


Figure 3-18

3.2 FUEL SELECTION

The fuel selection process for the high-temperature explosive program was very complex. While the number of oxidizers which qualified for this application was very small, a large number of fuels had to be screened for potential usefulness. Initially, the screening process included organic as well as inorganic fuels. Examples for inorganic fuels are hydrazine, sulfur, carbon, ammonium polysulfide or sodium polysulfide. However, these inorganic fuels were eliminated early in the program because they are too unstable or too reactive with the oxidizers. This left only the organic fuels for further evaluation.

It is estimated that there are currently close to 3 million organic compounds described in the literature. The criteria used to narrow this number down to a few candidate fuels for further experimental investigation were:

Good thermal stability
Low melting point ($<473^{o}K$)
Low vapor pressure (<1 bar at $505^{o}K$)
High density
High heat of combustion
Nonreactive with oxidizers
Miscible with inorganic oxidizers
High autoignition temperature in air
High flash point in air
Noncorrosive
Low vapor toxicity
No skin/eye hazard
Easy cleanup with water
No toxic combustion products
Readily available/low cost

Table 3-3 is a compilation of the physical and thermochemical properties of 43 organic fuels which were considered as candidates for a geothermal explosive. The compounds are arranged in the order of increasing numbers of carbon atoms per molecule, similar to the indexing system used by Chemical Abstracts.

In view of the large quantities of fuel which will eventually have to be handled at high temperatures and high pressures, the safety properties of the fuel are considered an important evaluation criterion. Fire, explosion and toxicity hazard data are compiled in Table 3-4.

Table 3-5 presents a summary of candidate fuels listed in order of increasing vapor pressures. From a standpoint of low volatility, the first compounds on this list would be the most desirable fuels to use. Typically, this list includes organic compounds which are currently used as plasticizers in plastics or as heat transfer fluids.

Table 3-3
PHYSICAL AND THERMOCHEMICAL PROPERTIES OF CANDIDATE FUELS

Formula	Compound	Molecular Weight	Melting Point °K	Boiling Point at 1.01325 bar °K	Density		Dielectric Constant		Heat Capacity		Heat of Formation		
					g/cm^3	@ °K	at °K		cal/g °K	@ °K	$(\Delta H)_{298}^f$ kcal/mol	kJ/mol	State
CH_3NO	Formamide	45.04	275.5	483.7 d	1.133	293	109	293	0.551	292	-61.6	-257.7	S
$CH_6N_4O_3$	Guanidinium nitrate	122.08	489	d	1.436	303					-93.0	-389.1	S
C_2H_5NO	Acetamide	59.07	355.3	494.2	1.159	293	59	356			-75.9	-317.6	L
C_2H_6OS	Dimethylsulfoxide	78.1	291.4	462	1.100	293					-47.2	-197.5	L
$C_2H_6O_2$	1,2-Ethanediol (Glycol)	62.1	284.5	471	1.113	293	37	298	0.571	288	-108.73	-454.9	L
$C_3H_6N_6$	Melamine	126.12	627 d	Sub	1.573	523			0.351	313	-15.35	-64.2	S
C_3H_7NO	Dimethylformamide	73.09	202.5	422	0.944	298							
$C_3H_7O_2$	2-Methoxyethanol	76.1	187.9	383							-114.8	-480.3	L
$C_3H_8O_3$	1,2,3-Propanetriol (Glycerol)	92.1	293	563 d	1.262	298	42.5	298	0.669	373	-159.8	-668.6	L
$C_4H_8O_2S$	Sulfolane	120.17	299	558	1.276	289	44		0.26	473			
$C_4H_{10}O_3$	Diethyleneglycol	106.12	262.5	518	1.118	293					-149.7	-626.3	L
C_5H_5N	Pyridine	79.1	231	388.5	0.982 0.978	293 298	12.3	298	0.431	294–381	+23.9	+100.0	L
C_5H_9NO	N-Methyl-2-pyrrolidone	99.1	248.7	475	1.027	298	32.2		0.40	293			
$C_5H_{12}O_4$	Pentaerythritol	136.2	542	Sub							-219.7	-919.2	S
$C_6H_4N_2O_4$	m-Dinitrobenzone	168.1	363	564	1.571	273	34.8	298	0.405	363	-6.2	-25.9	S
$C_6H_5NO_2$	Nitrobenzene	123.1	278.7	483.8	1.205	288			0.339	303	+3.8	+15.9	L
$C_6H_6O_2$	Resorcinol	110.1	384	554	1.272				0.452	273	-85.7	-358.6	S
$C_6H_{12}N_2$	Triethylenediamine	112.2	431	447							-3.4	-14.2	S
$C_6H_{14}O_3$	Diethylene glycol di-me-ether	134.2		435									
$C_6H_{14}O_3$	Diethylene glycol mono-et-ether	134.2		475	0.988	293							
$C_6H_{14}O_4$	Triethyleneglycol	150.2	268	551.3	1.127	288					-191.4	-800.8	L

d = decomposes

Sub = Sublimes

Table 3-3 (Concluded)
PHYSICAL AND THERMOCHEMICAL PROPERTIES OF CANDIDATE FUELS

Formula	Compound	Molecular Weight	Melting Point °K	Boiling Point at 1.01325 bar °K	Density		Dielectric Constant		Heat Capacity		Heat of Formation		
					g/cm³	@ °K	at °K		cal/g °K	@ °K	$(\Delta H)_{298}^{f}$ kcal/mol	kJ/mol	State
$C_6H_{15}NO_3$	Triethanolamine	149.2	294.2	550	1.124	293					-159.5	-667.3	L
$C_7H_6N_2O_4$	2,4-Dinitrotoluene	182.14	344	573 d							-16.3	-68.2	S
$C_7H_7NO_2$	2-Nitrotoluene	137.1	263.5	493.4	1.162	292	27.4	293			-6.0		L
$C_8H_4N_2$	Phthalonitrile	128.14	414	Subl.							+66.35	-25.1	S
$C_8H_5NO_2$	Phthalimide	147.14	511								-73.0	+277.6	S
C_8H_9NO	Acetanilide	135.17	387	578	1.219	288	2.9	293			-50.3	-305.4	S
$C_8H_{18}O_4$	Triethylene glycol di-me-ether	178.23		493								-210.5	
$C_9H_{14}O_6$	Triacetin	218.21	277.1	531	1.156	298					-316.1		L
$C_{10}H_7NO_2$	1-Nitronaphthalene	173.2	334.5	577 Sub	1.331				0.365	331.6	+11.0	-1323	S
$C_{10}H_8$	Naphthalene	128.2	353.6	491	1.162	293	2.52	293	0.402	360.5	+18.66	+46.0	S
$C_{10}H_{10}O_4$	Dimethylphthalate	194.2	273	556.8	1.192	293	8.5	297			-161.6	+78.1	L
$C_{10}H_{18}O_6$	Triethylene glycol diacetate	234.25		573								-676.1	
$C_{12}H_{10}O$	Diphenylether	170.2	299.8	531	1.075	293	3.65	303	0.38	298	-3.48		L
$C_{12}H_{10}O_2S$	Diphenylsulfone	218.3	396	652							-53.3	-14.6	L
$C_{12}H_{10}O_2S$	4,4'-Thiodiphenol	218.3	425.4		1.385	298						-223	
$C_{16}H_{22}O_4$	Di-n-butylphthalate	278.4	233	613	1.042	298					-198.3	-829.7	L
$C_{18}H_{15}O_4P$	Triphenylphosphate	326.3	323		1.286								
	Dowtherm G		<277										
	Therminol 55	~340							0.670	533			
	Therminol 60	~250							0.518	450			
	Therminol 66	~240							0.555	505			
	Silicone oil												

Table 3-4
SAFETY PROPERTIES OF CANDIDATE FUELS

Formula	Compound	Flammability Limit in air, % by Volume		Flash Point °K	Autoignition Temp in air °K	Auto-decomposition Temp. °K	TLV (1975) ppm (mg/m^3)	LC_{50} ppm	LD_{50} mg/kg B.W.	Mode Animal
		Lower	Upper							
CH_3NO	Formamide						20		5,700	Skin-G-pig
$CH_6N_4O_3$	Guanidinium nitrate									
C_2H_5NO	Acetamide									
C_2H_6OS	Dimethylsulfoxide			368					20	Oral-rat
$C_2H_6O_2$	1,2-Ethanediol (Ethyleneglycol)	3.5		389	795		100		5,840	Oral-rat
$C_3H_6N_6$	Melamine								>3,200	Oral-rat
C_3H_7NO	Dimethylformamide			340	718		10	<100	1,122	Oral-mouse
$C_3H_8O_2$	2-Methoxyethanol	2.5	20	319	653		25	1500 lethal-mouse	2,460	Oral-rat
$C_3H_8O_3$	1,2,3-Propanetriol (Glycerol)			433	773		(10)		31,500 (lethal)	Oral-mouse
$C_4H_8O_2S$	Sulfolane			436					>2,000	Oral
$C_4H_{10}O_3$	Diethyleneglycol			411					3,300	Oral-cat
C_5H_5N	Pyridine	1.8	12.4	293	755		5	4,000 (lethal)	800	Oral-rat
C_5H_9NO	N-Methyl-2-pyrolidone	2.18	12.4	368	619			>Saturation	7,000	Oral
$C_5H_{12}O_4$	Pentaerythritol						(10)		Nontoxic	
$C_6H_4N_2O_4$	m-Dinitrobenzene			423		548 >573	(1)		27	Oral-cat
$C_6H_5NO_2$	Nitrobenzene			361	829		1		700 (lethal)	Oral-rabbit
$C_6H_6O_2$	Resorcinol			400			(10)		370 (lethal)	Oral-rat
$C_6H_{12}N_2$	Triethylenediamine									
$C_6H_{14}O_3$	Diethylene glycol di-me-ether			340						
$C_6H_{14}O_3$	Diethylene glycol monoethylether			369					9,740	Oral-rat

Table 3-4 (Concluded)
SAFETY PROPERTIES OF CANDIDATE FUELS

Formula	Compound	Flammability Limit in air, % by Volume		Flash Point °K	Autoignition Temp in air °K	Auto-decomposition Temp. °K	TLV (1975) ppm (mg/m^3)	LC_{50} ppm	LD_{50} mg/kg B.W.	Mode Animal
		Lower	Upper							
$C_6H_{14}O_4$	Triethylene glycol	0.9	9.2	439	644				2,206	Oral-rat
$C_6H_{15}NO_3$	Triethanolamine			358					8,000	Oral-rat
$C_7H_6N_2O_4$	2,4-Dinitrotoluene						(1.5)			
$C_7H_7NO_2$	2-Nitrotoluene				945		5			
$C_8H_4N_2$	Phthalonitrile						(5)			
$C_8H_5NO_2$	Phthalimide									
C_8H_9NO	Acetanilide	1.0			818				800	Oral-rat
$C_8H_{18}O_4$	Triethylene glycol di-me-ether									
$C_9H_{14}O_6$	Triacetin			416					>6,900	Oral-rat
$C_{10}H_7NO_2$	1-Nitronaphthalene									
$C_{10}H_8$	Naphthalene	0.88	5.9	352	799		10			
$C_{10}H_{10}O_4$	Dimethylphthalate			436	829		(5)		6,900	Oral-rat
$C_{10}H_{18}O_6$	Triethylene glycol diacetate									
$C_{12}H_{10}O$	Diphenyl ether	0.8		388	893		<1		5,660	Oral-rat
$C_{12}H_{10}O_2S$	Diphenyl sulfone									
$C_{12}H_{10}O_2S$	4,4'-Thiodiphenol								3,362	Oral-rat
$C_{16}H_{22}O_4$	Dibutylphthalate			430	676		(5)		8,000	Oral-rat
$C_{18}H_{15}O_4P$	Triphenyl phosphate			493			(3)		>6,400	Oral-rat
	Dowtherm G			425	1,030°F					
	Therminol 55				630					
	Therminol 60				719					
	Therminol 66				647					
	Silicone oil			522–541	588–611					

Table 3-5
VAPOR PRESSURE OF HITEX FUELS AT 533°K (500°F)
ASCENDING ORDER

Name	$P_{533°K}$	
	mm Hg	Bar
Triphenylphosphate	14	0.019
Dowtherm G	83	0.11
Dibutylphthalate	89	0.12
Carbazole	90	0.12
Triethanolamine	~90	~0.12
Therminol 55	100	0.133
Therminol 66	115	0.153
Tetraethylene glycol	150	0.20
Therminol 60	250	0.33
Glycerol	375	0.50
Dimethylphthalate	415	0.553
Sulfolane	420	0.56
Phthalic Anhydride	440	0.59

Name	$P_{533°K}$	
	mm Hg	Bar
Triethyleneglycol	450	0.60
Diphenyl ether	800	1.07
Diethylene glycol	1,250	1.67
Diacetamide	2,000	2.67
Nitrobenzene	2,000	2.67
Acetamide	2,250	3.00
Formamide	3,500	4.67
Ethyleneglycol	4,250	5.67
Dimethylsulfoxide	5,000	6.67
Methylpyrrolidone	7,000	9.33
1,2-Diethanolethane	10,000	13.3
Dimethylformamide	11,000	14.7
Pyridine	15,000	20.0

Despite the tremendous number of organic compounds that are potentially useful as fuel for high-temperature explosives, most of the organic compounds are not miscible with inorganic nitrate oxidizers. It has been found from the detonation tests that poorly mixed or nonmiscible oxidizer and fuel combinations resulted in poor or nondetonable mixtures. In those instances where normally immiscible combinations were induced to detonate, such as mixtures of nitrate with dimethylphthalate, silicone oil and triphenyl phosphate, physical methods were employed to create a fine suspension of the oxidizer-fuel components by high-speed stirring and the use of a gelling agent such as Cab-o-sil. In those tests where closed systems had to be employed such as the 24-hour detonation test, high pressure detonation test, etc., significant difficulties would be encountered in obtaining an intimate mixture of oxidizer and fuel if they are normally immiscible. Also, if such combinations were chosen, the field application would be plagued by the same problems. It will then be necessary to ensure that the oxidizer and fuel components remain "mixed" at the depth of 2,000 meters or more. Due to the amount of problems encountered with immiscible mixtures, more and more efforts were directed toward systems of miscible mixtures.

It was felt that in order for an organic fuel to have good solubility with inorganic nitrate, it should contain polar functional group(s) in the molecular structure. Such functional groups might be hydroxy, carboxylic, acid chloride, ester, amide and ether, etc.

A literature survey shows that only low molecular weight polar organics have good solubility for water. In addition, organic acids are likely to decompose (losing CO_2) when heated to high temperatures. The low molecular weight esters and ethers are generally too volatile while high molecular weight esters and ethers, e.g., dimethylphthalate, DEGDME, are generally immiscible with nitrates. These above compounds were thus largely eliminated during early stages of the development.

Considerable work was conducted with hydroxy group containing compounds such as glycerol, low molecular weight glycols and triethanolanine. These were all miscible with nitrates and, as a group, were powerful fuels. A number of pierced witness plates resulted from detonating mixtures containing oxidizer and glycols. However, the same functional groups that allow these compounds to be easily miscible with nitrates also allow the molecules to be readily oxidized. Prolonged heating of these hydroxy-containing compounds with oxidizer usually led to charring.

The next group to be considered were amides. Those amides under consideration were formamide, acetamide, and dimethylformamide. All are highly soluble in water. For example, at any temperature above 268°K, formamide is completely miscible with water. At 293°K, 100 g water will dissolve 225.8 g acetamide. Of the three, both formamide and acetamide are also miscible with the inorganic oxidizers. Acetamide has then received greater interest because of its slightly higher fuel value compared to formamide.

In comparison with the hydroxy group containing compounds, the fuel value of acetamide is considerably less. The fact that the latter is further oxidized than hydroxy group containing compounds reduces the amount of energy available. This shortcoming, however, is compensated by increased stability toward attack by an oxidizer.

During the course of this investigation, most compounds came to our attention within the above classifications. There were nevertheless a number that appeared as a result of constant and continuous efforts to seek additional alternatives. Among these were compounds such as sulfolane, guanidinium nitrate, N-methyl-2-pyrrolidone, melamine, phthalimide, and phthalonitrile, etc. Some of these remained under serious considerations until near the end, and eventually some of these became selected as the final candidates. In order to elucidate some of the selection processes and to provide a better understanding for some of these fuels, the following paragraphs are devoted to a more detailed description of the candidate fuels.

Acetamide – Acetamide is characterized by its remarkable solvent power. It is related to hydrocarbons through its methyl group; to polar compounds through its carbonyl group; to alcohol and water through its tautomeric hydroxy group, $CH_3C(OH) = NH$; and to ammonia, ammonium salts and ammonia derivatives through its amino group. Furthermore, its high dielectric constant enhances its solvent action on inorganic compounds (Reference S13).

It is commercially available as white to slightly yellow deliquescent crystals. When pure, it is odorless, but most purity grades have an odor which reminds one of a cage with mice, attributed to an unknown impurity. Acetamide has a metastable form that melts at 69°C but slowly changes to the stable form on standing. This change is accompanied by an evolution of heat. The neutral and amphoteric characteristics of acetamide make it valuable as an antiacid in the laquer, explosives, and cosmetic industries.

Sulfolane – Sulfolane (synonyms: tetrahydrothiophene-1,1-dioxide, tetramethylene sulfone) has found increasing use as a solvent for numerous reactions in the chemical processing industry. Sulfolane is a thermally stable, clear liquid. As a polar compound, it is completely miscible with water and aromatic compounds, but does not mix with paraffinic hydrocarbons. Sulfolane is even somewhat hygroscopic.

If heated, sulfolane begins to decompose and split off sulfur dioxide. At 513°K, the rate of SO_2 formation is 24 mg/h per 250 ml sulfolane. In intimate contact with an oxidizing material, the rate of SO_2 formation may increase above that observed with the material by itself. As long as the interaction with the oxidizer does not lead to a runaway reaction, some SO_2 off-gassing by the mixed explosive at elevated temperature could be tolerated. Part of the SO_2 may be oxidized further to SO_3 or H_2SO_4 depending on the oxidizing power of the oxidizer used in the explosive.

Guanidinium Nitrate – Guanidinium nitrate is the salt of a monoacid base, guanidine, which has a strength equivalent to sodium hydroxide. It is prepared from dicyandiamide with ammonium nitrate/ammonia at 160°C for 1 hour. The resulting guanidinium nitrate is completely stable in boiling water, from which it is recrystallized. Guanidinium nitrate production is closely related to the production of melamine. Melamine can be prepared from guanidine and dicyandiamide or the latter with ammonia. It has been chiefly used to form synthetic resins with formaldehyde. Because of its high melting point and its immiscibility with molten nitrates, it was not further considered. Its potential use as the fuel component in a solid booster explosive might be considered in the future.

N-Methyl-2-pyrrolidone – N-methyl-2-pyrrolidone is sold by GAF Corporation under the trade name M-Pyrol® It is widely employed as a chemical reaction medium, a selective solvent for industrial petrochemical fluids and gases and other solvent applications for polymers. Having no active hydrogen, this remarkably stable heterocyclic compound is classed as an aprotic solvent (Reference G2). It is miscible with water and a wide range of other polar solvents. In absence of air, methylpyrrolidone could be recovered virtually unchanged in tests at temperatures as high as 700°K. The compound is not hydrolyzed appreciably in the presence of water. The compound is weakly basic and will form salts with anhydrous strong acids. Methylpyrrolidone is a good solvent for many chemicals, but solubility of sodium nitrate is insufficient to make a homogeneous explosive.

3.3 MIXTURE RATIO SELECTION

When selecting an oxidizer:fuel ratio for an internal combustion engine, a rocket propellant or an explosive, the maximum energy release is usually achieved with a stoichiometric mixture ratio. This

optimum ratio can be calculated from theoretical considerations as soon as the molecular weights of the reactants are known. However, in the case of combustion of organic compounds, different results are obtained depending on if one assumes oxidation of all carbon to carbon monoxide or carbon dioxide. In the presence of excess oxidizer and at moderate temperatures, complete reaction to carbon dioxide is possible. However, at higher temperatures (above 2,000°K) carbon dioxide is unstable and decomposes to carbon monoxide and oxygen. Even with mixtures which are balanced to carbon dioxide, one can frequently observe carbon monoxide in the reaction products. Besides thermodynamic equilibrium, this may also have kinetic reasons. At the first glance, it does not appear to be useful to balance the stoichiometry of an explosive to carbon dioxide. Overoxidation would result in a loss of energy content per unit mass. The incremental energy gained by oxidizing from the carbon monoxide state to the carbon dioxide state is only small compared to the total amount of energy released.

While it is undesirable to have a two-phase explosive (either two nonmiscible liquids or liquid/solid combination) from the standpoint of maintaining a uniform mixture and difficulty in preventing separation (sedimentation, "unmixing") of the explosive downhole, it may be worthwhile to consider the benefit to be gained by addition of finely dispersed metal powder. The metal should have a high heat of combustion and must be readily available. Beryllium has a high heat of combustion, but it is toxic and expensive. The most economical metal additive is aluminum. Aluminum is used to increase the power of numerous explosives, including the TAL-1005C currently considered for oil and gas well stimulation. Aluminum was also tested in a castable explosive, but high-temperature capability was not yet demonstrated (H4).

In calculating reaction products and heats of detonation of CHNO explosives, it is common practice to assume the "water arbitrary", i.e., available oxygen first burns hydrogen to H_2O, then carbon to CO, then CO to CO_2. In the presence of alkali metals and earth alkali metals, the sequence of priorities will have to be rearranged. It must be assumed that the alkali metals or earth alkali metals have a higher affinity towards oxygen than hydrogen or carbon. Thus, if insufficient oxygen is available, alkali metal and earth alkali metal oxides will form first. After their oxygen demand is satisfied, water, carbon monoxide and carbon dioxide will form in that order. If there is an excess of oxygen, the metal oxides may form peroxides or superoxides. Secondary reactions could lead to hydroxides, carbonates or bicarbonates.

During the initial phases of the program, a CO stoichiometry was assumed when selecting mixture ratios, in particular those for open pipe tests where fuel loss by evaporation had to be anticipated. Evaporative fuel losses shift the mixture ratio in the direction of a CO_2 stoichiometry and beyond. For the sealed pipe tests, a CO_2 stoichiometry was chosen to start with because it was hoped that this would maximize the energy release. No fuel losses had to be feared for the sealed pipe tests. For the open pipe tests, the losses would depend on the vapor pressure of the fuel under test, the temperature, the rate of heating, the mode of agitation, the pipe geometry, the length of heating after reaching the desired test temperature, and the wind conditions. In view of this many variables, it was hard to predict the exact mixture ratio in open pipes at the moment when the detonator was inserted and fired. It is assumed that for most open pipe tests with volatile fuels, this ratio was somewhere between the CO and the CO_2 stoichiometry.

In a separate test series with the ultimately selected combination, fuel losses and oxidizer/fuel segregation upon cooling were tested by analyzing an explosive sample after heating to 477°K in an open pipe, and cooling to ambient temperature. The nitrate content had increased only insignificantly from 49 to 52 percent.

3.4 DISCUSSION OF CANDIDATE EXPLOSIVE COMBINATIONS

Theoretically, combining the 14 oxidizers and the 43 fuels listed in Tables 3-1 and 3-3, at least 602 combinations have to be considered for selection of mixtures for testing. However, the actual number tested is larger because the oxidizers were rarely used in the pure state, but oxidizer mixtures were preferred. Furthermore, many fuels were tested which were not worthwhile to include in Table 3-3.

The following paragraph discusses some explosive combinations which have received more attention in the course of this program or which have been reported by other investigators. However, none of the liquid combinations described in the literature to date is able to withstand 561°K for 24 hours without premature detonation or loss of detonability.

3.4.1 Nitric Acid Combinations

Explosive combinations with nitric acid have never found widespread use because the unpleasant handling characteristics of the concentrated acid. Nevertheless, nitric acid combinations have been re-investigated periodically, but the conclusions as to practical usefulness were either incomplete or nonexistent.

Mixtures of nitrobenzene, nitric acid, and water are explosive over a wide range of compositions and an explosion of such a mixture destroyed a commercial nitration plant in Kingsport in 1960. The fact that these mixtures are explosive is already known for more than 100 years, and early patents covering two-component explosives based on nitric acid and nitrobenzene date back as far as 1880 (References H1 and H2). The first publication on this system (as a matter of fact the first publication pointing out the safety advantages of two-component explosives per se) already states that:

> "The nitrobenzene mixture (28.08% nitrobenzene, 71.9% nitric acid, balanced to CO_2) explodes with intense violence if fired by a detonating fuse. Nitrobenzene is freely soluble in nitric acid, from which it separates again when diluted with water to about 1.42 specific gravity. Some heat is evolved at the beginning of the mixing; hence, larger quantities require cooling. I noticed a rise to 50°C in mixing 25 cc." (Reference S3).

The nitration of nitrobenzene to polynitrobenzenes is dependent on the concentration of nitronium ions. Pure nitric acid dissociates to a small extent to produce nitronium ions:

$$2\,HNO_3 \rightleftharpoons H_2NO_3^{\oplus} + NO_3^{\ominus}$$

$$H_2NO_3^{\oplus} \rightleftharpoons H_2O + NO_2^{\oplus}$$

The first reaction is fast, but the second one is relatively slow. The presence of water, which is frequently formed as a reaction product, retards further nitration. Vice versa, if concentrated sulfuric acid is added, concentration of $NO_2^{\oplus}$ is increased and nitration of benzene can be carried beyond the step of nitrobenzene. This would be undesirable for the use of nitric acid/nitrobenzene mixtures as two-component explosives. Studies on the nitration of nitrobenzene at ambient temperature using mixtures of nitric acid, water, and sulfuric acid indicate that (in the absence of sulfuric acid) no dinitrobenzene is formed until the nitric acid concentration exceeds 82% by weight (Reference G1).

The nitration of nitrobenzene to form dinitrobenzene could be tolerated and would not detract from the explosive value of the mixture, if it was not accommodated by side reactions leading to the release of nitric oxide and nitrogen dioxide. These nitrous gases could possibly autocatalyze further nitration and render the entire mixture less stable. This is one reason why formation of nitrous gases has to be carefully avoided during nitration of ethanol to produce ethyl nitrate. Mixtures of alcohols with nitric acid are powerful explosives, but they have to be avoided because the nitration may proceed in a runaway reaction.

There is also concern that ferric ion and other transition metals, which must be expected in a downhole environment with nitric acid, may catalyze further nitration of nitrobenzene and reduce the stability of nitric acid/nitrobenzene mixtures.

Kurbangalina (Reference K1) measured detonation properties and critical diameters of mixtures of nitric acid with nitrobenzene, m-nitrotoluene, dichloroethane, glycol and methanol in comparison to molten TNT and glycerin trinitrate. The nitric acid used for preparation of the explosive mixtures had a density of 1.51 g/cm^3, which corresponds to a concentration of 100%. The components were mixed several minutes before the explosion and were kept cooled in water or snow until used. This mode of testing was significantly different from the one used during the HITEX development with regard to the temperature environment of the explosive prior to testing. A mixture of 72% nitric acid and 28% nitrobenzene which was balanced for CO_2 stoichiometry ("zero oxygen balance") detonated in thin-walled glass tubes down to 0.6 mm, whereas such sensitive explosives such as glycerin trinitrate or methyl nitrate no longer detonated stably when the tube diameter was below 2 mm. If a heavy-walled glass capillary was used, the nitric acid/nitrobenzene mixture would propagate a detonation even through a 0.25 mm I.D. column of liquid. The stoichiometric mixture was also found to be more sensitive toward HVD initiation than glycerin trinitrate. While 80 mg lead azide were sufficient to initiate HVD, 300 mg of lead azide were required to induce HVD in glycerin trinitrate.

A very detailed investigation of the card gap detonability of the system nitric acid/nitrobenzene/water in 25 mm (1 inch) diameter charges showed that only homogeneous mixtures were detonable (zero cards) (Reference M5). The limits of detonability coincided with the miscibility limits except for mixtures close to the corners of the triangular chart. The detonability (expressed as card gap width) as a function of nitric acid concentration in nitrobenzene showed an optimum at the (CO_2) stoichiometric composition. Increasing the temperature from 298 to 353°K widened the detonable

range distinctly. The desensitization caused by low concentrations of water was quite marked. Eight percent water was sufficient to reduce the card gap sensitivity from >127 mm to about 51 mm (Reference M5).

Limited testing was carried out with nitric acid/nitrobenzene mixtures in the course of this contract. While the mixture seemed very attractive from the standpoint of cost and availability of ingredients, detonation velocity, and lack of residues after detonation, other properties, such as lack of thermal stability, excessive mechanical shock sensitivity, corrosiveness and toxicity eliminated these combinations from further consideration for geothermal applications.

Mixtures of 22% dimethyl ether, 77% nitric acid, and 1% water have been named "Disalite" and tested as explosives (Reference A2). A similar mixture called "Nisalite" was composed of 79.5% nitric acid and 20.5% acetonitrile also detonated at 6,250 m/s with 83 k bar. Addition of 18% water reduced the cap sensitivity of Nisalite to that of commonly handled explosives such as molten TNT. No data were given on thermal stability of these mixtures.

Solutions of amine nitrates, e.g., tetramethylammonium nitrate or pyridinum nitrate, in nitric acid have at one time or another been considered as monopropellants and could possibly be formulated to form explosives instead. However, all these organic amines and their nitrate salts are not very stable at elevated temperatures and do not fulfill the objective of the HITEX program.

During the development of monopropellants based on quaternary ammonium salts dissolved in nitric acid (Reference B6), general rules on the compatibility of amines and nitric acid have been derived which may also be useful in the selection of amines for nitric acid-based explosive combinations:

- Any unsaturation (olefinic, acetylenic, aromatic) must be avoided
- Strained rings (ethylene imine) must be avoided.
- Tertiary carbon bonded to hydrogen or nitrogen must be avoided.
- Flexible ring structures (piperazine) cannot be used.
- Terminal carbon chains must be as short and as few as possible. Methyl groups are more stable than ethyl groups. Three methyls are better than four. The length of carbon chains between two nitrogens does not seem to be so critical.

The thermally most stable propellant in this group was the bis-quaternary salt from triethylene-diamine and methyl (chloride) dissolved in nitric acid. This mixture, called Cavea, had a card gap sensitivity of positive at zero cards and could be heated in a sealed bomb at 433°K (320°F) for more than 48 hours without exothermic decomposition. Other combinations were more sensitive in the card gap test and would also autodecompose at lower temperatures. The other quaternary ammonium salts were:

$$(CH_3)_4N^{\oplus} \qquad (CH_3)_3C_2H_5N^{\oplus} \qquad i\text{-}C_3H_7(CH_3)_3N^{\oplus}$$

$$(CH_3)_3N^{\oplus} - CH_2 - CH_2 - N^{\oplus}(CH_3)_3 \qquad (CH_3)_3N^{\oplus}(CH_2)_3N^{\oplus}(CH_3)_3$$

Of these, only the first and the third were stable for more than 24 hours at 433°K (320°F). The card gap sensitivity was 5 and 15 cards, respectively. This is too sensitive for practical applications.

3.4.2 Eutectic Nitrates and Organic Fuels

One of the major shortcomings of nitric acid explosives is the high vapor pressure, corrosivity and toxicity of this oxidizer. The good oxidizer properties of nitric acid are preserved in the alkali metal and earth alkali metal nitrates, though at the expense of reduced useful oxygen content. It was expected that a larger group of fuels would be compatible with nitrates than with nitric acid. However, only few of these turned out to be miscible with the salt melts.

One of the initial choices of oxidizers was the heat transfer salt (HTS), mainly because it was readily available in large quantities and also because it has a relatively low melting point at 417°K. Nitrates and nitrites are, however, poor oxidizers compared to perchlorates of the same cation. A few of the fuels found detonable with other oxidizers (perchlorates or nitrates only) were nondetonable or inconsistently detonable with HTS. Those combinations that were detonable generally showed weaker detonating force. As a comparison, using ethylene glycol as the fuel, a relative indentation of 19 mm was observed for $NaClO_4$ oxidizer versus a relative indentation of only 3.4 mm for HTS as oxidizer.

In this series, some immiscible mixtures were explored as well. Remote stirring of the immiscible mixtures was necessary prior to initiation. These positive tests lend support to the postulation that most oxidizer-fuel systems can be caused to detonate, provided that the two components are well mixed and provided that sufficient activation energy is provided, i.e., by detonating the mixture at elevated temperatures.

A large number of explosive formulations of ammonium nitrate with organic compounds have been patented. They all lack the thermal stability required for the geothermal environment. Binary and ternary mixtures of ammonium nitrate, sodium nitrate and ethylene glycol can be used at temperatures up to 333°K (Reference N1).

The lithium-sodium-potassium nitrate eutectic, $(LiNaK)NO_3$, has the advantages of lower melting, 393°K (120°C), and of being a better oxidizer (only nitrates, no nitrite) than HTS. One drawback with this oxidizer is the cost of lithium nitrate which is comparatively expensive. As a result, $(LiNaK)NO_3$ was abandoned in favor of another nitrate oxidizer, substituting calcium nitrate for lithium nitrate. The sodium-potassium-calcium nitrate eutectic, $(NaKCa)NO_3$, was selected as the final oxidizer to be used. Early testing with this oxidizer gave inconsistent results because the water of hydration from hydrated calcium nitrate was retained in the eutectic. Thus, detonability of its mixture with fuels depended on how much water evaporated during the heatup period. Later on, only the dehydrated $(NaKCa)NO_3$ was used. Dehydrated $(NaKCa)NO_3$ was used in all the safety and performance tests of the candidate explosive. This series included some interesting findings. One of these was finding that $(NaKCa)NO_3$ and guanidinium nitrate ($GuNO_3$) mixture detonated with high order detonation velocity when initiated by just a number eight cap. Another was a test to see if detonation of a $(NaKCa)NO_3$ acetamide mixture would propagate through a 12-inch long pipe. This was confirmed.

Sulfolane as the fuel component in an explosive is probably a novel idea. The present investigators are unable to find any previous reference to its explosive application. The compound is obtainable through Phillips Chemical Company. It has been suggested as a solvent for aromatic extractions and acid gas removal. The low melting point of sulfolane at 299°K, with a boiling point at 558°K, made it a likely contender as the fuel component for the high temperature explosive for geothermal application. A severe dent on the witness plate resulted from detonating (NaKCa)NO_3-sulfolane mixture.

Finally, a surprising result that even a (NaKCa)NO_3-silicone oil mixture detonated prompted the investigators to reaffirm a suspicion that most oxidizer-fuel combinations are detonable given the "right conditions".

The investigators were very surprised to see eutectic mixtures of nitrates with acetamide proposed as phase change materials for the storage of solar or off-peak energy in homes without a precautionary note attached (Reference L2). The mixtures were described as "inoffensive and . . . low order of toxicity". The upper temperature for this proposed application would have been 378°K. Admittedly this temperature is significantly below the temperatures used during the current programs, but a large tank of the mixture in the basement of a house would constitute an undue hazard. Melting points of eutectic mixtures of nitrates and acetamide are listed in Table 3-6. The eutectic with lithium nitrate melts slightly above ambient temperature. The eutectic compositions are all fuel-rich. They may not be quite as powerful explosives as the stoichiometric mixtures tested during this program.

Table 3-6
COMPOSITION AND MELTING POINTS OF NITRATE/ACETAMIDE EUTECTICS

Nitrate	Weight-% Nitrate	Melting Point °K
Acetamide only	0	353
Potassium nitrate	9.8	345
Sodium nitrate	20	332
Ammonium nitrate	39	311
Lithium nitrate	23	298

Source: Lorsch, et. al (Reference L2)

From the previous discussions thus far, one can say in general that perchlorate oxidizers are more powerful oxidizers than nitrate in explosive applications; but owing to the high melting property of most perchlorates, it is difficult to seriously consider them as the main oxidizer component for the intended applications here. It is, however, possible to add up to about 20% by weight of the perchlorate to a nitrate-based oxidizer to increase the performance of the resultant explosive. A comparison of the indentations of witness plates with those obtained with nitrate oxidizer alone does indicate improved performance of the perchlorate-spiked explosives.

3.4.3 Perchlorate Oxidizers and Organic Fuels

As a safety precaution, perchlorates should never be mixed with organic compounds in the laboratory. Accidents have occurred when attempting to digest organic materials with perchlorates in preparation for metals analysis. When handled with appropriate care, it would be conceivable that powerful high temperature explosives could be formulated from perchlorates and organic compounds. The main disadvantage of perchlorate oxidizers is the high melting point, even of eutectic perchlorates.

Numerous explosive formulations with perchlorates have been reported in the literature. These include heterogeneous as well as homogeneous systems, but none was intended to be used as a liquid at high ambient temperatures. A castable explosive has been described using sodium perchlorate and hydracrylonitrile, glycolic acid, acetamide and ethanolamine (Reference H4). Several low-melting eutectics of lithium perchlorate with other oxidizers or fuels have been proposed as ingredients for explosives or propellants. The solubility of lithium perchlorate in many organic solvents, such as diethyl ether, acetone, n-propane, ethanol or methanol make it possible to obtain homogeneous explosive solutions. Eutectics of lithium perchlorate with triamino guanidinium perchlorate melt at temperatures from room temperature to 355°K (Reference B3). The thermal stability of these mixtures at higher temperatures is unknown. A mixture of 74.3% potassium perchlorate and 25.7% carbon was found to ignite at 633°K (Reference G3). Organic compounds would most likely be more reactive than elemental carbon, and decomposition would occur at lower temperatures. Mixtures of potassium perchlorate and carbon would be very difficult to handle as a well stimulation explosive because the oxidizer melts only at a very high temperature.

Magnesium perchlorate is used as a desiccant because, in the anhydrous state, it has a high affinity toward water. However, it is not as deliquescent as other desiccants. As an oxidizer in explosives, it has been considered in solutions of 32 to 57% by weight magnesium perchlorate in mixtures of 22 to 57% nitroalkane and 5 to 27% of a polyglycol ether (Reference V1). Apparently, it is more soluble than the alkali metal perchlorates. Thermal stability of the above mixtures is unknown, but probably insufficient for geothermal applications. The magnesium perchlorate itself also is less stable than its counterparts derived from alkali metals. Its melting point is so high that it would be difficult to pump and meter it in the molten state.

A barium perchlorate/carbazole premixed solid explosive has been patented for high temperature applications (Reference P4). A stoichiometric mixture of 87.7% by weight barium perchlorate and 12.3% carbazole (balanced to CO_2 as reaction product) gave the highest indentation in a

mortar/bullet type testing device. The material could be heated to 490°K at a rate of 3.1°/minute and could be held at that temperature for at least two hours without change in ballistic properties when fired after cooling to ambient temperature. The composition was intended for explosively actuated devices in oil wells, such as bullet perforators, core takers, bridge-plug setting tools, and well tool valves. These applications do not necessarily require a high detonation velocity, and the compositions may have to be classified as "propellants" rather than "explosives".

3.5 CANDIDATE SELECTION

The final candidate explosive selected is one consisting of $(NaKCa)NO_3$, guanidinium nitrate, and acetamide where the latter two substances are combined in the ratio of 7:3 by weight and considered as the fuel component.

In tracing the steps leading to the above selection, it may be well to reiterate here some of the criteria of a chemical explosive for geothermal well fracturing. First, it is desirable to develop a two-component liquid explosive such that both the oxidizer and the fuel component can be pumped into the ground separately and then combined below ground to form the explosive. To be practical, both components should be liquids at or below about 422°K (300°F). The advantage of a final liquid explosive is its ability to penetrate into fissures extending from the borehole and cause a more effective fracturing. Secondly, the candidate explosive must tolerate the high temperatures found in the geothermal wells and remain detonable for at least the length of the loading period. Many of these temperatures are above 477°K (400°F). Thirdly, the candidate should be compatible with the well environment such as the rock formation, the types of well fluids present, and the equipment involved in the stimulation process.

One of the preliminary explosive formulations was a mixture containing just $(NaKCa)NO_3$ and acetamide. This combination appeared to have satisfied the above-mentioned requirements, except that it is not a particularly powerful explosive.

The possibility of adding another ingredient to the preliminary formulation was considered. The impressive detonation test result from the $(NaKCa)NO_3$-guanidinium (= Gu) nitrate mixture stirred renewed interest in the latter component. Guanidinium nitrate had been somewhat ignored because it was said to be an explosive by itself (Reference M6), although it is extremely insensitive to explosive primers. In addition, the high melting temperature of guanidinium nitrate at 488°K (215°C) discouraged any serious consideration unless a suitable solvent could be found. Incidentally, the thermal stability test of $(NaKCa)NO_3$ - $GuNO_3$ indicated it to be a rather stable mixture.

Since acetamide is well known for its excellent solvent ability, consideration was given to combining it with guanidinium nitrate to form the fuel component. The effect of diluting guanidinium nitrate with acetamide served two purposes: 1) formation of a low melting mixture, and 2) creating a more oxygen-deficient and hopefully completely nondetonable mixture.

Additional test data suggest that 85:15, 75:25, 65:35 mixtures of guanidinium nitrate to acetamide are not detonable at 505°K (450°F). Even guanidinium nitrate was not detonable at 505°K with a number eight cap. The present choice of guanidinium nitrate to acetamide ratio in the mixture is 70% to 30% by weight, respectively, resulting in a fuel mixture melting at 437°K (327°F). A pumpable slurry, however, is formed below this temperature. As this ratio is presently an arbitrary one, it can be varied in actual application depending on the required melting point. Increasing guanidinium nitrate concentration would raise the mixture melting temperature and would also increase the force of the explosive. Decreasing guanidinium nitrate concentration would have the opposite effects. This ratio can conceivably be formulated according to the optimal detonation velocity associated with each type of geological formation. A possible future task may be to determine the variation of detonation velocity as a function of fuel mixture ratio.

Safety test results and performance test results of the candidate explosive are found in Section 4.0 of this report.

4.0 EXPERIMENTAL RESULTS

The sequence of experimental results reported and discussed in this chapter follows the same outline as that used in Chapter 3 for describing the experimental methods used.

In reporting results of the various tests with explosive combinations, the following rationale has been chosen to arrange the data in a readily retrievable format: The combinations are grouped by oxidizer. The oxidizers are listed by cation in the sequence of the atomic numbers of the periodic table of elements. Within oxidizers with the same cation, the anions are arranged in the same sequence. Where more than one cation or anion is contained in the oxidizer, the oxidizer mixture is listed at the first possible location.

The fuels are listed in ascending number of carbon atoms, then hydrogen atoms, then nitrogen atoms, and eventually oxygen or other hetero atoms.

4.1 DEVELOPMENT TEST RESULTS

Results of development tests, including screening tests, differential scanning calorimeter tests, thermal stability tests, and material compatibility tests are presented in the following paragraphs. It is very difficult to condense the results of several months of laboratory work into a few pages and tables. In doing so, a large number of less successful experiments are being omitted for the sake of brevity of the report. All these negative tests are properly documented in the RRC laboratory notebooks to avoid any repetition of an unsuccessful experiment should additional reformulation work, for instance in an attempt to raise the temperature limitation even further, become necessary at a later time.

4.1.1 Screening Test Results

The objective of the screening tests was to eliminate combinations of oxidizers and fuels which react prematurely below the target temperature of 561°K (550°F). Some tests were also conducted with the fuel component alone to see if it would pyrolyze or ignite in air. Pyrolysis would eliminate the fuel from further consideration. Interaction with air is undesirable. Contact of fuel with air could be avoided by handling it in a hermetically-sealed system and blanketing it with nitrogen. However, the added complexity of handling fuels with low autoignition temperatures may be a reason to eliminate fuels which autoignite in air at temperatures below 561°K.

Only few of the mixtures, mostly those including nitric acid as oxidizer, reacted immediately upon mixing the constituents at ambient temperature. These reactions between organic bases and a strong inorganic acid were anticipated. One way to circumvent this reaction is to mix the nitrate of the base with nitric acid and still obtain a useful monopropellant or explosive. For example, the heat of solution of an amine nitrate in nitric acid is significantly less than the heat of neutralization.

Most organic compounds, except for low molecular weight glycols and amides and highly polar organic molecules, are not miscible with the inorganic oxidizers at the temperature range tested. For the most part, immiscible systems gave little indication of reaction between the oxidizer and the fuel. However, on prolonged heating, many fuels became discolored due to the breakdown of the organic compound by contact with the oxidizer at their interface.

Among the miscible mixtures, hydroxy group containing compounds reacted most readily. Except for ethylene glycol, mixtures of these compounds with oxidizers turned brown shortly after the mixture became fused. Glycols and nitrates tended to turn to dark brown or char, while with perchlorates the reaction at times led to ignitions or explosions. For example, during screening tests calcium perchlorate mixtures with glycerol or triethylene glycol exploded, ammonium perchlorate mixtures with glycerol and triethanol amine ignited.

Summaries of fuels heated with various oxidizers are presented in Tables 4-1 through 4-8. Essentially, the screening tests eliminated those combinations that readily reacted and those that reacted violently from serious considerations as high temperature explosives. They also helped to point out the difficulties that one may have in handling the mixtures such as sublimation and evaporation of the fuels. Inevitably, screening tests revealed that there is only a limited number of fuels miscible with inorganic oxidizers, specifically nitrates. Considerable efforts would have to be made in order to work with immiscible systems, and indeed considerable time and ingenuity were devoted to them until more promising completely miscible systems were identified.

4.1.2 Differential Scanning Calorimeter Results

Differential scanning calorimetry results are partly incorporated in the tables of screening test results (previous section) for ready comparison. A more complete set of data is presented in Tables 4-9 and 4-10. The temperatures reported are the onset of exotherms. If the DSC trace had a well defined peak exotherm, the temperature at which the maximum deflection occurred is reported under the column "Comments".

A typical DSC data trace is shown in Figure 4-1.

Besides for explosive mixtures, DSC was also used to analyze thermal stability of ingredients such as fuel or oxidizer mixtures. It was not attempted to quantify any of the exothermic or endothermic peaks in terms of surface area, which is proportional to the amount of energy released or absorbed. This type of analysis would require extremely accurate determination of sample weight in a controlled humidity environment. Most materials were very hygroscopic which made accurate weighing to 10^{-5} g very difficult. The DSC was also used to determine critical mass relationships as discussed in paragraph 4.5.3.

As the result of DSC tests, the field of candidates was narrowed to approximately 150 combinations. However, many of those combinations which passed the test were not acceptable based on other criteria, e.g., excessively high melting point or lack of miscibility. Surprisingly, the ultimately selected explosive (NaKCa) $NO_3/AcNH_2$ + $GuNO_3$, does not stand out among other

Table 4-1
EXPLOSIVE FORMULATION SCREENING TESTS – NITRIC ACID WITH ASSORTED FUELS

Fuel	Miscible	Screening Result at 561°K
70% Aqueous Nitric Acid		
Dimethyl sulfoxide	Yes	No reaction, reflux 394°K
Ethylene glycol	Yes	Brown gas
Pyridine	–	Charred
Methyl pyrrolidone	Yes	Brown gas
Pentaerythritol	Yes	Brown gas
m-Dinitrobenzene	Yes	Evaporation
Nitrobenzene	Yes	Evaporation
Triethylenediamine	–	Evaporation
Diethylene glycol di-me-ether	Yes	Brown
Diethylene glycol mono-et-ether	Yes	Brown
Triethylene glycol	Yes	Brown gas
Triethanolamine	–	Charred
2,4-Dinitrotoluene	Yes	Light yellow
2-Nitrotoluene	Yes (hot)	No reaction
1-Nitronaphthalene	Yes	Yellow
Naphthalene	No	Brown
Dimethyl phthalate	Yes	No reaction
Phenyl ether	No	Brown
Phenyl sulfone	Yes	No reaction
Dibutyl phthalate	No	Light brown
Triphenylphosphate	No	Yellow
Pluronic F38	Yes	Brown oil
Pluronic 25R8	–	Brown
Silicone oil	Yes	No reaction
Therminol 55	No	Brown gas
Therminol 60	No	Grown gas
Therminol 66	No	Brown gas, 395°K
90% Nitric Acid		
Formamide	Yes	Light yellow, foamed, 439°K
Guanidine nitrate	Yes	No reaction
Dimethylformamide	Yes	Light yellow
Pyridine	Yes	Brown gas
m-Dinitrobenzene	Yes	No reaction
Nitrobenzene	Yes	Red
Acetanilide	–	Brown gas, foamed, 397°K
1-Nitronaphthalene	Yes	Brown gas
Dimethyl phthalate	Yes	Slightly yellow
Dibutyl phthalate	Yes	Brown
Mineral oil	No	Brown gas
Therminol 55	No	Brown gas, foamed, 380°K

Table 4-2

EXPLOSIVE FORMULATION SCREENING TESTS – EUTECTIC NITRATE-NITRITE MIXTURE HTS (40 : 7 : 53% BY WT $NaNO_2$: $NaNO_3$: KNO_3) WITH ASSORTED FUELS

Fuel	Miscible	Screening Result at 561°K	DSC Exotherm
Formamide	Yes	Reflux	487°K
Guanidinium nitrate	Yes	Foamed, 494°K	485°K
Acetamide	Yes	No reaction, reflux 524°K	526°K
Dimethyl sulfoxide	Yes	Reflux 480°K	474°K +
Ethylene glycol	Yes	Yellow, reflux 487°K	483–513°K - large
Dimethylformamide	No	Reflux 427°K	
2-Methoxyethanol	No	Reflux	
Glycerol	Yes	Brown	550°K
Diethyleneglycol	Partially	Dark Brown	511°K+
Pyridine	–	Pyridine evaporated	
Methyl pyrrolidone	No	Brown, reflux 477°K	
Pentaerythritol	–	Charred	
m-Dinitrobenzene	No	No reaction	584°K+ - large
Nitrobenzene	No	Reflux 485°K	507°K+ - weak
Resorcinol	Yes	Charred	422, 541°K+
Triethylenediamine	–	Amine evaporated	507°F - sharp
Diethylene glycol di-me-ether	No	Reflux 437°K	
Diethylene glycol mon-et-ether	No	Reflux	660°F - weak
Triethylene glycol	No	Dark brown, reflux 558°K	489°K+
Triethanolamine	Yes	Brown	540°K+
2,4-Dinitrotoluene	No	Dark brown	
Benzoic acid	No	Decomposition	545°K+, 651°K
2-Nitrotoluene	No	Reflux 495°K	
Acetanilide	No	Red	
Triethylene glycol di-me-ether	No	Reflux 497°K	
1-Nitronaphthalene	No	No reaction	
Naphthalene	No	No reaction	None
Dimethyl phthalate	No	Light yellow, reflux 554°K	

Table 4-2 (Concluded)

EXPLOSIVE FORMULATION SCREENING TESTS – EUTECTIC NITRATE-NITRITE MIXTURE HTS (40 : 7 : 53% BY WT $NaNO_2$: $NaNO_3$: KNO_3) WITH ASSORTED FUELS

Fuel	Miscible	Screening Result at 561°K	DSC Exotherm
Phenyl ether	No	No reaction	546°K+
Phenyl sulfone	No	Yellow	None
Dibutyl phthalate	No	Light yellow	620°K - sharp
Triphenylphosphate	No	Yellow	580°K
Aluminum powder	No	No reaction	None
Graphite	No	No reaction	None
Dowtherm G	No	Reflux	
Mineral oil	No	No reaction	450, 600°K+
Pluronic F108	No	Brown	510°K - sharp
Pluronic F38	No	Brown	499°K - weak
Pluronic L31	No	Brown	
Pluronic L92	No	Brown	
Pluronic 17R4	No	Brown	
Pluronic 25R8	No	Brown oil	480, 601°K+
Polyglycol P-2000	No	No reaction	
Silicone oil	No	No reaction	None
Sodium polysulfide	–	Decomposition	610°K - large
Sulfur and charcoal	No	Sulfur evaporated	
Therminol 55	No	No reaction	
Therminol 60	No	No reaction	
Therminol 66	No	No reaction	

Table 4-3

EXPLOSIVE FORMULATION SCREENING TESTS – MIXED NITRATES (75 : 25% BY WT.)
GUANIDINIUM NITRATE-SODIUM NITRATE MIXTURE WITH ASSORTED FUELS

Fuel	Miscible	Screening Result at 561°K	DSC Exotherm
Formamide	Yes	Reflux 487°K	533°K
Acetamide	Yes	Red	546°K+
Dimethyl sulfoxide	Yes	Reflux 477°K	510°K+ - large
Ethylene glycol	Yes	Brown, reflux 470°K	490°K+
Dimethylformamide	Yes	Reflux 430°K	
2-Methoxyethanol	Yes	Reflux 411°K	
Glycerol	Yes	Charred	480+, 574°K - sharp
Pyridine	No	No reaction, reflux 383°K	
Methyl pyrrolidone	Yes	Charred	
Pentaerythritol	Yes	Charred	
m-Dinitrobenzene	No	No reaction	
Nitrobenzene	No	Reflux 485°K	
Resorcinol	Yes	Dark red	577°K
Triethylenediamine	—	Amine evaporated	
Diethylene glycol di-me-ether	Yes	Light yellow, reflux 472°K	499°K
Triethylene glycol	Yes	Dark red	505°K+
Triethanolamine	Yes	Dark red	
2,4-Dinitrotoluene	—	Brown	
2-Nitrotoluene	No	Reflux 495°K	
Triethylene glycol di-me-ether	No	Reflux 494°K	
1-Nitronaphthalene	No	No reaction	
Naphthalene	No	Red, reflux 494°K	
Dimethyl phthalate	No	Yellow	
Phenyl ether	No	Orange, reflux 533°K	
Phenyl sulfone	No	Yellow	
Dibutyl phthalate	No	Brown	
Triphenylphosphate	No	Yellow	
Dowtherm G	No	Red	
Mineral oil	No	No reaction	
Polyglycol P-2000	No	Yellow	
Silicone oil	No	No reaction	
Therminol 55	No	Yellow	
Therminol 60	No	No reaction	
Therminol 66	No	No reaction	

Table 4-4
EXPLOSIVE FORMULATION SCREENING TESTS – EUTECTIC NITRATE MIXTURE (23.3 : 16.3 : 60.4% BY WT. $LiNO_3$: $NaNO_3$: KNO_3) WITH ASSORTED FUELS

Fuel	Miscible	Screening Result at 561°K	DSC Exotherm
Formamide	Yes	Light yellow	528°K+
Guanidine nitrate	Yes	No reaction	600°K
Acetamide	Yes	No reaction, reflux 549°K	540°K
Dimethyl sulfoxide	Yes	Foamed	515+, 567°K
Ethylene glycol	Yes	Reflux 480°K	509+, 531°K - sharp
Dimethylformamide	No	Reflux 425°K	485°K
2-Methoxyethanol	No	Reflux 401°K	533, 556°K
Glycerol	Yes	Dark brown	450, 593°K - large
Diethyleneglycol	Yes	Brown	513°K
Pyridine	No	Pyridine evaporated	
Methyl pyrolidone	No	Brown	None
Pentaerythritol	Yes	Brown	573°K+
m-Dinitrobenzene	No	No reaction	455°K+
Nitrobenzene	No	Reflux 485°K	None
Resorcinol	Yes	Dark red	542°K+
Triethylenediamine	–	Amine evaporated	
Diethylene glycol di-me-ether	No	Reflux 436°K	None
Diethylene glycol mono-et-ether	No	Reflux	None
Triethylene glycol	No	Brown	526°K
Triethanolamine	Yes	Dark brown	501, 538°K
2,4-Dinitrotoluene	No	Brown	
Benzoic acid	No	Decomposition	521°K+
2-Nitrotoluene	No	No reaction, reflux 499°K	None
Acetanilide	No	Brown	
Triethylene glycol di-me-ether	No	Light yellow, reflux 499°K	428–497, 561°K
1-Nitronaphthalene	No	No reaction	533°K+
Naphthalene	No	Naphthalene evaporated	
Dimethyl phthalate	No	Yellow	None

Table 4-4 (Concluded)
EXPLOSIVE FORMULATION SCREENING TESTS – EUTECTIC NITRATE MIXTURE (23.3 : 16.3 : 60.4% BY WT. $LiNO_3$: $NaNO_3$: KNO_3) WITH ASSORTED FUELS

Fuel	Miscible	Screening Result at 561°F	DSC Exotherm
Phenyl ether	No	Reflux 537°K	
Phenyl sulfone	No	Yellow	None
Dibutyl phthalate	No	Yellow	566+, 635°K - sharp
Triphenylphosphate	No	Brown	508°K+
Aluminum powder	No	No reaction	–
Graphite	No	No reaction	–
Mineral oil	No	No reaction	
Pluronic F38	No	Brown	
Pluronic L92	No	Brown	
Polyglycol P-2000	No	No reaction	
Silicone oil	No	No reaction	
Sodium polysulfide	–	Exploded 558°K	590, 614°K - sharp
Sodium sulfide	–	Exploded 539°K	
Sulfur and charcoal	–	Sulfur evaporated	
Therminol 55	No	No reaction	
Therminol 60	No	No reaction	
Therminol 66	No	Yellow	

Table 4-5

EXPLOSIVE FORMULATION SCREENING TESTS – EUTECTIC NITRATE MIXTURE
(11.2 : 44.3 : 44.5% by Wt. $NaNO_3$: KNO_3 : $Ca(NO_3)_2 \cdot 4H_2O$)
WITH ASSORTED FUELS

Fuel	Miscible	Screening Result at 561°K	DSC Exotherm
Formamide	Yes	Brown	462°K+
Acetamide	Yes	Yellow, reflux 561°K	
Dimethyl sulfoxide	Yes	No reaction	
Ethylene glycol	Yes	No reaction, reflux 497°K	
Dimethylformamide	Yes	No reaction, reflux 504°K	
2-Methoxyethanol	Yes	No reaction	
Glycerol	Yes	Brown	
Diethyleneglycol	Yes	Charred	442°K+
Methyl pyrrolidone	No	Dark brown – charred	
Pentaerythritol	Yes Brown		
m-Dinitrobenzene	No	No reaction	
Nitrobenzene	No	No reaction, reflux 495°K	
Resorcinol	Yes	Charred	
Diethylene glycol di-me-ether	No	No reaction, reflux 514°K	
Diethylene glycol mono-et-ether	No	No reaction, reflux 475°K	
Triethylene glycol	Yes	Dark brown	
Triethanolamine	Yes	Charred	
Triethylene glycol di-me-ether	No	No reaction	
Dimethyl phthalate	No	Yellow	
Phenyl sulfone	No	No reaction	
Dibutyl phthalate	No	No reaction	
Triphenylphosphate	No	Brown	
Dowtherm G	No	No reaction	
Sodium polysulfide	–	Sulfur evaporated	

Table 4-6
EXPLOSIVE FORMULATION SCREENING TESTS –
STABILIZED AMMONIUM PERCHLORATE*
(90 : 10% By Wt. NH_4ClO_4 : NH_4BF_4)
WITH ASSORTED FUELS

Fuel	Miscible	Screening Result at 561°K
Formamide	Yes	Reflux, 475°F
Ethyleneglycol	No	Brown
Glycerol	Yes	Ignited
Methyl pyrrolidone	Yes	Black
Diethylene glycol mono-ethyl-ether	No	Brown
Triethylene glycol	Yes	Charred
Triethanolamine	Yes	Ignited
Dibutyl phthalate	No	Brown

*Reference M2

Table 4-7
EXPLOSIVE FORMULATION SCREENING TESTS – MIXED PERCHLORATES (25 : 75% By Wt. NH_4ClO_4 : $KClO_4$) WITH ASSORTED FUELS

Fuel	Miscible	Screening Result at 561°K	DSC Exotherm
Acetamide	–	Light yellow, reflux 505°K	
Dimethyl sulfoxide	–	Flashed	500°K+
Ethylene glycol	Yes	Brown	500°K+ - weak
Dimethylformamide	No	Reflux 431°K	
2-Methoxyethanol	No	Reflux 399°K	
Glycerol	–	Charred	
Pyridine	–	Charred	
Methyl pyrrolidone	Yes	Charred	
Pentaerythritol	–	Charred	533°K
m-Dinitrobenzene	No	DNB sublimes	
Nitrobenzene	No	Reflux	
Triethylenediamine	–	Amine evaporated	
Diethylene glycol di-me-ether	No	Reflux 435°K	
Diethylene glycol mono-et-ether	No	Reflux 467°K	
Triethylene glycol	No	Dark brown	532°K
Triethanolamine	No	Dark brown	
2,4-Dinitrotoluene	–	Brown	
2-Nitrotoluene	No	Reflux 494°K	
Triethylene glycol di-me-ether	No	Brown, reflux 495°K	
1-Nitronaphthalene	–	Orange	
Naphthalene	–	Evaporation	
Dimethyl phthalate	No	Yellow, reflux 549°K	
Phenyl ether	No	Brown, reflux 529°K	
Phenyl sulfone	No	Light brown	
Dibutyl phthalate	No	Light brown	
Triphenylphosphate	No	Yellow	
Pluronic F38	–	Charred	
Silicone oil	No	No reaction	
Sodium polysulfide	–	Decomposition	555°K - large

Table 4-8
EXPLOSIVE FORMULATION SCREENING TESTS – ANHYDROUS AND HYDRATED SODIUM PERCHLORATE WITH ASSORTED FUELS

Fuel	Miscible	Screening Result at 561°K	DSC Exotherm
Formamide	Yes	Yellow (a)*	545°K+
Guanidinium nitrate	Yes	No reaction (a)	568°K
Acetamide	No	Brown (a)	
Dimethyl sulfoxide	Yes	Reflux (a) 483°K	530°K - large
Ethylene glycol	Yes	Reflux (h)* 472°K	505, 609°K - large
Dimethylformamide	Yes	Reflux (a) 455°K	
2-Methoxyethanol	No	Reflux (a) 420°K	
Glycerol	Yes	Brown (a)	575°K
Diethylene glycol	Yes	Dark brown (a)	542°K
Pyridine	–	Evaporation (h), reflux 389°K	
Methyl pyrrolidone	Yes	Charred (a)	None
Pentaerythritol	–	No reaction (h)	600°K - large
m-Dinitrobenzene	No	No reaction (a)	
Nitrobenzene	No	No reaction (h), reflux 485°K	None
Resorcinol	Yes	Brown (a)	573°K+
Triethylenediamine	–	Evaporation (a)	460, 535, 690°K
Diethylene glycol di-me-ether	No	Reflux (a) 436°K	
Diethylene glycol mono-et-ether	Yes	Reflux (a) 487°K	510°K
Triethylene glycol	Yes	Brown (a), reflux 563°K	600°K - large
Triethanolamine	Yes	Brown (h)	540°K - large
2,4-Dinitrotoluene	No	Brown (a)	
Benzoic acid	No	No reaction (a)	573°K
2-Nitrotoluene	No	Reflux (a) 495°K	
Triethylene glycol di-me-ether	No	Light yellow (a), reflux 504°K	
1-Nitronaphthalene	No	No reaction (a)	
Naphthalene	No	Evaporation (a)	502°K - sharp
Dimethyl phthalate	No	No reaction (a), reflux 555°K	
Phenyl ether	No	No reaction (a), reflux 533°K	
Phenyl sulfone	No	No reaction (a)	None
Dibutyl phthalate	No	No reaction (h)	587°K
Triphenylphosphate	No	No reaction (a)	
Dowtherm G	No	No reaction (a)	
Mineral oil	No	No reaction (a)	
Pluronic F108	–	Brown (h)	None
Pluronic F38	–	Charred (h)	
Pluronic 25R8	–	Brown (h)	
Polyglycol P-2000	No	No reaction (a)	
Silicone oil	No	No reaction (h)	None
Sodium polysulfide	–	Exploded (h)	580, 645, 680°K large
Therminol 55	No	No reaction (a)	
Therminol 60	No	No reaction (a)	
Therminol 66	No	No reaction (a)	

* h = $NaClO_4 \cdot H_2O$ a = $NaClO_4$

Table 4-9

DIFFERENTIAL SCANNING CALORIMETER RESULTS WITH NITRATE OXIDIZERS

Oxidizer	Fuel	Endotherm (°K)	Exotherm (°K)	Comments
Nitric acid	M-dinitrobenzene	360	None	Leaked
	Diethylene glycol monoethylether	400+	---	Leaked at 482
	Silicone oil	---	336+	Max at 374, leaked at 430
HTS	Formamide	---	487	
	Guanidinium nitrate	392+	485	Max at 517
	Acetamide	363+	526	Weak exo
	Dimethylsulfoxide	351+	474+	
	Ethylene glycol	None	483–518	Large exo at 513, pan leaked at 538
	Melamine	402, 415+, 597, 640	604	
	Glycerol	473	550	
	Sulfolane	401, 412+	527+	Max at 587
	Diethylene glycol	366+	511+	
	N-methyl-2-pyrrolidone	None	None	Ruptured pan at 512
	m-Dinitrobenzene	359, 414	584+	Large exo
	Nitrobenzene	398, 403	507+	Shallow exo, ruptured pan
	Resorcinol	376, 380, 400	422, 541+	Max at 551 and 593, sharp
	Triethylenediamine	344, 357, 362	507	Sharp exo
	Diethylene glycol monoethylether	443, 445, 464+	660	Slight exo
	Triethylene glycol	---	489+	
	Triethanolamine	---	540+	
	Phthalonitrile	402, 412, 418	560+	
	Naphthalene	411	None	
	Dimethylphthalate	400	625	
	Diphenylether	399, 408	546+	
	Diphenylsulfone	395, 398, 410	None	
	Dibutylphthalate	390, 394	620	Sharp exo
	Triphenyl phosphate	410	580	
	Mineral oil	411	450, 600+	
	Silicone oil	398, 410	None	
	Sodium polysulfide	---	610	Large exo

Table 4-9 (Continued)

DIFFERENTIAL SCANNING CALORIMETER RESULTS WITH NITRATE OXIDIZERS

Oxidizer	Fuel	Endotherm (°K)	Exotherm (°K)	Comments
75/25 GuN/ $NaNO_3$	Formamide	---	533	Max at 546
	Acetamide	---	546+	Max at 600
	Dimethyl sulfoxide	---	510+	Large exo, max at 555
	Ethylene glycol	513	490+	Max at 533
	Glycerol	397+	480, 574	Large exo at 574, sharp
	Resorcinol	378, 425+	577	Max at 605
	Diethylene glycol monoethylether		499	Max at 510
	Triethylene glycol	---	505+	Max at 536
$(LiNaK)NO_3$	Formamide	---	520	Leaked at 557
	Guanidinium nitrate	410+	600	Max at 630
	Acetamide	343	540	Leaked at 590
	Dimethlysulfoxide	344, 356	515+, 567	Max at 567
	Ethylene glycol	---	509+, 531	Sharp exo at 531
	Melamine	370, 610	652+	
	Dimethylformamide	360+, 460+	485	Leaked at 536
	2-Methoxyethanol	361+	533, 556	
	Glycerol	587	450, 593	
	Sulfolane	382	540 (?)	Leaked at 600
	Diethylene glycol	371+	513	
	N-methyl-2-pyrrolidone	397, 475–542	None	
	Pentaerythritol	---	573+	Max at 604
	m-Dinitrobenzene	360, 405	455+	
	Nitrobenzene	398+	None	
	Resorcinol	369+, 539	542+, 610	Max at 610
	Diethylene glycol dimethylether	380+	None	
	Diethylene glycol monoethylether	380+	None	
	Triethylene glycol	379–385	526	
	Triethanolamine	537	501, 538	
	2 Nitrotoluene	380+	None	
	Phthalonitrile	350+	575 (?)	

Table 4-9 (Concluded)

DIFFERENTIAL SCANNING CALORIMETER RESULTS WITH NITRATE OXIDIZERS

Oxidizer	Fuel	Endotherm (°K)	Exotherm (°K)	Comments
$(LiNaK)NO_3$ (Continued)	Triethylene glycol dimethylether	540–560	428, 497+, 561	Sharp exo at 561
	l-Nitronaphthalene	---	533+	Broad exo
	Dimethylphthalate	545–580	None	
	Diphenylsulfone	395	None	
	Dibutylphthalate	---	566+, 635	Sharp exo at 635
	Triphenyl phosphate	390, 505	590, 614	Sudden exo at 614
$(NaKCa)NO_3$	Formamide	---	462+	Max at 500
	Guanidinium nitrate	475	516, 584, 588	Max at 599
	Acetamide	360+, 528	537	Leaked at 596
	Ethylene glycol (1)	384	454	Max at 489
	Melamine (1)	---	520+	
	Dimethylformamide	370+	484	Leaked at 492
	Sulfolane (1)	---	410	Max at 490
	Diethylene glycol (1)	400	442+	Max at 494
	N-methyl-2-pyrrolidone	---	367, 495, 537	Sharp exo at 537
	Triethylene diamine	350, 435, 490	459, 507	
	Triethylene glycol (1)	---	494	Leaked at 600
	Phthalimide	500, 581, 610	536	Leaked at 581
	4, 4'-thiodiphenol	425	550, 600	Sharp exo at 600
	Dibutylphthalate	420+, 580+	---	
	Triphenylphosphate(1)	----	542	Max at 570
	$AcNH_2 + GuNO_3$(2)	350+, 470	506	Leaked at 588
	Dowtherm G(1)	----	453	

(1) Hydrated $(NaKCa)NO_3$ used with these fuels.

(2) This is 30%:70% by weight acetamide:guanidinium nitrate mixture.

Table 4-10

DIFFERENTIAL SCANNING CALORIMETER RESULTS WITH PERCHLORATE OXIDIZERS

Oxidizer	Fuel	Endotherm (°K)	Exotherm (°K)	Comments
25:75	Dimethylsulfoxide	None	500+	Max at 522
NH_4ClO_4:	Ethyleneglycol	None	500+	Shallow exo
$KClO_4$	Pentaerythritol	455–463	533	Pan left holder at 545
	Triethyleneglycol	None	532	
	Sodium polysulfide	300, 429	555	Huge exo
	Formamide	595	545+, 598	Max at 598
	Guanidinium nitrate	430	568	Max at 610
	Acetamide	---	518	
	Dimethylsulfoxide	485	530	Large, sharp exo
	Ethyleneglycol	590	505+, 609	Large, sudden exo at 609
	Melamine	380, 630	563, 664	Huge exo at 664
	Glycerol	None	575	
	Sulfolane	---	500	Huge exo
	Diethyleneglycol	None	542	Max at 600
	N-methyl-2-pyrrolidone	None	None	Pan ruptured below 500
	Pentaerythritol	460	600	Large exo
	Nitrobenzene	482	None	Pan ruptured
	Resorcinol	374, 377	573+, 615	Max at 615
	Triethylenediamine	345, 380	460, 535, 690	Sharp Exo at 690
	Diethyleneglycol dimethylether	430	None	Pan ruptured
	Diethyleneglycol monoethylether	---	510	Leaked at 538
	Triethyleneglycol	None	600	Large exo
	Triethanolamine	480	540	Large exo
	Phthalonitrile	401	477+	Leaked at 609
	Phthalimide	474, 613	553+, 630	Huge exo at 630
	Naphthalene	350	502	Sharp, sudden exo
	Dimethylphthalate	None	None(?)	
	Diphenylsulfone	395, 620	None	
	Dibutylphthalate	None	587	
	Dowtherm G	530+	478+, 592	Sharp, sudden exo at 592, burst pan
	Mineral oil	---	473	
	Silicone oil	None	None	
	Sodium polysulfide	560, 600	580, 645, 680	Large exo at 680

Table 4-10 (Concluded)

DIFFERENTIAL SCANNING CALORIMETER RESULTS WITH PERCHLORATE OXIDIZERS

Oxidizer	Fuel	Endotherm (°K)	Exotherm (°K)	Comments
	Therminol 55	547	452, 477	
	Therminol 60	---	454+, 548	Sharp, sudden exo at 548
	Therminol 66	497+	552	Sharp, sudden exo at 552
$Ca(ClO_4)_2$	Glycerol	440+, 525	570	Huge exo
$\cdot 6\ H_2O$	Triethyleneglycol	499, 695	480, 540	Huge exo at 540

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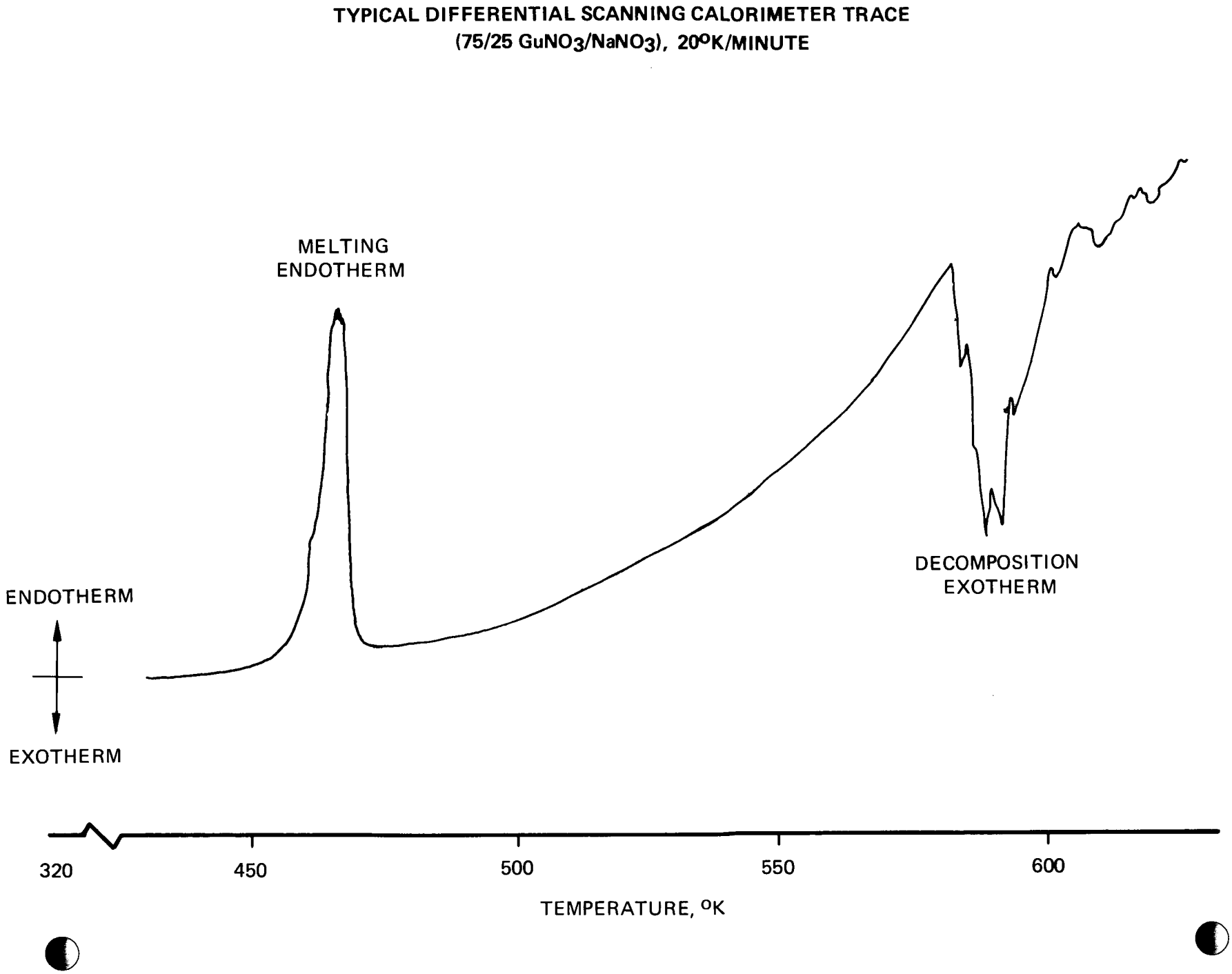


Figure 4-1

formulations with regard to a high onset of exotherm. It appears that some decomposition begins to occur at 506°K, but the rate of this reaction is small compared to that of other oxidizer/fuel combinations. A high-temperature explosive cannot be selected based on DSC data alone.

4.1.3 Thermal Stability Test Results

Thermal stability tests served to complement results obtained with the screening tests and the DSC. They were essentially a scaled-up version of either test, using a larger sample (6 g instead of 0.5 g or 10 mg, respectively). The samples were large enough so that chemical analysis of gases evolved or remaining explosive could be conducted after the heating period. Two different techniques were used as described in paragraph 2.1.3, sealed glass tubing and flanged bomblets.

The results of tests in the sealed glass tubes are summarized in Table 4-11. Of all tests with nitrate oxidizers, glycerol and acetamide showed the best thermal stability.

The majority of the 24-hour heating tests in the flanged bomblets relied on temperature excursions and burst disc ruptures as an indication of insufficient thermal stability. The selected test temperatures ranged from 477°K (400°F) to 561°K (550°F). Fluctuations of ±10 around the nominal test temperature were caused by environmental conditions in the semi-protected open test bay. The results of the initial series of bomblet tests are summarized in Table 4-12. On all samples which were recovered without explosion, the amount of discoloration was a qualitative indication of the degree of decomposition. Many combinations were completely charred, and, therefore, eliminated from further consideration. In particular, the glycol derivatives and glycerol fared very poorly in this test, leaving black residues. In contradistinction, acetamide, guanidinium nitrate, sulfolane, dimethylformamide, M-pyrol, and to a limited extent formamide survived these tests in contact with oxidizers suffering only minimal discoloration and without premature rupturing of burst discs.

In reviewing the fuels selected for this test, a bias toward miscible fuels is apparent. It was not meaningful to include immiscible combinations in this test, because the reaction rate is proportional to the interface area between the two liquids. It was not possible to maintain an emulsion throughout the duration of these tests.

More quantitative data were obtained by carefully weighing the initial ingredients to ±0.001 g and analyzing the remaining nitrate using an ion-selective electrode. The percent nitrate loss, as reported in Table 4-13, is proportional to the amount of undesirable chemical interaction during the heating. The lowest nitrate losses from (NaKCa) NO_3 were obtained with guanidinium nitrate, acetamide, formamide or sulfolane as a fuel. Nitrate losses with phthalimide or phthalodinitrile were also very low, but this may be caused only by the lack of miscibility. Nitrate loss from heating (NaKCa) NO_3 by itself was surprisingly high, 16 percent after 24 hours at 533°K. It appears that some of the nitrate decomposes to form an equilibrium concentration of nitrite.

In addition to nitrate analysis, gases vented from the bomblets were analyzed on the gas chromatograph for carbon dioxide, carbon monoxide, methane, hydrogen or water. Selective wet chemical reactions with moist reagent-soaked test paper were used to identify ammonia or oxides of nitrogen.

Table 4-11
RESULTS OF THERMAL STABILITY TESTS IN SEALED GLASS TUBES[1]

Sample	Results
83% HNO_3 + Nitrobenzene	Burst at 439°K
83% HNO_3 + Nitrobenzene[2]	Burst or exploded at 534°K
80% HNO_3 + m-Dinitrobenzene[2]	Burst or exploded at 577°K
75% HNO_3 + 2,4-Dinitrotoluene[2]	Burst or exploded at 495°K
HTS + Ethyleneglycol	Exploded at 566°K
HTS + Dimethylsulfoxide	Burst 552°K
HTS + Glycerol	Burst or exploded at 590°K
HTS + Nitrobenzene	No reaction when heated to 594°K
HTS + Dibutylphthalate	Burst at 601°K
HTS + Triphenylphosphate	Burst at 594°K
(LiNaK) NO_3 + Formamide	Burst at 581°K
(LiNaK) NO_3 + Acetamide	Burst or exploded at > 640°K
(LiNaK) NO_3 + Ethyleneglycol	Charred at 583°K
(LiNaK) NO_3 + Dimethylsulfoxide	Exploded at 561°K
(LiNaK) NO_3 + Glycerol	Exploded at 644°K
$NaClO_4$ + Ethyleneglycol	Burst or exploded at 607°K
$NaClO_4$ + Dimethylsulfoxide	Exploded at 522°K
$NaClO_4$ + Diethyleneglycol-monoethylether	Burst at 553°K

1 All except three were sealed in standard 10 mm by 75 mm Pyrex test tubes with wall thickness of 1 mm.

2 These were conducted in heavy wall tubes of wall thickness 2.5 mm and approximately the same outer dimensions as above.

Table 4-12
RESULTS OF 24-HOUR HEATING TESTS IN FLANGED BOMBLETS[1]

Sample	Test Temp. (°K)	Results and Comments[2]
90% HNO_3	539–555	Ruptured disc, black residue
90% HNO_3	544–555	Black residue[3]
83% HNO_3 + Nitrobenzene	550–572	Ruptured disc, black residue
90% HNO_3 + m-DNB	544–555	Ruptured disc, black residue
75% HNO_3 + 2,4-DNT	544–566	Ruptured disc, dark residue
HTS + Formamide	–	Ruptured disc (455°K), white and brown residues
HTS + Guanidinium nitrate ($GuNO_3$)	489–502	Gases, white solids
HTS + Acetamide	544	Gases, white solids
HTS + Acetamide	500–511	Gases, white solids, brown spots
HTS + Ethyleneglycol (EG)	550–552	Gases, charred residues, exotherm at 494°K
HTS + EG	505–522	Moist, black residue
HTS + Glycerol	555–561	Gases, charred residue
HTS + Sulfolane	477–561	Gases, pale yellow solids, brown liquid
HTS + Diethyleneglycol (DEG)	–	Ruptured disc (533°K), brown and charred residues
HTS + DEG	505–519	Gases, black solids, brown liquid
HTS + Triethanolamine (TEA)	450+	Ruptured disc (533°K)
(LiNaK) NO_3 + Formamide	550–555	Gases, black residue
(LiNaK) NO_3 + $GuNO_3$	500–511	White solids, orange spots
(LiNaK) NO_3 + Acetamide	525–533	Gases, beige-gray residue
(LiNaK) NO_3 + Acetamide	511–516	Brown, yellow & black solids
(LiNaK) NO_3 + EG	544–561	Gases, black residue
(LiNaK) NO_3 + Glycerol	541–555	Brown spots on white solids
(LiNaK) NO_3 + Sulfolane	477–561	Gases, white solids, brown liquid
(LiNaK) NO_3 + DEG	505–511	Yellow & brown solids, some chars
(LiNaK) NO_3 + TEA	450–572	Gases, charred residue
(NaKCa) NO_3 + $GuNO_3$	494–505	Orange tint on white solids
(NaKCa) NO_3 + Acetamide	533	Gases, black & brown residues
(NaKCa) $NO_3 \cdot 4H_2O$ + EG	502–522	Gases, white solids, brown liquid

Table 4-12 (Concluded)
RESULTS OF 24-HOUR HEATING TESTS IN FLANGED BOMBLETS[1]

Sample	Test Temp. (°K)	Results and Comments[2]
(NaKCa) NO_3 + Dimethylformamide	533	White residue, some chars, fishy odor
(NaKCa) NO_3 + Sulfolane	533	Gases, white solids, brown liquid
(NaKCa) $NO_3 \cdot 4H_2O$ + DEG	500–519	Gases, moist white & brown solids
(NaKCa) NO_3 + M-Pyrol	533	Gases, white solids, brown stains
(NaKCa) NO_3 + DEGDME	533	Gases, yellow & white solids
(NaKCa) NO_3 + DEGMEE	533	Gases, white and brown solids
(NaKCa) NO_3 + Triethyleneglycol	533	Gases, black residue
(NaKCa) NO_3 + TEA	450–572	Gases, charred residue
(NaKCa) NO_3 + Phthalonitrile	533	Gases, sublimate, dark brown solids
(NaKCa) NO_3 + Phthalimide	533	Sublimate, puffed yellow solids
(NaKCa) NO_3 + Dibutylphthalate	533	Black and yellow solids
(NaKCa) NO_3 + Triphenylphosphate	533	Gases, brown, black & yellow solids
$NaClO_4$ + Formamide	500–502	Yellow solids, some chars
$NaClO_4$ + $GuNO_3$	486–494	Beige solids
$NaClO_4$ + Acetamide	500–502	Dark brown slurry residue
$NaClO_4$ + EG	497–505	Ruptured disc (505°K), glass tube shattered
$NaClO_4$ + Melamine	533	Gases, sublimate, light brown solids
$NaClO_4$ + Sulfolane	477+	Exploded at 519°K
$NaClO_4$ + DEG	505	Ruptured disc, glass tube shattered
$NaClO_4$ + TEA	450+	Exploded at 514°K

[1] Bomblet setup is described in methods section

[2] Unless otherwise specified, the burst disc remained intact

[3] A thin stainless burst disc of unknown thickness was used

Table 4-13
ANALYTICAL RESULTS OF POST-TEST THERMAL STABILITY SAMPLES – 24 HOURS

Sample[1]	Test Temp. (°K)	% Nitrate Loss	Gases Detected
HTS + Guanidinium Nitrate ($GuNO_3$)	505	8	
HTS + Ethyleneglycol (EG)	505	34	
HTS + Sulfolane	505	12	
HTS + Diethyleneglycol (DEG)	505	40	
(LiNaK)NO_3 + Formamide	505	14	
(LiNaK)NO_3 + $GuNO_3$	505	21	
(LiNaK)NO_3 + EG	505	28	
(LiNaK)NO_3 + Sulfolane	505	23	
(NaKCa)$NO_3 \cdot 4H_2O$ + $GuNO_3$	505	12	
(NaKCa)$NO_3 \cdot 4H_2O$ + Acetamide	505	38	
(NaKCa)NO_3 + Acetamide	533	35	CH_4, CO, CO_2, NO_x
(NaKCa)$NO_3 \cdot 4H_2O$ + EG	505	32	
(NaKCa)NO_3 + Dimethylformamide	505	45	H_2, CH_4, CO, CO_2, NO_x
(NaKCa)NO_3 + Sulfolane	505	31	CO_2, NO_x
(NaKCa)NO_3 + Sulfolane	533	57	
(NaKCa)$NO_3 \cdot 4H_2O$ + DEG	505	25	
(NaKCa)NO_3 + M-Pyrol	533	50	CO_2, NO_x
(NaKCa)NO_3 + DEGDME	533	40	
(NaKCa)NO_3 + DEGMEE	533	60	
(NaKCa)NO_3 + Triethyleneglycol	533	43	
(NaKCa)NO_3 + Phthalonitrile	533	7	
(NaKCa)NO_3 + Phthalimide	533	13	
(NaKCa)NO_3 + Dibutylphthalate	533	10	
(NaKCa)NO_3 + Triphenylphosphate	533	55	CO, CO_2, NO_x
(NaKCa)NO_3 only	533	16	

[1]The initial sample size is 4 g

Several samples were heated to 505°K for only 6 hours in an effort to obtain crude kinetic data which might identify the predominant decomposition mechanism which limits the thermal stability. In this series shown in Table 4-14, the nitrite in the residual solid was analyzed quantitatively by a spectrophotometric method. In addition, the carbon dioxide released upon acidifying the sample was swept into a U-tube filled with Ascarite and weighed. The amount of nitrite and carbon dioxide also served as an indication of incompatibility. Based on the results of Table 4-14, dimethylformamide and sulfolane showed maximum interaction even in the abbreviated 6-hour tests. In the group of miscible fuels, acetamide and ethylene glycol behaved equal.

Table 4-14
ANALYTICAL RESULTS OF POST-TEST THERMAL STABILITY SAMPLES – 6 HOURS AT 505°K

Sample	% Nitrate Loss	Nitrite as mg $NaNO_2$	Carbonate as mg CO_2	Gases Detected
$(NaKCa)NO_3$ + Acetamide	3.4	0.004	4.3	CO_2, NO_x
$(NaKCa)NO_3$ + Ethyleneglycol	3.4	0.036	1.6	CO, CO_2, NO_x
$(NaKCa)NO_3$ + Dimethylformamide	31	0.03	202.5	$H_2, CH_4, CO, CO_2, NO_x$
$(NaKCa)NO_3$ + Sulfolane	21	0.76	58	CO, CO_2, NO_x
$(NaKCa)NO_3$ + Phthalimide	0	0.003	0.5	CO_2, NO_x
$(NaKCa)NO_3$ + Dimethylphthalate	0	0.80	–	CO, CO_2, NO_x
$(NaKCa)NO_3$ + 4,4'-Thiodiphenol	0	0.084	–	CO_2, NO_x
$(NaKCa)NO_3$ + Triphenylphosphate	9.4	0.80	4.1	CO, CO_2, NO_x

It would have been desirable to have more than one indicator of oxidizer/fuel interaction. The nitrite and carbonate determinations were time consuming. It was attempted to develop quantitative analysis methods for remaining acetamide or guanidinium nitrate in the explosive. However, the methods were not yet perfected to the point where they could be used for kinetic studies.

Unfortunately, it was very difficult to obtain a reproducibly good seal on the flanged bomblets. There was such a multitude of mechanical seals for the thermocouple feedthrough, the burst disc, and a vent valve, that it was very difficult to contain all gases and preserve the pressure generated during high temperature stability testing. The temperature differential was sufficient to cause most bomblets to leak upon cooling and contracting. Pressure readings were taken on several bomblets after cooldown, but the data do not correlate with nitrate loss or carbon dioxide formation. The bomblets had to be designed and tested such that there was no cold spot in the system allowing vapor to condense and solidify. This would have resulted in separation of oxidizer and fuel by distillation or sublimation. If a pressure transducer could be found which is capable of withstanding

561°K, it would be desirable to record pressure rise data. Pressure rise rates at different temperature could be used to determine the energy of activation of the stability-limiting reaction.

4.1.4 Materials Compatibility Test Results

Samples of typical downhole materials commonly found in geothermal wells were obtained from Union Geothermal, Los Alamos Scientific Laboratories, and Terra Tek. Compatibility of the ultimately selected explosive with these materials was determined using the same thermal stability bomblets used in the preceding paragraph. An increase in nitrate loss beyond 7 percent was taken as an indication of incompatibility. Distinct incompatibility was noted with rust scraped from old geothermal well casing or drill pipe (Table 4-15). Medium incompatibility was noted with dry cement, cement additives, and Invermul Baryte drilling mud. The majority of the samples had no effect or even a diluting effect on the rate of nitrate loss.

The incompatibility, as indicated by nitrate loss, may not necessarily lead to premature detonations if the explosive contacts the materials in the well. However, the explosive force may be reduced as the result of interactions catalyzed by the materials. The ratio of material to explosive was grossly exaggerated in these tests in order to enhance any suspected incompatibility. The preliminary tests conducted here serve as an indication of potential problem areas where additional work is required. Another variable which has not yet been tested is the combination effect of well fluids (H_2S-rich water, H_3SO_3-rich water) and minerals or iron pipe on the stability of the explosive. More quantitative data were obtained by testing some of the mineral samples finely ground on the DSC. No incompatibility was apparent in these tests.

Materials compatibility tests, so far, were restricted to materials, minerals, and well fluids expected in the downhole environment. However, prior to the design of a mobile mixing unit for a field demonstration, compatibility of the explosive and its ingredients with materials of construction will have to be demonstrated. While the ingredients above ground are not exposed to such high temperatures as the explosive downhole, it would be best to conduct the planned construction materials compatibility tests at elevated temperatures as well in order to accelerate any effects which otherwise could be observed only after months or years of exposure in the pumping/mixing equipment. As a preliminary test in this direction, copper powder was added to (NaKCa) $NO_3/AcNH_2$ + $GuNO_3$ in the same way as the mineral samples tested above. The nitrate loss after 24 hours at 505°K was 73 percent, indicating decomposition beyond the point of detonability. Consequently, copper, brass, or bronze parts must be avoided in selecting components for the mixing rig which are wetted by the explosive or its ingredients.

4.2 SAFETY TEST RESULTS

Safety tests were conducted on a variety of combinations during the development phase as well as on the ultimately selected single combination toward the end of the program. Safety tests were also conducted on the explosive ingredients alone, prior to mixing, to assure that they were not detonable by themselves.

Table 4-15

RESULTS OF MATERIALS COMPATIBILITY TESTS AT 505°K FOR 24 HOURS

Sample	% Nitrate Loss
HTS + acetamide + graywacke, unidentified	10
[(NaKCa)NO_3 + acetamide] = X	13
X + graywacke, from Geysers, CA	4
X + LASL EE-1 well sample from Jemez Mt., NM	4
X + Volcanic tuffs from Weiraki, New Zealand	6
[NaKCa)NO_3 + guanidinium nitrate + acetamide] = Y	7
Y + graywacke, from Geysers, CA	7
Y + LASL EE-1 well sample from Jemez Mt., NM	0
Y + Volcanic tuffs from Weiraki, New Zealand	7
Y + Dextrid - XC polymer KCl mud(1)/$BaSO_4$	7
Y + Carbonox-Q-Broxin mud(1)/$BaSO_4$	11
Y + Invermul mud(1)$BaSO_4$	18
Y + Pipe thread lubricant, UOCS(2) #1	7
Y + Scrapings from an old 13-3/8-inch diameter casing, UOCS #2	14
Y + Scrapings from a rusty 4-1/2-inch diameter drill pipe, UOCS #3	32
Y + Unisteam, UOCS #4	11
Y + Drilling mud, UOCS #5	0
Y + Cement sample, UOCS #6	0
Y + Cement and micrograywacke cuttings, UOCS #7	0
Y + Unwashed greenstone cuttings, UOCS #8	4
Y + Unwashed graywacke cuttings, UOCS #9	7
Y + Unwashed serpentine cuttings, UOCS #10	0
Y + Used bearing from a well, UOCS #11	7
Y + Perlite, UOCS #12a	0
Y + HR-T, UOCS #12b	30
Y + SAA1 silica flour, UOCS #12c	6
Y + HR-12, UOCS #12d	25
Y + POZ, UOCS #12e	11
Y + Class "G" cement, UOCS #12f	6
Y + CFR 2, UOCS #12g	14
Y + Steam condensate, UOCS #13	6

(1) These mud samples were obtained from Dr. A. Spencer. They were combined with 20% by weight $BaSO_4$.

(2) UOCS = Union Oil Company Sample. These samples were obtained from Union Geothermal Division of Union Oil Company of California, located in Santa Rosa. Additional details of these samples can be found in the correspondence from Jack Hartz of Union Oil Company to Dr. E. Schmidt of ROCKCOR, dated September 21, 1977.

4.2.1 Drop-Weight Sensitivity Test Results

Drop-weight sensitivity tests were performed both at ambient and at elevated (505°K) temperatures. At ambient temperature, the majority of mixtures examined did not appear to be sensitive to the impact of 120 kg-cm (3 kg weight suspended at 40 cm height). In many cases, emission of some mist or smoke was observed at the time of the impact. However, neither was accompanied by audible sounds of explosion. These emissions were probably evaporating liquids resulting from impact heat-ups, or possibly from dust generated by the impacts. Ambient drop-weight tests were performed as a safety check before mixing large quantities (100 g) of explosive.

Impact sensitivity data for mixtures with (NaKCa)NO_3 as oxidizer were difficult to conduct because the nitrate eutectic is quite hygroscopic. The absorbed water could easily invalidate the drop-weight tests by desensitizing the mixtures. A number of tests was performed with hydrated (NaKCa)NO_3 as oxidizer, all showing negative results.

As with friction sensitivity, solids, in particular very hard solids, are more likely to give positive drop-weight impact tests than the same material as a liquid. At the tip of crystals the sample will experience significant concentrations of energy which may be sufficient to ignite it. In molten samples, the liquid acts as a lubricant. It reduces friction considerably and equilibrates impact load or stress concentrations. On the other hand, the increased temperature in molten explosive may raise the initial energy level sufficiently that already a minor impetus such as a falling drop weight is sufficient to raise the local energy in so-called hot spots to the threshold barrier of initiation (Figure 4-2).

A few drop-weight sensitivity results were obtained at elevated temperature. The drop-weight apparatus was modified as described in paragraph 2.2.1 for use at elevated temperature. After preliminary testing to verify that the assembly was operational and could be heated to 561°K (550°F), two trial runs were made. In the first test, a sample of heat treatment salt (KNO_3:$NaNO_3$:$NaNO_2$ = 53.7 : 7.0 : 40.0% by weight) and graphite was heated to 561°K and tested at 120 kg-cm. The result was positive in that the steel diaphragm ruptured; however, there was no noise or flash of light which generally accompanies a positive result. A second sample consisting of $LiNO_3$:$NaNO_3$:KNO_3 (23.3 : 16.3 : 60.4% by weight) eutectic with acetamide was tested at 505°K (450°F) with a force of 120 kg-cm. Again, the steel diaphragm was ruptured, but no noise or fire accompanied the test.

Since the strength of the steel diaphragm probably is diminished by the elevated temperature and the pressure within the sample cell may be increased, depending on the tightness of the sealing surfaces, a hydraulic rupture of the steel diaphragm is probably occurring. Positive drop-weight tests almost always are accompanied by readily discernible noise, smoke, odors, and often a flash of light in addition to the rupture of the steel diaphragm. These criteria were eventually substituted in place of the rupturing of the diaphragm as evidence of a positive or negative result. Results of drop-weight sensitivity tests at elevated temperature of some mixtures of particular interest are reported in Table 4-16.

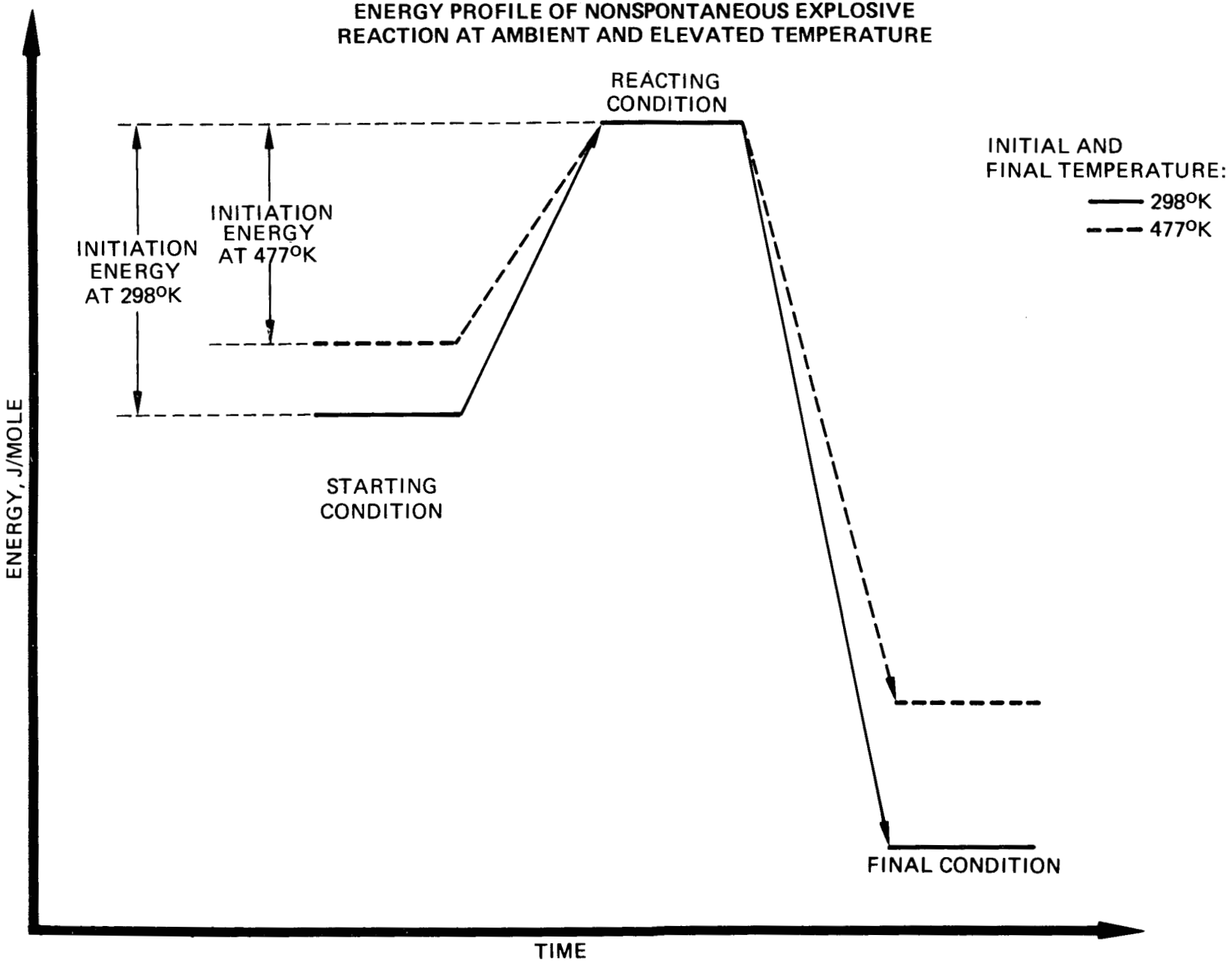

ENERGY PROFILE OF NONSPONTANEOUS EXPLOSIVE
REACTION AT AMBIENT AND ELEVATED TEMPERATURE
REACTING
CONDITION
INITIAL AND
FINAL TEMPERATURE:
298°K
477°K
INITIATION
ENERGY
AT 298°K
INITIATION
ENERGY
AT 477°K
STARTING
CONDITION
FINAL CONDITION
ENERGY, J/MOLE
TIME

Figure 4-2

Table 4-16

RESULTS OF IMPACT SENSITIVITY TESTS AT 505°K

Composition	Result at 120 kg-cm	Estimated 50%-Point (kg-cm)
$NaClO_4$ + $GuNO_3$	+	90 – 97.5
(NaKCa) NO_3 + $GuNO_3$	-	120 – 150
(NaKCa) NO_3 + $GuNO_3$ + acetamide	-	>300
(NaKCa) NO_3 + acetamide	-	>300
(NaKCa) NO_3 + sulfolane	-	200 – 225

As is usually found with nitrate based explosives, those containing nitrate oxidizer are not very impact sensitive. On the other had, perchlorate containing explosives are relatively more sensitive. One may compare, for example, results for $NaClO_4$ – $GuNO_3$ and (NaKCa)NO_3 – $GuNO_3$. One might also note that the addition of acetamide to (NaKCa)NO_3 – $GuNO_3$ makes it a less sensitive mixture than (NaKCa)NO_3 – $GuNO_3$ alone.

4.2.2 Drop Tower Test Results

Three drops were made with 200 g of the candidate explosive at 561°K (550°F), contained in a sealed stainless steel pipe bomb, onto a 2 1/2-inch-thick steel target located at 40 feet below the bomb. The impacts had no effect on the hot explosive. In view of the drop-weight sensitivity test performed earlier on the mixture, these results were not surprising. The drop-weight sensitivity test had suggested an E_{50} value of greater than 300 kg-cm, which qualitatively implied its low impact sensitivity.

Shortly after the 40-foot drops, the pipe bomb was disposed of while it was still hot. This was accomplished by attaching a shaped-charge to the side of the pipe, as was done in the sealed-pipe detonation tests. A loud report was heard following the initiation, indicating that the explosive was viable throughout the drop-tower test.

4.2.3 Adiabatic Compression Test Results

Prior to conducting HITEX explosive adiabatic compression sensitivity tests, the apparatus was checked out with eutectic oxidizer alone as a baseline to study a purely hydraulic shock rupture of the sample holder U-tube. Subsequently, it was attempted to produce a positive test result by heating and rapidly compressing anhydrous hydrazine. This monopropellant had previously shown positive results when compressed at rates above 20.7 k bar/s (300,000 psi/s) and temperatures above 373°K (212°F) (Reference V2). In our tests, only one of of three tests with hydrazine gave a positive result (Table 4-17). Because a heating tape was used instead of a constant temperature bath

Table 4-17
ADIABATIC COMPRESSION TEST RESULTS[1]

Sample	Sample Size (g)	Temperature °K	Heating Time (min)	Result
N_2H_4	3.2	387 (238°F)	17	–
N_2H_4	3.2	394 (250°F)	14	–
N_2H_4	4.1	422 (300°F)	8.5	+
(NaKCa)NO_3	3.2	533 (500°F)	12.5	–
$GuNO_3$-$AcNH_2$[2]	3.2	533 (500°F)	12	–
(NaKCa)NO_3-$GuNO_3$-$AcNH_2$[3]	3.2	550 (530°F)	20	+
(NaKCa)NO_3-$GuNO_3$-$AcNH_2$[3]	3.2	533 (500°F)	8.5	–
(NaKCa)NO_3-$GuNO_3$-$AcNH_2$[3]	4.1	561 (550°F)	15	–
(NaKCa)NO_3-$GuNO_3$-$AcNH_2$[3]	4.1	568 (563°F)	15.5	–

[1] Each sample was suddenly compressed with 2,000 psi of N_2 within 3 ms, at an average rate of 670,000 psi/s

[2] This is 70 to 30% by weight mixture of guanidinium nitrate and acetamide, respectively.

[3] This is a 58.7% – 28.9% – 12.4% by weight mixture. The mixture was premolten in a test tube and later transferred to the sample U-tube.

in all tests, it took several minutes to reach the desired test temperature. The time interval is an undesirable added variable in the interpretation of the test results. It will be attempted to use a preheated constant temperature bath which can be raised and lowered remotely in future tests.

Only one out of four tests with the (NaKCa)NO_3/$AcNH_2$ + $GuNO_3$ HITEX explosive was positive (Figure 4-3). It appears, thus, that sudden compression of a dead space gas pocket in the system must be avoided. The positive result may also be associated with a flammable acetamide vapor/air mixture in the closed end of the U-tube. No effort was made to replace the air from the test fixture prior to the test.

4.2.4 Spark Sensitivity (ESD) Test Results

Spark sensitivity tests were conducted under subcontract by Hercules/Allegany Ballistics Laboratory on the ABL ESD test machine (Reference G4). The sample of premixed, pre-fused (NaKCa)NO_3/$AcNH_2$ + $GuNO_3$ was placed in a special heated sample holder which maintained the temperature at 477°K (400°F) and assured that the discharge passed through the sample. The threshold initiation level (TIL) is that level of energy above which initiation can occur. For the HITEX sample, it was 0.075 Joule, based on 20 consecutive failures to initiate at this level. Table 4-18 shows the test results, and Figure 4-4 is a probit plot of these results. The probit analysis is a

ADIABATIC U-TUBE TEST RESULTS

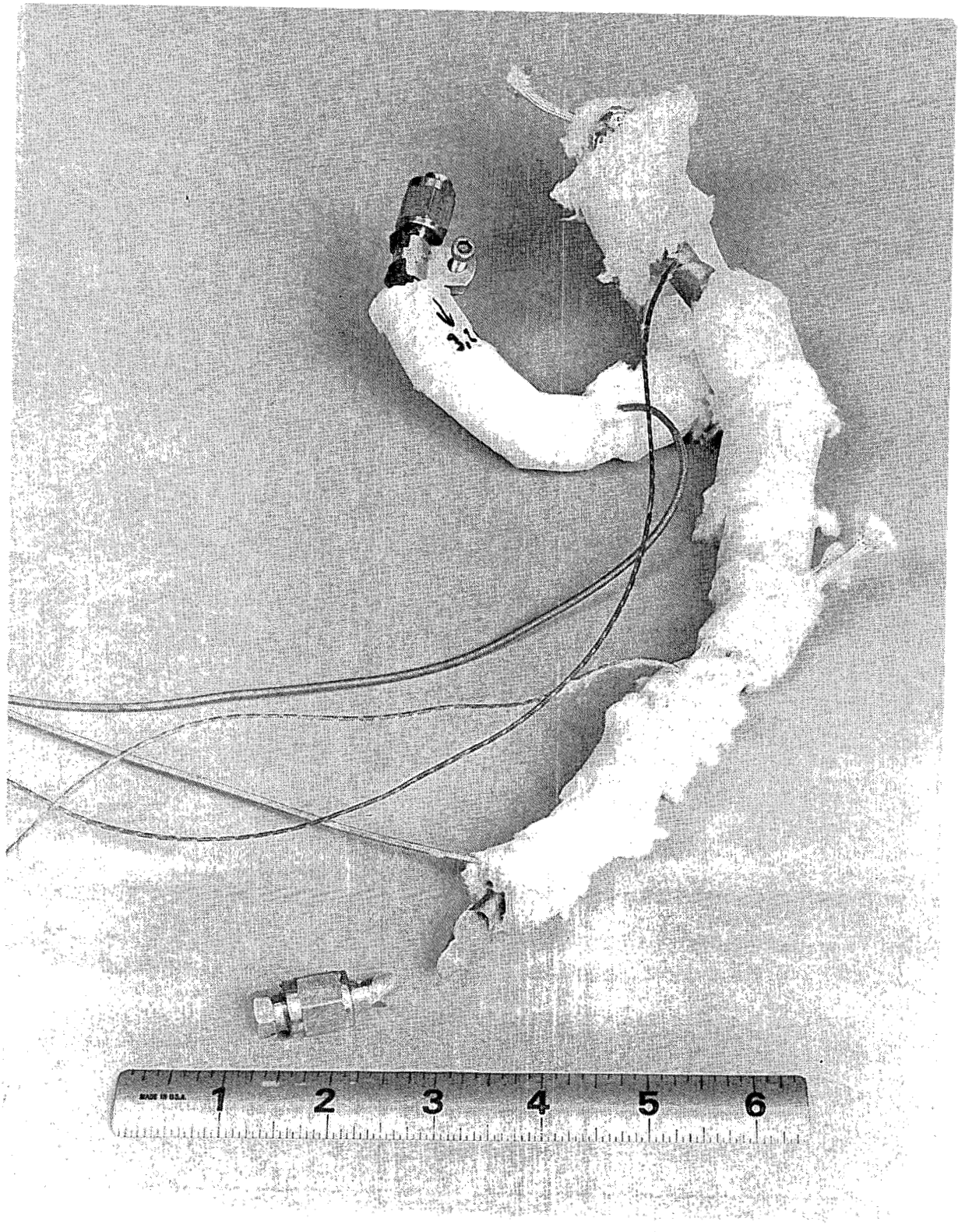


Figure 4-3

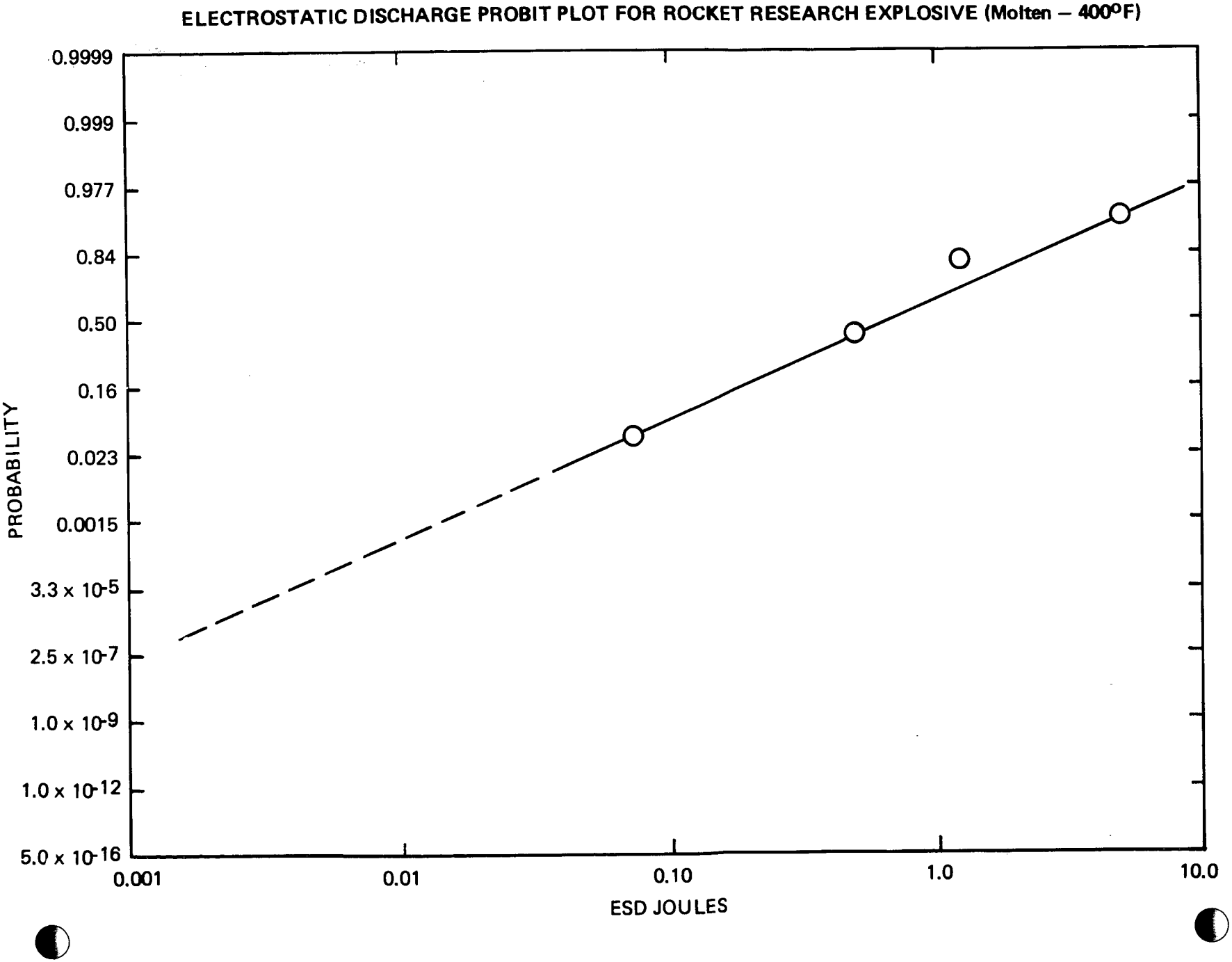

ELECTROSTATIC DISCHARGE PROBIT PLOT FOR ROCKET RESEARCH EXPLOSIVE (Molten – 400°F)
PROBABILITY
0.9999
0.999
0.977
0.84
0.50
0.16
0.023
0.0015
3.3 x 10-5
2.5 x 10-7
1.0 x 10-9
1.0 x 10-12
5.0 x 10-16
0.001
0.01
0.10
1.0
10.0
ESD JOULES

Figure 4-4

statistical technique developed to show the probability of initiation as a function of the amount of energy input as stimulus to the test material. There was no indication of burning of any sample for which reaction was noted by the infrared analyzer. While some sample decomposition was occurring, there was no evidence of flame or sustained reaction.

For comparison, the ESD sensitivity of Composition B, a commonly used military explosive, is 0.05 Joule at 361°K (190°F). ESD sensitivity of glycerol trinitrate is 0.024 Joule. In dry weater, the human body can accumulate 0.015 Joule.

The LIRA infrared analyzer (Reference R1) is presumably tuned to the wavelength of carbon dioxide, a common combustion product. The carbonyl group in acetamide, the most volatile constituent of HITEX, absorbs in the same range. Acetamide liquid which is evaporated or atomized by the spark energy may, therefore, feign a positive reaction at much lower energies than those required for actual ignition.

4.2.5 Friction Sensitivity Test Results

The friction sensitivity test was conducted by Hercules ABL under subcontract on a single sample of $(NaKCa)NO_3/AcNH_2$ + $GuNO_3$ HITEX, using the ABL friction test machine (Reference G4). The test was conducted on solid rather than liquid molten material in order to maximize the friction coefficient. The sample was placed on the anvil and subjected to friction between the stationary wheel and the movable anvil plate under known contact pressures and velocities. For this test series, both the wheel and anvil were steel and two anvil velocities, 2.4 m/s and 3 m/s were used. The TIL at 2.4 m/s was $> 9.9 \times 10^8$ N/m^2. There were no reproducible positive shots at the highest friction level attainable under test conditions. At 3 m/s, the TIL was 7.5×10^8 N/m^2. Numerical results are listed in Table 4-19 and illustrated as a probit plot in Figure 4-5. The material is relatively insensitive to friction, with only three reactions recorded at 3 m/s and none at 2.4 m/s. The friction sensitivity of the material is at the maximum energy boundary of the ABL test machine. Consequently, it will be very safe to handle at ambient temperature even in the mixed state.

For comparison, the friction sensitivity of Composition B, a commonly used military explosive, is 1.82×10^8 N/m^2 at 3 m/s and 361°K (190°F), and 3.4×10^8 N/m^2 at 2.4 m/s and 361°K. Heating the explosive from ambient to 361°K lowers the friction initiation energy from above 3.5×10^8 N/m^2 to 1.82×10^8 N/m^2 (at 3 m/s). Glycerol trinitrate requires only 0.4×10^8 N/m^2 at 1.2 m/s for initiation.

4.2.6 Detonation Arrestor Test Results

Five kg $(NaKCa)NO_3$ were filled into the annulus and 1.45 kg of a 70:30 mixture of guanidinium nitrate and acetamide were filled into the core of the detonation test fixture described in paragraph 2.2.6. The upper donor section was filled with 4.3 kg of mixed explosive. During the warmup and after the test fixture had reached a uniform temperature of 505°K, the explosive in the donor section was mixed repeatedly (four times) by bubbling nitrogen gas through it for 1 minute. The donor charge was then initiated from the top with a No. 8 cap and a 20-g booster made of C-4 PBX.

Table 4-18
ELECTROSTATIC DISCHARGE (ESD) TEST RESULTS

Sample conditions: Molten, temperature 400°F

Test conditions: Room temperature – 70°F
Relative humidity – 15%

Test Level (Joules)	No. of Shots	Total No. of Trials
5.0	10	10
1.26	8	10
0.50	4	10
0.075	0	20

Table 4-19
FRICTION SENSITIVITY TEST RESULTS

Sample conditions: Solid

Test conditions: Temperature – 66°F
Relative humidity – 61°F
Steel components

Test Velocity (mps)	Energy Level (N/m^2)	No. of Shots	Total No. of Trials
3.0	12.1×10^8	1	18
	10.2×10^8	1	10
	8.8×10^8	1	10
	7.5×10^8	0	20
2.4	9.9×10^8	0	20

NOTE: LIRA inrared analyzer used to detect reaction.
For the 2.4 mps friction test, 9.9×10^8 N/m^2 was the highest test level attainable consistent with a proper test.
TIL is 7.5×10^8 N/m^2 for 3 mps friction.
TIL is greater than or equal to 9.9×10^8 N/m^2 for 2.4 mps friction.
Friction sample was 0.080" thick sheet.

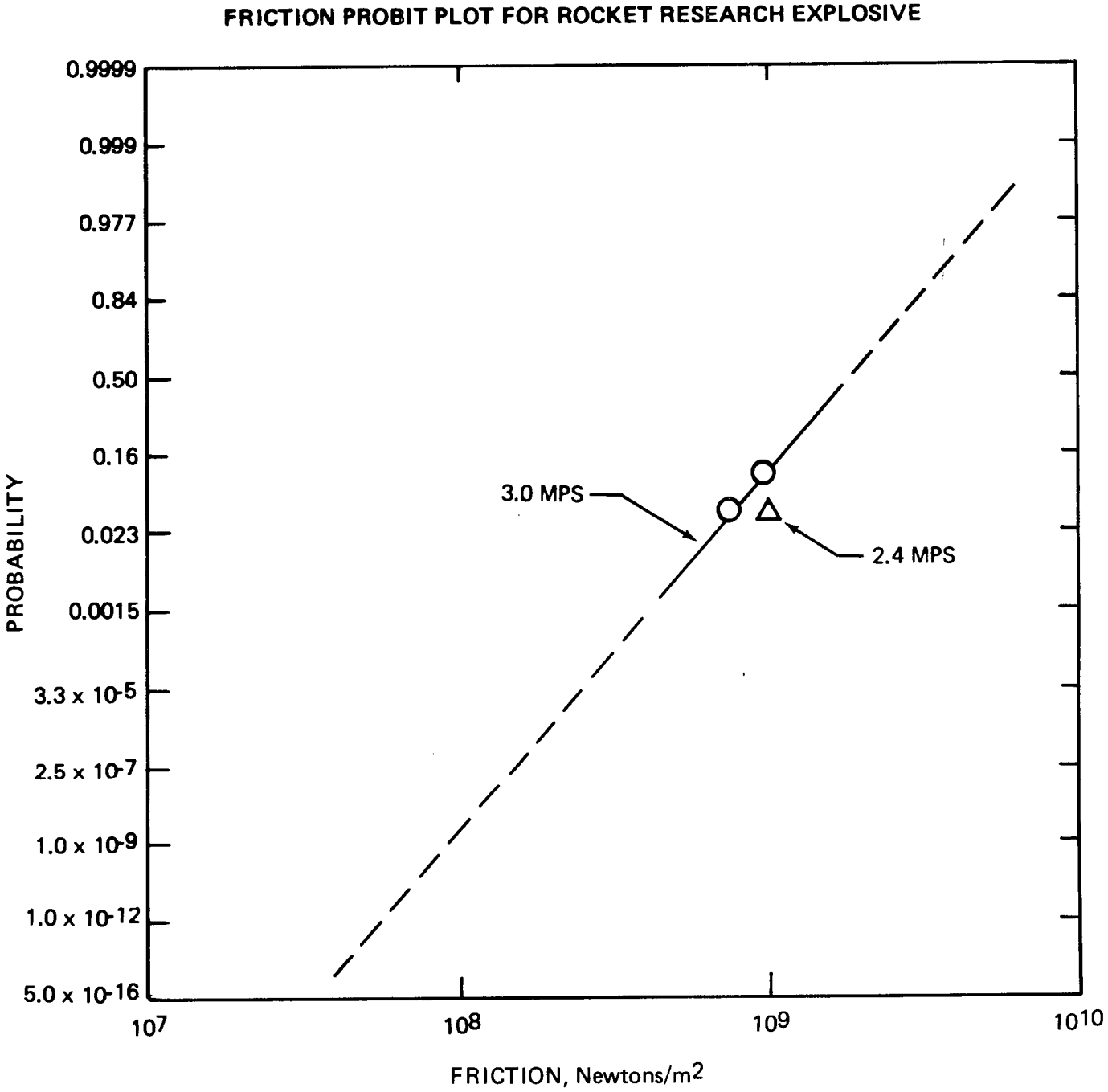

FRICTION PROBIT PLOT FOR ROCKET RESEARCH EXPLOSIVE
0.9999
0.999
0.977
0.84
0.50
0.16
0.023
0.0015
3.3 x 10-5
2.5 x 10-7
1.0 x 10-9
1.0 x 10-12
5.0 x 10-16
PROBABILITY
3.0 MPS
2.4 MPS
10^7
10^8
10^9
10^10
FRICTION, Newtons/m2

Figure 4-5

The donor section disintegrated completely, and only a single coin-sized fragment of it could be found. The shock wave penetrated into the acceptor section and ruptured the upper third of the pipe, presumably by hydraulic pressure rather than by reaction between the oxidizer and fuel. The acceptor section was initially 36 inches long. As can be seen in Figure 4-6, the lower 24 inches were recovered undamaged.

This test successfully demonstrated the inherent safety of two component explosives in general and HITEX in particular. The test is significant because it was not conducted with a sealed-down model, but with true dimensions identical to those expected for downhole mixers. If this had been a premature detonation in a geothermal well, the detonation would not have propagated past the mixer, and the personnel and equipment on the surface would not have suffered any damage.

4.2.7 Cook-Off Test Results

In the cook-off tests, 150 to 175-g samples were heated at an average rate of 6°K/minute in a sealed pipe bomb with continuous mixing until the pipe burst.

Each cook-off test bomb was arranged such that the thermocouple which dipped into the sample was able to detect the onset of an exotherm. This became obvious on the strip chart recording if the sample temperature exceeded the outside surface temperature of the pipe. This arrangement essentially constituted an oversize differential thermal analysis apparatus. Of all combinations tested, the (NaKCa)NO_3/acetamide explosive showed the highest onset of exotherm, 586°K (596°F) (Table 4-20). However, the temperature at which the pipe failed was generally above the initially observed exotherm. The highest temperature in this category was achieved by sodium perchlorate/guanidinium nitrate, which reached 744°K (880°F) before the pipe failed. Five samples only blew the top cap off the pipe and stripped the thread (Figure 4-7). The unthreaded part of the pipe was undamaged. This failure is similar to the one observed during hydrotesting the pipes for burst pressure and would occur at pressures above 482 bar (7,000 psi) at room temperature. Four of the remaining samples burst above the lower threaded cap leaving the latter and the witness plate undamaged. These are also considered to be resulting from pressure build-up inside the bombs rather than from autodetonation. Had they autodetonated, the lower threaded caps would have been flared and the witness plates would have been distorted.

In a few cases, there was a fire after the cap was blown off. The fire could also have been started by unreacted chemicals being spattered on the heating tape. Only one mixture, (NaKCa)NO_3 with sulfolane, deflagrated and there was a loud report when the pipe burst. On close examination, the lower threaded cap from this mixture was slightly flared.

The cook-off temperature is size dependent and is inversely proportional to the sample size. In spite of the disparity in sample size between the cook-off test and the DSC, there was good correlation between the onset of exotherms in the cook-off test and the DSC (Table 4-20).

The cook-off tests have demonstrated that many explosives, including the ultimately selected candidate, can be heated beyond the design temperature without premature detonation. However,

DETONATION ARREST FIXTURE AFTER DETONATION OF MIXED UPPER SECTION

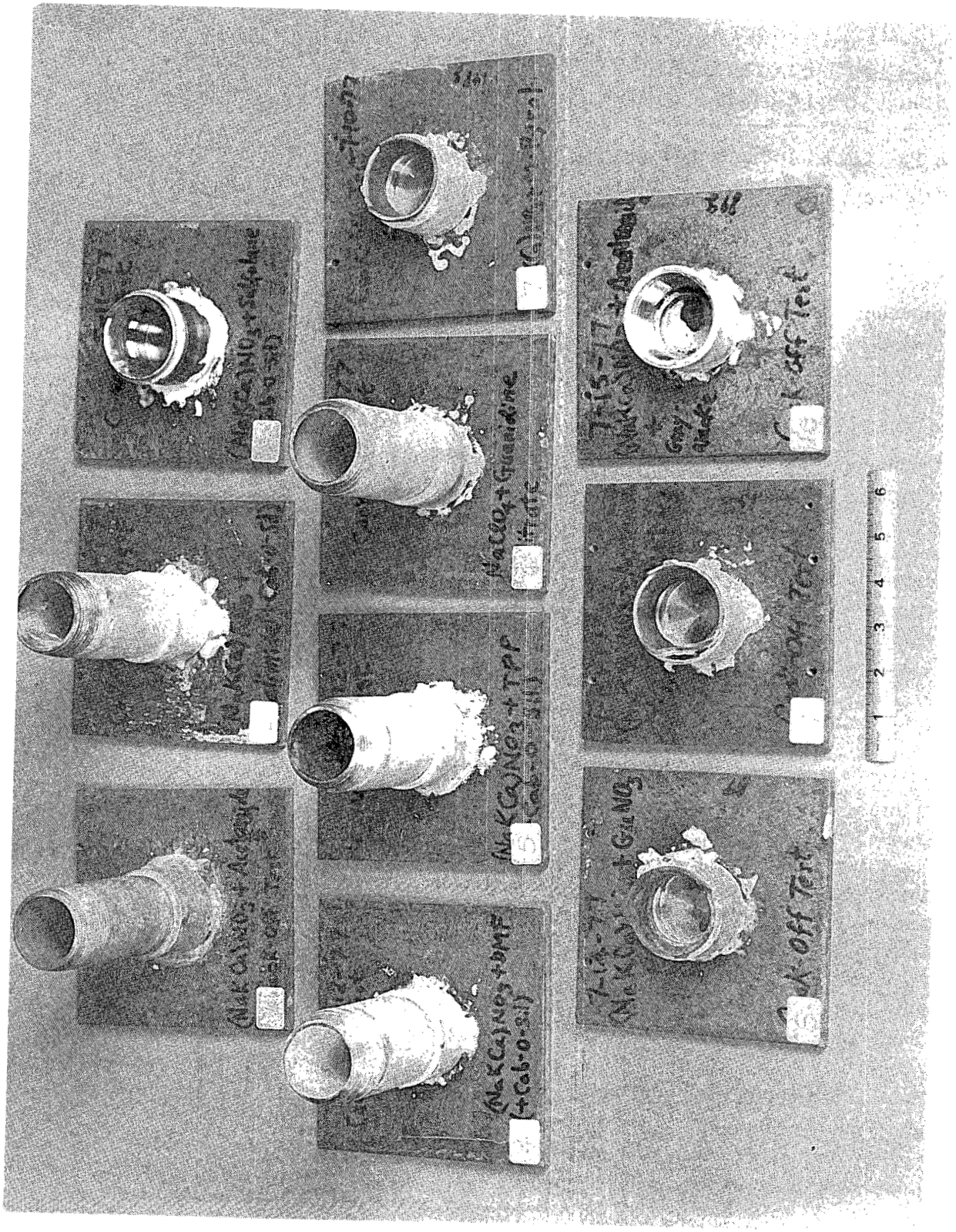
Table 4-20

COOK-OFF TEST RESULTS[1]

Sample	Average Heating Rate		Result	Beginning of Exotherm	Heating Rate at Exotherm Temp.		DSC Exotherm[2]
	°K/min	°F/min			°K/min	°F/min	
1. (NaKCa) NO_3 + acetamide	5.1	9.2	Blew top at 639°K (690°F)	586°K (596°F)	2.6	4.6	537°K
2. (NaKCa) NO_3 + phthalimide	5.6	10.0	Blew top at 575°K (575°F)	537°K (508°F)	1.4	2.5	536°K
3. (NaKCa) NO_3 + sulfolane	7.5	13.5	Deflagrated at 585°K (594°F)	543°K (518°F)	5.9	10.7	410°K
4. (NaKCa) NO_3 + dimethylformamide	6.4	11.5	Blew top at 525°K (485°F)	516°K (470°F)	2.0	3.7	484°K
5. (NaKCa) NO_3 + triphenylphosphate	6.5	11.7	Blew top at 581°K (586°F)	553°K (536°F)	5.6	10.0	542°K
6. $NaClO_4$ + guanidine nitrate	3.0	5.4	Blew top at 744°K (880°F)	563°K (554°F)	0.6	1.0	568°K
7. (NaKCa) NO_3 + N-methyl-2-pyrrolidone	6.2	11.0	Burst at 511°K (460°F)	505°K (450°F)	Unknown		495, 537°K
8. (NaKCa) NO_3 + guanidine nitrate[3]	2.8	5.1	Burst at 691°K (785°F)	585°K (593°F)	0.94	1.7	588°K
9. (NaKCa) NO_3 + guanidine nitrate[3] + acetamide	3.0	5.5	Burst at 592°K (606°F)	568°K (563°F)	0.78	1.4	506°K
10. (NaKCa) NO_3 + acetamide +unidentified graywacke[4]	5.0	9.0	Burst at ~639°K (~690°F)	555°K (540°F)	1.3	2.3	531°K

1. These were 175-g samples unless otherwise specified. Each was shaken for 5 minutes after the sample temperature reached 400°F.
2. The DSC exotherms were determined at a heating rate of 20°K/min.
3. These were 150-g samples.
4. This contained 130 g of the explosive mixture (slightly underoxidized due to a mix-up) and 10 g of graywacke.

REMAINS OF COOK-OFF TESTS



11111-76

Figure 4-7

depending on the size and geometry of the charge, deflagration-detonation transition may occur under uncontrolled conditions. The thermal stability of the combination sodium perchlorate/ guanidinium nitrate is significantly above that of the ultimately chosen formulation. However, the melting point of sodium perchlorate is too high to allow easy handling of the molten oxidizer.

4.2.8 Open Burning Test Results

The explosive sample was heated in the test fixture described in paragraph 2.2.8 to 477°K and mixed by bubbling nitrogen gas through it. The igniter was inserted remotely with the same solenoid/pneumatically operated apparatus used for inserting detonators. When firing the igniter, liquid from the upper 5 cm of liquid evaporated, but the remaining melt did not burn in the 37 mm-diameter pipe. In a separate test, a small quantity of solid, premixed explosive was placed on a spatula and held into the flame of a Bunsen burner. The solids melted, but did not support combustion.

4.3 PERFORMANCE TEST RESULTS

Performance tests were conducted during the development phase on numerous candidate explosives as well as during the qualification phase on the ultimately selected explosive formulation. Of all tests conducted during this program, the detonability tests were the most important tests in identifying useful explosives and eliminating useless candidates. Detonability cannot be simulated using small-scale laboratory samples, but has to be tested full-scale. Because of the hazard involved in handling explosives which were not yet fully characterized, in particular in handling them at high temperature, extreme precautions had to be taken throughout the test program. The time required to plan and carry out such tests safely and the destructive nature of the test which makes reusability of hardware (e.g., heating tapes or a wedge test fixture) impossible, account in part for the comparatively high expense in conducting an explosive development program compared to a study of physical properties of rock formations in preparation for hydraulic fracturing.

If the development and characterization of high-temperature explosives should be continued at some later time, it would be desirable to include some more quantitative tests, e.g., an equivalent of the Trauzl block test or a mortar test to determine and compare explosive pressure and impetus of the explosive. None of these tests is commonly done at the temperatures required for HITEX explosives, and the methods would have to be modified significantly to accommodate hot samples and correct for the effect of temperature on the lead or aluminum blocks. In the case of high-pressure detonability testing, it would be desirable to include detonation velocity instrumentation in the high-pressure bomb and use an internal booster rather than an outside shaped charge for initiation.

4.3.1 Detonability Test Results

Three different types of detonability tests were conducted during this program: open pipe tests for ambient temperature or low vapor pressure explosive tests; sealed pipes for high vapor pressure, high temperature tests; and detonability tests preceded by a 24-hour heating period.

4.3.1.1 Open-Pipe Detonability Tests

It was the desire to develop the plate bending test into a quantitative method to assess the explosive force of candidate explosives. As part of this effort, the depth of indentation was measured on the weaker explosives. The more powerful explosives would perforate the plate. In those cases where a clean hole was punched out of the plate, indentation had to be reported as "infinity". A qualitative assessment was possible by looking at the pipe fragment size, if fragments could be found at all.

Throughout the development of the high-temperature explosive for geothermal applications, the Petroleum Technology Corporation explosive PTC-4 has been carried along as a baseline because field data have already been obtained on its effectiveness in stimulating oil and gas wells. Figure 4-8 (left) shows the effects of a typical high-order detonation on the witness plate, resulting in a cleanly sheared hole with a diameter close to that of the sample. As shown on the right-hand of Figure 4-8, one of the high melting, two-component explosives developed during this program created witness plate perforations very similar to those of the powerful PTC-4.

A summary of the open-pipe detonation tests is presented in Table 4-21. They are listed in the order of descending indentation of the witness plates. The relative indentation measurements were done by averaging the results of measuring depths from two axes paralleling the edges of the witness plate and intersecting over the center of the dent. The nondetonable mixtures are also included in the table. These are grouped by their common oxidizers.

Some of the negative tests, such as those of (LiNaK)NO_3 with ethylene glycol or acetamide most likely reflect mixing problems rather than nondetonability. If properly homogenized, most of the combinations listed as negative would probably be detonable if tested in large-diameter pipes.

One variable which is not yet reflected in Table 4-21 is the quality of mixing. The homogeneity of the mixture depended on the type of mixer used. Table 4-21 includes tests with three different types of mixers as well as a few tests where no mechanical mixer was used at all. The importance of mixing and the degree of emulsification became apparent in the test of (NaKCa)NO_3 with silicone oil, two completely immiscible fluids. Surprisingly, even silicone oil, which is considered an inert, nonflammable fluid, can be made to detonate when homogenized with an oxidizer, although the explosive force was only very weak. Also, heat transfer salt and Dowtherm G, commonly used heat transfer fluids, gave a weak reaction. This points at potential hazards in the design of heat exchange systems in the chemical process industry.

All negative detonability tests were the result of attempts to initiate with a cap only. Many of these cap-insensitive combinations could be detonated successfully when the shock from the cap was boosted by 20 g of C-4 plastic bounded explosive (PBX) in a subsequent test. Combinations in this category include HTS/dibutylphthalate and (LiNaK)NO_3/ethylene glycol.

Another variable which is included in Table 4-21 is the test temperature. Thus, it was surprising to note that (NaKCa)NO_3/acetamide or (NaKCa)NO_3/acetamide plus guanidinium nitrate are not detonable at ambient temperature, but detonate at temperatures above 477°K (400°F). The

RESULTS OF POSITIVE DETONABILITY TESTS

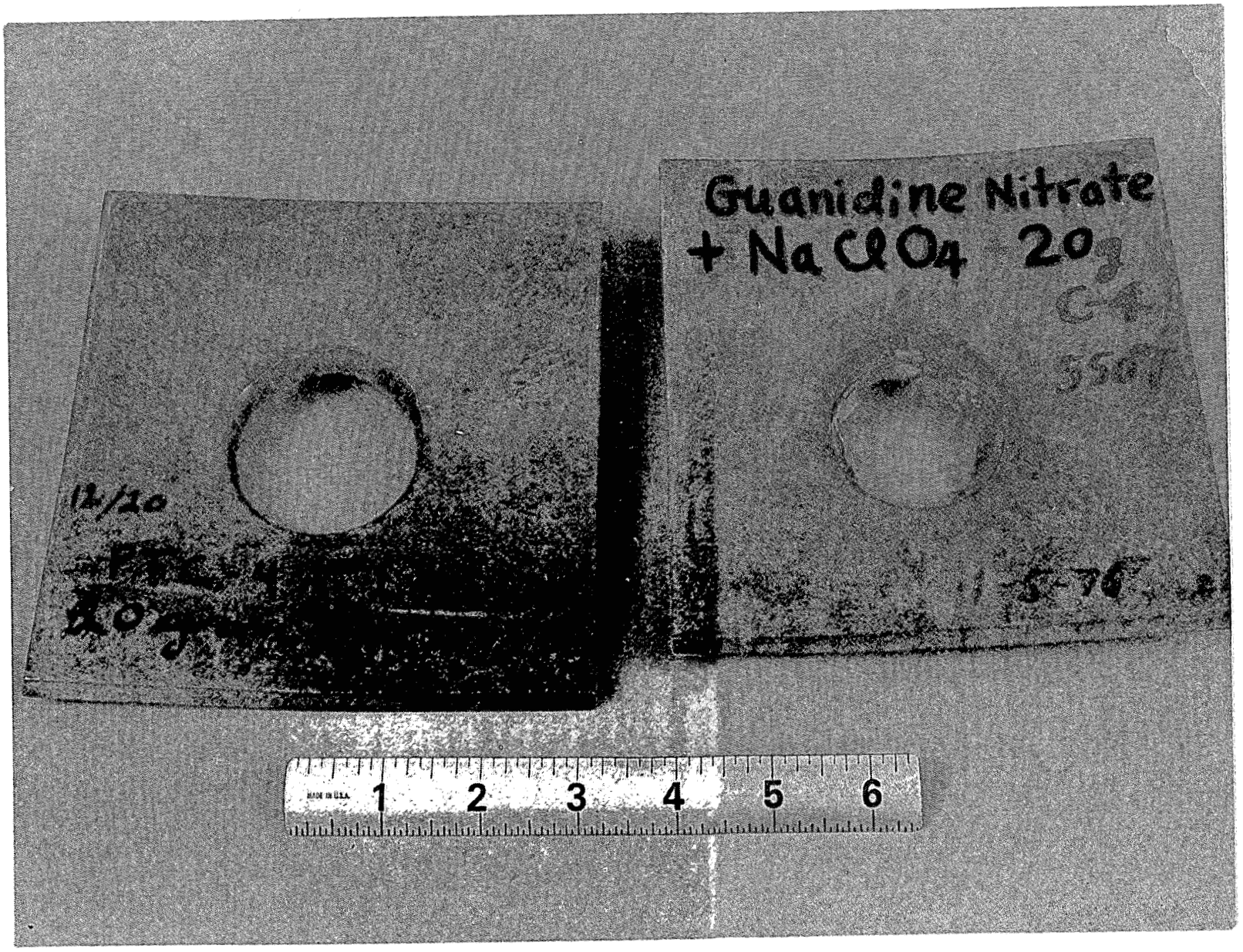


Figure 4-8

Table 4-21
DETONATION TEST RESULTS – OPEN PIPE TESTS

Oxidizer	Fuel	Temperature		Initiation	Witness Plate Indentation (mm)
		°K	°F		
C-4	C-4	293	68	Cap	∞
PTC-4[1]	PTC-4	293	68	Cap + C-4[2]	∞
$NaClO_4$	Guanidinium nitrate	561	550	Cap + C-4	∞
$NaClO_4 \cdot H_2O$	Triethylene glycol	552	534	Autodetonated	∞
(NaKCa) NO_3	Guanidinium nitrate	561	550	Cap	∞
(NaKCa) NO_3	Acetamide	480	405	Cap + C-4	37[3]
$NaClO_4$	Diethylene glycol	519	475	Cap + C-4	30[4]
$NaClO_4$	Ethylene glycol	469	385	Cap + C-4	28[4]
(NaKCa) $NO_3 \cdot 4H_2O$	Sulfolane	533	500	Cap	28[4]
(LiNaK) NO_3 + $NaClO_4$	Glycerol	555	540	Cap + C-4	25
$HNO_3 + H_2O$	Nitrobenzene	293	68	Cap	25
$NaClO_4$	Ethylene glycol	472	390	Cap	19[4]
$NaClO_4$	Diethylene glycol	505	450	Cap	18
$NaClO_4$	Guanidinium nitrate	561	550	Cap	17
(LiNaK) NO_3	Ethylene glycol	477	400	Cap + C-4	17
(NaKCa) $NO_3 \cdot 4H_2O$	Triphenylphosphate	533	500	Cap	16
(NaKCa) $NO_3 \cdot 4H_2O$ + $NaClO_4$	Dibutylphthalate	561	550	Cap	14
$NaClO_4 \cdot H_2O$	Acetamide	505	450	Cap	13
(LiNaK) NO_3 + $NaClO_4$	Glycerol	561	550	Cap	13
None	m-Dinitrobenzene	561	550	Cap	12
$KClO_4$	m-Dinitrobenzene	550	530	Cap	10
HTS[5]	Melamine	561	550	Cap	10
HTS + $NaClO_4$	Dibutylphthalate	533+	500+	Cap	9

Table 4-21 (Continued)
DETONATION TEST RESULTS – OPEN PIPE TESTS

Oxidizer	Fuel	Temperature		Initiation	Witness Plate Indentation (mm)
		°K	°F		
(NaKCa) $NO_3 \cdot 4H_2O$	Acetamide	505	450	Cap	8
(LiNaK) NO_3	Diethylene glycol	505	450	Cap	8
HTS	Dimethylphthalate	550	530	Cap	7
None	2,4-Dinitrotoluene	522	480	Cap + C-4	7
None	2,4-Dinitrotoluene	561	550	Cap	6
(LiNaK) NO_3	Glycerol	544	520	Cap	6
None	m-Dinitrobenzene	547	525	Cap + C-4	5
(NaKCa) NO_3	Silicone oil	505	450	Cap	5
HTS	Dibutylphthalate	561	550	Cap	4
HTS	Ethylene glycol	466	380	Cap	3
HTS	Dowtherm G	533	500	Cap + C-4	3
HTS	Dibutylphthalate	561	550	Cap + C-4	3
HTS	Acetamide	505	450	Cap	1
HTS	Dibutylphthalate	293	68	Cap	None
HTS	Glycerol	477	400	Cap	None
HTS	Formamide	477	400	Cap	None
HTS	Mineral oil	505	450	Cap	None
HTS	Dowtherm G	533	500	Cap	None[6]
HTS	Therminol 55	561	550	Cap	None
HTS	Triphenylphosphate	561	550	Cap	None
HTS	Sulfolane	533	500	Cap	None[6]
(LiNaK) NO_3	Ethylene glycol	472	390	Cap	None
(LiNaK) NO_3	Acetamide	505	450	Cap	None

Table 4-21 (Concluded)
DETONATION TEST RESULTS – OPEN PIPE TESTS

Oxidizer	Fuel	Temperature		Initiation	Witness Plate Indentation (mm)
		°K	°F		
(LiNaK) NO_3	Dibutylphthalate	561	550	Cap	None
(LiNaK) NO_3 + $NaClO_4$	Dibutylphthalate	561	550	Cap	None[6]
(NaKCa) $NO_3 \cdot 4H_2O$	Dibutylphthalate	561	550	Cap	None
(NaKCa) $NO_3 \cdot 4H_2O$	Dimethylphthalate	550	530	Cap	None[6]
(NaKCa) $NO_3 \cdot 4H_2O$	Therminol 66	561	550	Cap	None
(NaKCa) NO_3	Acetamide	293	68	Cap	None
(NaKCa) NO_3	Guanidinium nitrate + acetamide (70/30)	297	75	Cap	None
$NaClO_4$	Melamine	293	68	Cap	None
None	m-Dinitrobenzene	373	212	Cap	None
None	Guanidinium nitrate + H_2O	293	68	Cap	None

ANNOTATIONS:

1 PTC-4 – Proprietary explosive of Petroleum Technology Corporation, a subsidiary of ROCKCOR, Inc.

2 A Hercules No. 8 blasting cap and 20 g booster charge of composition C-4.

3 This was a 1-5/8" (dia) x 12" open pipe containing slightly over one pound of the explosive mixture. All the others in the table were 100 g mixtures.

4 Witness plate penetrated, but not to the extent that a high order detonation occurred.

5 HTS = heat treatment salt = KNO_3 : $NaNO_3$: $NaNO_2$ (53 : 7 : 40% by weight).

6 The explosion was somewhat louder than just the blasting cap.

NOTE: All immiscible mixtures contained 2% Cab-O-Sil and were stirred while hot, just prior to initiation, by a remotely activated stirrer.

transition temperature has not yet been pinpointed. Most likely it coincides with the melting point. The fact that the prime candidate explosive is not detonable at ambient temperature (at least not in a 37-mm pipe) is a significant safety feature of the HITEX explosive. Normally, mixed explosive would not have to be handled above ground. After use and before disassembling, the equipment can be flushed with water, in which the explosive is readily soluble. Even if some explosive should evade the flushing and remain in the mixer or tubing removed from the well, it would not constitute a hazard to the stimulation crew.

The appearance of witness plates after typical tests with (NaKCa)NO_3 oxidizer/fuel combinations is illustrated in Figure 4-9. A similar collection of witness plates from tests with sodium perchlorate as an oxidizer is shown in Figure 4-10.

After it was decided to choose a guanidinium nitrate-acetamide mixture as the fuel component of the candidate explosive, a series of detonability tests was conducted with different ratios of the two components to determine if they were detonable without (NaKCa)NO_3 oxidizer. The results were encouraging. None of the mixtures listed in Table 4-22 was detonable. It was especially reassuring that a 2.27 kg (5 lbs) mixture in a 76-mm (3-inch) diameter 380-mm pipe (15-inch) long pipe also failed to detonate. Figure 4-11 shows the outcome of this latter test. The bulging distortion in the upper half of the pipe resulted from the 20-g of C-4 booster used for the initiation.

These results are not surprising in view of the fact that all mixtures were underoxidized. The two components of the mixture, however, have been noted to decompose at elevated temperatures in test tubes and in previous thermal stability tests. In fusing guanidinium nitrate, there was usually some evolution of gases, such as ammonia, and after samples containing acetamide were retrieved from thermal stability tests in bomblets, the residual solids were usually discolored (light brown to black) showing decomposition products although the nitrate analysis of the sample showed only a slight nitrate loss. When acetamide alone was heated to 533°K (500°F) for 24 hours, it turned dark brown. Thus, a comprehensive study of the fuel mixture of guanidinium nitrate and acetamide is essential before tank car size batches are prepared for field operation.

4.3.1.2 Sealed Pipe Detonability Test Results

The interpretation of data from detonability tests in sealed pipe bombs is more difficult. The plate indentation could no longer be used as indication of the explosive force because the heavy-walled threaded cap of the pipe bombs attenuated the shock wave significantly. Consequently, one had to rely on fragment size studies. Also the amount of flaring of the bottom cap attached to the witness plate was an indication of the explosive force.

A continuing problem with the sealed pipe bombs was the inability to initiate high-order detonations with the jet of a penetrating shaped charge alone. Even PTC-4 would not detonate high-order when initiated in this mode. The size of fragments indicated that PTC-4 detonated at a low order. The results did not improve if the shaped charge jet penetrated the pipe bomb horizontally or vertically.

WITNESS PLATES FROM OPEN PIPE DETONABILITY TESTS – (NaKCa) NO_3 AS THE OXIDIZER

Figure 4-9

WITNESS PLATES FROM OPEN PIPE DETONABILITY TESTS – $NaClO_4$ AS THE OXIDIZER

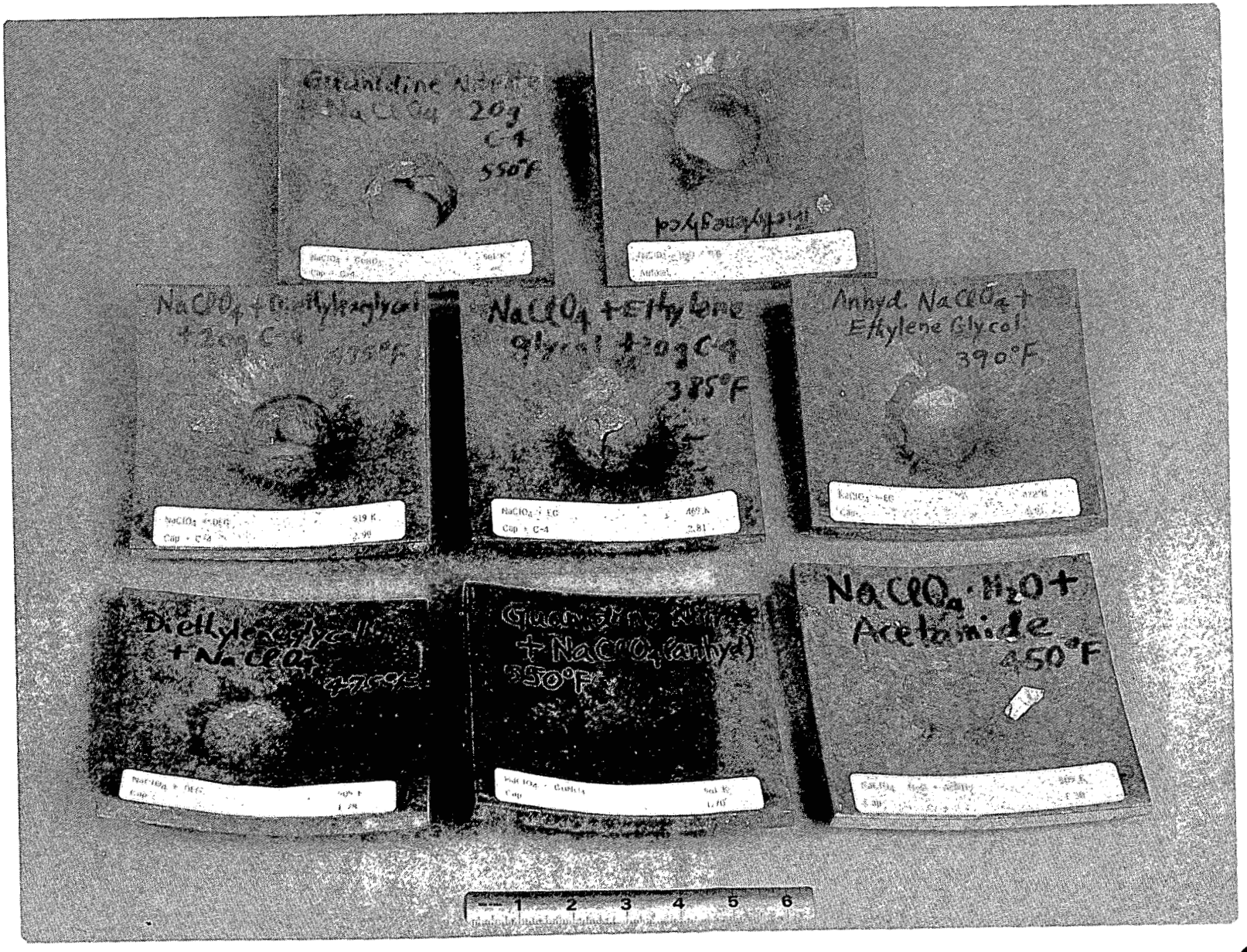


Figure 4-10

Table 4-22
DETONABILITY TEST RESULTS OF SOME MIXTURES
OF GUANIDINIUM NITRATE AND ACETAMIDE

Sample[1]	Temperature		Initiation	Result
	°K	°F		
Guanidinium nitrate + acetamide (65/35) [3]	505	450	Cap[2]	Negative
Guanidinium nitrate + acetamide (75/25)	505	450	Cap	Negative
Guanidinium nitrate + acetamide (85/15)	505	450	Cap	Negative
Guanidinium nitrate	505	450	Cap	Negative
Guanidinium nitrate + acetamide (70/30) [4]	477+	400+	Cap + C-4 (20g)	Negative

[1] Unless otherwise specified, these were 80 g samples in 37 mm diameter pipes

[2] Hercules No. 8 detonator

[3] The numbers in parentheses indicate percent by weight of each, respectively

[4] This was a 5 lb mixture. It was tested in a 3-inch diameter pipe

It would have been desirable to include a booster charge inside the pipe bomb in close contact with the sample. The booster of high explosive then presumably would have been initiated by the shaped charge to detonate at high order. However, no booster material was available which would withstand the high temperature and which had a critical diameter below the diameter of the pipe.

Three different methods of initiation were tested for sealed pipe bombs. Initially, horizontal penetration by the jet from a shaped charge was considered a good method for initiation. However, this method failed to initiate PTC-4 to a high-order detonation. Similarly, promising explosive combinations might have been overlooked if one had relied on horizontal shaped charge jets only.

Repeating the PTC-4 test with vertical penetration of the jet did not improve the order of detonation. Vertical penetration through the sample is generally undesirable for test purposes because the jet arrives at the target plate prior to the detonation front from the sample and will weaken the witness plate.

THREE-INCH DIAMETER PIPE
CONTAINING GUANIDINIUM NITRATE-ACETAMIDE MIXTURE –
AFTER DETONABILITY TEST THIS WAS INITIATED WITH 20g OF C-4 BOOSTER

Another mode of initiation was to insert a stainless steel well with a du Pont X-321-K detonator. The walls of the well tube were machined down to 0.76 mm (30-mil) thickness, sufficient to withstand a sample pressure of 6.9 bar (100 psia). The detonator was inserted prior to the test and was heated up along with the sample.

In a blank test, the detonator alone was fired in the stainless steel tube. The detonator was very powerful, and the tube was completely fragmented. It is believed that the attenuation by the 0.76-mm stainless steel wall adds only insignificantly to that of the 0.5-mm aluminum wall in which the booster part (8 grains = 0.52 g TACOT) of the X-321-K cap is contained.

A summary of detonability tests in sealed pipes is presented in Table 4-23. As already mentioned, it would have been desirable to include a 20-g booster charge of high explosive inside the pipe bomb which would have reproducibly initiated the explosive sample to high-order detonation, if the explosive under test had the ability to propagate in this mode. The booster charge would have had to be in close contact (partially submerged) with the sample and would have had to be encapsulated to prevent its chemical interaction with or dissolving in the sample. The only material which could possibly withstand the high temperature is TACOT, a high-temperature explosive manufactured by Du Pont. Throughout the program, RRC repeatedly attempted to obtain TACOT samples from Du Pont; however, RRC was told that TACOT is not available as pellets or bulk material and Du Pont elects to sell it in manufactured items (e.g., X-321-K caps) only. In looking for a substitute high-temperature booster material, a thorough literature survey was conducted. The only other high explosive which was found to be commercially available was hexanitrostilbene, HNS. Its thermal stability ranks between that of TACOT and RDX on Figure 1-3.

4.3.1.3 Twenty-Four Hour Detonability Test Results

The experimental technique used for the detonability tests preceded by a 24-hour heating period was the same as that used for the sealed pipe bomb tests. The mixtures were shaken every 30 minutes for 5 minutes to assure a uniform mixture. Because the tests at the remote test site continued in three shifts around the clock, a guard service was provided during night hours to assure that no unauthorized persons would approach the explosive sample while it was being heated. After the 24-hour (counting from the time the sample had reached the desired test temperature) heating period was over, the sample holder was moved to an upright position and the shaped charge was detonated on command.

The 24-hour detonation test results are summarized in Table 4-24. The remains from the bombs are displayed in Figure 4-12. The sample numbers on Table 4-24 correspond to the numbers found at the lower left-hand corner of witness plates in Figure 4-12. A number of these combinations show potential for use as high temperature explosives. Combinations of (NaKCa)NO_3 with acetamide, sulfolane and/or guanidinium nitrate and combinations of $NaClO_4$ with guanidinium nitrate are thermally stable and remain detonable after 24 hours. Obviously, the usefulness of the various combinations depends on the upper temperature limit of the environment where the explosive will be applied and also on the duration of exposure to such environment. For example, a comparison of the $NaClO_4$-$GuNO_3$ mixture at various conditions in Figure 4-13 shows that its effectiveness was

Table 4-23
DETONATION TEST RESULTS – SEALED PIPE

Oxidizer	Fuel	Temperature		Initiation	Result
		°K	°F		
C-4	C-4	293	77	Cap + S.C.[1]	Positive } High order detonation
PTC-4	PTC-4	293	77	Cap + S.C.	Positive
(NaKCa) $NO_3 \cdot 4H_2O$	Formamide[2]	>394	>250	Cap + S.C.	Negative[3]
(NaKCa) $NO_3 \cdot 4H_2O$	Acetamide[2]	505	450	Cap + S.C.	Negative[3]
$NaClO_4$	Guanidinium nitrate	550	530	Cap + S.C.	Positive[3]
(NaKCa) NO_3	Dimethylformamide	511	460	Cap + S.C.	Positive
(NaKCa) NO_3	Acetamide	~519	~475	X-321-K Cap	Positive
(NaKCa) NO_3	Acetamide	516	470	Cap + S.C.[4]	Positive
(NaKCa) NO_3	Acetamide	516	470	Cap + S.C.	Positive
(NaKCa) NO_3	N-methyl-2-pyrrolidone	505	450	Cap + S.C.	Negative
(NaKCa) NO_3	Triethylene glycol	494	430	Cap + S.C.	Positive
(NaKCa) NO_3	Phthalonitrile	511	460	Cap + S.C.	Negative
(NaKCa) NO_3	Phthalimide	533	500	Cap + S.C.	Positive

NOTES:

[1] A Hercules No. 8 blasting cap attached to the groove of a shaped charge. The groove of the shaped charge was filled with approximately 2 g of C-4. The shaped charge was aimed through the side of the sealed pipe at a 45° downward angle at the liquid surface.

[2] The fuel was sealed in a polyethylene bag.

[3] These were 100 g mixtures. All the others were 175 g mixtures.

[4] The shaped charge was initiated through the top of the sealed pipe for this test only.

Table 4-24
TWENTY-FOUR-HOUR DETONATION TEST RESULTS

Sample[1]	Test Temperature		Duration (hrs)	Result
	(^{o}K)	(^{o}F)		
1. (NaKCa)NO_3 + acetamide	491 ± 10	425 ± 20	23	Detonated on command[2]
2. (NaKCa)NO_3 + sulfolane	491 ± 10	425 ± 20	21	Detonated on command
3. $NaClO_4$ + Guanidinium nitrate ($GuNO_3$)	533 ± 10	500 ± 20	24	Detonated on command
4. (NaKCa)NO_3 + triphenylphosphate	505 ± 10	450 ± 20	24	Negative
5. (NaKCa)NO_3 + dimethylformamide	478 ± 10	400 ± 20	1.3	Burst by itself
6. (NaKCa)NO_3 + phthalimide	505 ± 10	450 ± 20	10	Burst by itself
7. (NaKCa)NO_3 + acetamide	561 ± 10	550 ± 20	24	Burst or deflagrated on command[3]
8. $NaClO_4$ + $GuNO_3$	561 ± 10	550 ± 20	24	Burst or deflagrated on command
9. (NaKCa)NO_3 + $GuNO_3$	561 ± 10	550 ± 20	24	Burst or deflagrated on command
10. (NaKCa) + $GuNO_3$ + acetamide	505 ± 10	450 ± 20	24	Detonated on command

[1] Sample sizes varied from 100 g (for No. 3 and No. 9), 150 g (for No. 10), to 175 g (for the rest), depending on the ease of loading the 1.5-inch diameter pipe bombs.

[2] The top and main body of the pipe were blown into fragments. The threaded bottom cap of the pipe was flared and the witness plate was distorted.

[3] The pipe sheared off above the bottom cap leaving it and the witness plate essentially intact with minimal distortion.

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REMAINS FROM TWENTY-FOUR-HOUR DETONABILITY TESTS

Figure 4-12

DETONABILITY OF $NaClO_4$ -$GuNO_3$ MIXTURE UNDER VARIED CONDITIONS

Figure 4-13

diminished as the exposure time to high temperature was lengthened (compare the left and the middle witness plates). As the soak temperature was increased, the power of the explosive also diminished (compare the middle and the right witness plates). Similar comparisons might also be made with the (NaKCa)NO_3-acetamide series in Figure 4-14, although the trend is not as obvious owing to the greater differences in test temperatures. The effectiveness of the (NaKCa)NO_3-acetamide mixture appears to diminish going from 491°K to 510°K (compare the middle and left witness plates) as the 24-hour soak temperature.

4.3.2 High-Pressure Detonability Test Results

The bomb for high-pressure detonability test was heated to 586°K (595°F), pressurized to 345 bar (5,000 psi) with nitrogen gas and detonated with a shaped charge filled with one pound of C-4. The shaped charge was positioned at a height of two diameters of the shaped charge cone above the top of the bomb. When detonated, it gave a loud report. Examination of the test site afterwards and of the fragments left by the explosion suggested that the pressurized candidate explosive detonated with a high-order detonation velocity.

To insure that the above effect was not caused by the shaped charge alone, a blank test was performed by firing a same size shaped charge through the top of a sealed container (1.5-inch diameter by 6-inch length pipe with threaded caps on the top and bottom) containing water. The shaped charge perforated the upper and lower caps of the container, but otherwise caused no fragmentation.

The difference between the two tests is so pronounced that it must be concluded that the explosive remains detonable at high pressure.

4.3.3 Detonation Velocity Test Results

Three explosive formulations were tested for detonation velocity using the equipment described in paragraph 2.3.1.

Three tests were performed using the primary candidate ((NaKCa)NO_3/acetamide/guanidinium nitrate). The average detonation velocity was 6,050 meters per second for the three shots. The nominal test temperature was 505°K (450°F). In one shot, the initial pin shorted, but consistent data were obtained from the remaining three pins. For the two other shots, all pins functioned normally. However, the explosive could not be mixed prior to firing since the nitrogen gas line was plugged; apparently, some explosive had backed up into the tube during the loading procedure, had solidifed and did not remelt when the test was run. This was not considered to be a serious problem since the explosive in all cases was mixed during the loading process before it was allowed to solidify. Analysis of top and bottom samples from explosive mixed and cooled in this manner showed identical nitrate results, indicating that the explosive mixed uniformly and did not separate upon cooling. Therefore, failure to remix the explosive upon remelting was not deemed significant. The detonation velocity did not deviate significantly in any of the three samples tested as can be seen from Table 4-25.

DETONABILITY OF (NaKCa) NO_3-$AcNH_2$ MIXTURE UNDER VARIED CONDITIONS

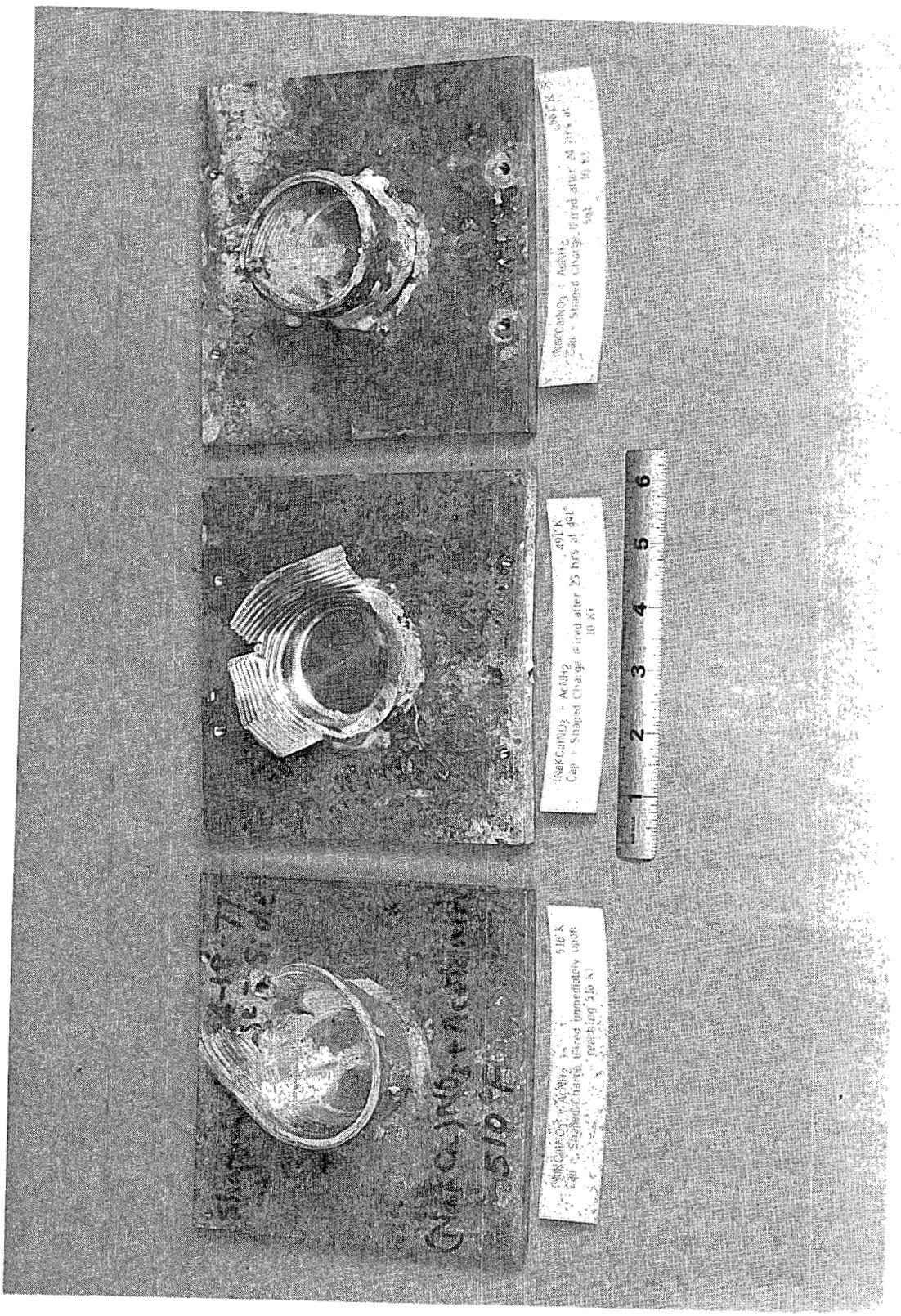

Figure 4-14

Table 4-25
DETONATION VELOCITY TEST RESULTS

Explosive Sample	Average Detonation Velocity (m/s)	Test Designation	Remarks
$(NaKCa)NO_3/AcNH_2 + GuNO_3$	6,096	A	Mixed OK
	6,016	B	Mixing problems
	6,000	C	Mixed OK
$(NaKCa)NO_3/AcNH_2$	3,810	F	Mixed OK
$(NaKCa)NO_3$/Sulfolane	2,454 4,675 5,562	H	Mixed repeatedly. Detonator not fully inserted.

The results from the backup candidate explosive $(NaKCa)NO_3$/acetamide were disappointing and unexpected. Of the first three tests run, two failed to detonate and the third shot showed a low order detonation velocity of 3,810 m/sec with the velocity decreasing over the last 3 inches. This was totally unexpected and is still not explainable. This formulation had been tested previously using 18-inch long, 1-1/2-inch diameter pipes as well as the shorter pipes used in preliminary detonability tests and in all cases the explosive had detonated. A fourth test was run, mixing the explosive and running the test the same day to see if possibly the preparation of the explosive samples a week before testing had any effect. This sample also failed to detonate. Since all tests were run with the same lots of chemicals, the same lots of parts and were prepared by the same personnel, there seems to be no ready explanation for these results.

One additional test was conducted on an alternate candidate explosive $(NaKCa)NO_3$/sulfolane which detonated at high velocity; however, the measurement of detonation velocity was not valid since the remotely operated device to place the detonator apparently did not fully insert the detonator before it was set off. The detonation velocity gave results showing an increase in rate as the detonation wave proceeded through the explosive as shown in Table 4-25.

This is the result one would expect from a weak initiation such as that obtained by a detonator going off before being fully inserted in the explosive so that some of the energy was attenuated by the air gap. No further testing could be done since all of the test fixtures had been used; also, schedule and financial limitations did not permit extra testing.

The remains of the detonation velocity test fixtures are shown in Figure 4-15. The clean cut holes punched out of the witness plates A, B, and C using $(NaKCa)NO_3$/acetamide + guanidinium nitrate

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REMAINS OF DETONATION VELOCITY TEST FIXTURES

Figure 4-15

visibly support the high-order detonation velocity measured electronically during the test. Test F with (NaKCa)NO_3/acetamide illustrates a low-order detonation which bent the plate but failed to perforate it. Plate H from the sulfolane test also indicates that in spite of weak initiation, the detonation bootstrapped itself to high-order propagation by the time it impacted on the plate.

4.3.4 Thin Film Propagation (Wedge) Test Results

The results of the wedge test for the primary candidate, (NaKCa)NO_3-acetamide-guanidinium nitrate, are best described by graphical representation as illustrated in Figure 4-16 which present the results from the two series of pins employed (upper and lower rows of drawing SK-5997). The detonation velocity shows a steadily decreasing rate as the thickness of the explosive wedge decreases, dropping off quite drastically at 15 mm (0.58 inch) thickness. The depth of the explosive was uniformly 100 mm (4 inches) from end to end. The initial width of the charge was 40 mm (1.6 inches). The explosive was known to have a high-order detonation velocity (in excess of 6,000 m/sec) in a thickness of 38 mm (1.5 inches) from previous testing so the initial width of 1.6 inches insured that the detonation wave started at high velocity which was confirmed by the results of this test. The detonation velocity dropped below 4,000 m/s at a gap width of 20 mm (0.79 inch). At detonation velocities measured in the narrower end of the wedge, the explosive would be considered to be undergoing a low-order burn or even be extinguishing rather than detonating. This transition may occur at lower wedge gap widths if more confinement was provided allowing increased pressure buildup. The remains of the wedge test fixture are shown in Figure 4-17.

The question has been raised what effect confinement and increased initial pressure may have on the critical wedge gap width. Studies reported in the literature on the effect of a steel shell on the critical diameter of detonation of condensed explosives show that the critical diameter as a function of the wall thickness of the shell decreases sharply at comparatively low wall thickness (Reference K4). At increasing wall thickness, further decreases in critical diameter become insignificant. The wedge gap width and detonation velocity obtained in the 6-mm steel shell is probably very close to that which can be experienced in an explosive sample confined by rock below ground.

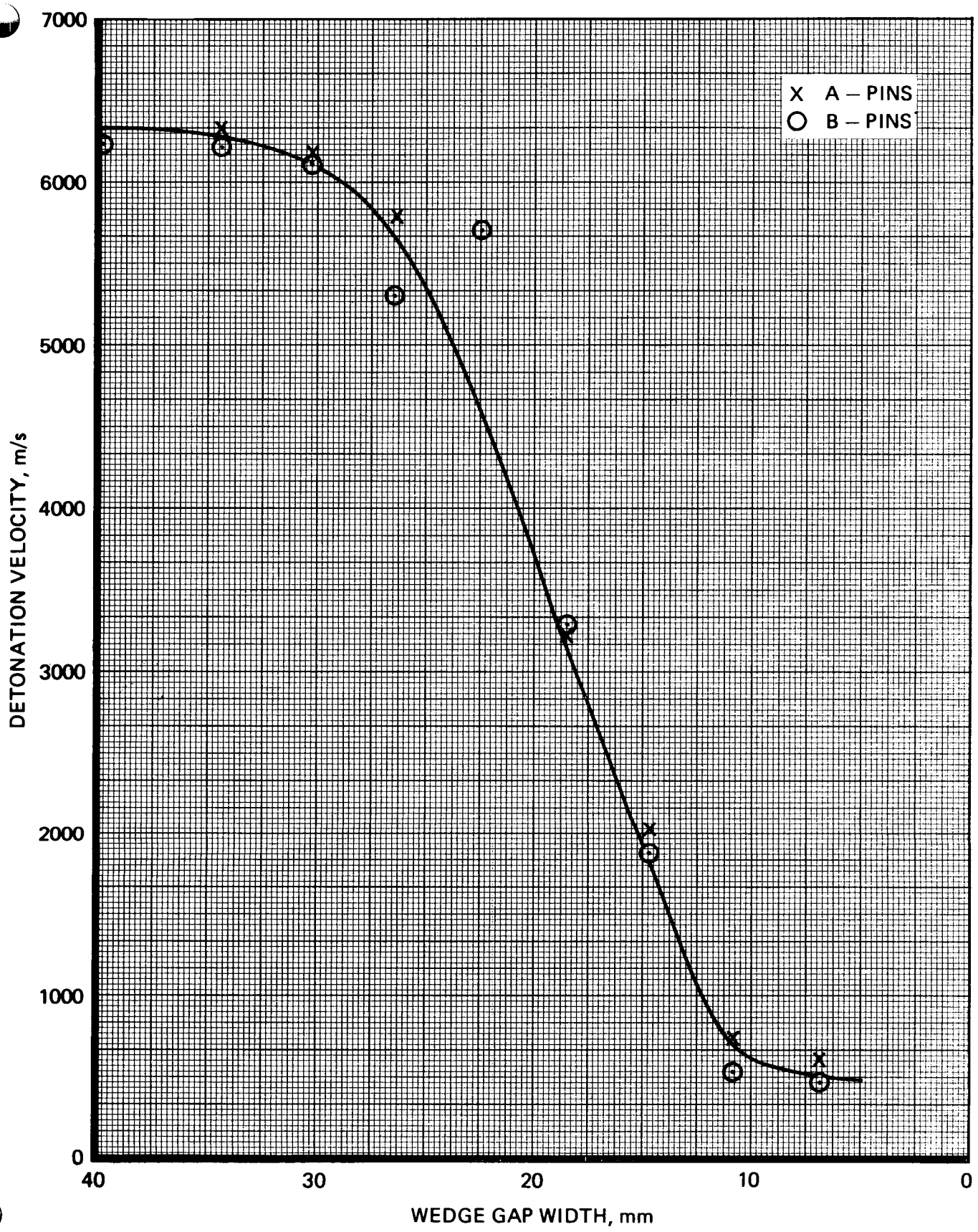
In studies with isopropyl nitrate as an explosive, it was noted that not only the wall thickness and the wall material, but also the smoothness of the wall had a pronounced effect on the critical diameter (Reference F5). In order to conclusively answer the question with regard to the effect of pressure on critical wedge gap width, it may be advisable to repeat the wedge test in a test fixture designed to withstand high pressure.

4.4 RESULTS OF PHYSICAL PROPERTY MEASUREMENTS

A preliminary set of physical properties of the explosive and its ingredients have been determined. These data may be used for sizing studies of the mobile mixing unit to be used for the field demonstration test. Because some of the physical properties of the explosive had to be measured remotely, the data lack the accuracy which can typically be achieved with nonexplosive ingredients.

A summary of physical properties of the prime candidate explosive is compiled in Table 4-26. A more detailed discussion of the individual physical properties follows in the subsequent paragraphs.

HITEX DETONATION VELOCITY AS A FUNCTION OF WEDGE GAP WIDTH



REMAINS OF THIN FILM PROPAGATION TEST-WEDGE TEST FIXTURE

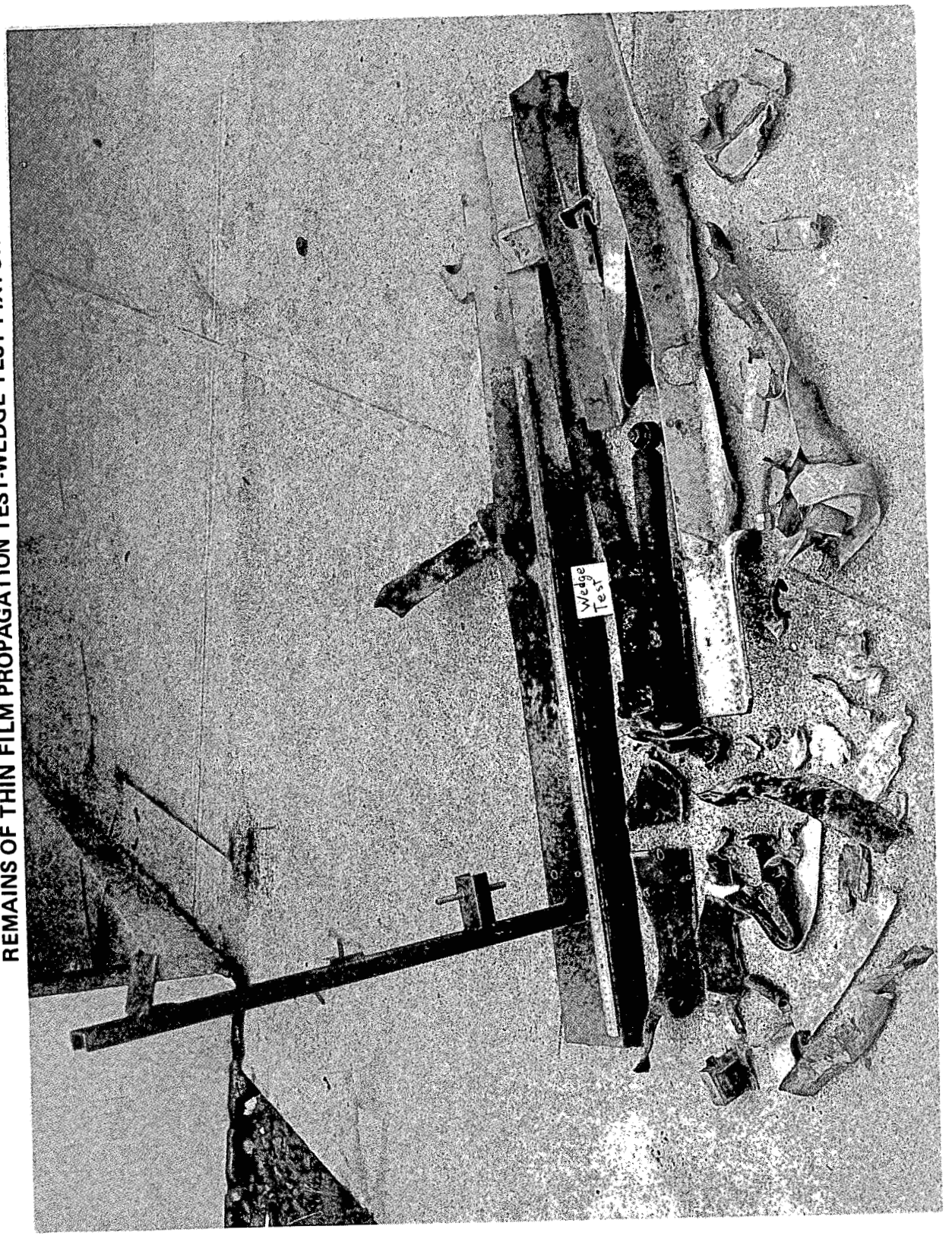


Table 4-26
PHYSICAL PROPERTIES OF CANDIDATE HIGH TEMPERATURE EXPLOSIVE (HITEX) AND ITS COMPONENTS

	Oxidizer $(NaKCa)NO_3$ (11.2%–44.3%–44.5%)	Fuel $GuNO_3$-$AcNH_2$ (70%–30%)	Mixture $(NaKCa)NO_3$-$GuNO_3$-$AcNH_2$ (58.7%–28.9%–12.4%)
Melting point, °K	406	<338–437	332–427 375–427 – Slurry 332–375 – Paste
Solubility, g/100g H_2O			
295°K	71	19	27
313°K	–	–	66
333°K	217	89	122
Viscosity, centipoise			
410°K	460	–	
423°K	250	300	
427°K	210	58	
430°K	185	–	
435°K	150	7.5	
570°K	20	–	
Density, g/cm^3			
295°K	2.32	1.25	1.65
425°K	2.11	1.22	1.58
475°K	2.02	1.18	(1.39)*
500°K	1.99	1.16	–
Conductivity, ohm^{-1} cm^{-1}			
400°K	0.004	–	0.050
425°K	0.014	0.088	0.080
475°K	0.063	0.194	(0.150)*
500°K	0.096	0.210	–

*Extrapolated point

4.1 Melting Point Determinations

ıe (NaKCa)NO_3 eutectic was prepared from fused $NaNO_3$, KNO_3 and $Ca(NO_3)^2 \cdot 4\ H_2O$ in the tio of 9.4, 37.0, and 53.6% by weight, respectively. The water-containing mixture was then heated a 423°K drying oven overnight to obtain the dehydrated eutectic with a weight ratio of 11.2, 4.3 and 44.5%. When the molten (NaKCa)NO_3 cooled, it went through a glass-like transition stage. olid (NaKCa)NO_3 became transparent. Depending on the quality of nitrates used, the solid varied :om completely clear to amber-colored. The (NaKCa)NO_3 eutectic melted at 406°K, but remained elatively fluid down to 366°K (200°F) and became quite viscous at 361°K (190°F). A complete lot of melting point versus other compositions of the three nitrates was already shown in Figure -11.

A mixture of 70%–30% by weight $GuNO_3$ and acetamide exhibited a melting range from below 338°K to 437°K. Unlike (NaKCa)NO_3 which gradually thickened on cooling, the $GuNO_3$–$AcNH_2$ mixture solidified readily on cooling. When chilled to 423°K, the mixture consisted of 20–30% solids. A melting point diagram of various mixtures of $GuNO_3$ and $AcNH_2$ is shown in Figure 4-18.

The candidate explosive has a melting range of 332°K to 427°K. Due to the combined effects of its oxidizer and fuel components, it remained a slurry down to 375°K, below which it assumed a paste-like consistency until it froze at 332°K.

The phase change by melting is accompanied by an increase in the specific volume of the explosive ingredients. The only exception to this rule is the melting of water ice. For all other substances, the melting point increases with pressure. It will be necessary to determine molar volumes of the solid and liquid explosive in the vicinity of the melting point. The increase in melting point as a function of pressure can then be calculated. It would be very undesirable to operate the molten explosive in the vicinity of the melting point and have it solidify in the formation as soon as pressure is applied or hydrostatic pressure builds up.

4.4.2 Solubility Determinations

Solubilities were already presented in Table 4-26. An interesting observation was made while determining the solubility of the $GuNO_3$-$AcNH_2$ mixture. The solvation process of this mixture was noticeably endothermic. The cooling of a solution of guanidinium nitrate in water was similar to that of ammonium nitrate. A plot of the solubility data of the candidate explosive is shown in Figure 4-19, extrapolating to about 343°K. Technical grade guanidinium nitrate contained insoluble solids in the order of <0.5%. They formed a turbid suspension in the fuel and candidate explosive solutions causing the latter to appear turbid even though all the nitrates and acetamide had gone into solution.

Solubility and miscibility also depend on pressure. No changes are expected during normal operation and cleanup of the mixing rig. However, solubility at great depth under high pressures may be different from that determined at ambient pressure at the surface.

MELTING POINT DIAGRAM OF THE SYSTEM GUANIDINIUM NITRATE/ACETAMIDE

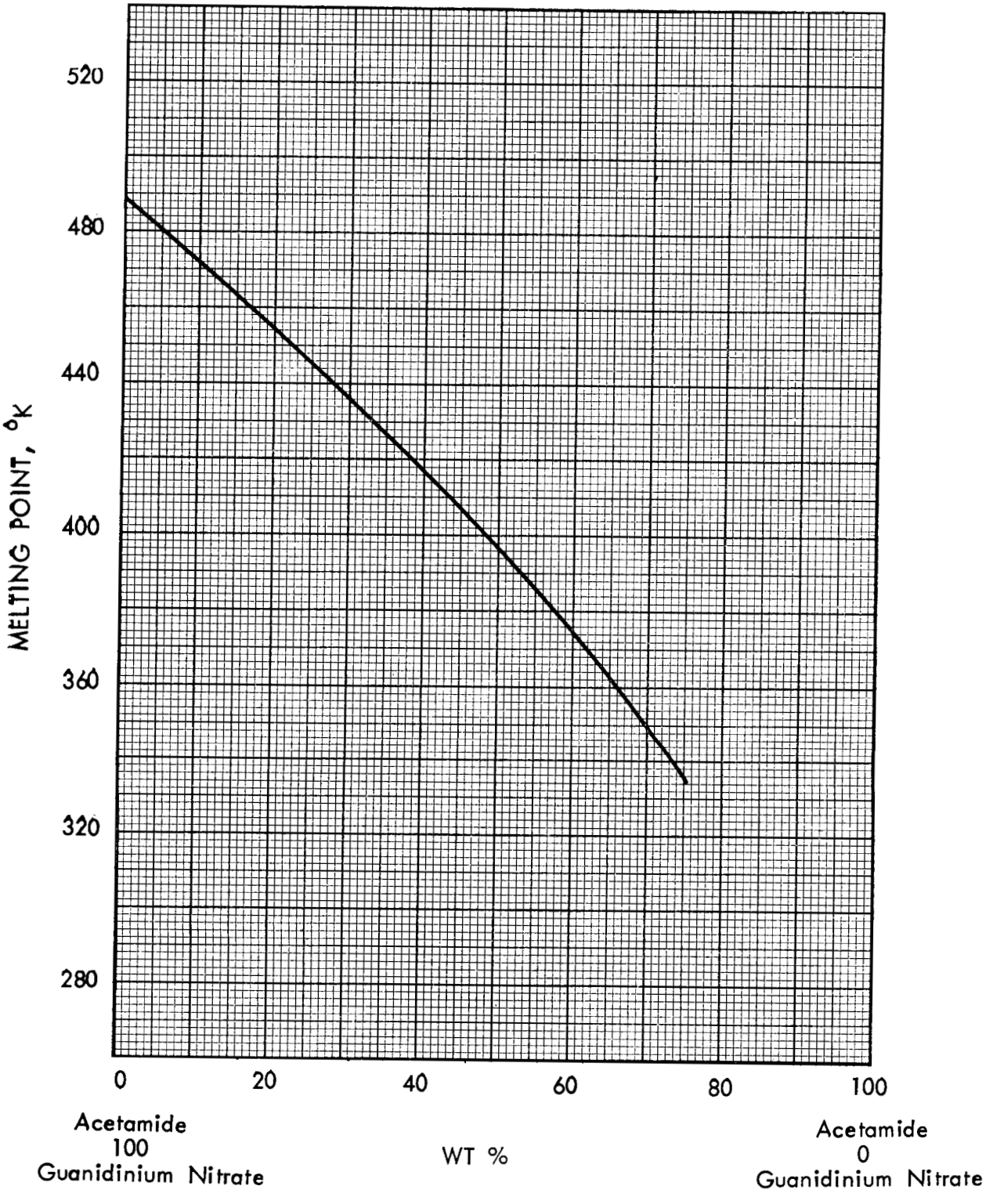
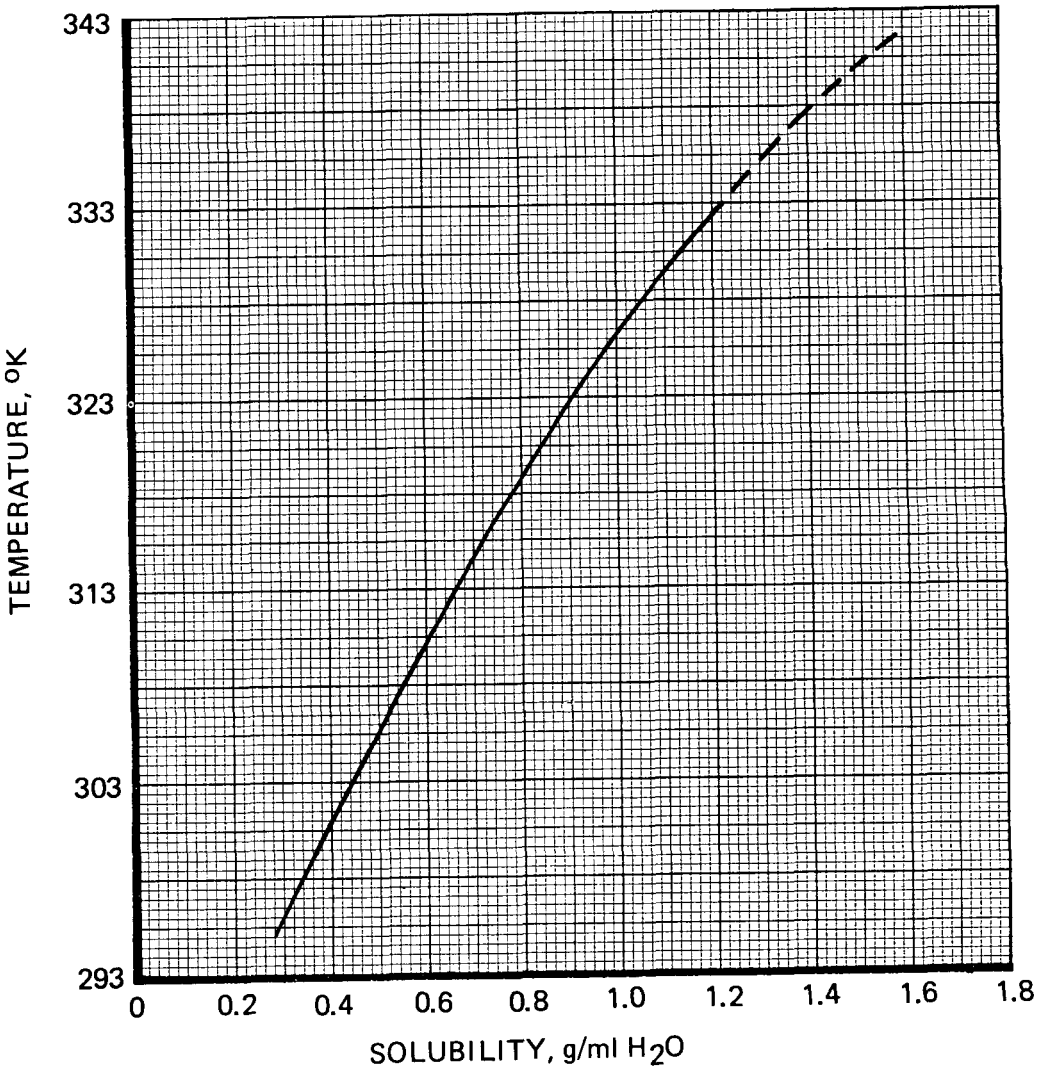


Figure 4-18

SOLUBILITY OF $(NaKCa)NO_3$ - $GuNO_3$ - $AcNH_2$ MIXTURE (58.7% - 28.9% - 12.4% BY WEIGHT) AT VARIOUS TEMPERATURES



4.4.3 Viscosity Determinations

It was mentioned earlier that the (NaKCa) nitrate melt passed through a glassy stage prior to solidifying. Its viscosity change tended to be very gradual within the temperature range from 570° to about 370°K. A more complete plot of data is shown in Figure 4-20.

Only a few data points were obtained for the viscosity of the $GuNO_3$-$AcNH_2$ mixture (Table 4-26). At 15 degrees below its melting point at 437°K, sufficient solids were present in the mixture to prevent accurate measurements with the Brookfield viscometer. At the temperatures where these data were obtained, evaporation of acetamide was already apparent. Evaporation became quite rapid beyond the temperature where the last measurement was taken.

4.4.4 Density Determinations

Results at some selected temperatures are already presented in Table 4-26 for comparison. Additional data are found in Figures 4-21, 4-22, and 4-23. In the fuel mixture and the candidate explosive mixture, bubbling became quite vigorous during upper temperature measurements. This was partly due to the presence of moisture in the mixture, and perhaps partly attributable to decomposition. Also, at these higher temperatures, the vapor pressure of acetamide became rather substantial as the sample temperature approached the boiling point of acetamide at 494°K.

The bulk density of unmelted material is needed for sizing the mixing unit tanks and determining the number of loading sequences until the tanks are filled to capacity with molten material. The bulk density of a physical mix of (NaKCa) nitrate was 1.01 g/cm^3, that of practical grade acetamide 0.7 g/cm^3 and that of guanidinium nitrate 0.81 g/cm^3. These numbers may fluctuate depending on the particle size of the material.

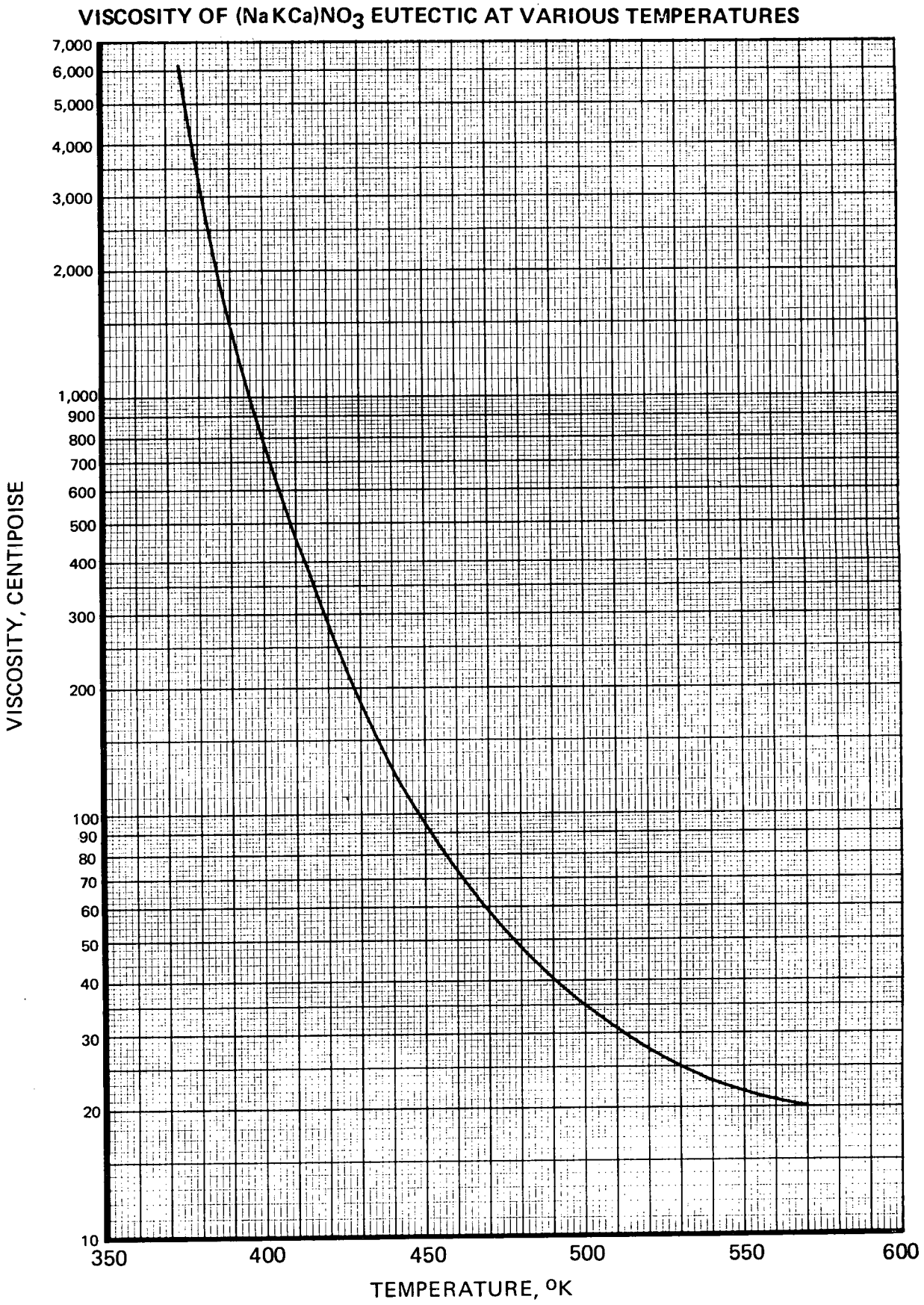
4.4.5 Electrical Conductivity Determinations

Plots of electrical conductivity versus temperature of the oxidizer, the fuel, and their mixture are shown in Figure 4-24. It is interesting to note that the fuel mixture has better conductivity than the completely ionic $(NaKCa)NO_3$ system. The curve for the fuel system reflects the physical transition which takes place near its melting point. A rapid reduction in conductivity below 437°K corresponds to the precipitating of guanidinium nitrate from the mixture.

It appears that electrical conductivity would be a useful method to monitor the mixture ratio of the mixed explosive after it leaves the downhole mixer. An electrical conductivity measurement probe would not occupy much space and could easily be incorporated in the design of the mixer.

4.5 SUPPORTING STUDIES

In the course of supporting studies, various problems or potential problems associated with the use of the high temperature explosive for stimulation of geothermal reservoirs have been studied. Some of the studies were conducted in support of the theoretical explosive component selection considerations; others were of an experimental nature, such as the selection of high-temperature detonators. An abbreviated form of a field test plan is included here. The more comprehensive field test program plan will be submitted to DOE as a separate document.


VISCOSITY OF (NaKCa)NO3 EUTECTIC AT VARIOUS TEMPERATURES
VISCOSITY, CENTIPOISE
7,000
6,000
5,000
4,000
3,000
2,000
1,000
900
800
700
600
500
400
300
200
100
90
80
70
60
50
40
30
20
10
350
400
450
500
550
600
TEMPERATURE, °K

DENSITY OF (NaKCa)NO_3 EUTECTIC AT VARIOUS TEMPERATURES

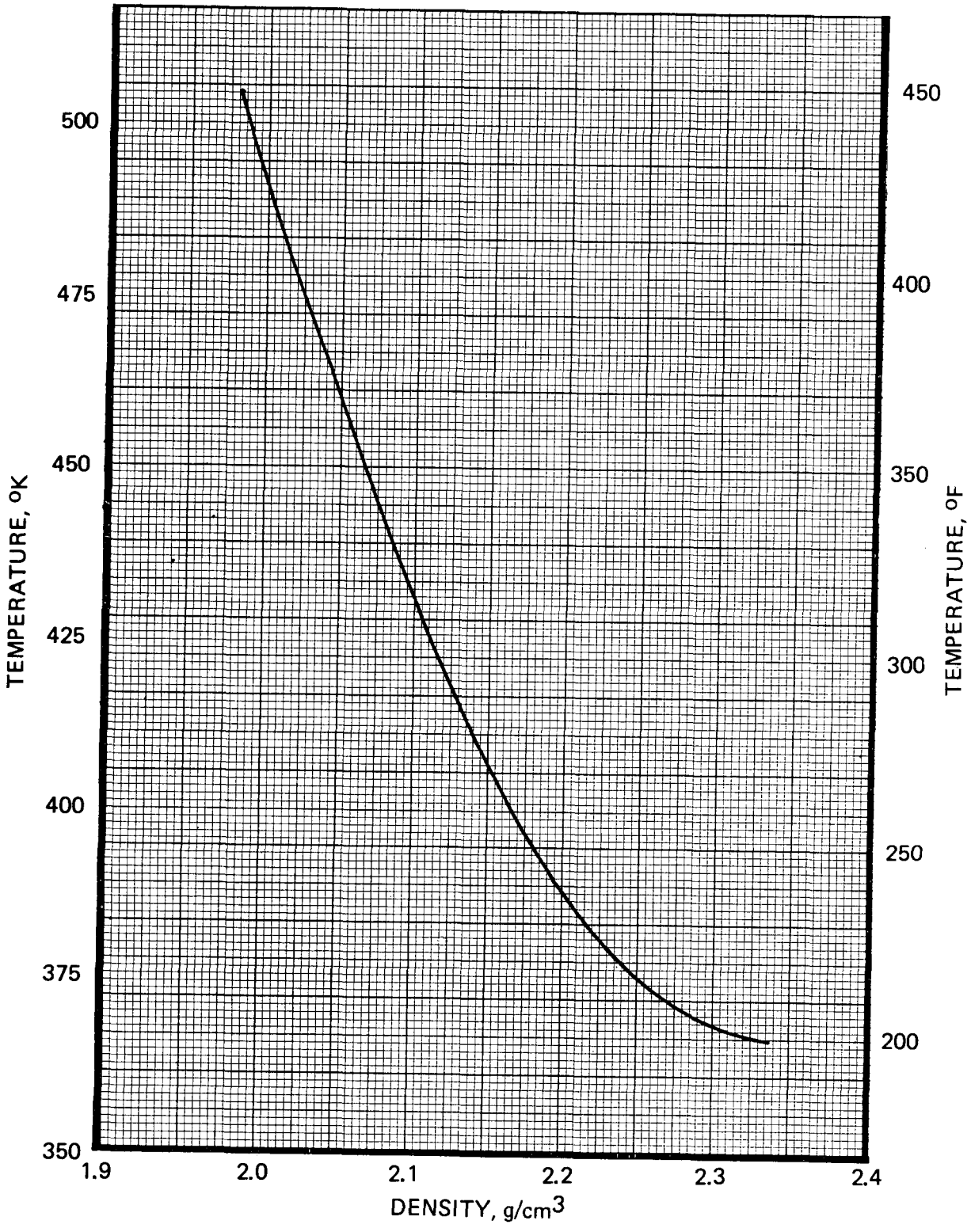


Figure 4-21

DENSITY OF $GuNO_3$ - $AcNH_2$ MIXTURE
(70% - 30% BY WEIGHT) AT VARIOUS TEMPERATURES

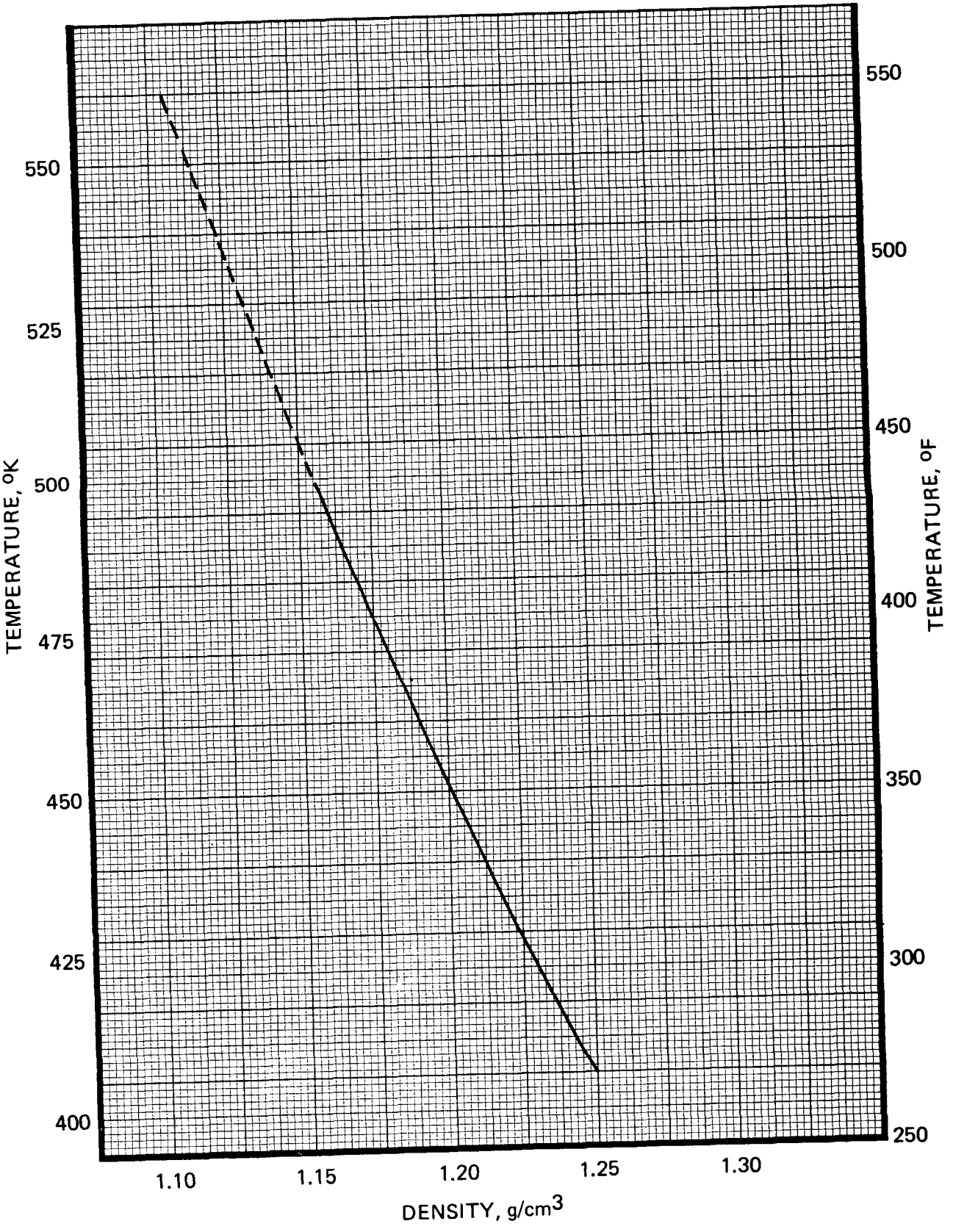


Figure 4-22

DENSITY OF $(NaKCa)NO_3$ - $GuNO_3$ - $AcNH_2$ MIXTURE (58.7% - 28.9% - 12.4% BY WEIGHT) AT VARIOUS TEMPERATURES

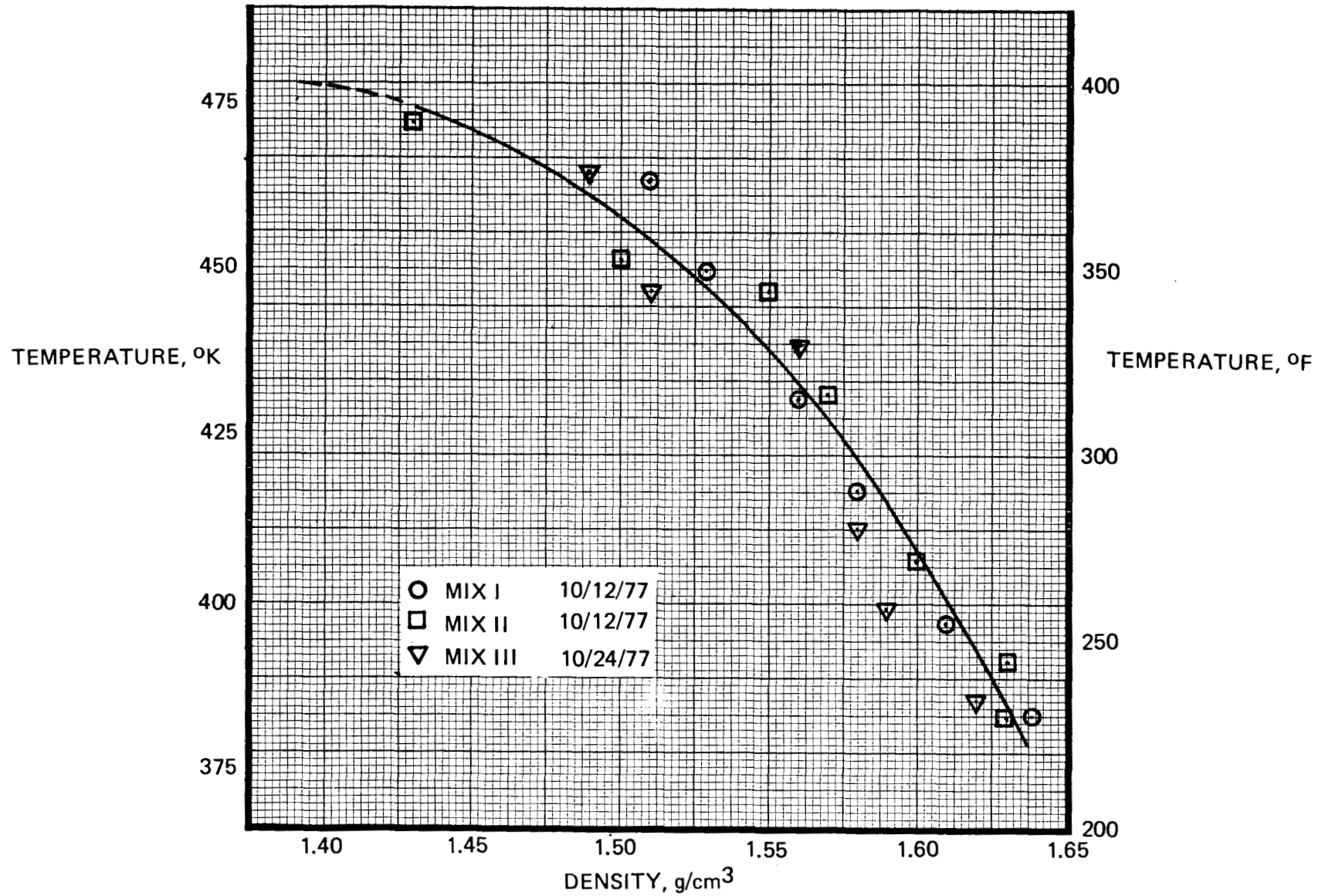


Figure 4-23

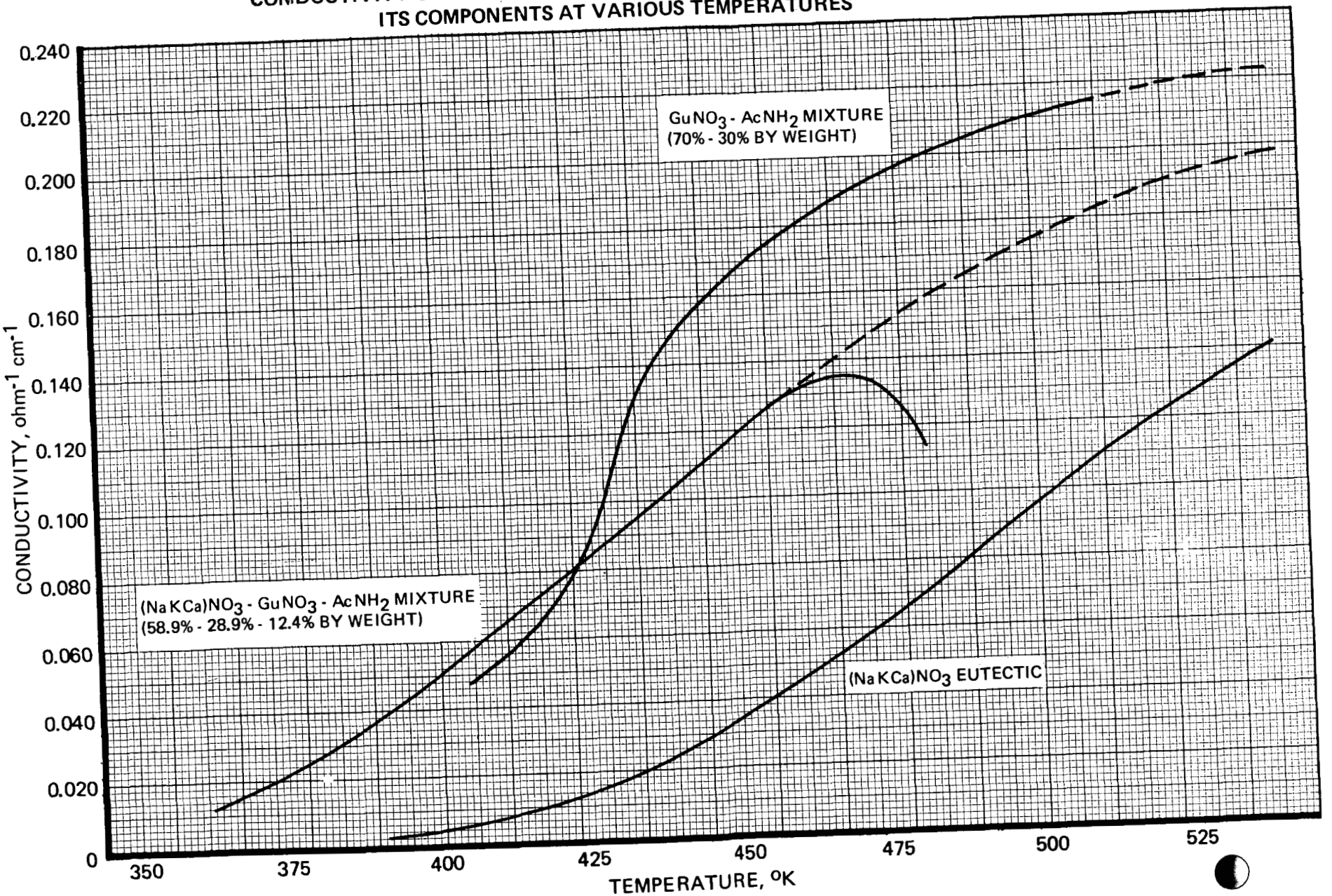

CONDUCTIVITY OF THE CANDIDATE HIGH TEMPERATURE EXPLOSIVE AND ITS COMPONENTS AT VARIOUS TEMPERATURES
CONDUCTIVITY, ohm-1 cm-1
0.240
0.220
0.200
0.180
0.160
0.140
0.120
0.100
0.080
0.060
0.040
0.020
0
350
375
400
425
450
475
500
525
TEMPERATURE, °K
GuNO3 - AcNH2 MIXTURE (70% - 30% BY WEIGHT)
(NaKCa)NO3 - GuNO3 - AcNH2 MIXTURE (58.9% - 28.9% - 12.4% BY WEIGHT)
(NaKCa)NO3 EUTECTIC

Figure 4-24

4.5.1 COMPUTER CALCULATIONS

Several computer codes have been described in the literature for the calculation of detonation velocities and detonation pressures from thermodynamic and physical properties data of the explosive and anticipated explosion products (References M8 and W5). Rocket Research Company has routinely used the TIGER code. While this program operates satisfactorily if the reaction products are all gaseous, problems may be encountered if the exhaust products contain condensed species. The data library of the copy of the 1968 program available at RRC did not contain all species which must be expected as explosion products of HITEX. Data which were needed to expand the program library were the heat of formation, the heat capacity as a function of temperature, the entropy of formation and the molar volume as a function of pressure and temperature (equation of state). These data were extremely hard to obtain within the amount of time allocated to the TIGER program support effort. While several new species have been added to the program library using the STARFIT subroutine, the list still is not complete enough to allow a representative calculation of the theoretical performance of HITEX.

Of the several cases attempted to run on the TIGER code, only two were executed at the first try. Cases involving alkali metal nitrate oxidizers were rejected because they took an excessive number of iterations and the energy of the system did not converge at a solution. The two cases which were executed without difficulty were Dithekite-00 (a mixture of 57.1 percent nitric acid and 42.9 percent nitrobenzene) and PTC-4 (a proprietary formulation included as test case because it had been calculated several times before). The C-J condition results for Dithekite-00 were a shock velocity of 6,974 m/s and a detonation pressure of 178 kbar. The corresponding numbers for PTC-4 were 7,753 m/s and 201 kbar.

During the proposal phase prior to award of the contract, a mixture of sodium nitrate, sodium nitrite and pentaerythritol had been calculated on the same program, giving a detonation velocity of 6,568 m/s and a pressure of 140 kbar. Even though the composition and temperature of this explosive differ from that of HITEX, the calculated detonation velocity is in the same range as that measured during experimental tests. The comparatively low pressure of only 140 kbar indicates that explosives with alkali metal nitrate oxidizers cannot be as powerful as explosives with nitric acid or ammonium salt oxidizers. This is explained by the low vapor pressure of the alkali metal oxides formed as combustion products.

It was the intention to use the TIGER program to optimize the oxidizer:fuel mixture ratio. While the absolute numbers for detonation velocity and pressure may vary from those determined experimentally, the location of the maximum of either parameter is expected to agree quite well between theory and practice. An attempt will be made to obtain a more complete copy of a program library as required. This effort will continue as a company-sponsored effort beyond the period of performance of the current contract. The improved TIGER code with an expanded library may become available in time to select an optimized oxidizer:fuel mixture ratio immediately prior to the field test demonstration program.

4.5.2 Raw Material Availability and Economic Considerations

The large-scale application of HITEX explosives will depend on economically justifiable cost and availability of the ingredients. It is a major advantage of the currently selected composition that the ingredients are in abundant supply and readily available at low cost.

All three oxidizer ingredients are currently produced in mega tonnage quantities. In 1977, potassium nitrate sold for $197.50/short ton fertilizer grade and $285/short ton technical grade. Sodium nitrate likewise sold for $100 to $150/short ton. Calcium nitrate sold for $140/short ton. The oxidizer constitutes 58.7 percent by weight of the explosive and its cost dominates the cost of the ultimate explosive. The mixed oxidizer should be available at a cost of approximately $0.10/lb which includes an allowance for manufacturing and blending.

The 1967 U.S. consumption of sodium nitrate was 281 Gg (310,000 short tons); practically all of that amount came from Chile. Only a small amount of sodium nitrate is made synthetically. In 1964, the U.S. consumed 48 Gg (53,000 short tons) sodium nitrate for explosives and pyrotechnics alone. Sodium nitrate is the main oxidizer in the production of magnesium flares for battlefield illumination. The use of sodium nitrate as fertilizer is declining worldwide because ammonia and ammonium nitrate have become more economical sources of fertilizer nitrogen. This situation should free significant amounts of sodium nitrate for use as oxidizer in explosives.

Guanidinium nitrate is an important chemical intermediate in the production of melamine plastics. Melamine plastics are well-known because they are high-temperature resistant and nontoxic. For this reason, they are the main polymer used for dishwasher-resistant plastic dinnerware. This market sector alone consumes 16 Gg (35 million lbs) melamine resin every year. The resin sells for $0.6/lb which is probably not different from the large-scale price of guanidinium nitrate which goes into production of the melamine. In 1977, 45 kg (100 lbs) quantities of guanidinium nitrate were quoted as $1.75/kg ($1.25/lb) and $1.32/kg ($0.60/lb) in tonnage quantities. The 1973 world melamine capacity and production was listed as 360,000 metric tons per year and 242,000 tons per year, respectively. The U.S. annual capacity and production that year was 70 and 40 metric tons, respectively. In view of excess capacity, extra use of guanidinium nitrate is not expected to have a major impact on the market and availability of this chemical. The U.S. Army is also looking at improved methods for the production of guanidinium nitrate as an intermediate for the production of smokeless gun propellants (Reference L6).

Little information could be found on industrial uses and production data of acetamide. Acetamide is currently sold at $2.75/kg ($1.25/lb) in small quantities below 100 pounds. It is assumed that this price will drop to near the price of acetic anhydride ($0.23/lb) and ammonia ($120/short ton) from which it can be prepared in a single-step reaction. All indications are that HITEX can be prepared and emplaced at approximately $0.30/lb. Thus, the explosive cost for a typical full-scale stimulation test using 9,000 kg (20,000 lbs) of explosive would be of the order of $6,000. This is but a small fraction of what it may have cost to drill a dry hole, and there may be sufficient economic incentive to attempt to recover this investment by stimulating the well using chemical explosives.

A recent survey of stimulation methods for geothermal wells has concluded that explosive fracturing appears particularly promising in the highly permeable graywacke formations at The Geysers, California (Reference O2). It appears that sometimes producing sections were missed by only 15 meters (50 feet) because if nonproducing wells were sidetracked and redrilled at a slant, a producing formation was intersected in close proximity to the nonproducing well. It may be more economical to establish horizontal communications by the use of explosives. Even if only one out of ten wells drilled was a marginal or below nominal producing well, there would be ample activity for an explosive stimulation rig. Similar considerations apply to hot dry rock and hydrothermal reservoirs. A more detailed economic evaluation will be required before private enterprise will take over the stimulation process once the technology has been demonstrated under government-sponsored contracts. A long-range prediction should be made of the potential effect of explosive stimulation technology on the contribution by geothermal energy to the overall United States energy consumption.

4.5.3 Critical Mass Relationship

A detonation will occur whenever the heat generated in an explosive undergoing isolated auto-decomposition cannot be dissipated outside the material and hence continues to raise the internal temperature. The geometry and size of an explosive where run-away exothermic reactions can occur at a specific temperature is known as the critical mass. If the temperature is below the critical temperature while decomposition may take place, no thermal autodetonation will occur.

The critical temperature is a function of kinetic constants, geometrical factors and heat transfer considerations. It can be analytically calculated from kinetic and physical property data. The equation relates the critical temperature to the radius of spheres or cylinders or the half-thickness of a slab.

$$\frac{E}{T_M} = 4.58 \log \left\{ \frac{a^2 \rho Q Z E}{T_M^2 \delta \lambda R} \right\}$$

where:

- E = activation energy (cal/mole)
- Z = Arrhenius pre-exponential factor (sec^{-1})
- Q = heat of reaction (cal/g)
- ρ = density (g/ml)
- a = radius or half-thickness (cm)
- R = gas constant, 1.9872 (cal/mole ^oC)
- λ = thermal conductivity (cal/cm sec ^oC)
- δ = geometrical factor, 3.32 (sphere); 2.00 (cyl); 0.88 (slab)
- T_M = critical temperature for self-heating to thermal explosion (^oK).

The results of this equation have been experimentally verified in "cook-off" tests of various military explosives that melt and enter a total liquid phase before they reach their critical temperature. Accuracy has been found to be on the order of 2% of the temperature at a given configuration.

Results – Kinetic constants are required for the solution of the equation. The kinetic data for HITEX were determined with the aid of a Perkin-Elmer Differential Scanning Calorimeter (Reference R6). Many programmed temperature runs were made to obtain preliminary kinetic data and provide information as to where isothermal runs should be made. Figure 4-25 is a plot of the logarithmn of the reaction rate constant, k, versus the reciprocal of the absolute temperature, 1/T. The straight line is from a least squares calculation for best fit of the data.

The Arrhenius equation is:

$$k = Ze^{-E/RT}$$

where:

k	=	reaction rate constant (sec^{-1})
Z	=	frequency factor (sec^{-1})
E	=	activation energy (cal/mol)
R	=	gas constant (cal/mol ^{o}K)
T	=	absolute temperature (^{o}K)

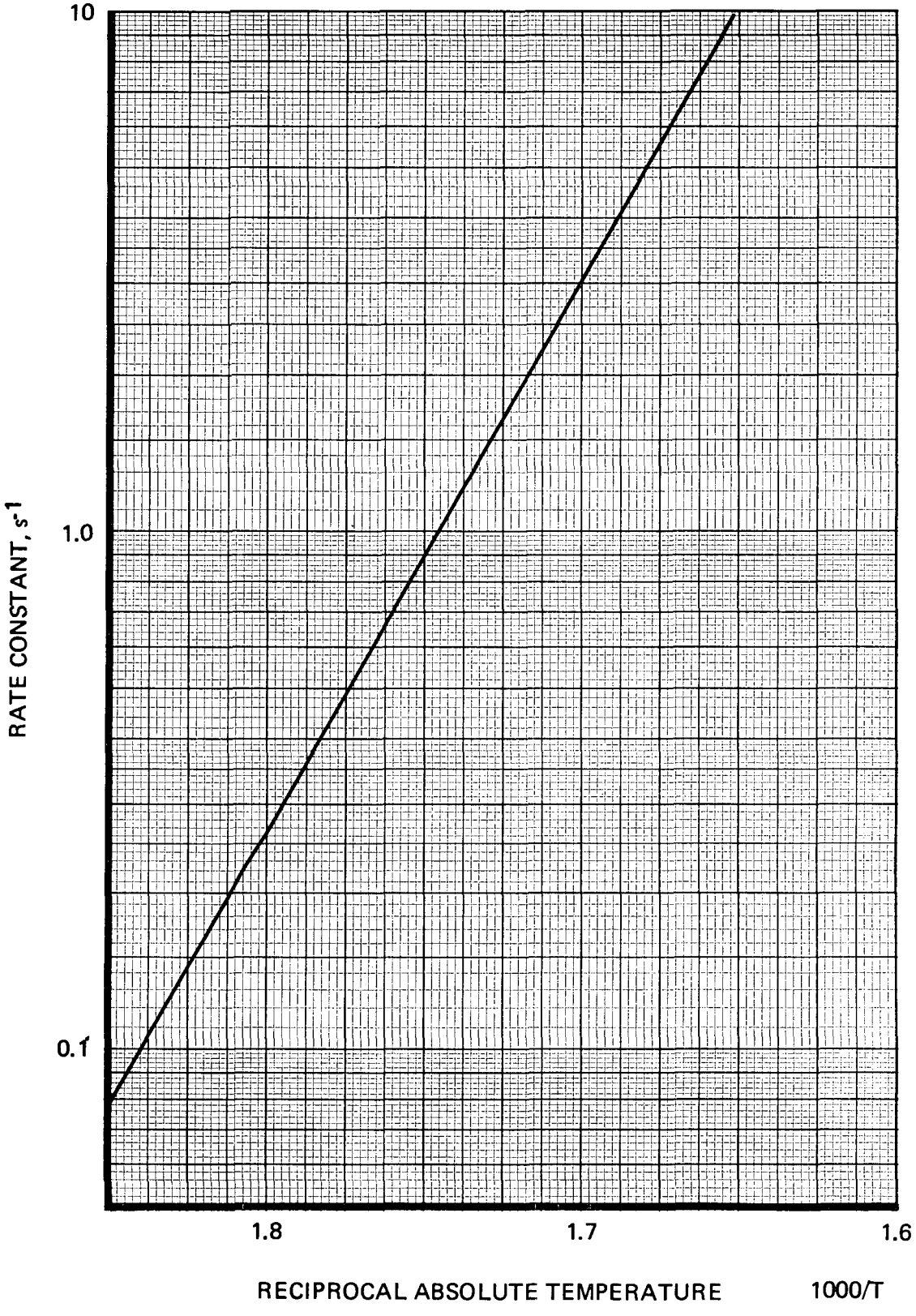
E and Z were determined from the straight line in Figure 4-25. The slope is $-E/R$ and the intercept is Z, or two values of ln k and 1/T may be taken from the graph and E and Z determined algebraically thus:

$$\ln k = \ln Z - E/RT$$

These kinetic constants and physical property constants (ρ = 1.4 g/ml; Q = 400 cal/g and λ = 0.00136 cal/cm sec ^{o}C) were used to calculate the critical mass-temperature relationship. The results of this iterative calculation are shown in Figure 4-26 for the cylinder and slab geometries.

In actual use, the explosive will be in the "cylinder" borehole and in the "slab" fractures in the rock formation. From the curves in Figure 4-26, one can obtain the theoretical maximum temperature that can be safely tolerated at the bottom of the well. For example, consider a 20-cm (8-inch) diameter hole with a 12-mm (1/2-inch) wide hydraulic fracture in the formation. From Figure 4-26 it appears that the maximum recommended operating temperature would be on the order of 440^{o}K (330^{o}F) for the borehole and 500^{o}K (440^{o}F) for the fracture system. Hence, the borehole temperature is critical. However, this calculated temperature is much lower than temperatures which were already proven to be safe in pipes with diameters up to 7.6 cm (3 inch). The physical properties may have to be determined more accurately to represent experimental conditions more closely. These curves are idealized in the sense that they represent the behavior of the

TEMPERATURE DEPENDENCE OF DECOMPOSITION RATE OF HITEX



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CRITICAL MASS RELATIONSHIP FOR (NaKCa)NO_3/$GuNO_3$/$AcNH_2$ HITEX EXPLOSIVE

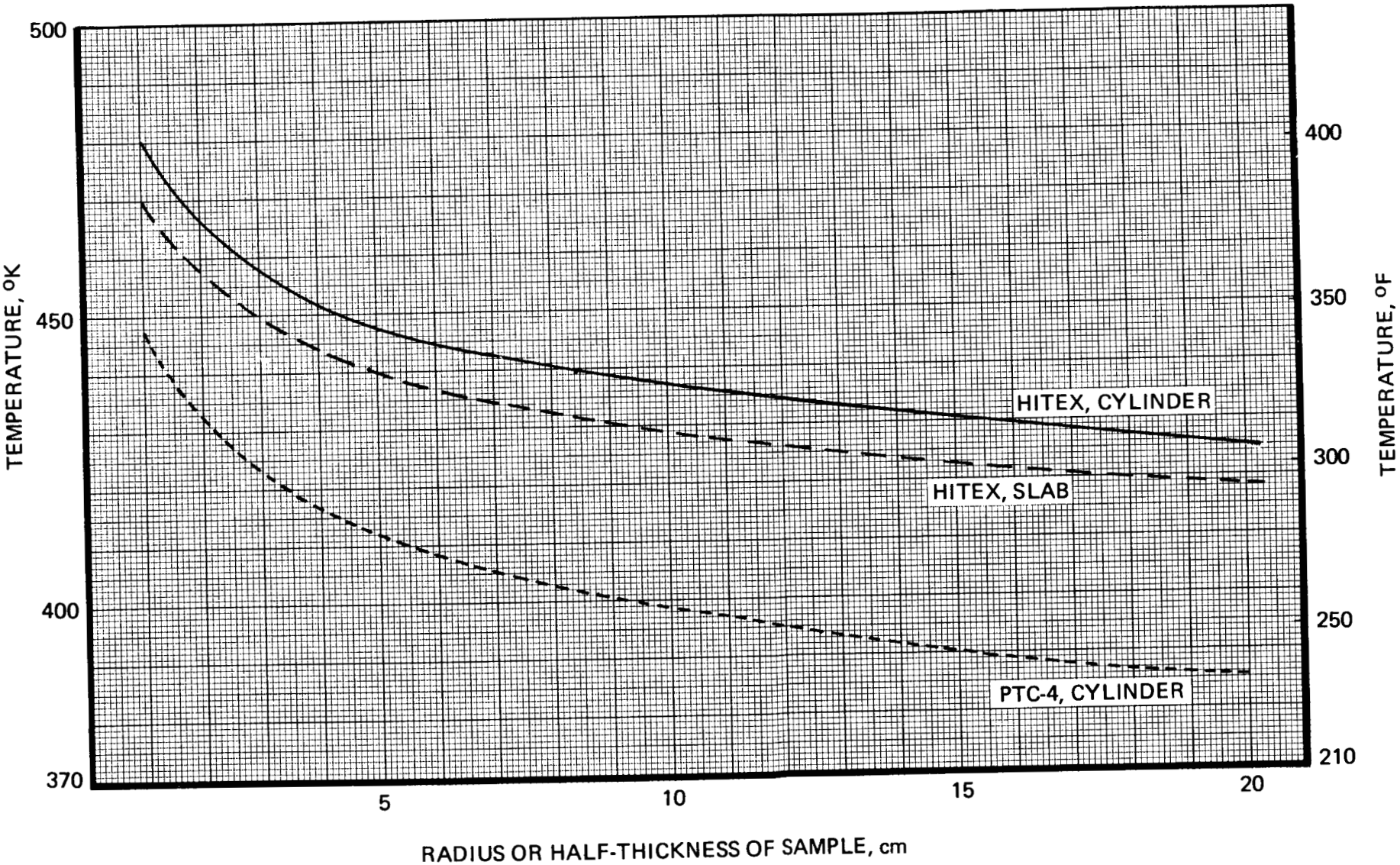


Figure 4-26

uncontaminated explosive. The critical temperature data can be refined for selected contaminated systems such as the marginal cases found in the compatibility study. Limited test data indicates the curves will not require great downward adjustment. Preliminary tests have been run with HITEX confined in large diameter, mild steel pipes and heated to destruction. The limited data gathered suggests that the effect of the contaminant on the critical temperature of the material was minimal.

As shown in Figure 4-26, HITEX is more stable than the currently used PTC-4.

4.5.4 Detonator Evaluation

A market survey was conducted for high-temperature high-pressure detonators and boosters. None of the commercially available detonators listed in Table 4-27 is rated for 24-hour operation at 561°K (550°F). The best commercially available detonators for operation at 533°K (500°F) appear to be the Du Pont X-637 or X-321-K, which are recommended by the manufacturer for up to 1 hour at 533°K (100% fire). One shipment of X-321-K detonators was ordered and used during this contract. However, these do not appear to be an off-the-shelf item because it took several months to have them built and delivered. There is no detonator on the market which combines the pressure resistance of the E-96 cap with the temperature resistance of the X-637 or X-321-K detonators.

Table 4-27
MANUFACTURER'S RATINGS OF HIGH PRESSURE/HIGH TEMPERATURE ELECTRIC DETONATORS

Manufacturer	Designation	Max Temp		Max Pressure		Base Charge Explosive	Quantity	
		°K	°F	bar	psia		grains	grams
Du Pont	E-96	436	325	1,034	15,000	RDX	4.1	0.26
Du Pont	X-321-K	533	500	Unknown		TACOT	8	0.52
Du Pont	X-637	533	500	Unknown		TACOT	4	0.26

A number of commercially available detonators were tested for autoignition temperature ("volunteering," "cook-off") and operation after soaking at a temperature below the cook-off temperature (100% fire point). The results are shown in Table 4-28. The E-97, a high-pressure medium-temperature detonator was used for most of the tests. In four repetitive tests, it volunteered at temperatures between 460 and 466°K. In subsequent tests, the detonator was heated to five to twenty-five degrees below this temperature and then fired on command. Both tests were positive. These tests would have to be repeated with a larger number of samples to determine a reliable 100% fire point. However, it was quite obvious that the E-97 and related E-series detonators would not satisfy the extended heating geothermal environment requirements. By comparison, the

Table 4-28

DETONATOR COOK-OFF TEST RESULTS

Detonator	Manufacturer	Explosive Charge, g	Heating Rate °K/min	Temperature at Autoignition		Temperature		Time at Temperature, Minutes	Fired On Command
				°K	°F	°K	°F		
E-97	DuPont	0.356 RDX	5.6	460	368	---	---	---	---
E-97	DuPont		3.4	464	376	---	---	---	---
E-97	DuPont		3.6	466	379	---	---	---	---
E-97	DuPont		2.7	461	371	---	---	---	---
E-97	DuPont		1.1	---	---	435	324	30	Yes
E-97	DuPont		2.3	---	---	454	358	30	Yes
Number 8	Hercules		3.7	420	297	---	---	---	---
MS-250-9	DuPont		3.7	435	324	---	---	---	---
Lead azide squib	Atlas	$Pb(N_3)_2$	3.6	587	597 (605)	---	---	---	---
X-321-K	DuPont	0.52 TACOT	4.7	585	593	---	---	---	---

X-321-K detonator volunteered at 585°K, slightly above the 561°K temperature requirement of this contract. It functioned reliably and repeatedly in detonability tests, where it was heated to 533°K and fired on command very soon after reaching the test temperature.

The weak link in the X-321-K detonator appears to be the ignition bead of lead azide which is located between the bridgewire and the base charge. In a separate test, lead azide squibs volunteered at exactly the same temperature as the X-321-K detonator.

Under contract N00174-74-C-0171, RRC has developed a two-component detonator for ambient temperature operation (Reference R7). It has been considered to apply the same principle to the development of a high-temperature two-component detonator for geothermal applications. These devices would be safe to handle above ground, and would only be activated by the thermal environment or by a remote electrical signal preceding the electric detonator firing command.

Exploding bridgewire (EBW) detonators do not contain any heat sensitive primary explosive. All of the explosive in an EBW detonator is a secondary explosive which requires a shock wave for detonation. The secondary explosive may be of the thermally stable type such as HNS, TACOT, or TATB. To function an EBW detonator, a large amount of electrical energy must be supplied to the bridgewire at the proper rate to cause it to explode and transfer a shock wave into the secondary explosive. Just heating of the bridgewire will not cause the secondary explosive to detonate. The EBW requires a powerful capacitor discharge unit in close proximity (less than 100 feet) to the detonator. While EBW detonators can be built to withstand the geothermal environment, capacitors and firing circuits that withstand the high temperature are not now available and would require substantial development. The capacitor discharge unit could not be located at the surface due to the high impedance caused by the discharge cable.

Another approach is to use an electric explosive initiation system which will directly detonate a high density secondary explosive (Reference M7). This detonation concept (HDSEI) operates by an exploding foil, which accelerates a dielectric material into the explosive, which results in a detonation ("flyer plate," "slapper"). However, this type of detonator also requires a capacitor discharge unit or another powerful power supply in close proximity to the charge. The voltage losses upon wiring the device from the surface would be excessive, if all energy required for initiation was provided from the surface at the moment of initiation. Instead, a downhole high voltage generator and a capacitor bank can be charged from the surface with low voltage DC at low current until the unit is ready to be fired. The electronics can be packaged in a thermally insulated pressure resistant container. The electronics package, the initiator, and the booster can be designed to survive several hours after being lowered into the well.

Ordinary EBW detonators utilize a powdered secondary explosive which must be packed against the bridgewire at a specific and relatively low density. The bridgewire must be in contact with the explosive. In contradistinction, the high density secondary explosive initiation (HDSEI) system may prove of use for the geothermal applications. The HDSEI has several advantages over the standard EBW detonator. The metal bridge is completely separated from the explosive by an insulating film

and an air gap, the explosive can be packed to a high density, and the insensitive explosives, such as HNS, can be detonated. However, both the standard EBW and the HDSEI depend on a capacitor discharge unit as power supply. In the HDSEI, the wire of the EBW is replaced by a necked metal foil section etched on the back of a Mylar film. The exploding foil accelerates the plastic flyer plate down a cylindrical standoff until it impacts the explosive pellet. This impact energy translates a shock wave into the explosive causing it to detonate. Both EBW and HDSEI systems have the advantage of a short response time, and their reproducibility is better than that of conventional detonators. This may be of importance for applications where multiple initiation points have to be synchronized.

The success of the field demonstration program depends on the development of ancillary systems required for remotely detonating the emplaced explosive on command. Initiation techniques for downhole explosives can be subdivided in wireline and remotely activated systems on the one hand, and preprogrammed, on-site command-type systems on the other hand. The use of wireline systems is very undesirable because it is very difficult to run a length of wire and electric cable from the surface, through the well head, past the mixer, and down into the hole. Even if weighted down with a weight, the line has a tendency to hang up on minor protrusions or restrictions in the pipe or in the open part of the well. A jammed line is hard to retrieve, and a snapped cable dropped into a well causes a hopeless tangle which is extremely difficult to remove. Remotely activated systems are the preferred initiation method. Time bomb-type devices can be lowered into the well days or hours prior to explosive loading, utilizing wireline with a disconnect mechanism. As an alternate, the time bomb can be strapped to the string of tubing which feeds the explosive from the mixer to the bottom of the hole. This method is frequently used as a back-up system to the command-type initiation systems.

Previous explosive well stimulation efforts have used a variety of methods to detonate the explosive on command. Traditionally, mechanical time bombs have been used, which contain an alarm clock and an electric firing circuit. As soon as the hand of the clock closes the electric circuit, current from a battery fires an electric squib detonator which sets off the booster and/or the main charge. The mechanical part of this device could probably be made to work at elevated temperatures. However, no conventional batteries are available on the open market which will withstand the geothermal temperature regime. Generation of electricity by induction with another spring-driven device is also generally considered very unreliable.

Previous tests under ERDA contract E(34-1)-0001 have evaluated a command firing device developed by Motorola, which was integrated with a wiper plug. However, the device failed to detonate the explosive in three tests, and Motorola has since discontinued their development effort.

In the current field tests under ERDA contracts EY-76-C-08-0685, EY-76-C-08-0686, and EY-76-C-08-0687, Petroleum Technology Corporation is using an RRC-developed remote initiation system which is triggered by a magnet pumped downhole. The magnet travels through the same tubing as the mixed explosive, and can be attached to or integrated with the top wiper plug. In this mode, the magnet follows the slug of explosive as it is being displaced down the well by a layer of water. As soon as the wiper plug with the magnet is seated in the appropriate seat, the magnetic

field of the permanent magnet activates a Reed switch similar to those used in the electric burglar alarms on windows. The closing of the Reed switch activates the firing circuit.

At the present time, two downhole initiators are in work at PTC. The first is remotely controllable from the surface, while the second is a "time bomb". Both are powered with Mallory LO-32 Lithium Organic batteries. Both consist of a clock oscillator, a digital time delay circuit, and a capacitor discharge circuit to fire the initiators. The major difference is that the remotely controlled unit is started by sensing a magnet pumped into place from the surface, whereas the "time bomb" is started manually before being placed into the borehole.

However, none of the foregoing technology is directly applicable at 561°K (550°F) because no semiconductor will operate at a temperature near 523°K, let alone at 561°K. Military rated parts (highest temperature rating available) are specified to be derated to zero power at 523°K. That is, the junction temperature must be maintained at or below 523°K. In fact, very few devices even specify a short term (<10 seconds) lead temperature during soldering as high as 523°K. In addition, there is no conventional battery available that will function for any period of time at temperatures exceeding 423°K, although thermal batteries may be feasible.

This pumpdown detonator system depends on a secondary inert fluid which is used to displace the mixed explosive in the tubing between the mixer and the top of the zone to be stimulated. In the case of HITEX application in geothermal wells, the fluid which follows the explosive must be able to withstand the same temperature as the explosive, and must be hot enough to prevent the mixed explosive from solidifying at the boundary.

Other methods of initiation which have been considered depend on a coded ultrasonic or microwave signal sent from the surface. Only a signal with a certain frequency and amplitude sequence would be able to trigger the firing circuit. Such an initiator would allow completely free choice of the firing time from a control console at the surface and it would be independent of wire connections from the surface. Unfortunately, such a design has not yet been proven for oil- or gas-well stimulation, and no such device is known to exist.

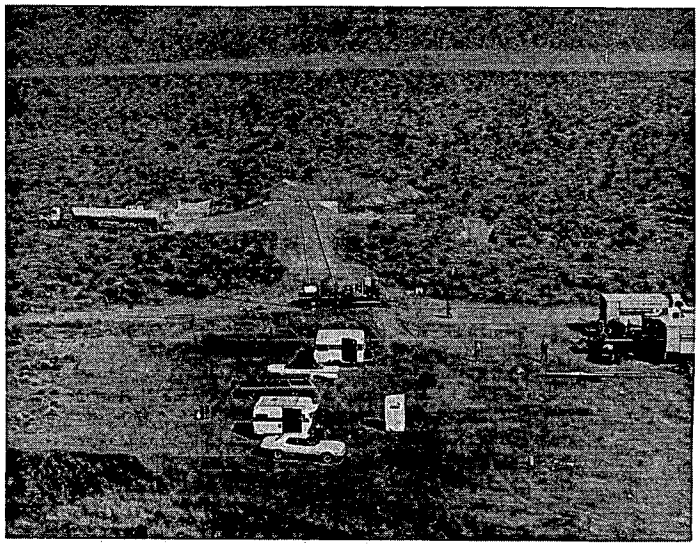
4.5.5 Field Test Program Plan

The next logical step after the so successful development of a high-temperature resistant two-component explosive would be to conduct a field demonstration test with a medium-size explosive charge in a geothermal well. The objective of the first test would be to demonstrate new technology and not necessarily to stimulate the well which happens to become available for the test. Most likely, a well which will be made available for a field demonstration test which may completely damage the well will be a nonproducing or marginally producing well with little potential of improvement. Of course, should an early field demonstration test open up new fissures and establish connection with a producing formation, such a by-product result would greatly support the concept of explosive stimulation of geothermal wells.

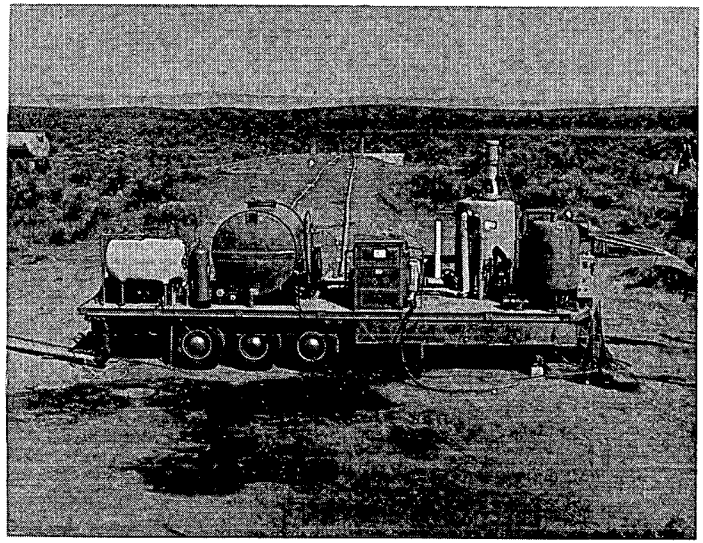
The program plan for a mobile explosive mixing rig and a field demonstration test would follow the same route as that established by Petroleum Technology Corporation, another ROCKCOR subsidiary, in the development and field testing of the Astro-Flow II process for stimulation of oil and gas wells. The next step would be to construct a flatbed truck trailer-mounted mixing unit capable of remotely mixing 1 ton of explosive. The unit would be checked out with an above-ground test similar to the one conducted by PTC at the AEC Hanford test site (Figure 4-27). Following the above-ground mixing test, the unit could be moved to a geothermal field and one ton of explosive would be loaded into a geothermal well and detonated. The unit would also provide valuable material and component compatibility data which are needed for the design of a full-scale mixing rig. The full-scale mixing rig capable of mixing 20 tons of explosive in a single batch would consist of separate vehicles for fuel and oxidizer melting and pumping and a data control unit. The on-site orientation of equipment is shown in Figure 4-28. In Figure 4-29, the PTC mixing rig truck fleet is leaving the RRC York Center facility for gas well stimulation work in West Virginia and Kentucky. Presumably, a similar fleet of trucks will handle geothermal stimulation jobs in the near future.

It is estimated that the flatbed trailer-mounted mixing unit will require approximately 1 year to build. Following checkout and the above-ground test, the first geothermal well test could be conducted within 20 months after receipt of the follow-on contract.

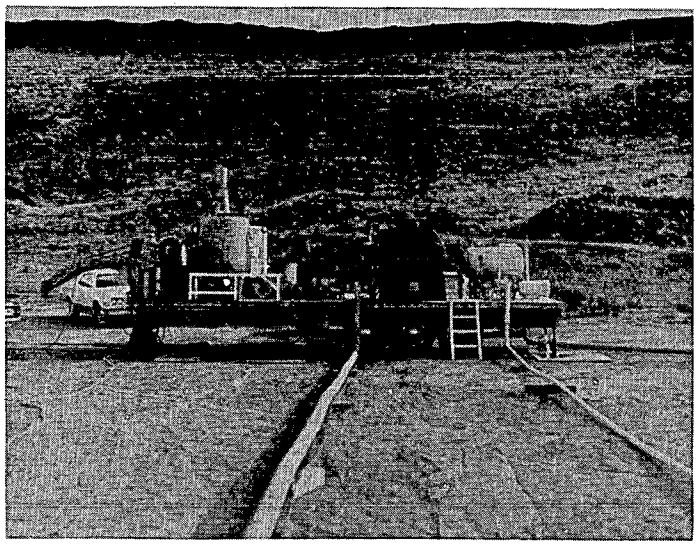
PETROLEUM TECHNOLOGY CORPORATION TEST AREA AND EQUIPMENT



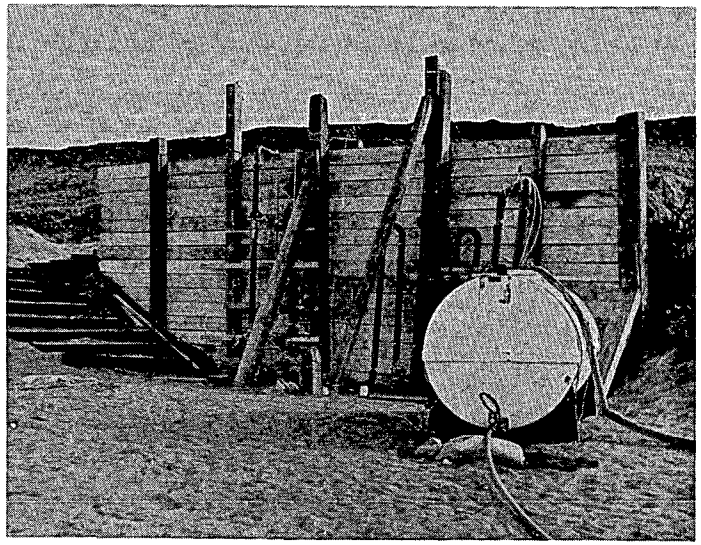
GENERAL LAYOUT



TRAILER-MOUNTED LOW PRESSURE RIG



RIG AND DELIVERY LINES FOR TWO COMPONENTS



EXPLOSIVE MIXING TEST SETUP AND CATCH TANK

LOCATION: ATOMIC ENERGY COMMISSION HANFORD RESERVATION WASHINGTON STATE

Figure 4-27

ON-SITE ORIENTATION OF EQUIPMENT

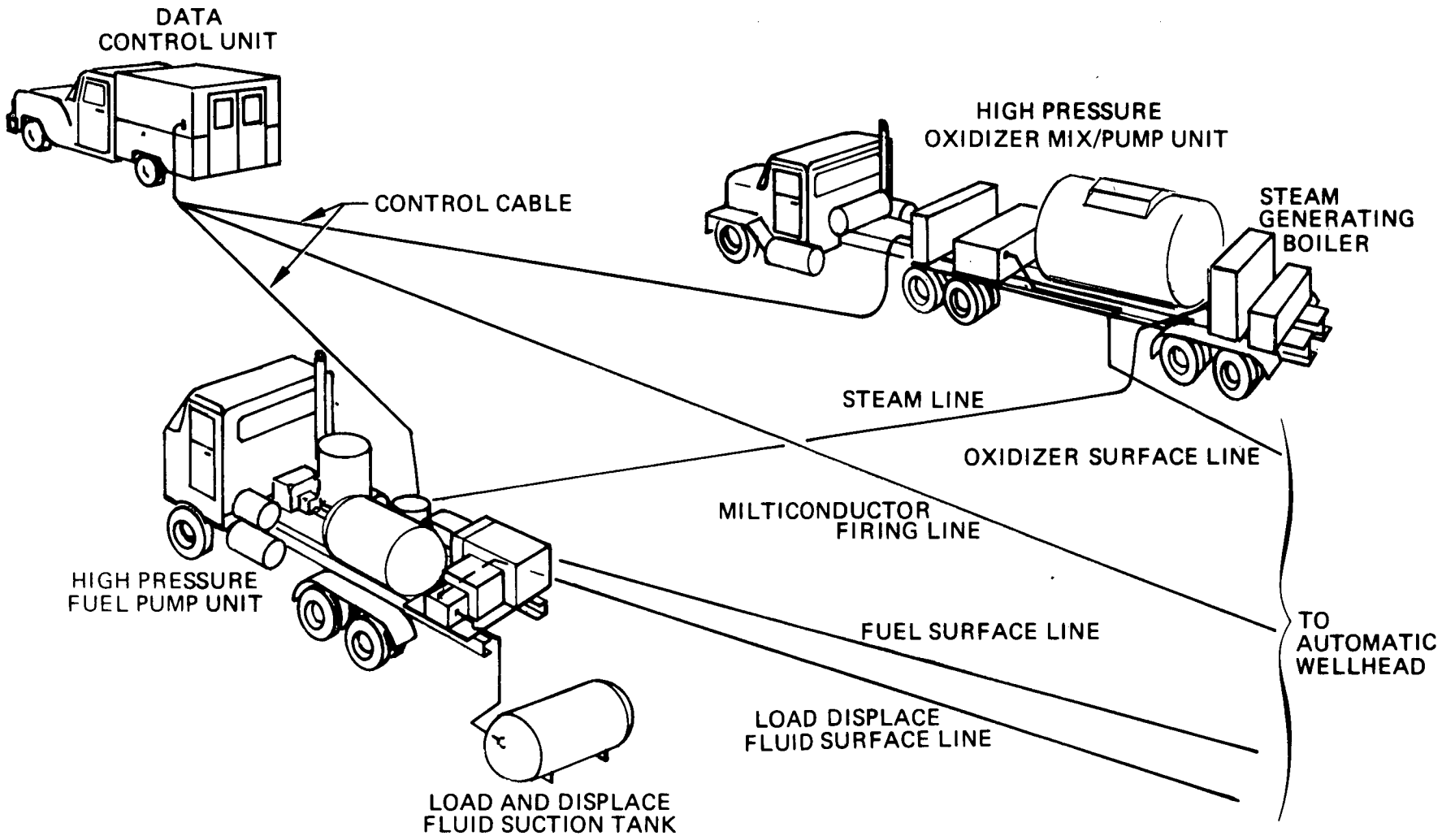


Figure 4-28

ASTRO FLOW II CHEMICAL EXPLOSIVE FRACTURING EQUIPMENT

40000-83 1743-9

4-87

Figure 4-29

5.0 SUMMARY AND CONCLUSIONS

A high-temperature resistant two-component explosive called HITEX has been developed and successfully tested in quantities up to 5 kg at temperatures up to 561°K (550°F). The prime candidate selected has the composition (% by weight) 6.57 sodium nitrate, 26.00 potassium nitrate, 26.12 calcium nitrate, 28.92 guanidinium nitrate and 12.39 acetamide. It can be successfully detonated after 24-hour exposure to 533°K (500°F). It detonates with a detonation velocity of 6,100 m/s and propagates at high order into gaps as narrow as 20 mm. The explosive ingredients are nondetonable and can be safely handled above ground. They are available at low cost. The ingredients and the explosive itself are environmentally compatible and excess explosive is easily desensitized and disposed of by dissolving it in water.

While the development of an explosive capable of operating at 561°K without premature detonation constitutes a major step forward in explosive technology, it is well recognized that some geothermal reservoirs have downhole temperatures in excess of 561°K. It would be desirable to come up with an explosive which can serve all geothermal reservoirs equally well. However, this goal was thought to be too ambitious at the beginning of the current program. The minimum temperature which a geothermal explosive has to withstand to be useful was assumed to be 477°K (400°F). The current work has far exceeded this goal and brought us closer to the reservoirs in excess of 561°K. Among the explosive combinations which were rejected during the current contract because of handling difficulties (excessively high melting point), there may be some promising formulations which deserve further study if reservoirs hotter than 561°K have to be stimulated. Additional work in this direction seems indicated.

With regard to the prime HITEX formulation, a few remaining questions have to be answered before a field demonstration can be initiated. These concern compatibility of the explosive and its ingredients with materials of construction, more accurate physical properties, environmental impact, residue analysis, detonation velocity and critical diameter (wedge gap width) at high pressure, steam/brine dilution effects and detonator development. It is estimated that these long-lead items tasks will require approximately 6 months before construction of the mixing rig can be started.

In conclusion, it is recommended that the development be continued and that a field demonstration test be conducted to demonstrate the ability of the explosive and the equipment to operate in a geothermal environment.

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A

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