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Characterization of Amatex-20K

by
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and
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Propulsion Development Department

MAY 1976

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Naval Weapons Center
CHINA LAKE, CALIFORNIA 93555

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FOREWORD

This study of the thermal properties of the experimental explosive Amatex-20K was undertaken to assist the U.S. Army, Picatinny Arsenal, Dover, New Jersey, in the development of an emergency fill explosive for general purpose bombs and shells. The work was performed by the Thermal Research Branch (Code 4546), NWC.

The study was conducted during FY75 on Military Interdepartmental Purchase Request number 5311-1010 under Picatinny Arsenal Customer Order number M156Z579GGFR.

This report was reviewed for technical accuracy by Barbara Stott.

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(U) *Characterization of Amatex-20K*, by Carl M. Anderson and Jack M. Pakulak, Jr. China Lake, Calif., Naval Weapons Center, May 1976, 30 pp. (NWC TP 5767, publication UNCLASSIFIED.)

(U) Amatex 20-K is a modification of the proposed alternate fill Amatex-20. The ammonium nitrate (AN) prills in Amatex-20 are replaced by prills of a solid solution of 10% potassium nitrate (KN) in AN. This substitution changes the temperature at which the large volume change transition of AN occurs from 32°C to 12-15°C, but does not completely eliminate the problem.

(U) The chemical and thermal stability of Amatex-20K has been given a "first look" survey via DTA/TGA, DSC, fast and slow cookoff, and isothermal decomposition techniques. With the exception of a less violent reaction occurring at a lower temperature on fast cookoff, all of the tests suggest that the substitution of AN/KN prills for the AN prills in the RDX/TNT matrix is detrimental to the stability of Amatex. More work will be needed, particularly in the isothermal decomposition and slow cookoff areas, to make a sure judgment of the desirability of the substitution.

CONTENTS

INTRODUCTION

Chemical and thermal stability study programs on candidate explosive systems are conducted to investigate the stability, storability, and compatibility of these new systems. All three characteristics are interrelated, either physically or chemically; however, no single test can be used as a measure of all three.

Amatex-20K, a variation of the proposed alternate fill Amatex-20, consists of a 40/40/20 weight percent mixture of prilled ammonium nitrate (AN)/potassium nitrate (KN) solid solution (90/10 weight percent), TNT, and RDX. Amatex-20K was proposed as a means of avoiding the drastic solid-solid AN IV→AN III transition that occurs at 32°C.[1] The transition is a complete change in crystal form that proceeds by the collapse of one form and reassembly in the other form with a concomitant volume change of about 3.8%. The solid-solid reaction at 32°C is slow so that when the AN is heated rapidly, a direct transition of AN IV→AN II usually occurs at about 56°C. A trace of water catalyzes in the AN IV→AN III rearrangement.

Storage at temperatures above 32°C for an appreciable period produces exudation from ordnance items loaded with Amatex-20 due to formation of the low density AN III form. KN, co-crystallized with AN from a melt or from a saturated solution, forms solid solutions in which potassium ions randomly replace ammonium ions in the AN crystal lattice. The addition of 10% KN lowers the transition temperature to about 15°C, but does not eliminate or prevent the change. Much work has been done on the AN/KN system; a recent study by Popolato and Cady[2] reports results making no essential change in the low temperature regions from the phase diagram published by R. Janacke, et al.[3] Figure 1 is a phase diagram of the AN/KN/water system reproduced from the report of footnote 3. The large volume change occurs in the AN III↔AN IV transition and the presence of KN does not eliminate the change. An X-ray study by Holden and Dickinson[4] of the structure of some of these phases indicates that in addition to a change in coordination number, hydrogen bonding can occur to further reduce the volume of AN IV phase. The substitution of potassium ions (K^+) for some of the ammonium ions (NH_4^+) in the AN IV lattice reduces the opportunities for hydrogen bonding, thus relaxing the crystal bonds forming a slightly larger crystal. However, the K^+ ion is smaller than the NH_4^+ ion and, when substituted in the AN crystal, produces a smaller crystal; so that, as a final result, the volume change in the AN III↔AN IV transition is less drastic in the AN/KN solid solution than in pure AN. The principal effect of the KN addition is to move the volume change difficulty to the low temperature storage ranges.

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[1] Naval Ordnance Laboratory. *Minol IV, A New Explosive Composition Containing Ammonium Nitrate-Potassium Nitrate Solid Solution*, by Carl Boyers, J. R. Holden and A. L. Bertram. White Oak, MD, NOL, 29 March 1973. (NOL TR 73-49.)

[2] Los Alamos Scientific Laboratory. *Joint Services Explosives Program, 1 December 1973 through 15 March 1974*. Quarterly report compiled by A. Popolato. Los Alamos, NM, March 1974. (LA-5616-R.)

[3] Janacke, R., H. Hamacher, and E. Rahlfs. "Das System KNO_3-NH_4NO_3-H_2O." ZEITSCHRIFT FUR ANORGANISCHE AND ALLEGEMEINE CHEMIE, Vol. 206 (1932), pp. 352, 368.

[4] Holden, J. R. and Dickinson, Co. JOURNAL OF PHYSICAL CHEMISTRY, Vol. 79 (1975), p. 249.

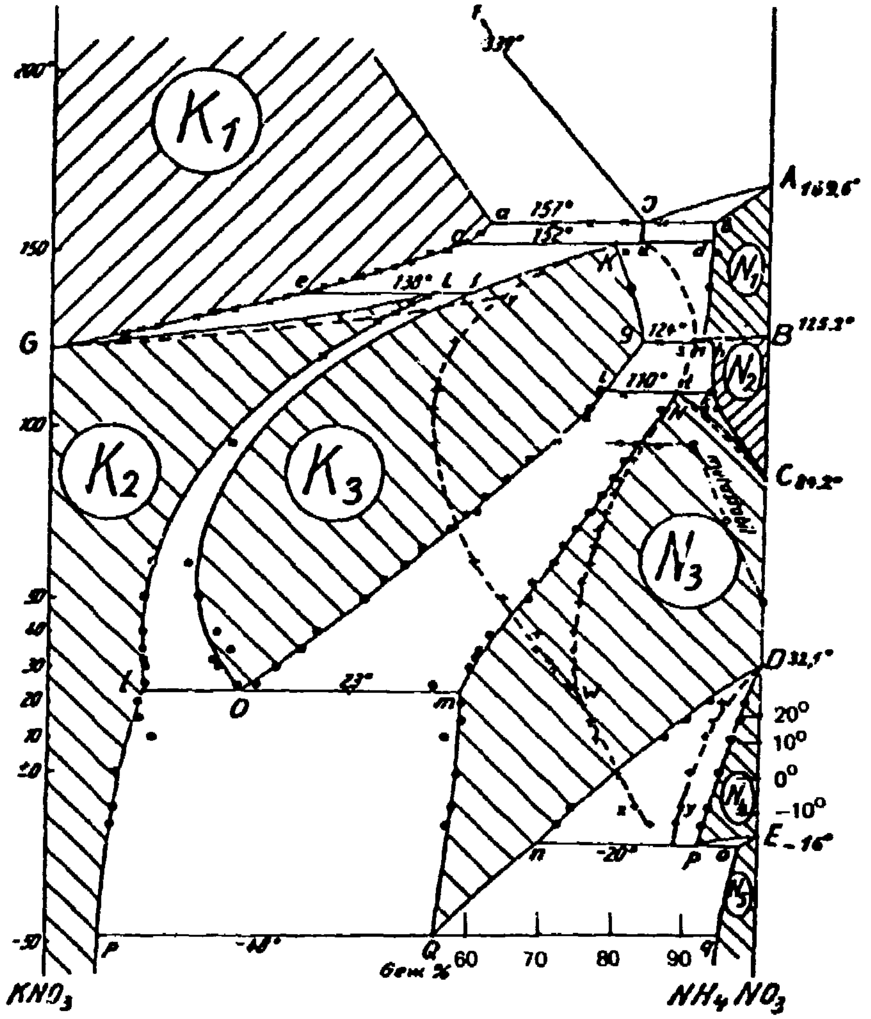

FIGURE 1. Phase Diagram of the AN/KN Water System.

The AN/KN prills used in this study were obtained from Ross Thermal Systems, Inc.,[5] which used a melt process for the preparation of the prills, and from Gulf Oil Chemical Co.,[6] which used a solution process. Ross has ceased production, so that data for samples containing these prills are inlcuded for information only.

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[5] Ross Thermal Systems, Inc., Englewood, Colorado

[6] Gulf Oil Chemical Co., Pittsburgh, Kansas

EXPERIMENTAL INVESTIGATIONS

An atomic absorption spectrometer was used to determine the potassium content of 100 prills from each source as a limited check on the composition of the AN/KN prills. Figure 2 is a histogram of the results. The results are a normal distribution of a range appropriate to the material and the analytical method. Since no one prill of either series is excessively rich or poor in KN, the tentative conclusion to be drawn is that the solid solution of AN/KN was obtained by both manufacturers.

COMPATIBILITY STUDIES

Simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) tests were conducted with a Thermoanalyzer-2.[7] The DTA/TGA results for Amatex-20K with Ross and Gulf AN/KN prills are shown in Figures 3 and 4, respectively. A second Amatex-20K sample formulated with Gulf prills was ground to a find powder: Figure 5 shows the DTA/TGA results. DTA/TGA results for an Amatex-20 sample[8] are presented for comparison in Figure 6. The principal features

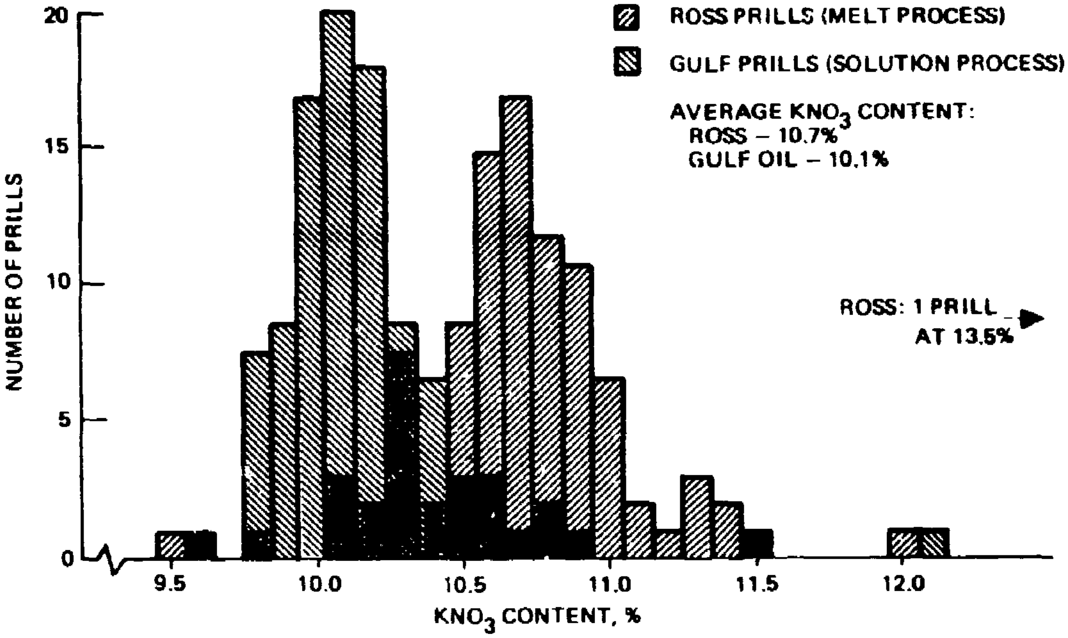

FIGURE 2. Histogram of Spectrometer Test of AN/KN Prills.

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[7] Mettler Instrument Co., Princeton, NJ

[8] Naval Weapons Center. *Characterization of Amatex-20*, by Jack M. Pakulak, Jr. and Edward Kuletz. China Lake, CA, NWC, February 1975. (NWC TP 5503, publication UNCLASSIFIED.)

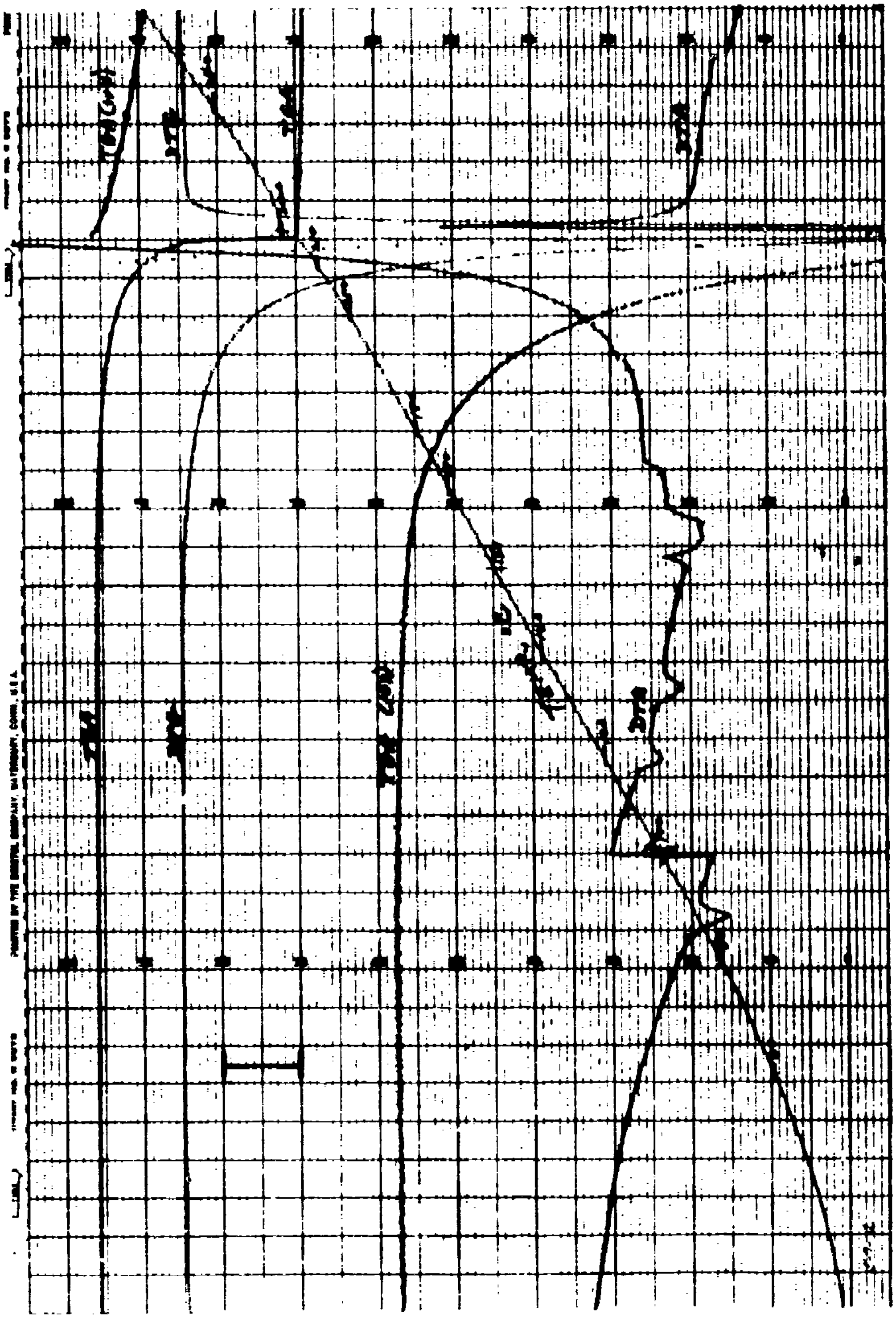

FIGURE 3. Thermal Patterns of Amatex-20K (With Ross AN/KN Prills) at 3°C/min Heating Rate. (Sample wt 29.025 mg; Run no. 5-7-2)

*Machine adjustment to shift DTA trace.

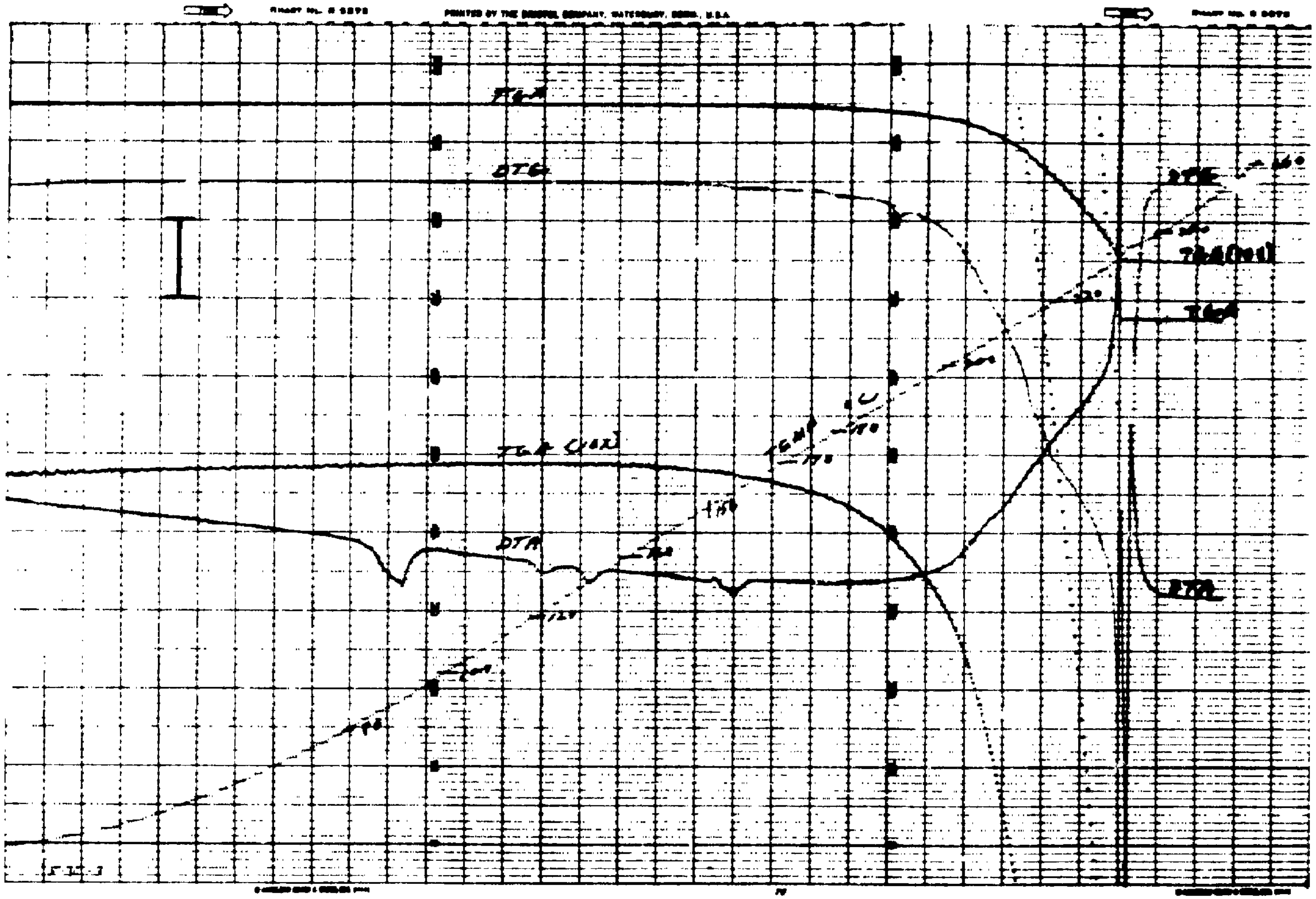

FIGURE 4. Thermal Patterns of Amatex-20K (With Gulf AN/KN Prills) at 3°C/min Heating Rate (Sample wt: 29.83 mg; Run no. 5-30-3)

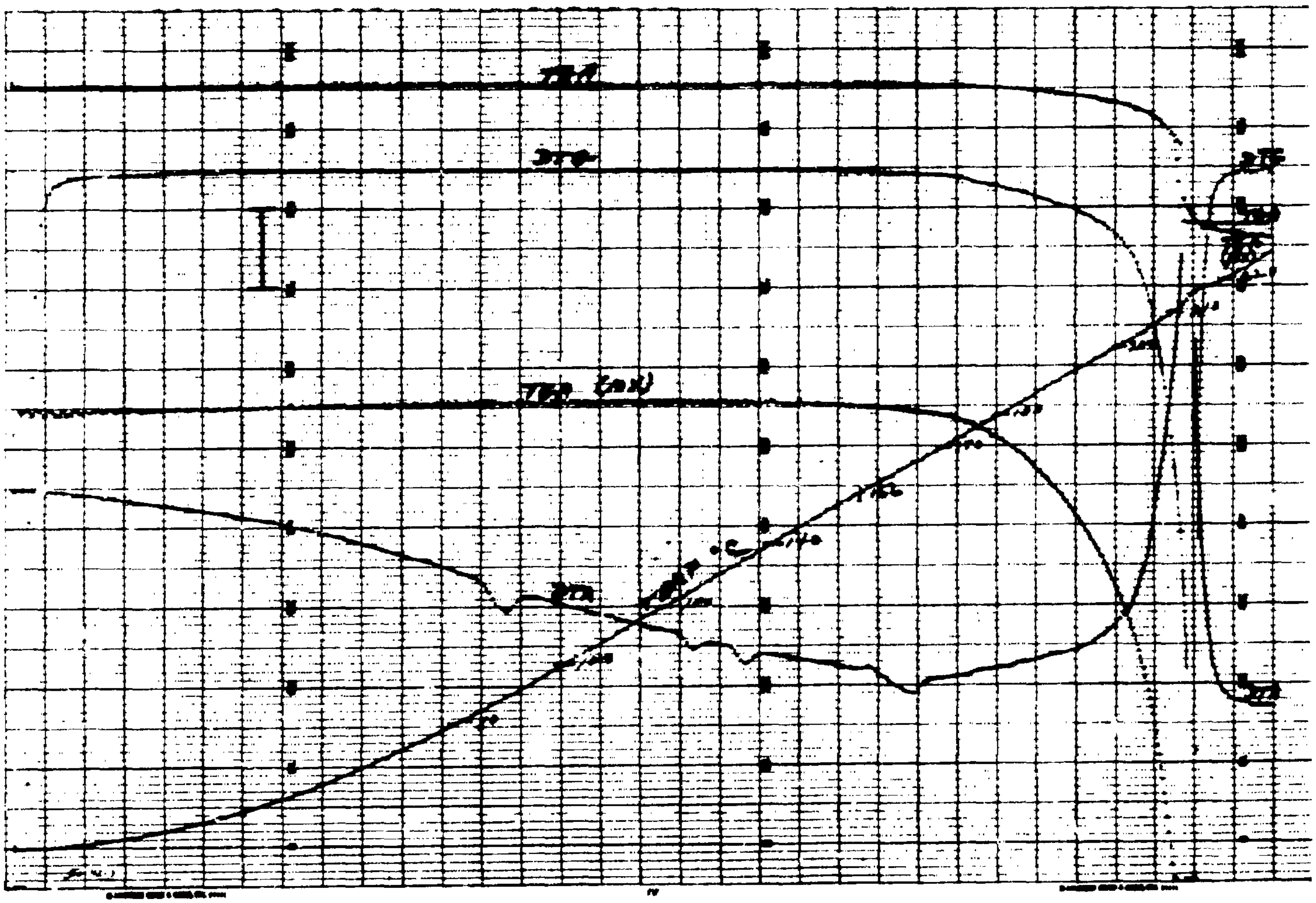

FIGURE 5. Thermal Patterns of Powdered Amatex-20K (With Gulf AN/KN Prills) at 3°C/min Heating Rate. (Sample wt: 20.96 mg; Run no. 5-42-3)

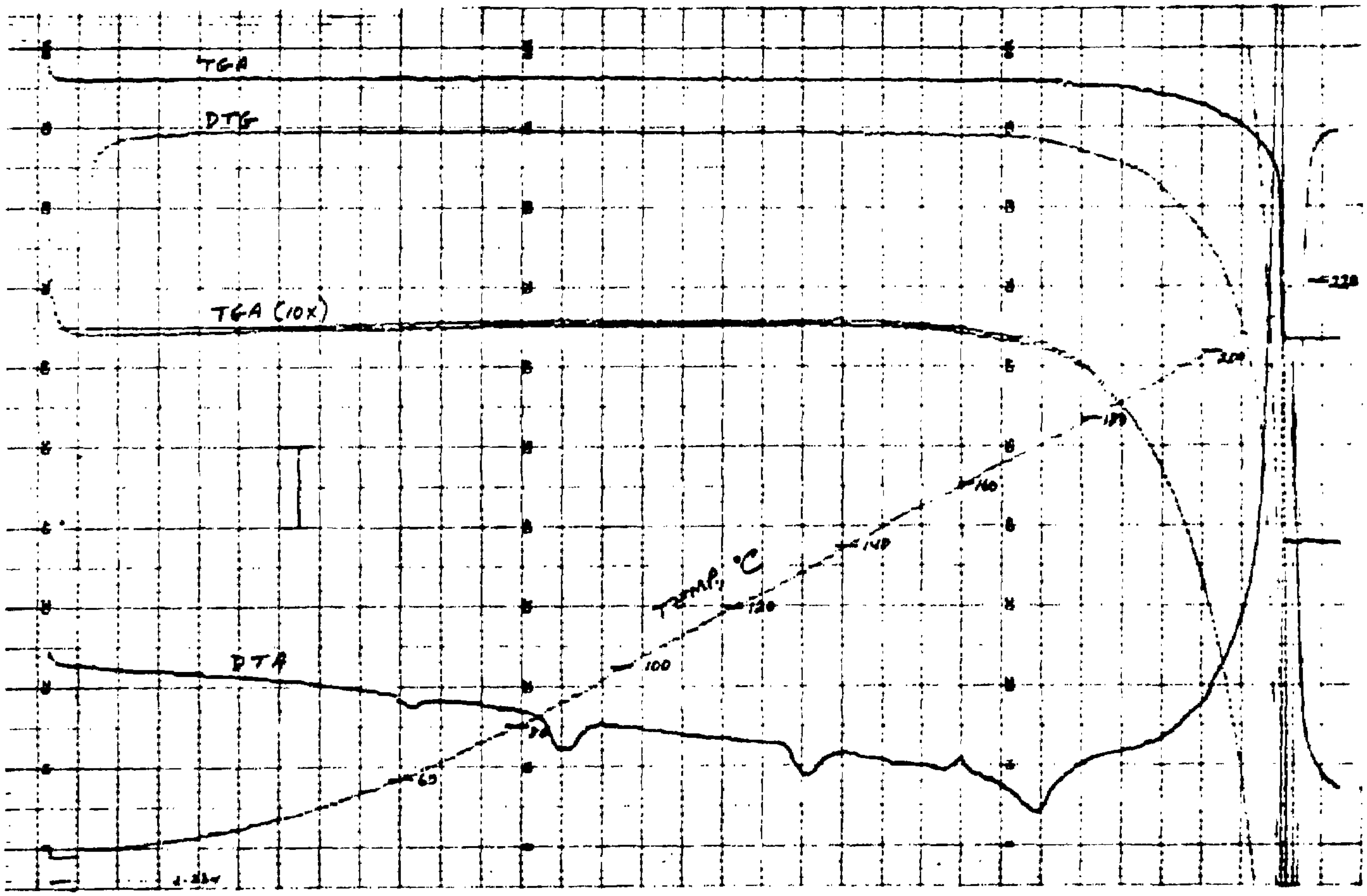

FIGURE 6. Thermal Patterns of Amatex-20 Explosive (NWC Mix) at 3°C/min Heating Rate. (Sample wt: 35.3 mg; Run no. 2-23-1)

of these records, listed in Table 1, include the endotherms at 83°C, TNT melt, AN/KN III↔II transition at 118°C, AN/KN II↔I at 130°C, and melting of AN/KN at 156°C. After the system melts, the liquid phase allows the rapid, exothermic decomposition to proceed, leading to a burst reaction at 212-215°C. Amatex-20 containing only AN shows endothermic transitions at 60°C, the metastable AN IV↔II change, the combination of melting TNT and AN III↔II at 84-90°C, AN II↔I at 130°C, and AN I melt at 164°C, followed by the decomposition to burst at 212°C. The burst reaction at 212-215°C in the liquid phase is characteristic of TNT/RDX mixtures. The thermal pattern variations between the two samples with Gulf prills were possibly due to sampling or to some coating on the prills which was broken up when the sample was ground. Another possibility was that water, taken up by the hygroscopic AN/KN, affected the reactions. To investigate this, a DTA/TGA test was conducted with 40 mg water added to 40 mg of Amatex-20K (Gulf prills). The results (Table 1 and Figure 7) show that the water boiled out independently of the Amatex-20K reactions, indicating that water absorption is not the cause of the different reaction series.

A differential scanning calorimeter (DSC)[9] was used to obtain further thermal data, particularly an activation energy for the exothermic "burst" reaction, which correlates well with cookoff data. The variation of the reaction peak temperature with heating rate and the method of Kissinger[10,11] were used for this determination. The

TABLE 1. DTA/TGA Reactions.

Material, source/reference	Endo reactions, °C								Exo reactions, °C			
	Initial	Peak	Initial	Peak	Initial	Peak	Initial	Peak	First weight loss	Initial	Burst	Weight loss, %
Amatex-20K Ross prills Figure 3	83	88	118	121			156	160	100	160	215	88
Amatex-20K Gulf Oil prills Figure 4	83	90	119	122	128	132	156	163	130	170	232	61
Ground Amatex-20K Gulf Oil prills Figure 5	84	90	103	107	133	136	160	163	140	170	212	86
Amatex-20 Figure 6	60	64	84	90	129	132	164	172	145	175	212	93
Amatex-20K w/water Gulf Oil prills Figure 7	85	88	120	125	127	130			175	175	212	92

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[9] Model DSC-1B, Perkin-Elmer Corporation, Norwalk, Connecticut

[10] Kissinger, Homer E. "Variation of Peak Temperature with Heating Rate in Differential Thermal Analysis," JOURNAL OF RESEARCH OF THE NATIONAL BUREAU OF STANDARDS, Vol. 57, No. 4 (October 1956). Research paper 2712.

[11] ———. "Reaction Kinetics in Differential Thermal Analysis," ANALYTICAL CHEMISTRY, Vol. 29 (1957), p. 1702.

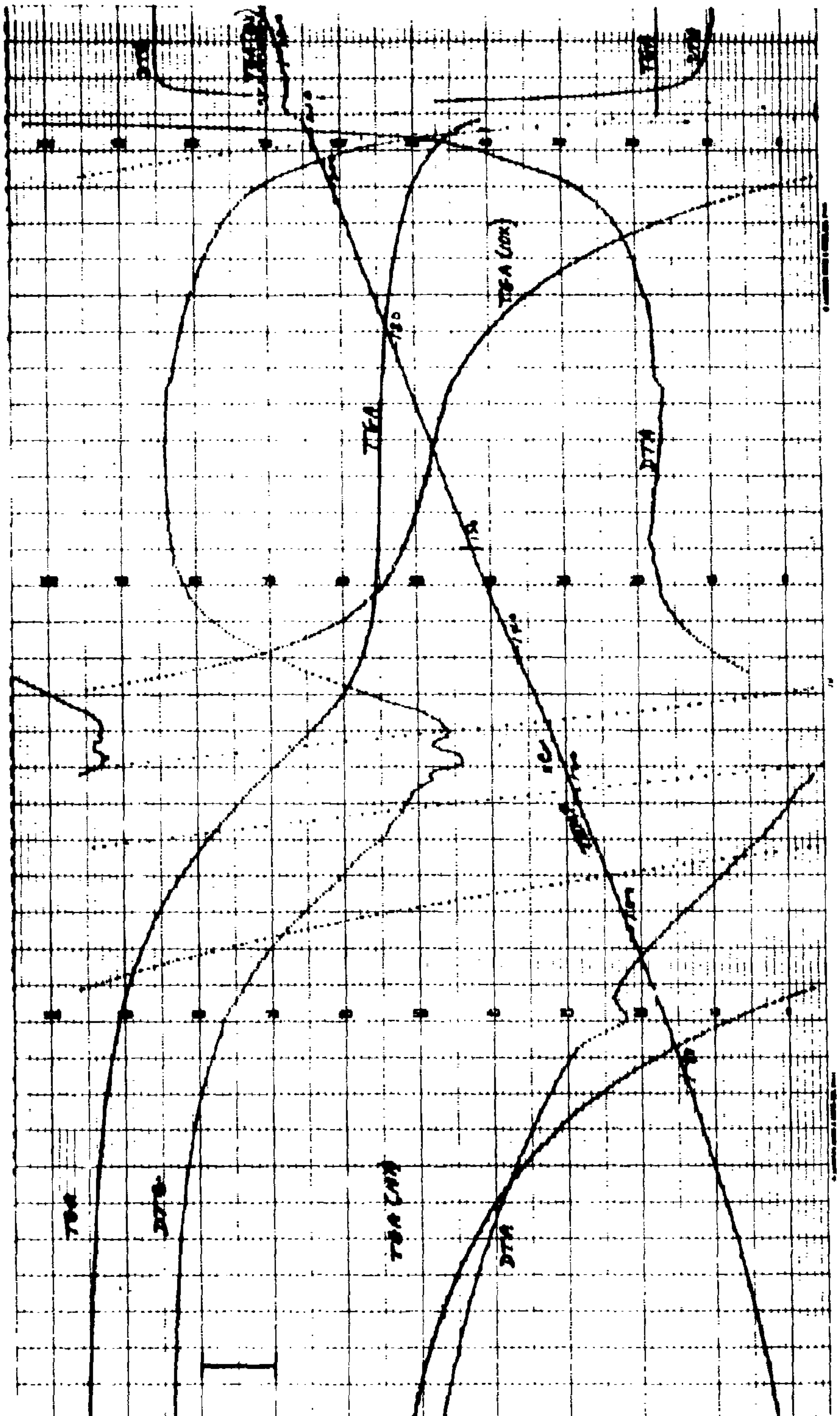

FIGURE 7. Thermal Patterns of Amatex-20K (With Gulf AN/KN Prills) at 2°/min Heating Rate. (Total sample wt: 82.30 mg; Run no. 5-42-1)

DSC results are given in Figures 8 and 9 for Amatex-20K with Ross and Gulf prills, respectively. Figure 10 contains plots of the Kissinger heating rate function (as log ϕ/T^2 versus $1/T$) as derived from the equation

$$\frac{\phi}{T^2} \cdot \frac{E^*}{R} = A \exp\left(-\frac{E^*}{RT}\right)$$

where

ϕ = heating rate, °C/sec
T = burst peak temperature, °K
R = universal gas constant
A = Arrhenius frequency factor
E^* = activation energy

The data for these determinations are listed in Table 2.

THERMAL DECOMPOSITION

The thermal decomposition of Amatex-20K was studied using an isothermal technique. The test consisted of holding a sample of a material at a constant temperature in a 45-ml general purpose Parr bomb fitted with a pressure transducer and a means of sampling the gas phase. The sample, about 1 gram, was held in a glass vial that fit snugly in the bomb. After loading the bomb and purging the air with argon, the loaded bomb was placed in an aluminum block furnace at the desired temperature. The temperature of the block and pressure in the bomb were continuously recorded until any reaction ceased. At this point the bomb was removed and allowed to cool. The gas phase in the bomb was sampled for mass spectrographic analysis and for IR identification. The residue in the bomb was weighed to determine the amount of reaction that had occurred. The results of this study are given in Figures 11 through 14 and Table 3.

A disturbing effect observed in this series was that both of the samples containing Ross prills and one of the samples containing Gulf prills cooked off at 170°C. These were 1-gram samples under the pressure of their own decomposition products. The cookoff was sufficiently energetic to shatter the glass vial liners holding the samples. The sudden reaction at cookoff produced an entirely different series of product gases; e.g., a low amount of N_2O, a high amount of N_2 and CO, and a trace of NH_3. The IR scans showed an appreciable amount of carbon monoxide (CO) in the final gas from the burst reactions, but little or no CO in the usual, non-violent thermal decomposition. The Amatex-20K prepared with Ross prills was less stable than that containing Gulf prills. That is, although both materials showed the same activation energy ($E^* = 33$ Kcal/mole), the frequency factors were 1.0×10^{12} sec^{-1} for Gulf prills and 1.4×10^{12} sec^{-1} for Ross prills, which produced the higher rate of decomposition of Amatex-20K with Ross prills. Figure 15 is an Arrhenius plot of the

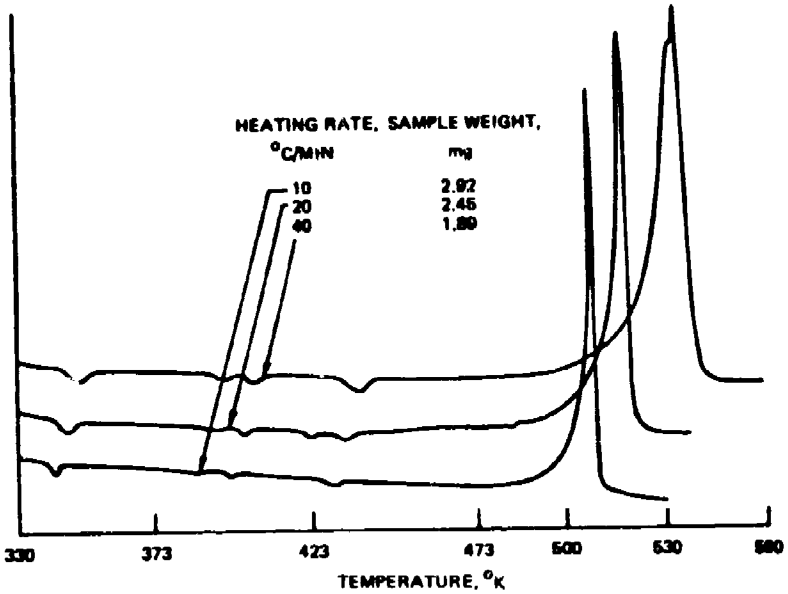

FIGURE 8. DSC Results for Amatex-20K (With Ross AN/KN Prills).

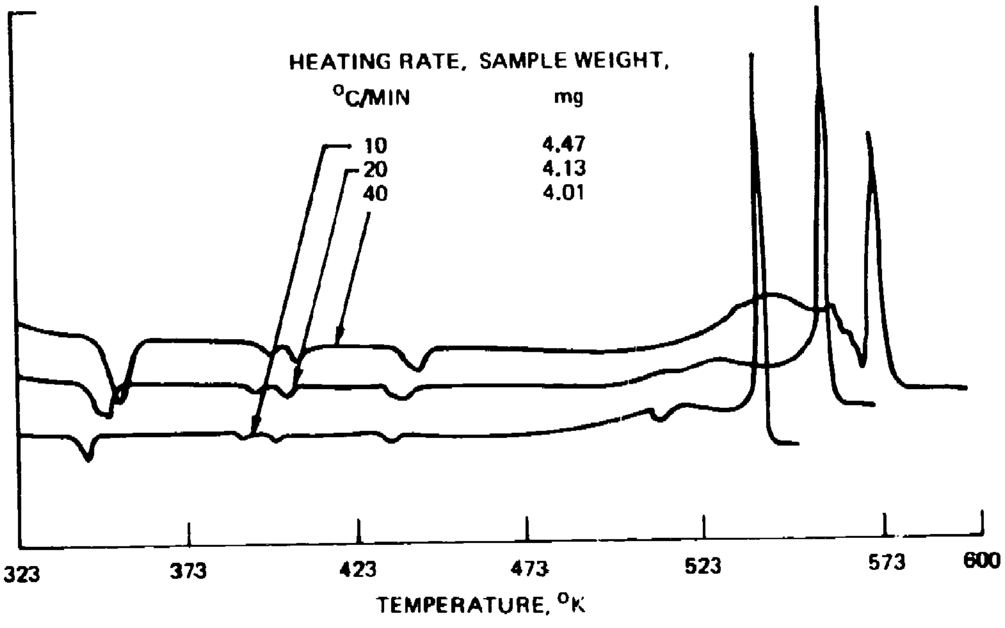

FIGURE 9. DSC Results for Amatex-20K (With Gulf AN/KN Prills).

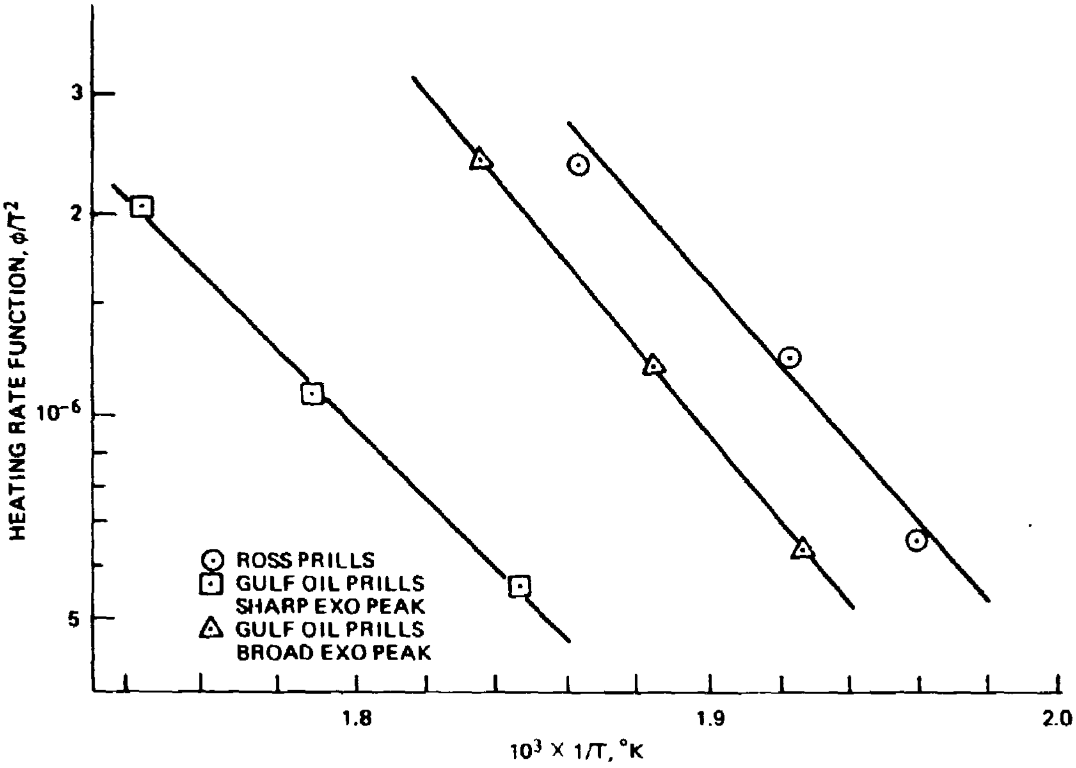

FIGURE 10. Plot of Heating Rate Function for Amatex-20K.

TABLE 2. DSC Data for Amatex-20K.

Sample	Heating rate, °/sec	Temperature, °K	1/T	ϕ/T^2	Activation energy	Frequency factor
Ross prills	0.167	509	1.963×10^{-3}	6.40×10^{-7}	26.8 Kcal	3.03×10^{9} sec^{-1}
	0.333	518	1.929×10^{-3}	1.24×10^{-6}		
	0.667	536	1.866×10^{-3}	2.32×10^{-6}		
Gulf Oil prills (sharp peak)	0.167	540	1.852×10^{-3}	5.71×10^{-7}	23.5 Kcal	2.13×10^{7} sec^{-1}
	0.333	559	1.789×10^{-3}	1.07×10^{-6}		
	0.667	573	1.745×10^{-3}	2.03×10^{-6}		
Gulf Oil prills (broad exo)	0.167	518	1.930×10^{-3}	6.20×10^{-7}	28.1 Kcal	6.80×10^{9} sec^{-1}
	0.333	529	1.890×10^{-3}	1.19×10^{-6}		
	0.667	544	1.838×10^{-3}	2.25×10^{-6}		

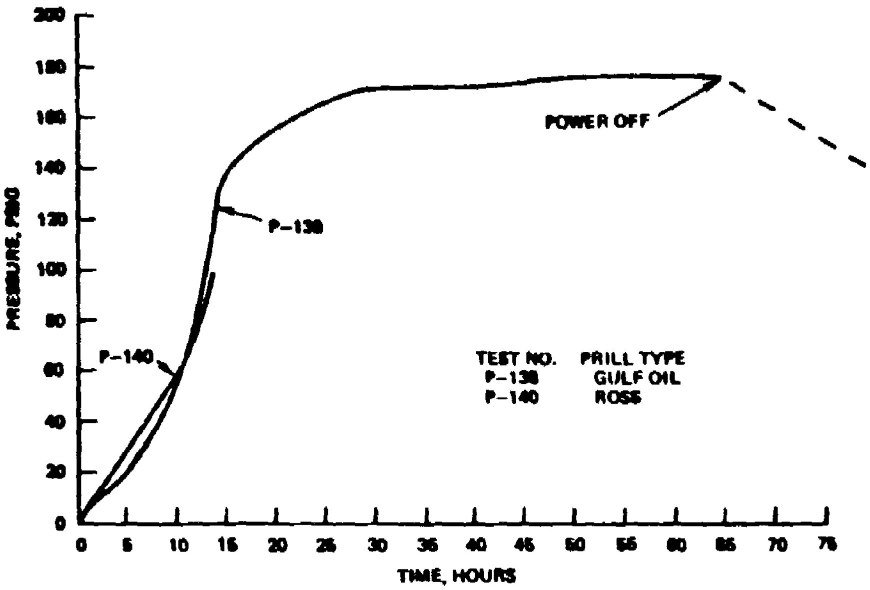

FIGURE 11. Thermal Decomposition of Amatex-20K at 155°C.

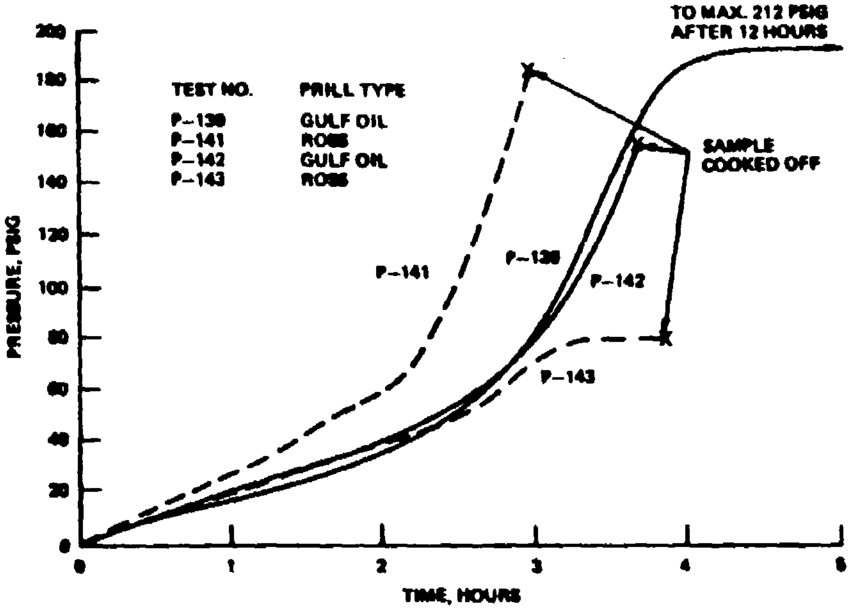

FIGURE 12. Thermal Decomposition of Amatex-20K at 170°C.

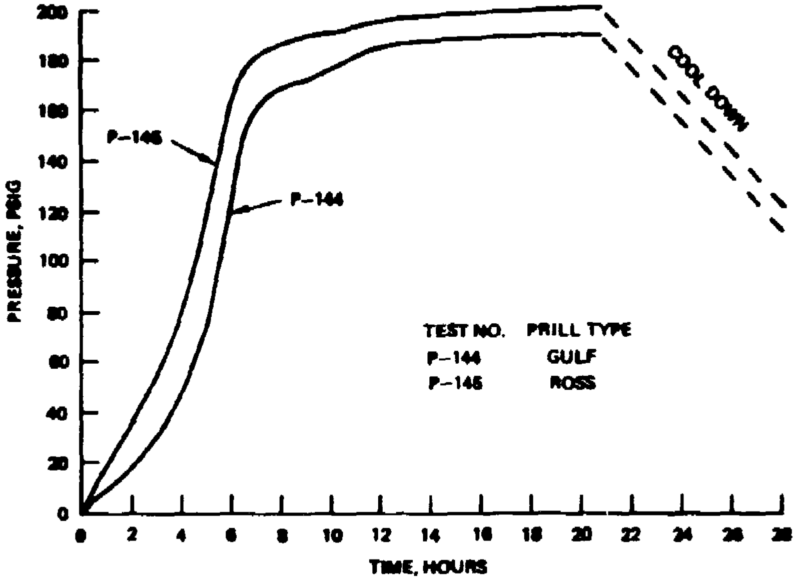

FIGURE 13. Thermal Decomposition of Amatex-20K at 165°C.

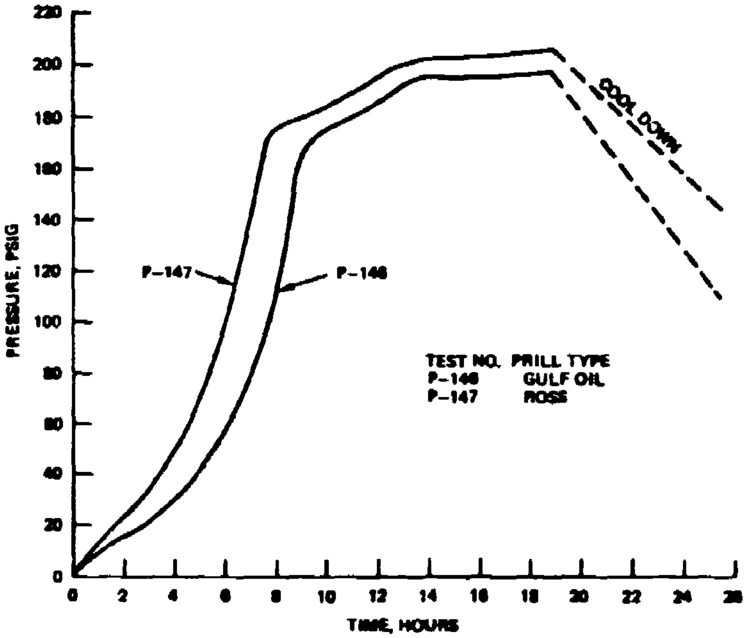

FIGURE 14. Thermal Decomposition of Amatex-20K at 160°C.

TABLE 3. Thermal Decomposition of Amatex-20K.

Test no.	Prill source	Temperature, °C	Maximum pressure at temperature, psig	Percent reacted	Gas analysis, volume %				Half-life ($t_{1/2}$), min.	10^3 x 1/T, °K^{-1}	Specific rate constant, 10^5 x sec^{-1}
					N_2O	CO_2	$N_2 + CO$	H_2O[a]			
138	Gulf	155	177	64	22	34	24	19	780	2.335	1.48
146	Gulf	160	197	66	24	21	36	19	468	2.308	2.5
144	Gulf	165	190	66	24	25	39	13	330	2.282	3.5
139	Gulf	170	212	66	11	38	32	20[b]	204	2.256	5.7
142	Gulf	170	157[c]	76	6	26	68	[d]	204	2.256	5.7
140	Ross	155	[e]	68	43	31	24	[d]	...	...	...
147	Ross	160	206	63	28	21	37	14	363	2.308	3.2
145	Ross	165	201	56	14	29	48	10	282	2.282	4.1
141	Ross	170	185[c]	79	1	28	71	[d]	156	2.256	7.4
143	Ross	170	83[c,e]	75	2	24	74	[d]	...	...	...

[a] Percent water calculated from final cold pressure in bomb

[b] Estimated

[c] Sample cooked off

[d] No estimate of water possible

[e] Bomb malfunction

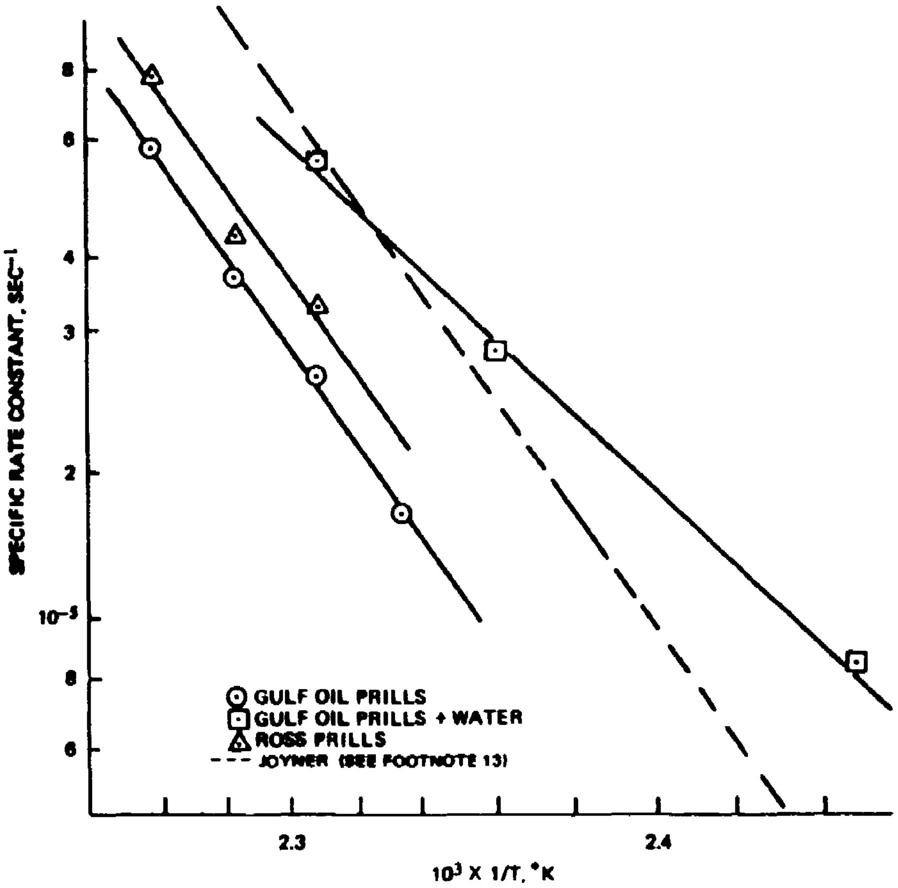

FIGURE 15. Arrhenius Plot of Thermal Decomposition of Amatex-20K.

first order specific rate constant derived from the half-life time and the reciprocal absolute temperature of the experiment. The equations

$$k = (\ln 2)/t_{1/2}$$

$$k = A \exp(-E^*/RT)$$

were used to calculate the specific rate constant, k, from the half-life time, $t_{1/2}$; the activation energy, E*, from the slope of the log k versus 1/T line.

$$\log k = \log A - E^*/2.303R$$

Joyner[12] reported that the thermal decomposition of Amatex-20 has an activation energy of 32.8 Kcal/mole and a frequency factor of 2×10^{12}. The dashed line in Figure 15 was calculated from these parameters and indicates that the presence of KN in the Amatex-20K has a slight stabilizing effect on the RDX/TNT/AN system.

As a worst case check on the effect of water on the thermal decomposition of Amatex-20K, 1-gram samples of the material containing Gulf prills with 1-gram of water were subjected to the isothermal Parr bomb tests. Data from these tests are listed in Table 4 and plotted in Figure 16. A plot of half-life time versus the reciprocal absolute temperature, included in Figure 15, produces an activation energy of 21.8 Kcal and a frequency factor of 5.2×10^6 sec^{-1}. This indicates that the presence of water is detrimental and should be avoided.

FAST COOKOFF

The small scale fast cookoff procedure is used to investigate the response of materials, propellants, explosives, liners, etc., to a flame environment.[13] The setup (Figure 17), called an SCB (small-scale cookoff bomb), consists of a 400-ml stainless steel can with 1/8-inch walls equipped with an electric ribbon heater to produce heating rates of 2.5 to 3°C/second, such as is seen by ordnance items in a fire. The severity of reaction with the 2-pound charge, lightly confined in the SCB, correlates directly with the response of the material in bombs and warheads.[14] The observed noise, dust cloud, and, in particular, the size, shape, color, etc. of the SCB fragments, range from a small pop and an opened case (deflagration) to a loud bang, a cloud of

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[12] Naval Weapons Center. *Thermal Decomposition of Explosives. Part II. The Thermal Decomposition of Amatex and Related Systems*, by Taylor B. Joyner. China Lake, CA, NWC, (in process). (NWC TP 4709, Part II, publication UNCLASSIFIED.)

[13] Naval Weapons Center. *Thermal Analysis Studies on Candidate Solid JPL Propellants for Heat Sterilizable Motors*, by Jack M. Pakulak, Jr. and Edward Kuletz. China Lake, CA, NWC, July 1970. (NWC TP 4258, publication UNCLASSIFIED.)

[14] Naval Ordnance Systems Command. *Standard Terminology for Ordnance Explosive Reactions Obtained by Cookoff*. Washington, DC, NOSC (ORD-93221), 23 April 1969. (NAVORDNOTE 8020.)

TABLE 4. Thermal Decomposition of Amatex-20K/Water.

Test no.	Prill source	Temperature, °C	Maximum pressure at temperature, psig	Gas analysis, volume %				Half-life ($t_{1/2}$), min.	$10^3 \times 1/T$, °K^{-1}	Specific rate constant, $10^5 \times$ sec^{-1}
				N_2O	CO_2	$N_2 + CO$	H_2O[a]			
148	Gulf Oil	110	17	1.4	1.4	29	60	[b]	2.609	[b]
149	Gulf Oil	130	110	2.0	35	42	15	1,350	2.480	0.86
150	Gulf Oil	150	177	15	31	39	15	432	2.363	2.7
151	Gulf Oil	160	210	14	36	32	17	213	2.308	5.4

[a] Estimated from pressure in bomb after cool-down.

[b] Run terminated at 66 hours. No half-life estimate possible.

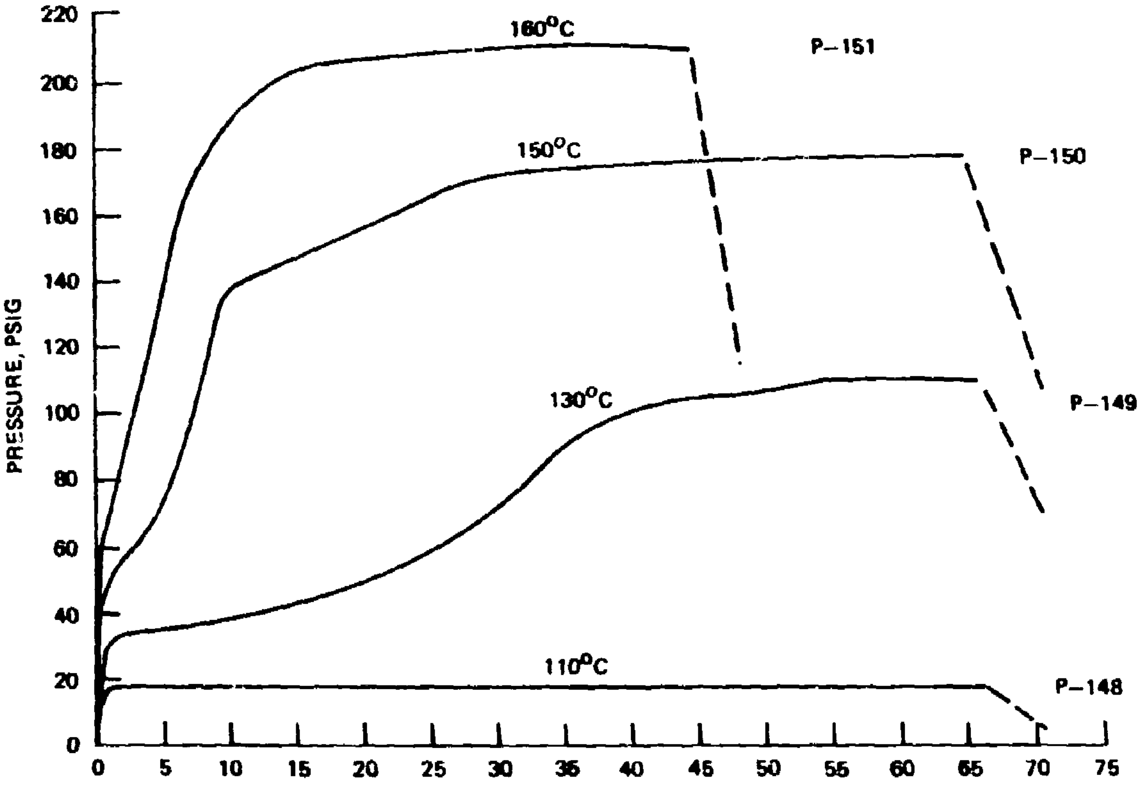

FIGURE 16. Thermal Decomposition of Amatex-20K (With Gulf AN/KN Prills).

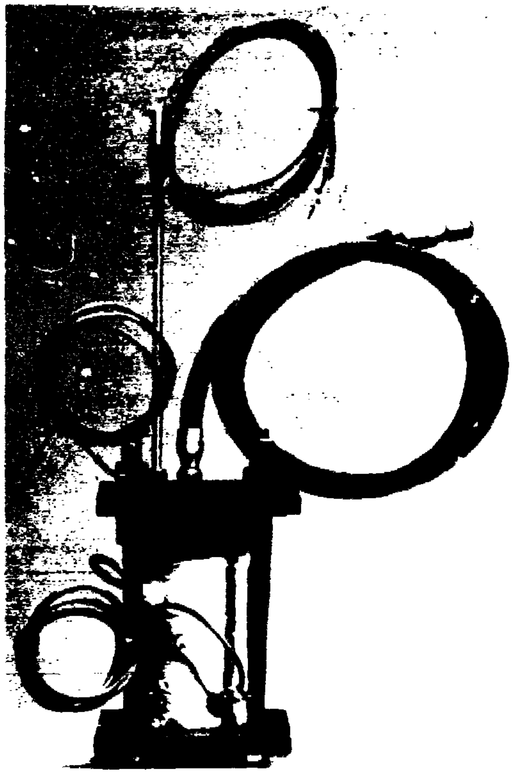

FIGURE 17. Small-scale Cookoff Bomb Setup. (LHL 182486)

dust, and case torn to small heat colored fragments (detonation). The SCB is instrumented with a thermocouple spot-welded to the inside wall of the container and with a take-off to a pressure transducer in the cover.

Two SCB tests were conducted with Amatex-20K loads, one with each of the two types of AN/KN prills. The time-temperature and time-pressure records are shown in Figures 18 and 19. Figures 20 and 21 show the SCB fragments from the two tests. The result with Ross prills was anomalous; an explosion was defined by the indicators, but about 1/3 of the explosive billet was recovered. Also, the thermocouple record was anomalous after 93 seconds and 210°C; the presence of molten material and gas bubbles behind the thermocouple could produce this result. Similar events were

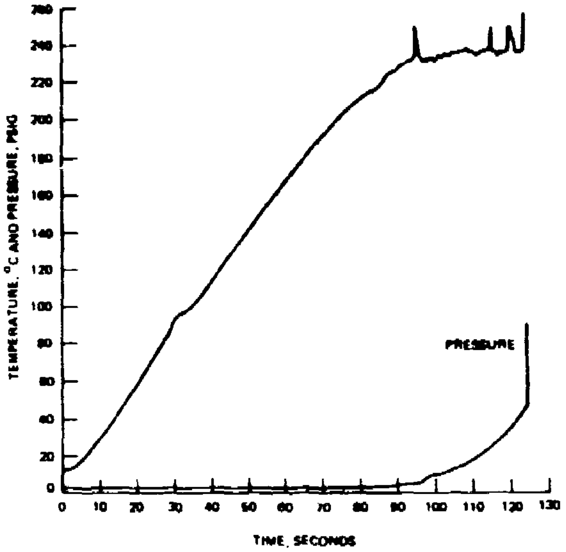

FIGURE 18. Time-Temperature vs. Time-Pressure for Amatex-20K (With Ross AN/KN Prills).

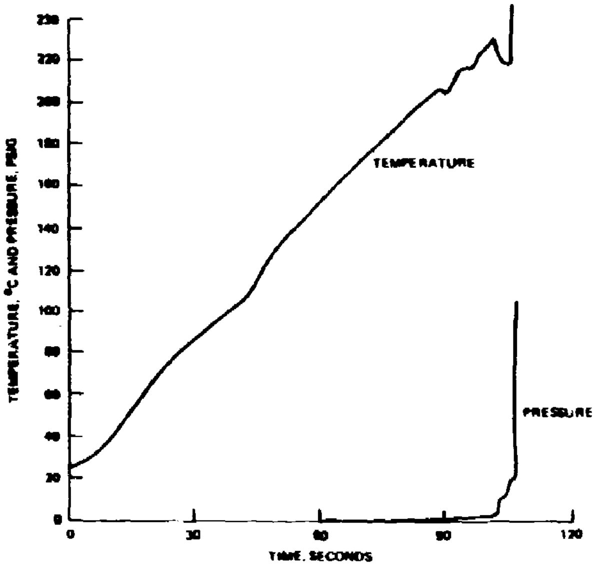

FIGURE 19. Time-Temperature vs. Time-Pressure for Amatex-20K (With Gulf AN/KN Prills).

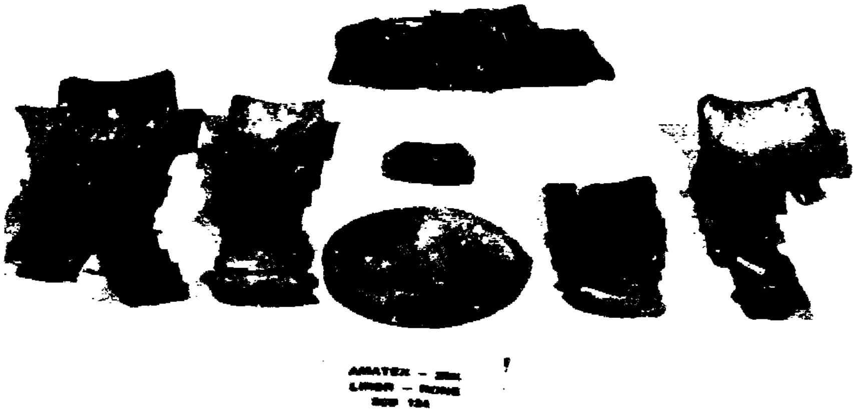

FIGURE 20. Fragments from SCB Test for Amatex-20K (With Ross AN/KN Prills). (LHL 186312)

FIGURE 21. Fragments from SCB Test for Amatex-20K (With Gulf AN/KN Prills). (LHL 187654)

apparent in the material containing Gulf AN/KN prills. Relative to Amatex-20, the Amatex-20K reactions were much milder, but they occurred at a much lower temperature. The data are summarized in Table 5; data for an earlier Amatex-20 test are included in the table.

SLOW COOKOFF

The slow cookoff procedure (see footnote 13) provides data for the prediction of time-to-reaction in various sizes and under assorted storage conditions. An insufficient number of samples were tested; therefore, the critical temperature values must be considered tentative. Since Amatex-20K is partially liquid at the experimental temperatures, samples were contained in vertical ovens. The ovens consisted of a heavy-walled aluminum tubing with a welded base plate. Heating elements were attached to the outside of the tubing and controlled from a thermocouple imbedded in the aluminium wall. The ovens were covered with heavy aluminum foil to minimize evaporation and sublimation of the sample. The ovens, and samples, were heated rapidly to the chosen temperature and controlled at that temperature until the cookoff reaction occurred. Continuous recording was maintained on thermocouples located at the exact center of the charge and on the inside wall at the explosive/aluminum interface. A third thermocouple was placed at a half-radius point in the larger samples to monitor the temperature distribution in the sample. Thermocouple data for the four slow cookoff runs are given in Figures 22 through 25. The data are summarized in Table 6. The equivalent time to cookoff in Table 6 is calculated as time at the oven temperature corrected for the amount of reaction that occurred during the warm-up period.[15]

TABLE 5. SCB Fast Cookoff Data.

Test no.	Explosive/source	Reaction		Type of reaction
		Time, sec	Temperature, °C	
124	Amatex-20K (Ross AN/KN)	125	237	Explosion
131	Amatex-20K (Gulf Oil AN/KN)	107	230	Explosion
45	Amatex-20	125	320	Detonation

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[15] Naval Weapons Center. *Cookoff Studies on the General Purpose Cast Explosives PBXC-116 and PBXC-117*, by Carl M. Anderson and Jack M. Pakulak, Jr. China Lake, CA, NWC, (in process). (NWC TP 5629, publication UNCLASSIFIED.)

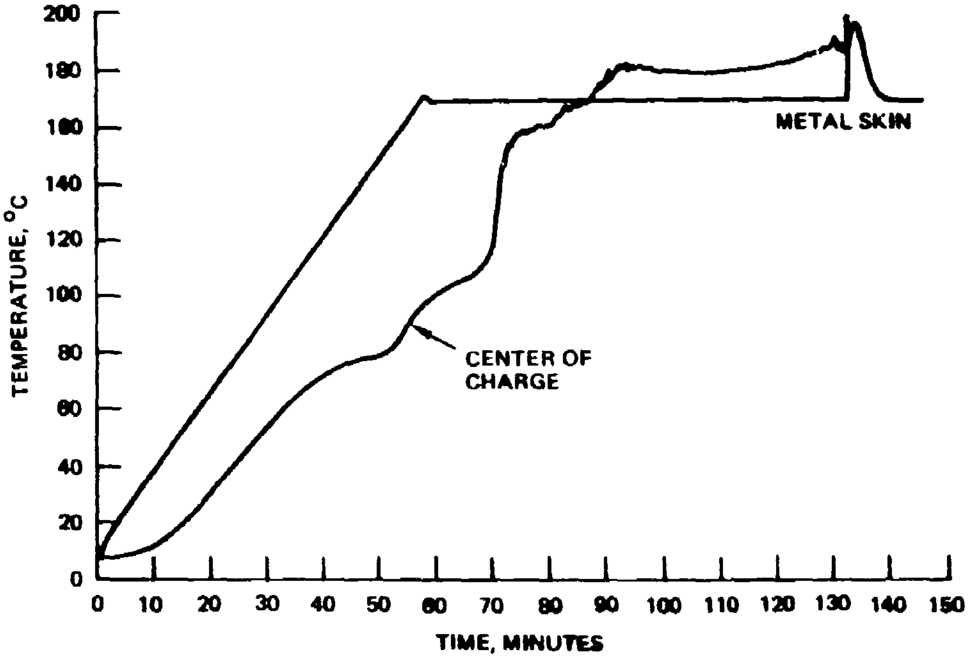

FIGURE 22. Thermocouple Data for Amatex-20K (With Ross AN/KN Prills) Tested at 170°C. (Sample 2-inch diameter by 6 inches long)

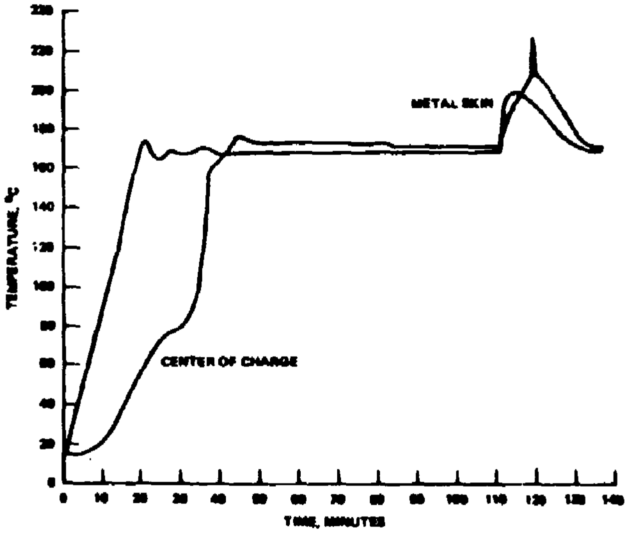

FIGURE 23. Thermocouple Data for Amatex-20K (With Gulf AN/KN Prills) Tested at 170°C. (Sample 2-inch diameter by 6 inches long)

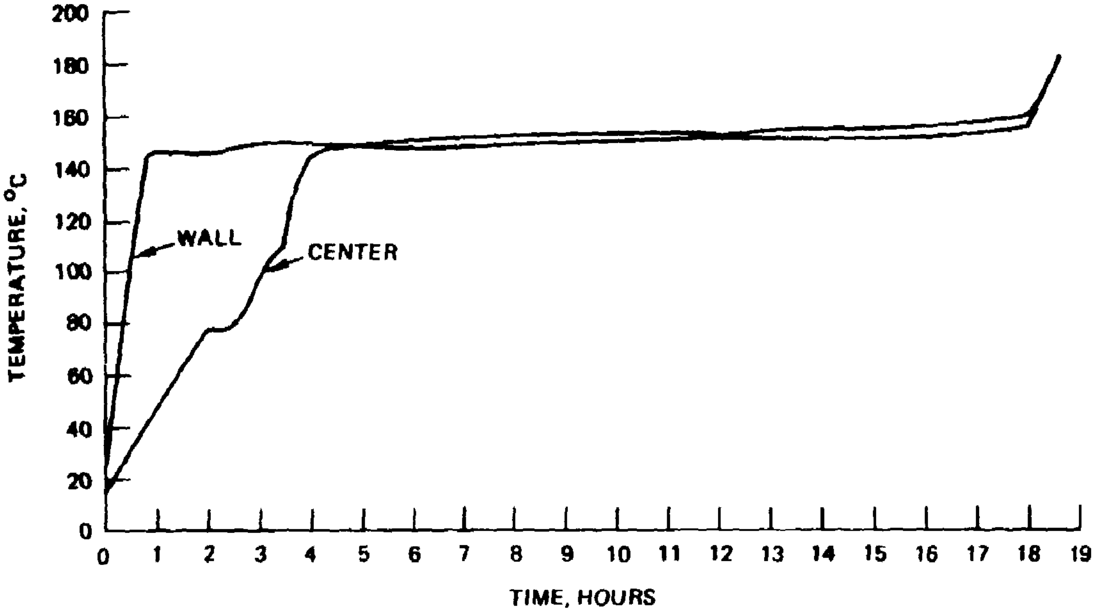

FIGURE 24. Thermocouple Data for Amatex-20K (With Ross AN/KN Prills) Tested at 150°C. (Sample 5 1/4-inch diameter by 8 inches long)

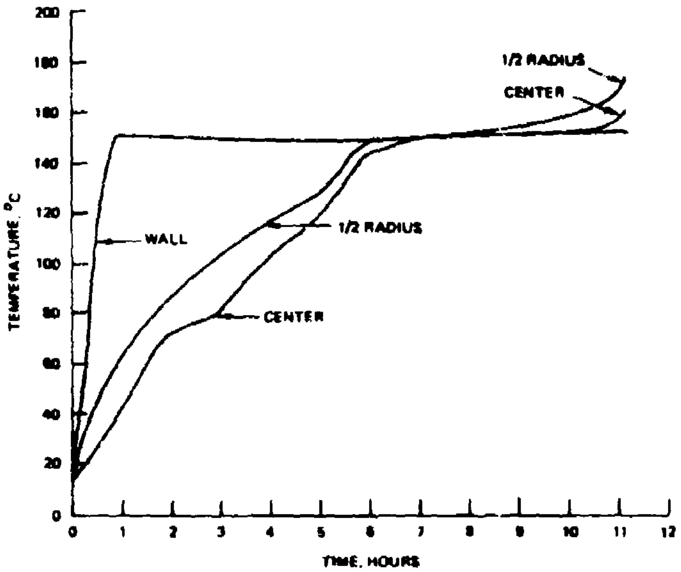

FIGURE 25. Thermocouple Data for Amatex-20K (With Gulf AN/KN Prills) Tested at 150°C. (Sample 5 1/4-inch diameter by 8 inches long)

TABLE 6. Slow Cookoff Data.

Test no.	AN/KN prill source	Size		Temperature, °C	Reference Figure no.	Time to cookoff	
		Diameter, in.	Length, in.			Total, hr:min	Equivalent, hr:min
206	Ross	2	6	170	20	2:33	0:57
220	Gulf	2	6	170	21	2:47	2:09
217	Ross	5-1/4	8	150	22	18:40	14:33
218	Gulf	5-1/4	8	150	23	11:15	5:44

A comparison of these single-point data with previous explosives data (see footnote 8 and Figure 26) indicates that, relative to Amatex-20, the use of AN/KN solid solution prills lowers the time to cookoff at a given temperature, or lowers the temperature required for a given time to cookoff. It also appears that Amatex-20K has a thermal stability comparable to Composition B. It should be emphasized that these are single-result, first-look data. Many more samples of the same and other sizes at other temperatures will be required to define the slow cookoff characteristics of Amatex-20K to make useful predictions.

CHARACTERISTIC "CRITICAL" TEMPERATURE

The characteristic "critical" temperature, T_m is defined by Zinn and Mader[16] as a unique temperature for each explosive and each size of billet, above which the explosive will self-heat to cookoff. Cookoff can occur below this temperature, but the reaction kinetics will not be a simple, zero-order, self-heating system. Zinn and Mader define this critical temperature by the equation

$$T_m = \frac{E^*}{2.303R \log\left(\frac{\rho a^2 QAE^*}{\lambda R T_m^2 \delta}\right)} \tag{1}$$

The values of the parameters for Amatex-20K are:

E^* = activation energy = 33 kcal/mole
A = Arrhenius frequency factor = 1.2×10^{12} sec^{-1}
Q = heat of reaction = 400 cal/g (estimated)
λ = thermal conductivity = 9.6×10^{-4} cal/sec/cm/°C
ρ = density = 1.6 g/cm^3
c = specific heat = 0.40 cal/g
δ = shape factor = 2 for cylindrical geometry
R = universal gas constant = 1.987 cal/mole/°C
a = radius of cylinder, cm

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[16] Zinn, J. and C. L. Mader. "Thermal Initiation of Explosives," JOURNAL OF APPLIED PHYSICS, Vol. 31 (1960), p. 323.

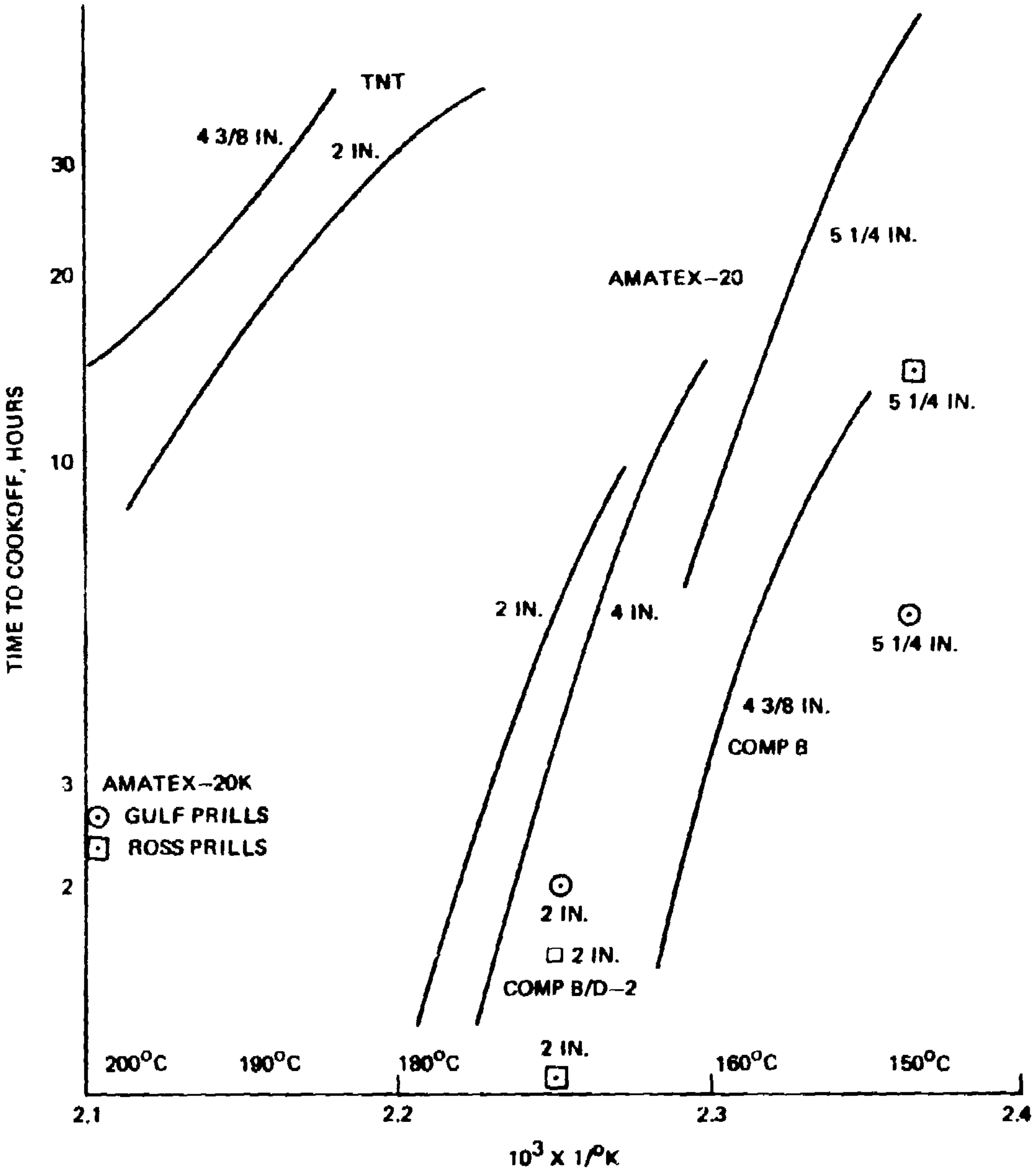

FIGURE 26. Comparison of Amatex-20K with TNT, Amatex-20, Composition B and Composition B/D-2.

An iteration on values of T_m converges rapidly to a solution for the equation, as shown in the table below.

2-inch-diameter cylinder	5 1/4-inch diameter cylinder
Amatex-20 K (using half-life kinetic data above)	
T_m = 141°C	T_m = 121°C
Ross prills (E^* = 26.8 Kcal; A = 6 × 10^9 sec^{-1})	
T_m = 116°C	T_m = 94°C
Gulf prills (E^* = 28.1 Kcal; A = 1.51 × 10^{10} sec^{-1})	
T_m = 124°C	T_m = 102°C

Another approach to locating a value for T_m, is the empirical function developed by Zinn and Rogers.[17] A plot of this function, given in the Zinn and Rogers article, is useful for predicting the time to reaction for other sizes and temperatures.

$$\log \frac{t_e}{\tau} = f\left[E^*\left(\frac{1}{T_m} - \frac{1}{T_1}\right)\right] \tag{2}$$

where t_e is the time to reaction, τ is a thermal time constant equal to a^2/α, and T_1 is the temperature of the surroundings. α is the thermal diffusivity of the material and is related to other thermal properties by $\lambda = \rho c \alpha$. With an experimental value of time-to-reaction, t_e, for a particular size and oven temperature, a value for the function is found from a plot of equation (2). Then

$$\frac{1}{T_m} = \frac{1}{T_1} + \frac{X}{E^*} \tag{3}$$

where X is the value of the function. Using the activation energy, E^*, value of 33 Kcal/mole from the thermal decomposition data, Amatex-20K T_m are calculated as follows.

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[17] Zinn, J. and R. N. Rogers. "Thermal Initiation of Explosives," JOURNAL OF PHYSICAL CHEMISTRY, Vol. 66 (1962), p. 2646.

Ross prills	
2-inch-diameter cylinder	5 1/4-inch-diameter cylinder
T_m = 156°C	T_m = 148°C
Gulf prills	
T_m = 168°C	T_m = 134°C

Slow cookoff data on Amatex-20 with no KN in the AN prills (see footnote 7) produced T_m values of 170°C for the 2-inch-diameter cylinder and 153°C for the 5 1/4-inch-diameter cylinder. Here again, on the basis of these single-run data, it appears that the AN/KN prills lower the stability of the Amatex-20K relative to Amatex-20.

SUMMARY

In summary, this study to characterize the thermal properties of Amatex-20K produced discouraging results relative to Amatex-20. The essential difference between Amatex-20K and Amatex-20 is the use of 90/10 AN/KN prills in Amatex-20K. The presence of KN as a solid solution in AN lowers the drastic volume change temperature of AN from 32°C to about 15°C and raises the upper large phase change from 84°C to 105°C. This results from the fact that the smaller K^+ ion, relative to the NH_4^+ ion, will tend to stabilize the AN III crystal form. This should make the volume change less, but certainly will not eliminate the difficulty.

With the exception of the change in temperatures at which phase changes occur, the presence of KN in the AN has little effect on the exotherms in the DTA/TGA records. This would indicate that the decomposition reactions leading to an exothermic "burst" reaction is that of the TNT/RDX in the Amatexes. However, the reaction kinetic data derived from the DSC records (Table 2) show that the activation energy for Amatex-20K is lower than for Amatex-20, indicating a lower stability. A more specific indication of possible difficulty with Amatex-20K is the explosive decomposition that occurred at 170°C under the pressure of its own decomposition products. This explosive reaction is evidently a different series of reactions than that observed in thermal decompositions in that the distribution of gaseous products changes from N_2O, CO_2, N_2 to CO_2, CO, and N_2 with little N_2O.

The results of the slow and fast cookoff experiments are confusing at best. The only real conclusion that can be drawn is that more samples will need to be run to define the properties of Amatex-20K under cookoff conditions. On fast cookoff, Amatex-20K reacts less violently and at a lower temperature than Amatex-20; the reaction is an unacceptable explosion (Amatex-20 detonated in the same test). On slow cookoff, Amatex-20K is again less stable than Amatex-20, reacting at a shorter time or lower temperature.

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