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TRANSITION METAL HE's - VII
ACP

G. L. Clink

DEVELOPMENT DIVISION

AUGUST - OCTOBER 1971

Normal Process Development
Endeavor No. 204

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One of a series of studies of the explosives characteristics of transition metal coordination compounds.

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ABSTRACT

Physical and physicochemical properties of hexaamminechromium III perchlorate (ACP) were investigated to determine its potentiality for HE and/or HE component application.

Physicochemical properties obtained through investigation of isothermally aged ACP under conditions of various system and boundary restrictions (open and closed; 50 and 80 C; 0.65 and 0.85 g/cc) show the material to be substantially stable under these simulated isothermal storage conditions from a standpoint of infrared and DTA thermal pattern behavior and chemical analysis of aged residues.

Spark sensitivity was 0.25 joules at 5 kv (by LASL type test) and impact sensitivity was about 23 and 14 cm on sandpaper (12A) and steel (12B), respectively.

DISCUSSION

INITIAL EVALUATION OF HEXAAMMINECHROMIUM III PERCHLORATE

An initial investigation of the physicochemical properties of hexaamminechromium II perchlorate (ACP)* was undertaken to obtain some insight into the nature of the compound prior to and during its simulated isothermal storage (aging) under various system boundary conditions.

The material was prepared by the reaction of anhydrous ammonia with the chloride, and subsequent conversion to the perchlorate by means of saturated (aqueous) sodium perchlorate metathesis. The product was filtered, ethanol washed repeatedly, and vacuum dried. The coordinate is an inner d^2sp^3 system.

The physicochemical investigation of ACP essentially involved its storage in uniform system configurations under specifically chosen thermal conditions with system variables including temperature, sample geometry, material density, and physical restriction (open and closed systems).

The physical aspects included spark and impact sensitivity, hot wire and EBW threshold, and Henkin Test.

For the remainder of this report the material will be referred to be a chemical acronym, ACP.

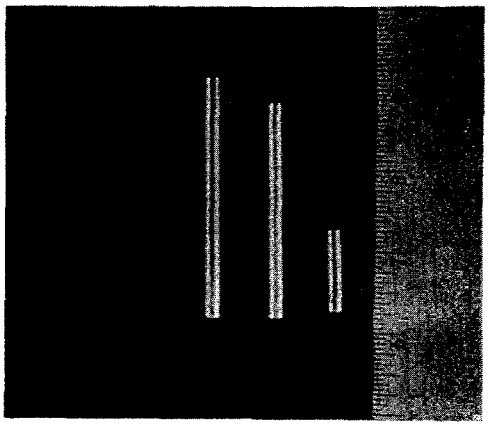


Fig. 1

Aluminum Sample Configurations

EXPERIMENTAL

THERMAL GROUP I (OPEN BULK CONFIGURATION)

Infrared spectral analysis of the unaged material was made in order to ascertain function group presence (qualitative), the results of which are presented in Fig. 2 and Table I.

Table I. Infrared Band Assignments for ACP

μ	Functional Group	Mode
3.00	NH_3	ν_{a+s}
6.15	NH_3	δ_d
7.40	NH_3 (Coordinated)	δ_s
8.8-9.1	ClO^{-4}	ν_d
10.6	ClO^{-4}	ν_s
13.4	NH_3 (Coordinated	ρ_t

Differential thermal analysis (DTA) of unaged ACP shows only one significant exotherm thresholding at ∿ 260 C, and cresting at ∿ 308 C (Fig. 2).

Chemical analysis of the material was restricted to hydrogen and nitrogen (Table II).

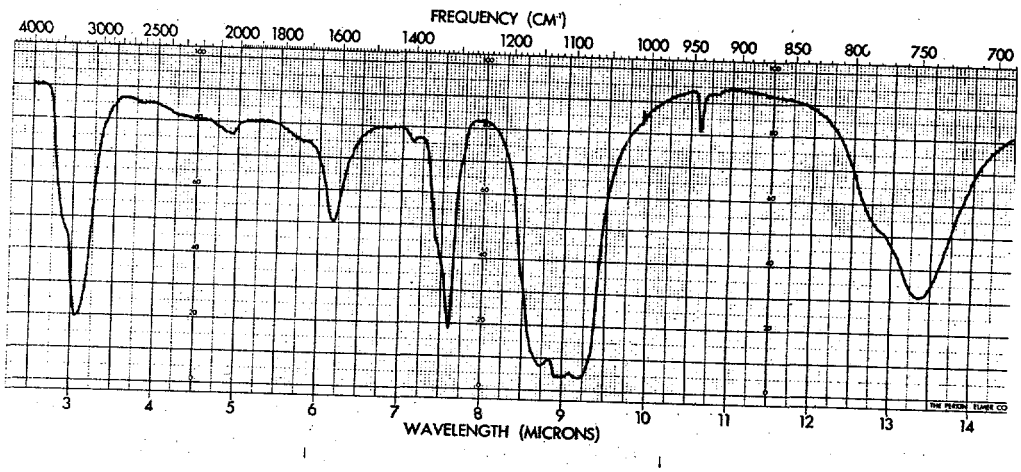
Table II. Chemical Analysis of ACP

	Hydrogen (wt %)	Nitrogen (wt%)	H/N Molar Ratio
ACP (theoretical)	4.01	18.57	3.00/1.00
ACP (original)	4.02	18.49	3.02/1.00

Based on nitrogen content, the material has an indicated purity of 99.6%.

Elemental Analysis (hydrogen and nitrogen) of ACP of the open bulk material following isothermal aging at 50 and at 80 C for periods up to 1000 hours give no indication of decomposition. Weight losses are 0.3% or less (Table III).

Infrared spectral analysis (Fig. 3) as well as DTA thermogram results (Fig. 4) give no indication of instability due to thermal aging.



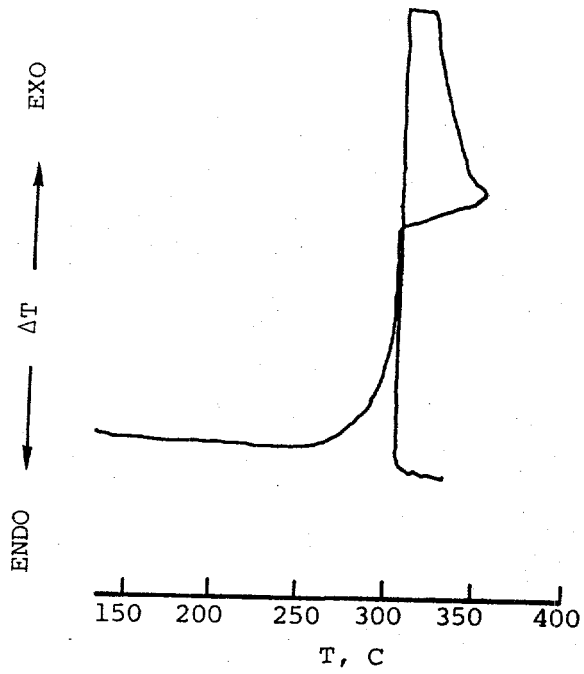


Fig. 2. Infrared and DTA Thermal Characteristics of ACP

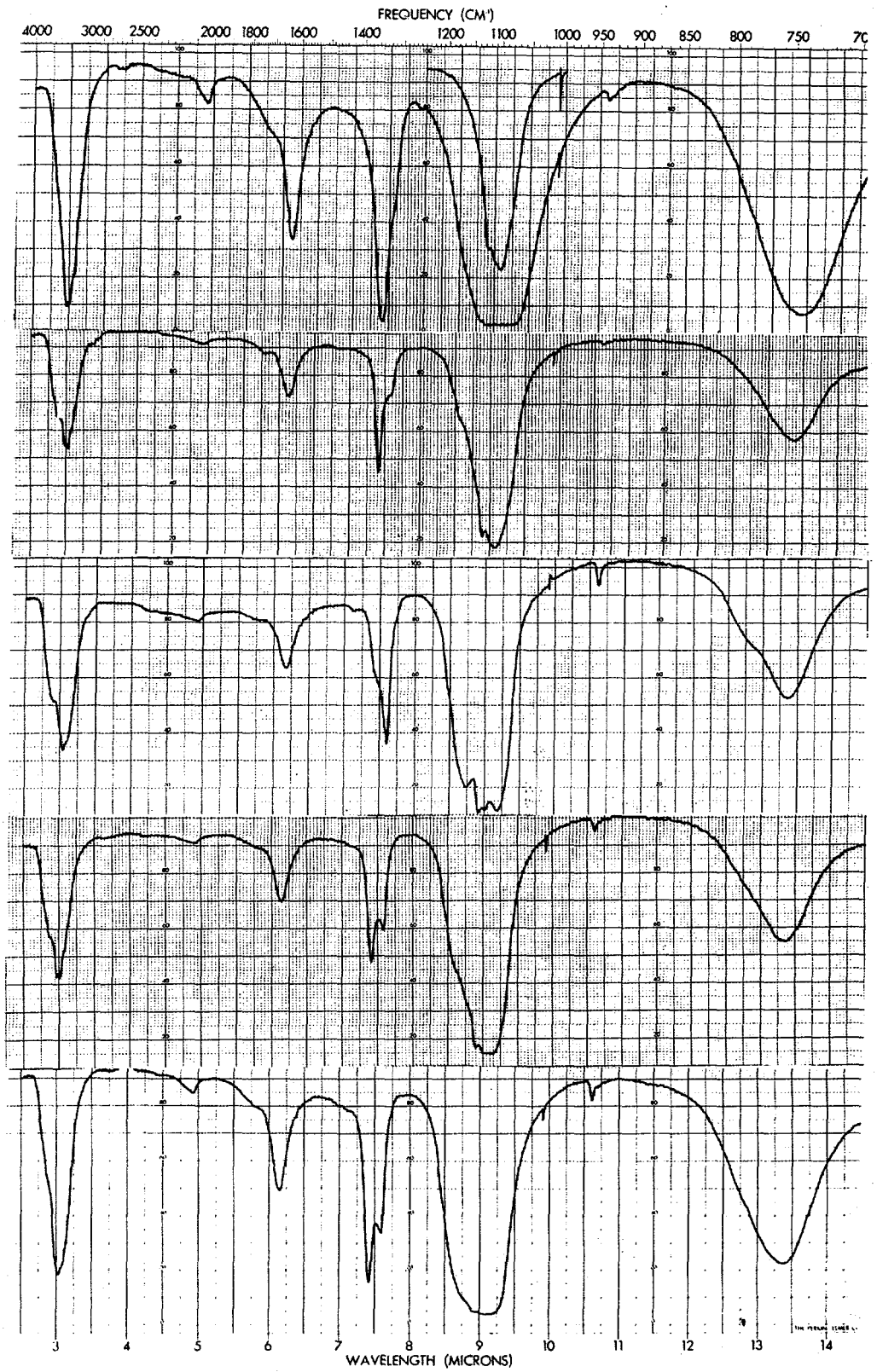


Fig. 3. Infrared Spectra of Open Bulk Residues

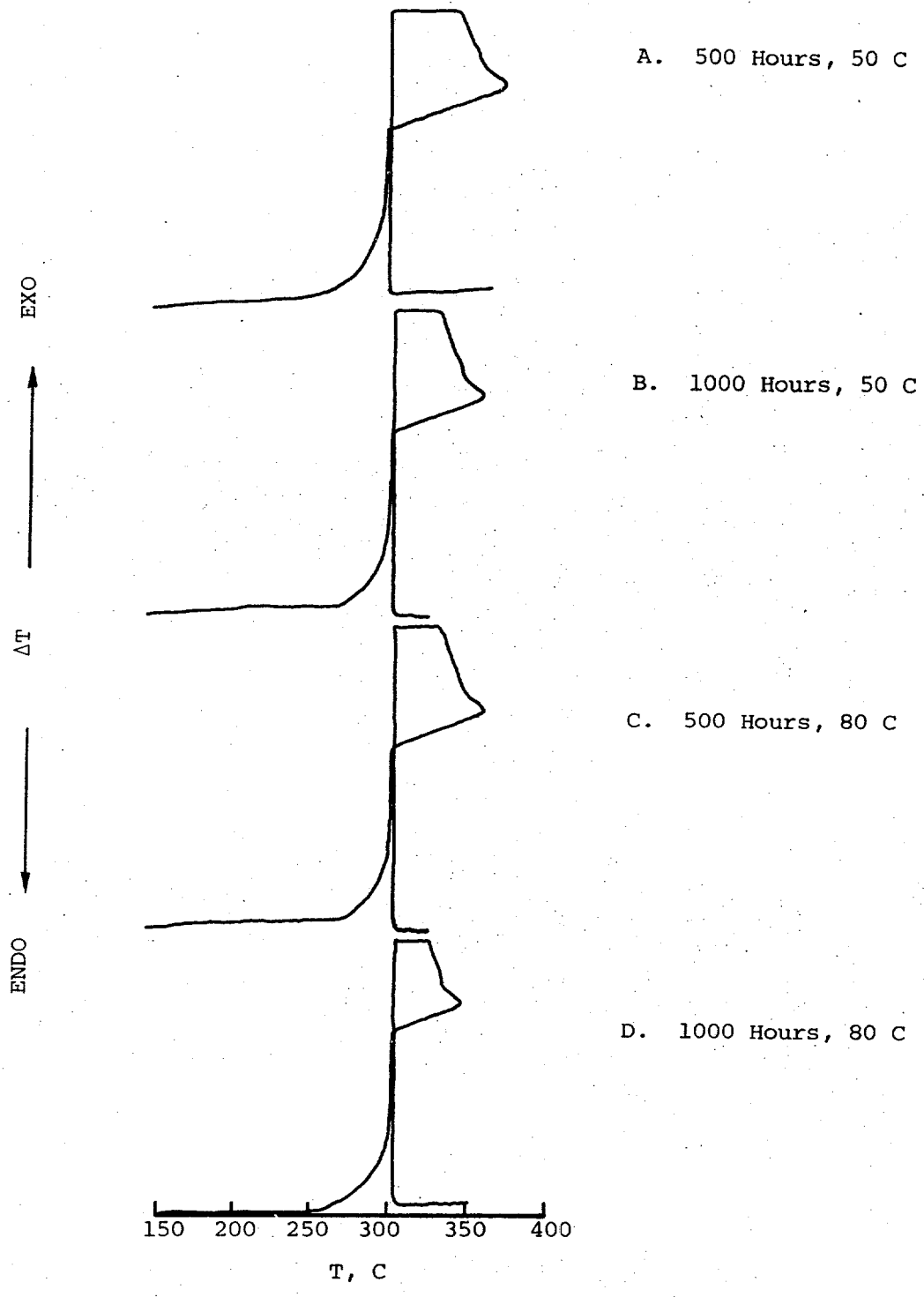


Fig. 4. DTA Thermograms of Open Bulk Residues

THERMAL AGING CONSIDERATIONS

Preliminary studies of ACP involved the determination of impact sensitivity (drop hammer, using an ERL machine) and the electrostatic sensitivity (spark gap, using a LASL type discharge). The results obtained were as follows:

Impact sensitivity (12A, sandpaper)	23.1 σ = 0.03
Impact sensitivity (12B, steel)	14.2 σ = 0.04
Spark sensitivity (5 kv)	0.25 joules

After drying the material, the study was systemized by placing a weighed amount in aluminum sample configurations (Fig. 1).

These sample configurations, as seen in Fig. 1, consisted of (left to right) a unibody right circular cylinder closed at one end, while the remaining items are solid right circular cylinders whose diameter matched the inside diameter of the former, so as to produce a nearly perfect closed system when the "plug" is set in place by means of a small pellet press. The longer of the two plugs is of such a length so as to produce a sample density of 0.85 g/cc, while the shorter is for maintaining a closed system at bulk density (0.65 g/cc). After the material was weighed and placed in the aluminum cylinders, they were modified so as to produce four system configurations:

1. Open bulk
2. Closed bulk
3. Open compact**
4. Closed compact

The completed configurations were placed in analytical ovens maintained at specific temperatures for an extended period of time divided into the following groups:

Thermal Group I
Open bulk configuration (0.65 g/cc), 50 & 80 C

Thermal Group II
Closed bulk configuration (0.65 g/cc), 50 & 80 C

Thermal Group III
Open compact configuration (0.85 g/cc), 50 & 80 C

Thermal Group IV
Closed compact configuration (0.85 g/cc), 50 & 80 C

** *This system is obtained by removal of the closure plug after attaining a sample density of 0.85 g/cc.*

Table III. Thermal Group I (Open Bulk Configuration)

	Original	500 hours		1000 hours	
		50 C	80 C	50 C	80 C
Hydrogen/nitrogen Molar Ratio	3.02	3.04	3.04	2.99	3.03
Weight Loss (%)	----	0.2	0.1	0.3	0.3
Infrared Spectrum (Figure)	3-A	3-B	3-C	3-D	3-E
DTA Thermogram (Figure)	2	4-A	4-B	4-C	4-D

THERMAL GROUP II (CLOSED BULK CONFIGURATION)

Chemical analysis of these thermal residues (Table IV) give no indications of decomposition, which is in agreement with weight loss results ($\leq$ 0.2%).

Infrared spectral results (Fig. 5) as well as DTA thermograms (Fig. 6) give no indication of molecular or thermal instability due to aging.

Table IV. Thermal Group II (Closed Bulk Configuration)

	Original	500 hours		1000 hours	
		50 C	80 C	50 C	80 C
Hydrogen/nitrogen Molar Ratio	3.02	3.02	3.01	3.00	3.02
Weight Loss (%)	----	0.2	0.1	0.2	0.2
Infrared Spectrum (Figure)	5-A	5-B	5-C	5-D	5-E
DTA Thermogram (Figure)	2	6-A	6-B	6-C	6-D

THERMAL GROUP III (OPEN COMPACT CONFIGURATION)

Chemical analysis and weight loss (Table V) as well as infrared spectral and differential thermal analysis (Figs. 7 and 8) of these thermal residues indicate no differences from the results found in the preceeding groups.

Table V. Thermal Group III (Open Compact Configuration)

	Original	500 hours		1000 hours	
		50 C	80 C	50 C	80 C
Hydrogen/nitrogen Molar Ratio	3.02	3.02	3.00	3.00	3.04
Weight Loss (%)	----	0.1	0.1	0.2	0.1
Infrared Spectrum (Figure)	7-A	7-B	7-C	7-D	7-E
DTA Thermogram (Figure)	2	8-A	8-B	8-C	8-D

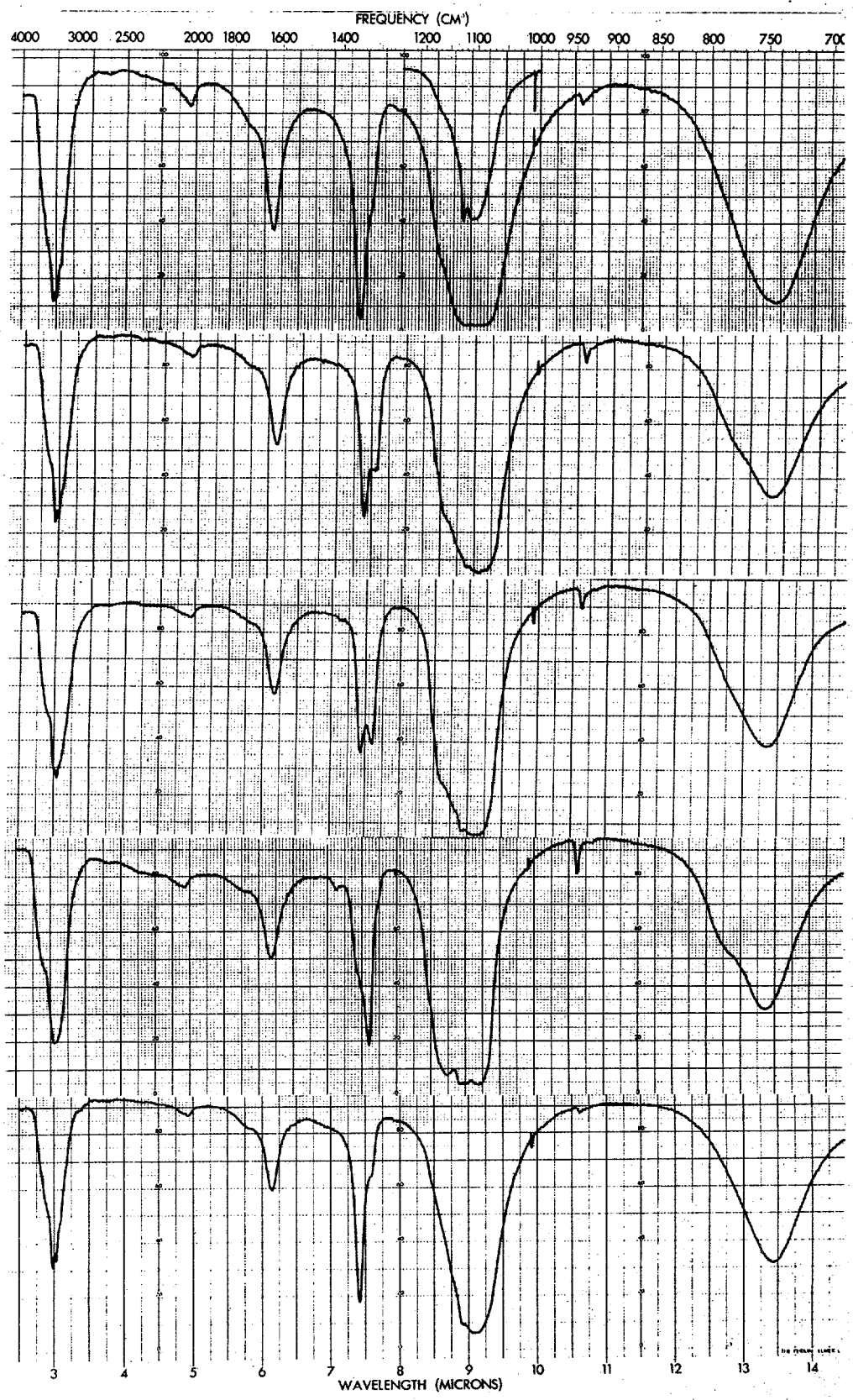


Fig. 5. Infrared Spectra of Closed Bulk Residues

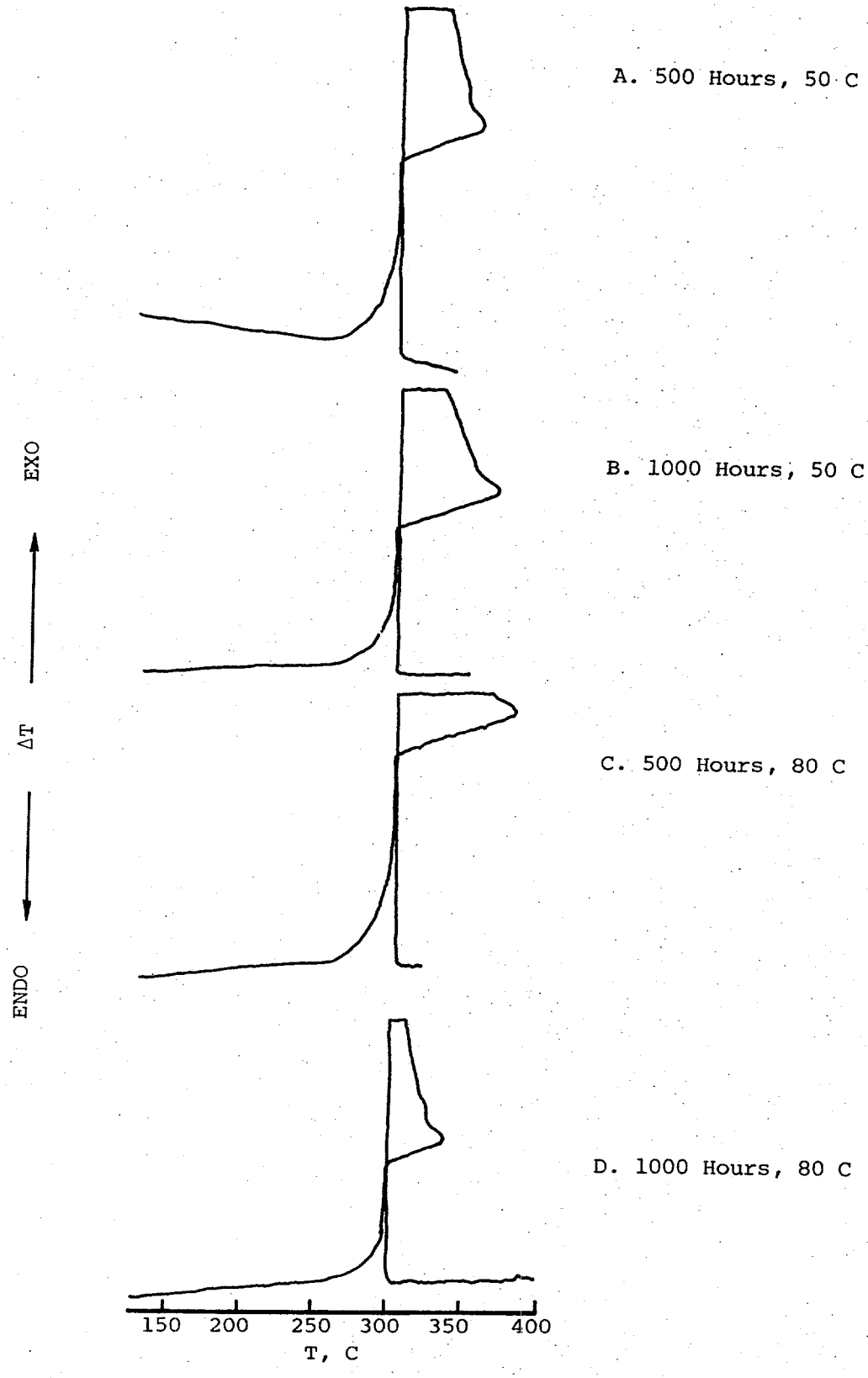


Fig. 6. DTA Thermograms of Closed Bulk Residues

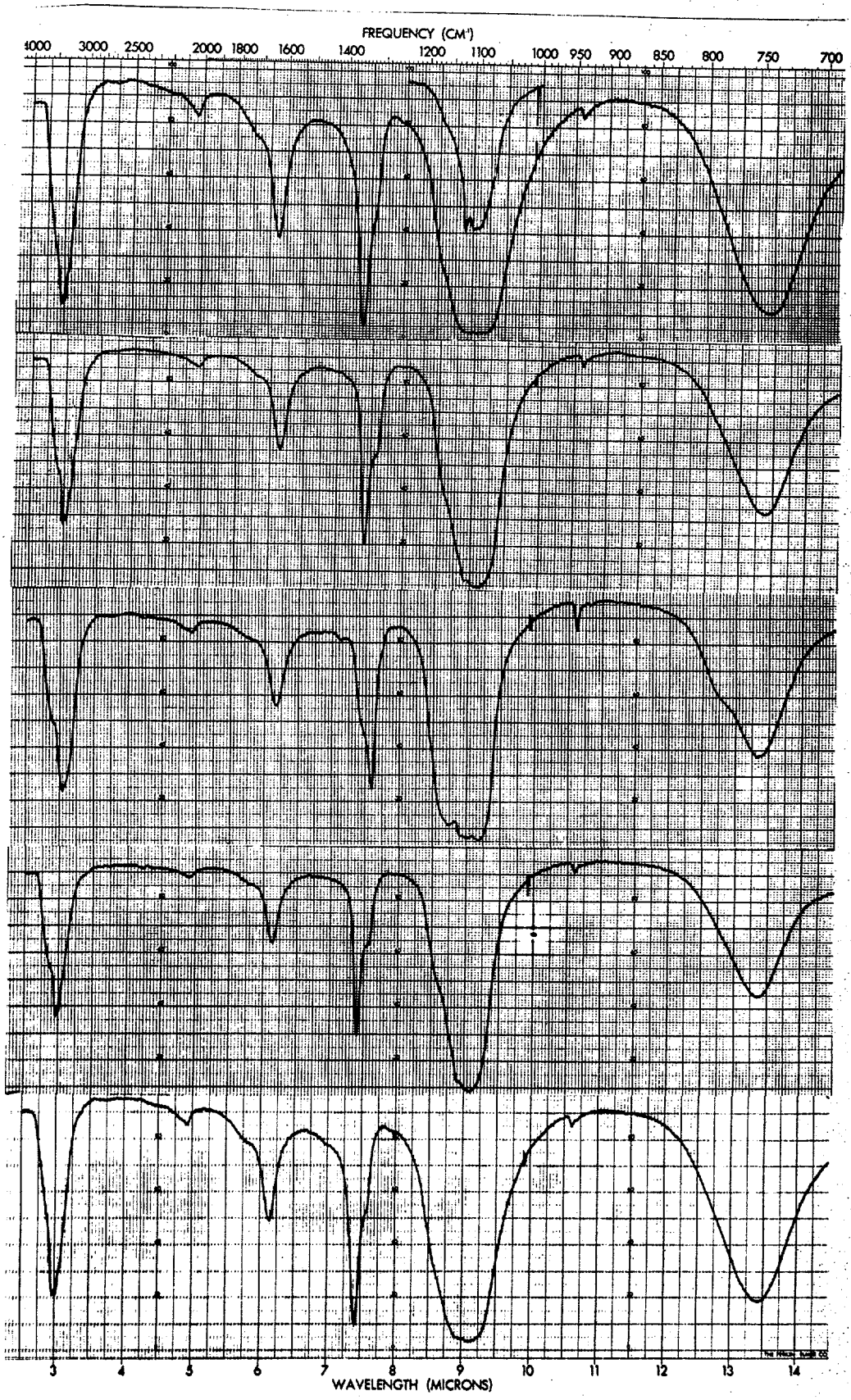


Fig. 7. Infrared Spectra of Open Compact Residues

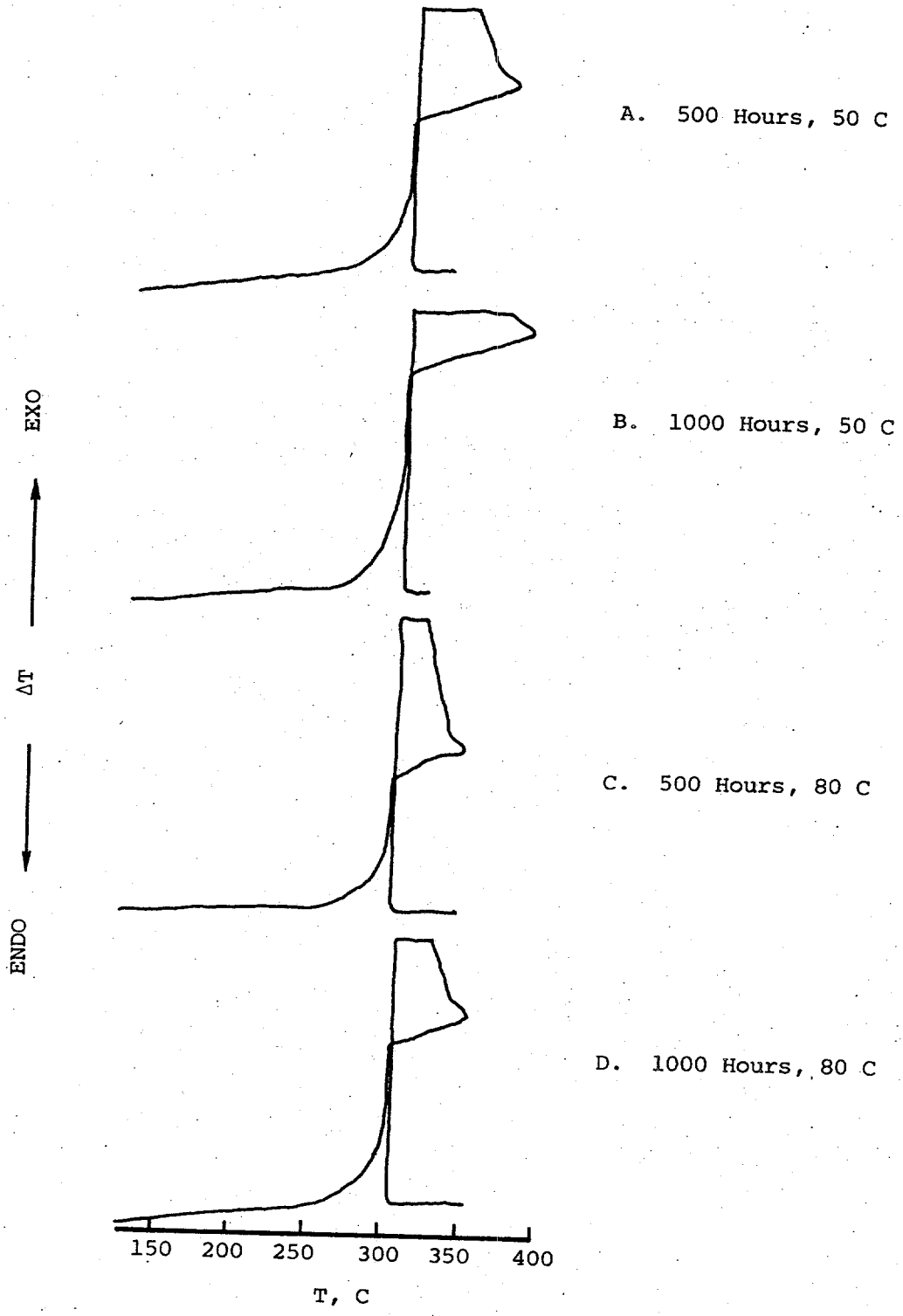


Fig. 8. DTA Thermograms of Open Compact Residues

THERMAL GROUP IV (CLOSED COMPACT CONFIGURATION)

There is no indication of anomalous behavior of this group relative to the previous three. Chemical, molecular, and thermal characteristics appear to be unaltered due to the thermal aging (Table VI, Figs. 9 and 10).

Table VI. Thermal Group IV (Closed Compacted Configuration)

		500 hours		1000 hours	
	Original	50 C	80 C	50 C	80 C
Hydrogen/nitrogen Molar Ratio	3.02	3.05	3.02	3.02	3.03
Weight Loss (%)	----	0.1	0.1	0.2	0.2
Infrared Spectrum (Figure)	9-A	9-B	9-C	9-D	9-E
DTA Thermogram (Figure)	2	10-A	10-B	10-C	10-D

SYSTEMS COMPARISON

The four system configurations, regardless of density difference (0.65 g/cc and 0.85 g/cc), temperature difference (50 C and 80 C), or elapsed time of aging (500 and 1000 hours) give no indication of instability in either molecular functionality (infrared spectral analysis) or thermal behavioral patterns (differential thermal analyses). Weight losses are $\leq$ 0.3% and are reasonably consistent. Hydrogen to nitrogen molar ratios remain essentially constant (0.1 - 0.3%).

The only anomalous behavior is in the spectral behavior of the symmetric deformation mode of the coordinated ammonia (NH_3, δs, $\sim$ 7.4μ). This same behavior was seen to occur in the cobalt III congener, HCP. It has been attributed to "inversion doubling" of the amine group in the d^2sp^3 ligand field(*1*). It is not considered a change in the molecular composition of the material.

The results of Henkin time-to-explosion runs (Fig. 11) show ACP to have much sharper temperature/time-to-explosion discrimination than that of HMX (used for relative comparison).

FIRING CHARACTERISTICS

EBW burst current studies with ρ = 0.92 g/cc show "go's" between 1.36 and 2.00 μsec at currents from 375 - 900 amps (Fig. 12). As found with the majority of amine perchlorate complexes of the transition metals, the material assumes slightly lower amperage thresholds after preaging of loaded systems (30 hours @ 100 C).

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(1) K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley (1963) p. 85.

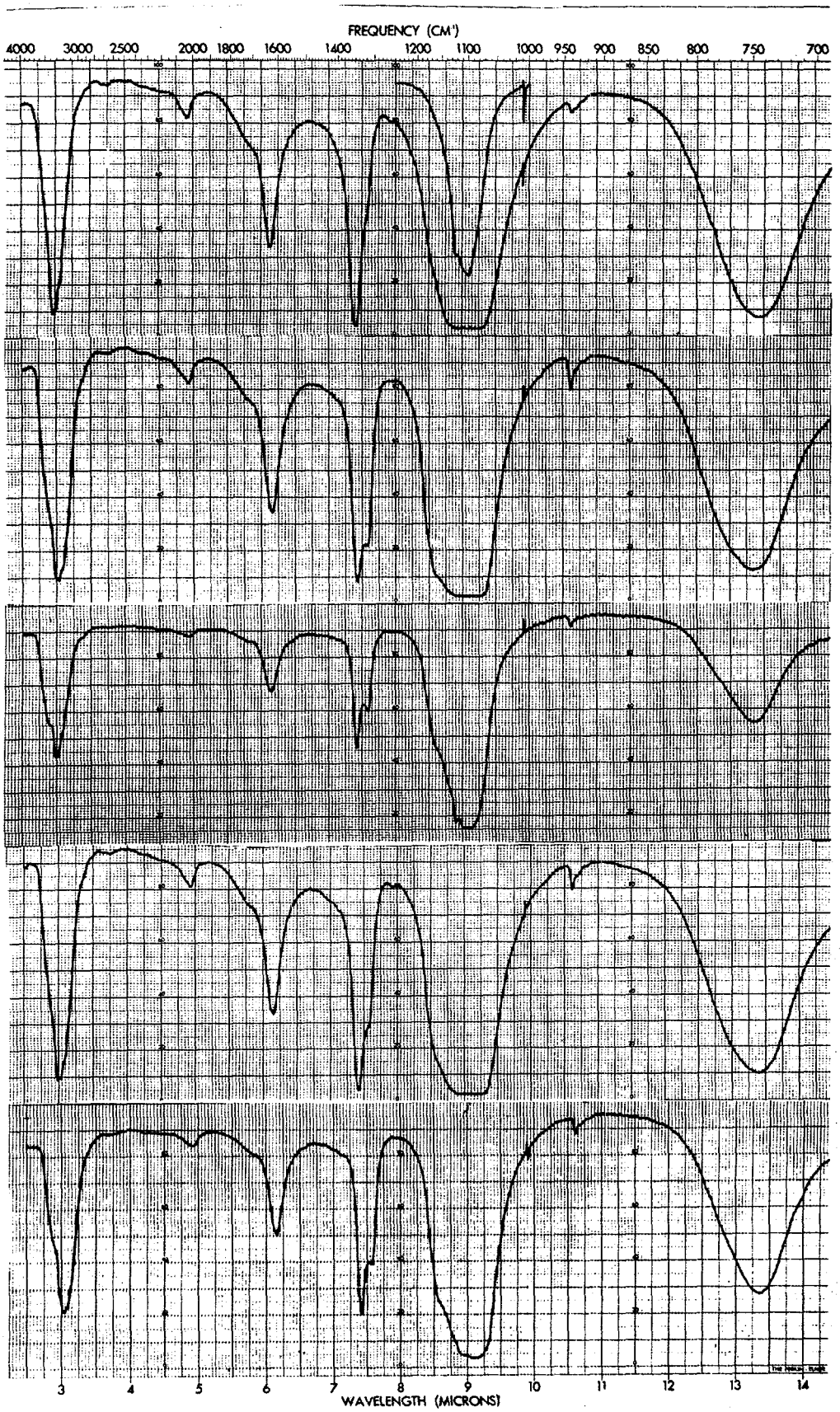

Fig. 9. Infrared Spectra of Closed Compact Residues

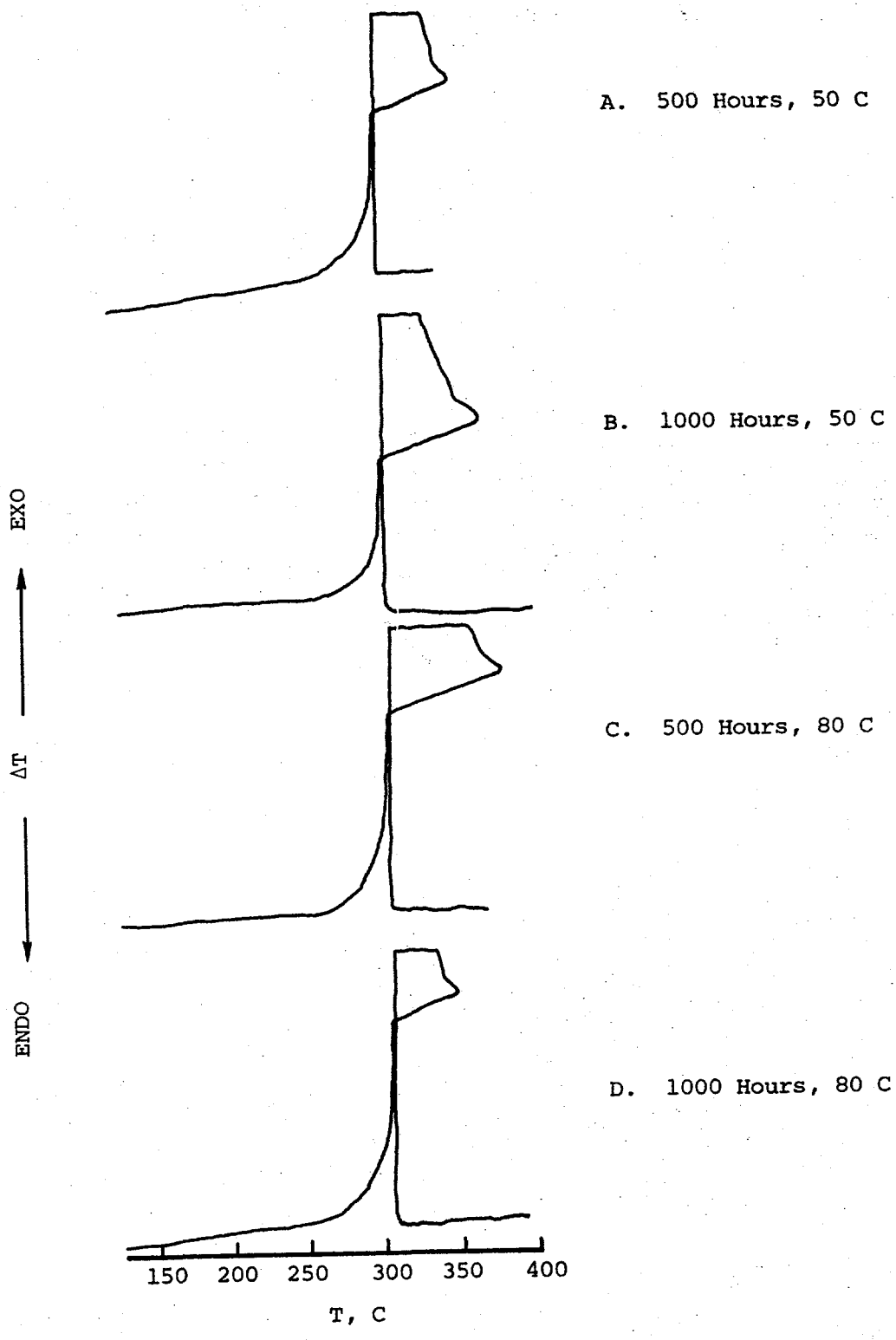

Fig. 10. DTA Thermograms of Closed Compact Residues

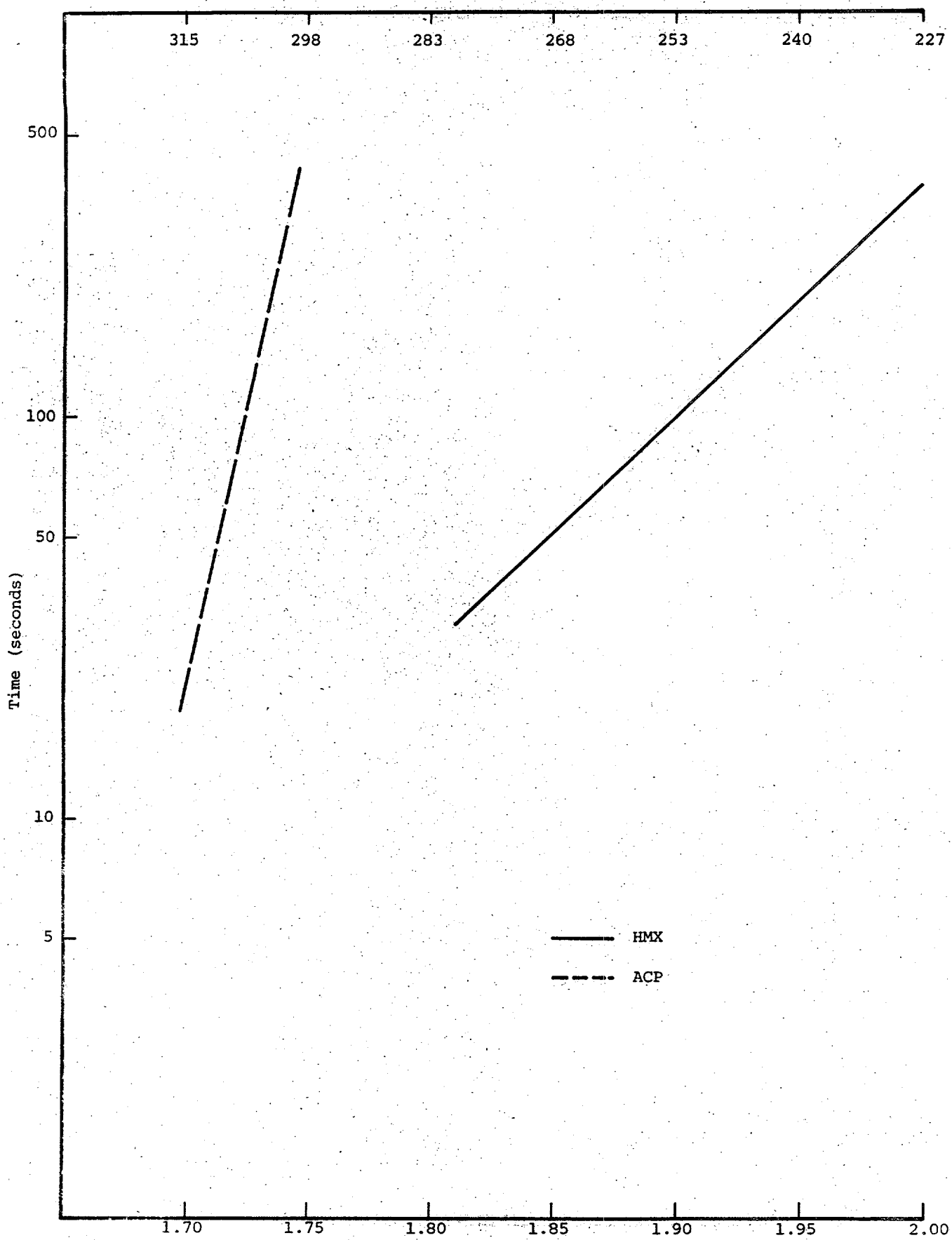

Fig. 11. Henkin Time-To-Explosion

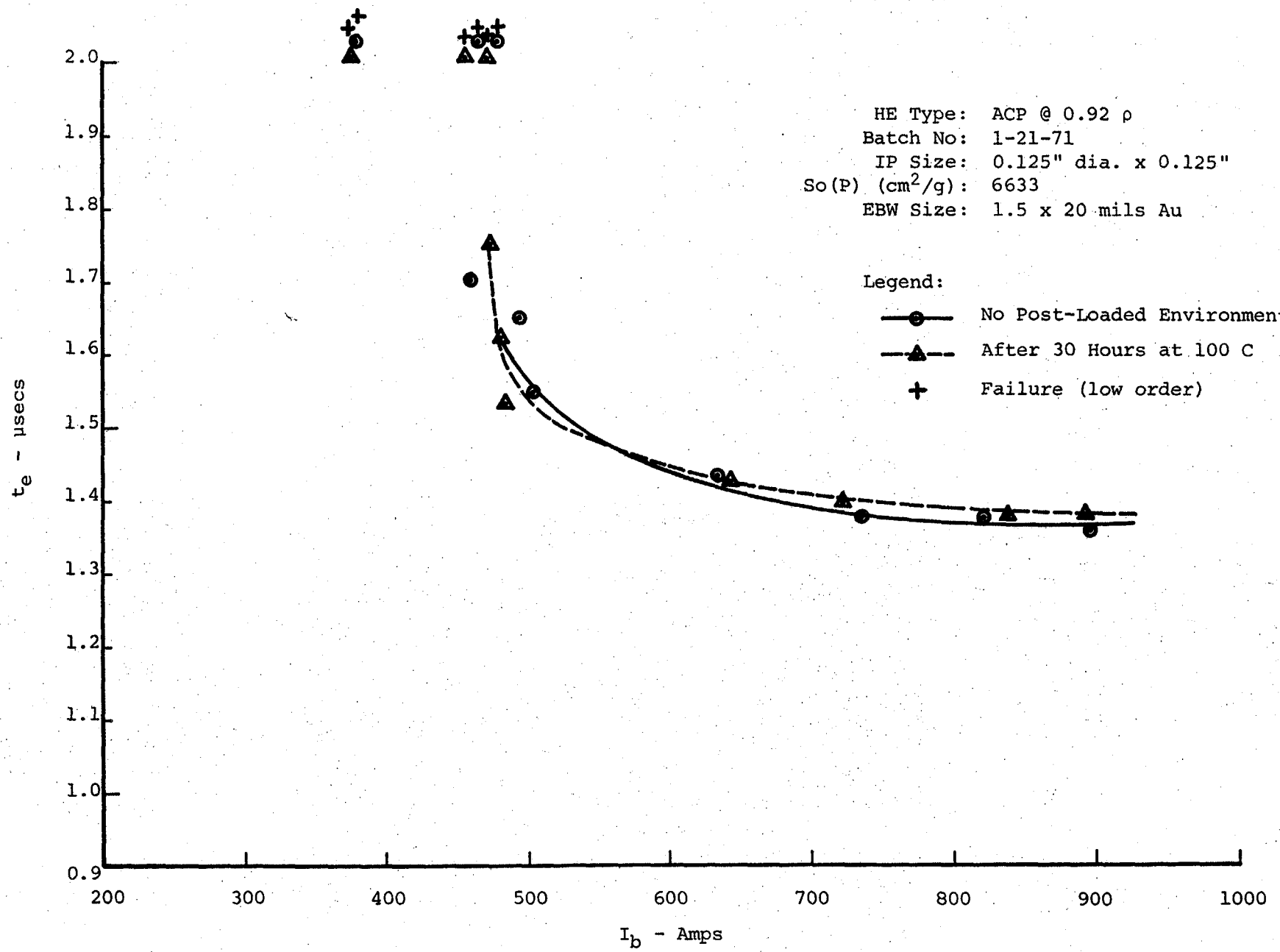

Fig. 12. Initial Pressing Transmission Time (t_e) vs. EBW Burst Current (I_b)

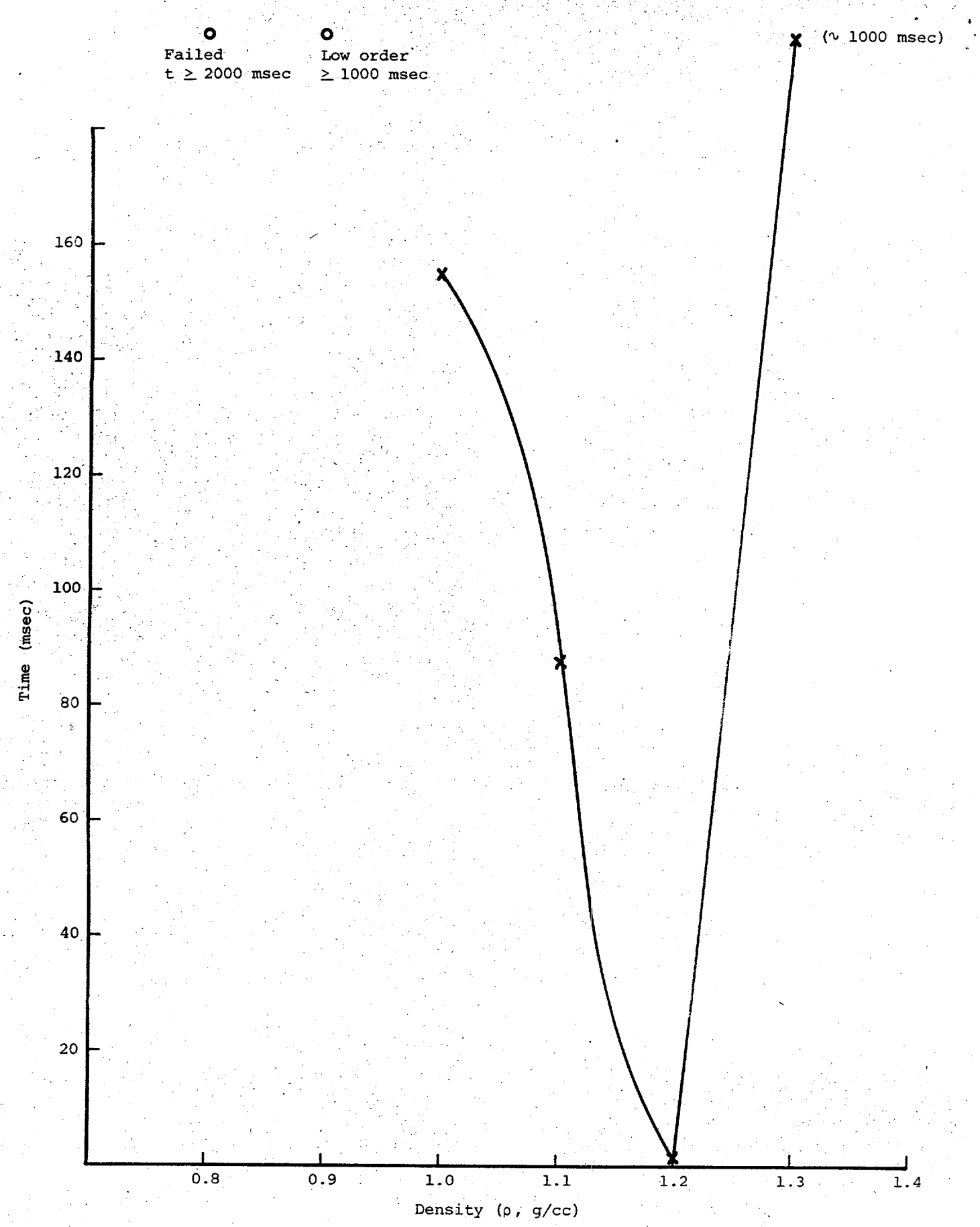

Fig. 13. Hot Wire Test Results (Firing Current 1.9 amps)

Hot wire test results (Fig. 13) show the optimum voltage threshold to be ∿ 5 watts (ρ = 1.2 g/cc, 1.5 msec). Beyond this density there is a sharp increase in time, similar to a sharp increase in time at densities below 1.2 g/cc.

COMMENTS

Based upon the apparent lack of chemical and thermal changes found in ACP as a result of thermal aging at 50 C and 80 C, this material, like its congener HCP, appears to be favorably stable and is quite similar in quiescent behavior to HCP, but has more attractive initiation characteristic (while probably not as promising as those of CEP).

These data will be utilized for the eventual overall evaluation of transition metal HE stability, firing characteristics and behavior as a cationic function.