

STABILITY AND COMPATIBILITY STUDIES WITH THE INORGANIC EXPLOSIVE  
2-(5-Cyanotetrazolato)pentaamminecobalt(III) Perchlorate (CP)<sup>\*</sup>

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ABSTRACT

2-(5-Cyanotetrazolato)pentaamminecobalt(III) perchlorate (CP) is an inorganic secondary explosive that has been developed for applications involving deflagration-to-detonation transition. Previously the primary explosives lead azide and lead styphnate had been used. Stability and compatibility studies with CP have been conducted for periods up to three years. By using the rate of formation of cobalt(II) as the prime stability measurement for CP no reaction above baseline has been observed at temperatures at or below 80°C. At 120°C, approximately 2.2% reaction has been measured after three years with the concentration approaching a constant value. With the typical materials of construction in low voltage detonators, no compatibility problems with CP have been found. Adhesives such as epoxies have also shown good compatibility characteristics with CP. The only material tested thus far that exhibits potential compatibility problems with CP has been copper.

INTRODUCTION

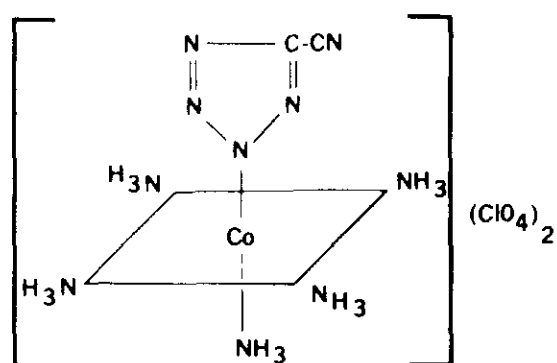
Nearly all low voltage, hot wire initiated explosive devices in the past have used primary type explosives as the initiating charge. In most designs the initiating primary explosive has been lead azide or lead styphnate. Because of the safety hazards involved in using such materials a major effort has been made at Sandia National Laboratories to develop new explosive materials that have the hot wire, low voltage initiating properties of a primary explosive but which do not exhibit the safety problems associated with such materials.

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A series of new explosive compounds based upon inorganic transition metal coordination compounds has been developed in this program (most of which were cobalt(II) perchlorate compounds (ref. 1)). In some cases the candidate materials possess the desirable safety properties such as impact insensitivity and low susceptibility to electrostatic initiation. But equally important, these materials can be initiated from a hot wire and achieve detonation within the short distances (less than 7 millimeters) required for detonator designs.

The explosive 2-(5-cyanotetrazolato)pentaamminecobalt(III) perchlorate has been the most promising material developed for these designs. Figure 1 shows the structure for this material which has been given the acronym CP.



2-(5-Cyanotetrazolato)pentaamminecobalt(III) Perchlorate

Fig. 1. Chemical Structure and Name of CP

Numerous reports have been published on the preparation, properties and use of CP, (refs. 2-5), some of which have been listed in Table 1. Because of its desirable properties, CP has been committed for use in several low voltage, hot wire detonators at Sandia National Laboratories. This study was initiated to provide data on the stability and compatibility of CP for use in long lived, high reliability explosive detonator designs.

#### CP STABILITY

Stability studies with CP have focused on three major areas of work. They are:

1. The stability of CP for use in long lived, high reliability components.
2. The effects of impurities and decomposition products on the decomposition of CP.
3. The effect of impurities and CP decomposition products on the compatibility of CP with other materials.

TABLE 1  
Properties of CP (refs. 4 and 5)

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Molecular Weight:	436.98 g/mol.
Color:	Yellow
Crystal Structure:	Monoclinic
Crystal Density:	1.974 Mg/m <sup>3</sup> (x-ray diffraction) 1.96 Mg/m <sup>3</sup> (Helium Pycnometer)
Coefficient of Thermal Expansion:	60 x 10 <sup>-6</sup> mm/mm-°K (25 to 50°C)
Heat Capacity:	$C_P \left( \frac{\text{cal}}{\text{g}^\circ\text{K}} \right) = 0.1545 + 0.0003 T \text{ (}^\circ\text{K)}$ (353 - 453°K)
Moisture Uptake at 95% RH:	0.15 w/o at ambient temperature
Impact Sensitivity:	~40 cm loose powder (2 kg weight)
Electrostatic Sensitivity:	Greater than 20 kV at 600 pF and 500 ohms (loose powder and unconfined pellet)
Detonation Velocity:	$D^* \left( \frac{\text{km}}{\text{s}} \right) = 0.868 + 3.608 \rho_0 \text{ (Mg/m}^3\text{)}$

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Searcy and Shanahan (ref. 6) have studied the thermal decomposition of CP at temperatures from 150°C to 260°C by a variety of techniques. Their work dealt with understanding the decomposition mechanisms of CP and the kinetics of decomposition in this temperature regime. They concluded that CP decomposition is a heterogeneous, solid-to-gas reaction that proceeds in three stages, with multiple and parallel paths (ref. 6). They also concluded by extrapolation that CP would be stable in the temperature range of ambient to 70°C.

The decomposition mechanisms proposed by Searcy and Shanahan may be summarized as follows (ref. 6). Stage I is an endothermic process which includes the dissociation of ammonia ligands from the cobalt atom, rearrangement of the 5-cyanotetrazolato ligand to produce a nitrogen molecule and unidentified solid species, and the oxidation-reduction reaction of cobalt(III) with ammonia to produce cobalt(II), nitrogen and ammonium ion. Stage II is the oxidation of the ligands around the cobalt atom by the perchlorate ion. Stage III is the oxidation of the residual solid products by the perchlorate ion.

Stability data have now been obtained with CP loaded components in the temperature range from ambient to 120°C. Hermetically sealed CP loaded devices have been aged for periods up to three years. After aging, the detonators were disassembled for examination by the scanning electron microscope and the CP removed for analysis.

The amount of cobalt(II) formed during aging was established as the stability criterion for CP since cobalt(II) formation occurs during the first stage of decomposition. A spectrophotometric technique was developed to determine the concentration of cobalt(II) (ref.

7). The detection limits of this technique have been established at 100 ppm cobalt(II) in the solid CP samples. However, due to the nature of the solvent system, sample sizes, instrumentation, and the nature of sample collection techniques, the accuracy of the method is limited to 500 ppm  $\pm$  200 ppm cobalt(II) (ref. 7).

Table 2 lists cobalt(II) analyses of CP from the detonator aging program. Even though cobalt(II) values of less than 500 ppm have been reported, these values are believed to be identical within experimental error. CP has shown no measurable decomposition at temperatures of 80°C or below for periods up to three years. At 120°C, CP decomposes in less than 612 days and displays a fairly constant cobalt(II) concentration for time periods from 612 to 1078 days (3 years). Calculations involving the cobalt(II) concentration indicate that approximately 2.2% of the CP has decomposed. One of the 1078 day (3 year), 60°C samples displayed an anomalous high cobalt(II) concentration (1370 ppm) which cannot be readily explained. This aging program has been continuing with the preliminary conclusion that no stability problems with CP are likely to exist in a detonator design for temperatures up to 80°C and three years.

TABLE 2

Co<sup>+2</sup> analysis of CP removed from aged mini-dets

Environment	PPM Co <sup>+2</sup> Present After Aging		
	612 Days	795 Days	1078 Days
Room Temp.	166	301	456 $\pm$ 215
	334	630	778 $\pm$ 209
	<100		
	<100		
60°C	254	383	639 $\pm$ 169
	<100	355	1370 $\pm$ 134
	313		
80°C	299	461	463 $\pm$ 93
	824	542	839 $\pm$ 171
120°C	3710	3070	3160 $\pm$ 218
	2270	4557	4180 $\pm$ 138
	2700		
	3150		

A comparison of these data with that obtained from Searcy and Shanahan's low temperature extrapolation indicates general agreement. The results of the two studies show that the cobalt(II) concentration from CP decomposition should be below 800 ppm at temperatures below 80°C and therefore not measurable. The average CP decomposition of

2.2% from the 1078 day, 120°C aging was also in reasonable agreement with the 1.3% decomposition predicted by Searcy and Shanahan.

Thermal analysis of CP shows the three stage heterogeneous decomposition process. Figure 2 is a differential scanning calorimeter (DSC) trace for CP under two different sets of conditions; the sample used for curve A was contained in a hermetically sealed minimum volume aluminum sample cup whereas the CP sample for curve B was in an open aluminum cup where the decomposition gases were swept away by a 100 cm<sup>3</sup> min<sup>-1</sup> argon purge gas. Curve A of Figure 2 shows the three stage decomposition process of CP starting with the weak endothermic response (Stage I) at about 270°C, quickly followed by a broad exothermic response (Stage II) and ending with a sharp second exothermic response (Stage III). Much of the magnitude of the endothermic response has been masked by the dominant, more energetic first exothermic response (Stage II). Curve B of Figure 2 shows the initial endothermic response as in Curve A but only one exotherm. In addition both the endothermic and exothermic responses have been shifted to lower temperatures in the open environment.

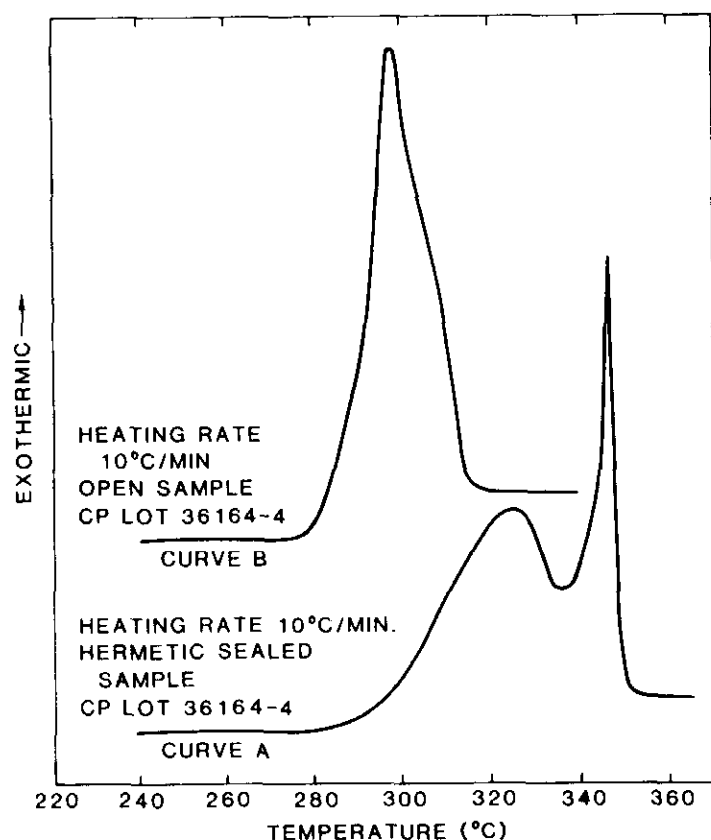


Fig. 2. CP DSC thermal analysis curves hermetically sealed sample versus open sample.

Since ammonia (NH<sub>3</sub>) plus other reaction products were part of the first stage of CP decomposition, it was felt that one of the decomposition products, particularly ammonia, could be inhibiting the decomposition reaction in the sealed environment (ref. 8). Further work

by Reed has established that the presence of excess gaseous ammonia shifts the decomposition reaction of CP to a higher temperature (ref. 9). For example the DSC exotherm was shifted some 20 to 30°C upwards while isothermal thermogravimetry at 235°C shifted the decomposition time from 50 minutes to more than 100 minutes.

Two thermal analysis procedures were used to determine the effects of impurities and reaction products on the decomposition of CP. The first procedure was based upon a first order reaction of a solid to a solid plus gas under nonisothermal conditions using the equation derived by Kissinger (refs. 10-12). The basic equation was:

$$\frac{d \ln(\phi/T_m^2)}{d(1/T_m)} = - \frac{E_A}{R}$$

where

$\phi$  = heating rate,

$T_m$  = temperature maximum or peak temperature of the DTA or DSC exotherm,

$E_A$  = Arrhenius activation energy, and

$R$  = universal gas constant.

For a first order reaction, a plot of  $\ln(\phi/T_m^2)$  versus  $1/T_m$  will yield the Arrhenius activation energy. The temperature shifts in the peaks were obtained by running the DSC at various heating rates (Figure 3.) Both open and hermetically sealed samples were investigated.

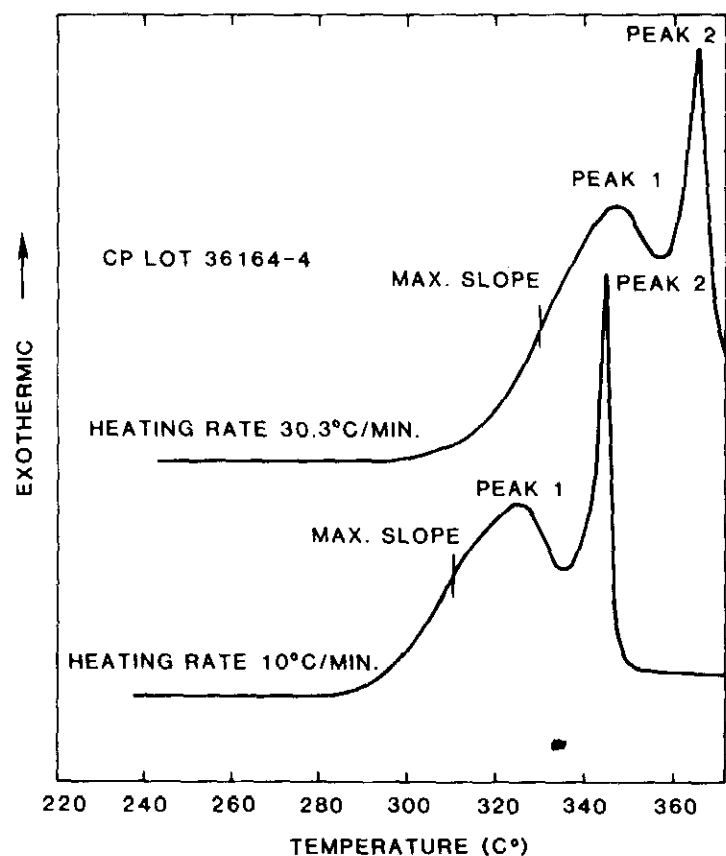


Fig. 3. Shift in DSC exotherm of CP with heating rate (hermetically sealed sample).

The second procedure was an isothermal technique which employs a Dupont 990 Thermal Analysis system and utilizes a modified procedure after the one developed by Rogers for organic explosive materials (ref. 13). The CP sample was loaded into an open cup configuration and placed in an isothermally stabilized DSC cell. The time to peak of the decomposition curve (Figure 4) was plotted against the reciprocal of the absolute isothermal temperature in a typical Arrhenius plot.

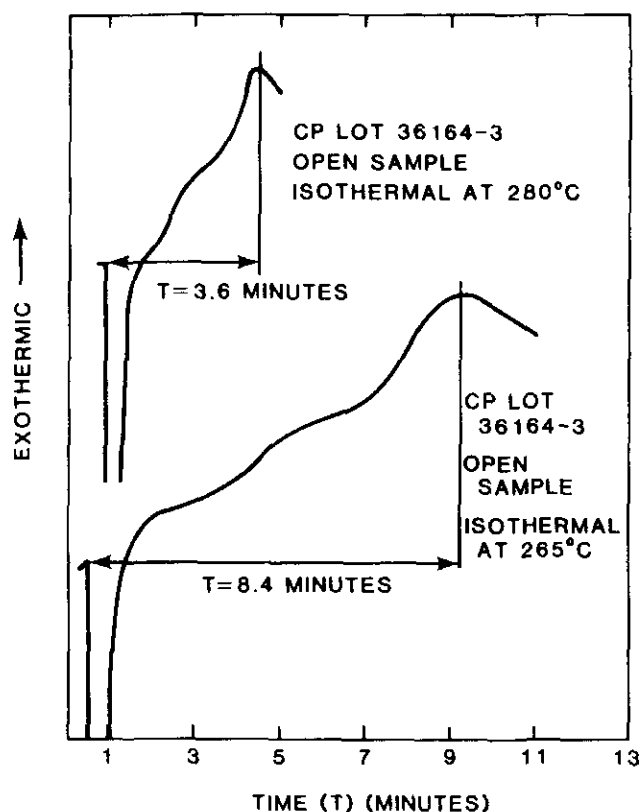


Fig. 4. Isothermal analysis of CP.

Figure 5 shows plots for three different lots of CP. As will be discussed later, this technique has been used as a screening procedure for CP compatibility.

During the preparation of CP, significant amounts of the impurity 5-carboxamidotetrazolatopentaamminecobalt(III) perchlorate (called the "amide complex") (Figure 6) have been obtained. Having a chemical structure and solubility properties similar to CP, amounts up to 10 percent have been found. By using the above thermal analysis technique no effect on the activation energy or shifts in the temperature (or rate) could be found for various CP lots containing varying amounts of the "amide complex" from one (1) to ten (10) percent. Tables 3 and 4 show no significant variations in the activation energy as a function of the "amide complex" concentration. These activation energies have a precision of  $\pm 3$  kcal/mol. Figure 5 shows the Arrhenius plots for the three lots of CP with varying amide complex concentrations showing

no shift in the curves which indicate no autocatalysis or inhibition of the decomposition reaction.

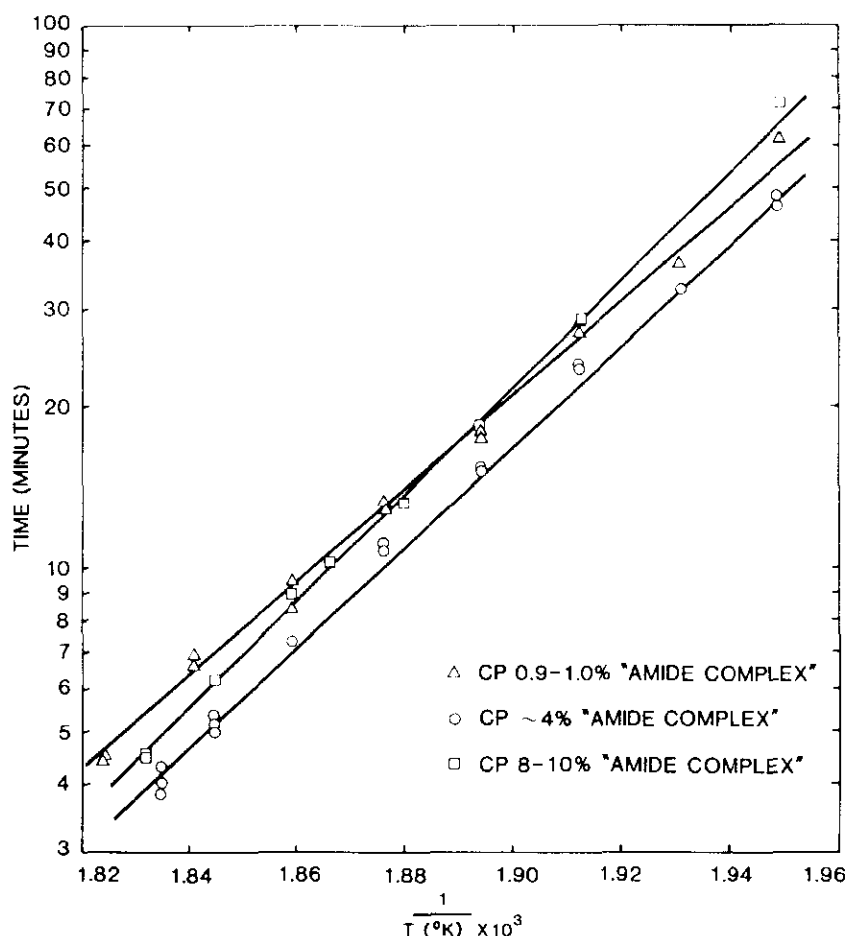


Fig. 5. Isothermal kinetic DSC analysis of CP effect of "amide complex" concentration.

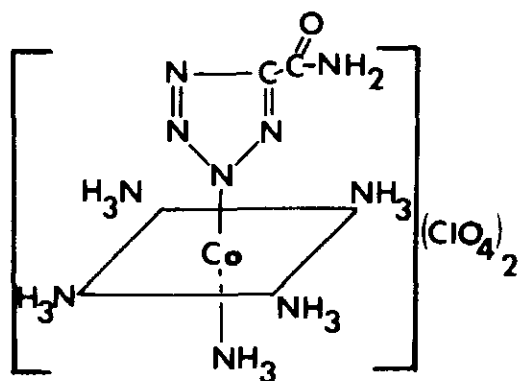


Fig. 6. Proposed chemical structure of the "amide complex".

In a similar manner, both procedures were used to examine any similar effects of the decomposition products on CP. Tables 5 and 6 list the activation energies obtained for the aged CP powders. Again the precision was  $\pm 3$  kcal/mol.

Figure 7 shows the Arrhenius plot for the isothermal experiments on the aged samples. No variation in the activation energy or shifts in the Arrhenius plots could be found, even for the 120°C aged CP containing 2.2% decomposition products.

The data listed in Tables 4 and 6 are a combination of the activation energies from all the competing reactions taking place in one



Table 3

Activation energy (kcal/mol) of CP with varying amounts of the "Amide Complex" (non-isothermal method - hermetically sealed sample)

Exothermic Response	Sample		
	Lot 36353A 0.9 - 1.0% "Amide Complex"	Lot 47344 ~ 4% "Amide Complex"	Lot 36164 8 - 10% "Amide Complex"
Maximum Slope (1st exotherm)	27.4	31.3	27.9
Peak Maximum (1st exotherm)	29.8	32.2	32.3
Peak Maximum (2nd exotherm)	34.4	43.7	42.1

Table 4

Activation energy (kcal/mol) of CP with varying amounts of the "Amide Complex" (open sample)

	Sample		
	Lot 36353A 0.9 - 1.0% "Amide Complex"	Lot 47344 ~ 4% "Amide Complex"	Lot 36164 8 - 10% "Amide Complex"
Non-isothermal method	44.4	49.6	39.2
Isothermal method	43.4	42.9	41.7

Table 5

Activation energy (kcal/mol) of CP from aged detonators (non-isothermal method - hermetically sealed sample)

Exothermic Response	CP Sample							
	Amb.	612 Days			Amb.	1078 Days		
		60°C	80°C	120°C		60°C	80°C	120°C
Maximum Slope (1st exotherm)	31.7	30.8	31.5	32.4	30.8	35.1	30.1	32.5
Peak Maximum (1st exotherm)	32.7	32.6	31.5	33.6	30.5	30.7	34.8	38.4
Peak Maximum (2nd exotherm)	45.6	44.8	42.3	40.9	48.7	39.7	44.4	46.8

Table 6

Activation energy (kcal/mol) of CP from aged detonators (isothermal method - open sample)

CP Unaged Powder	Sample		
	CP 60°C 812 Days	CP 80°C 812 Days	CP 120°C 812 Days
42.9	42.5	42.4	42.4

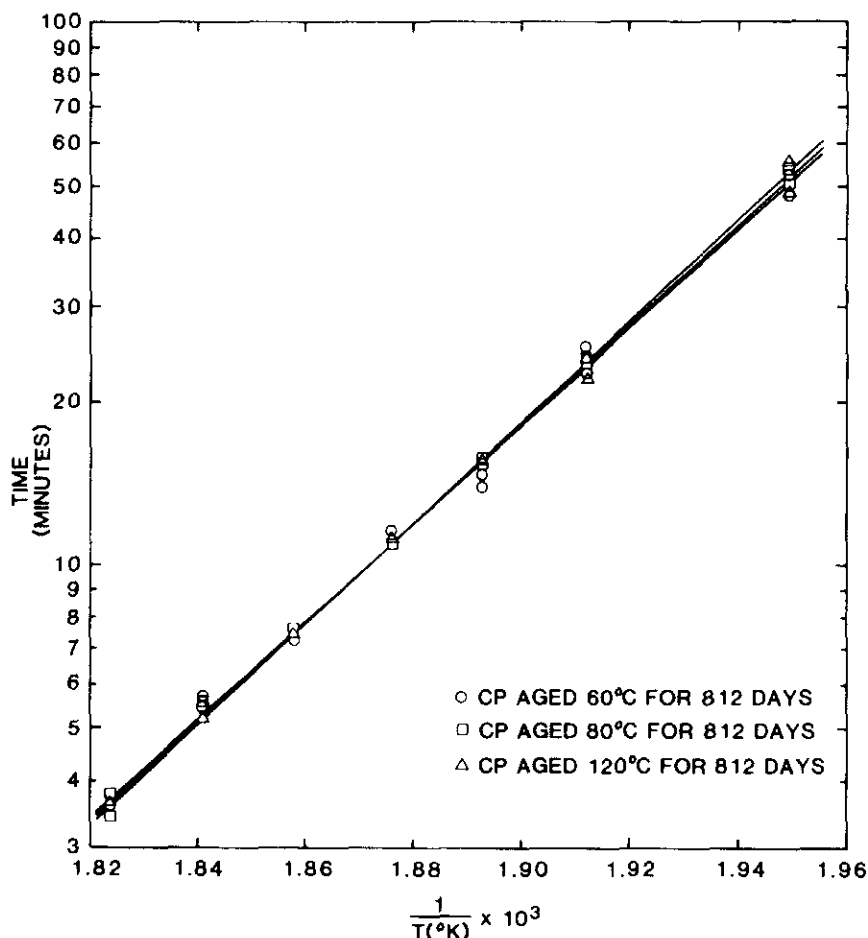


Fig. 7. Isothermal kinetic DSC analysis of CP, effect of decomposition products

single exothermic response whereas the data in Tables 3 and 5 are activation energies of two separate reaction steps. Therefore these data are not expected to be comparable. The variation in activation energies between the first and second exothermic responses in Tables 3 and 5 are consistent with the findings by Searcy and Shanahan.

From these results, it can be concluded that the solid decomposition products and impurities in this study have no apparent autocatalytic or inhibitive effect on the CP decomposition. Gaseous decomposition products such as ammonia inhibit the decomposition by shifting the reactions to higher temperatures.

#### CP COMPATIBILITY

In addition to being stable a new detonator material must also demonstrate compatibility with the environment around it. For our applications the material must be compatible with design materials, especially the detonator bridgewire, electrode pins and weld interface.

Various decomposition products can be produced from CP such as ammonia and water plus ammonium ( $\text{NH}_4^+$ ), chloride ( $\text{Cl}^-$ ) and cyanide ( $\text{CN}^-$ ) ions. For thermally reacted samples all of the above have been found to be present in CP. With other energetic materials some of these species have been known to cause corrosion directly or indirectly of

metallic materials. Impurities from the CP synthesis steps such as nitrate ( $\text{NO}_3^-$ ) and perchlorate ( $\text{ClO}_4^-$ ) ions can also be present and lead to compatibility problems.

The primary technique used to evaluate the compatibility of these materials with CP has been scanning electron microscopy (SEM) which can readily detect the presence of corrosion or reaction products on the various materials. Scanning electron microscopy has been previously used to evaluate compatibility of pyrotechnic materials with component design materials and has been successful in the detection and monitoring of corrosion which occurred in these designs (refs. 14-15).

Detonator housings with the CP removed for cobalt(II) analyses were examined for corrosion and other compatibility problems with the scanning electron microscope. No evidence of corrosion or reactions taking place were observed for periods up to three years and temperatures from ambient to 120°C for any of the materials listed in Table 7.

Table 7

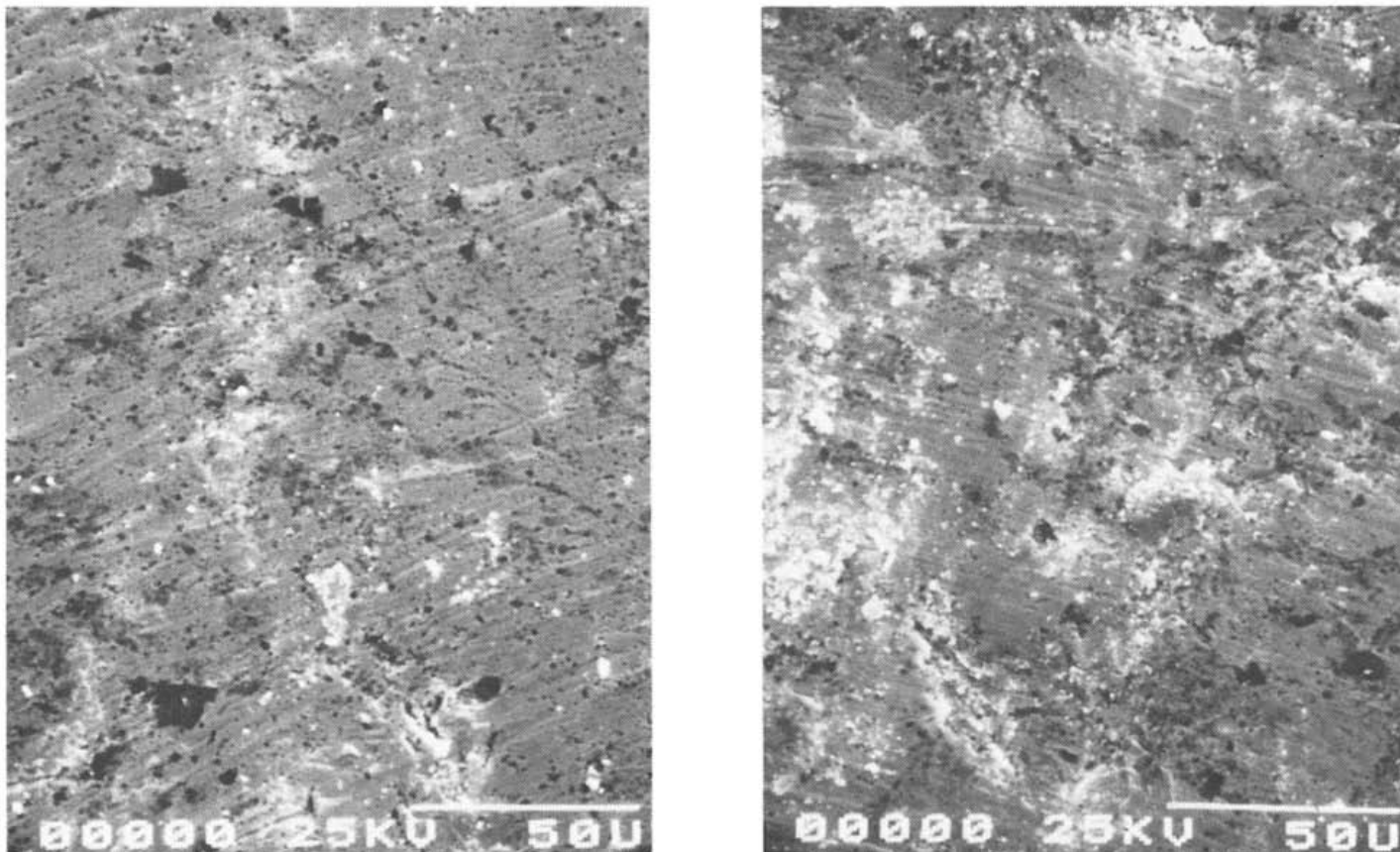
Detonator design materials employed in compatibility evaluations

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1. Bridgewire: Tophet A (Nichrome alloy)
  2. Electrode Pins: Kovar
  3. Weld Junction: Laser weld of the Tophet A and Kovar
  4. Metallizing: Molybdenum/Nickel Oxide
  5. Ceramic Braze: Silver
  6. Ceramic Insulator: Diamonite (95%)
  7. Detonator Housing and Closure Disk: Stainless Steel 304
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Figures 8 and 9 are typical SEM photomicrographs of the electrode pin and bridgewire surfaces, respectively, after three years aging at 120°C. No compatibility problems were observed, although significant reaction of the CP powder had occurred for the 120°C samples resulting in potentially active decomposition products.

Other compatibility studies with CP have also been conducted. CP mixed with the pyrotechnic boron/calcium chromate ( $\text{B/CaCrO}_4$ ) and pressed with Tophet A and Kovar wires have shown no compatibility problems of the wire materials after eight (8) months aging at ambient 50 and 92 percent relative humidities and thermal environments up to 120°C. No reaction between the calcium chromate and CP has been observed for thermally aged samples up to 120°C or the ambient and 50 percent relative humidity samples. At 92 percent relative humidity, a few small (5 microns or less) crystals of the chromate analog of CP were identified within the mixture after eight (8) months aging. Solution chemistry experiments with CP and chromate ( $\text{CrO}_4^{2-}$ ) ions dissolved in



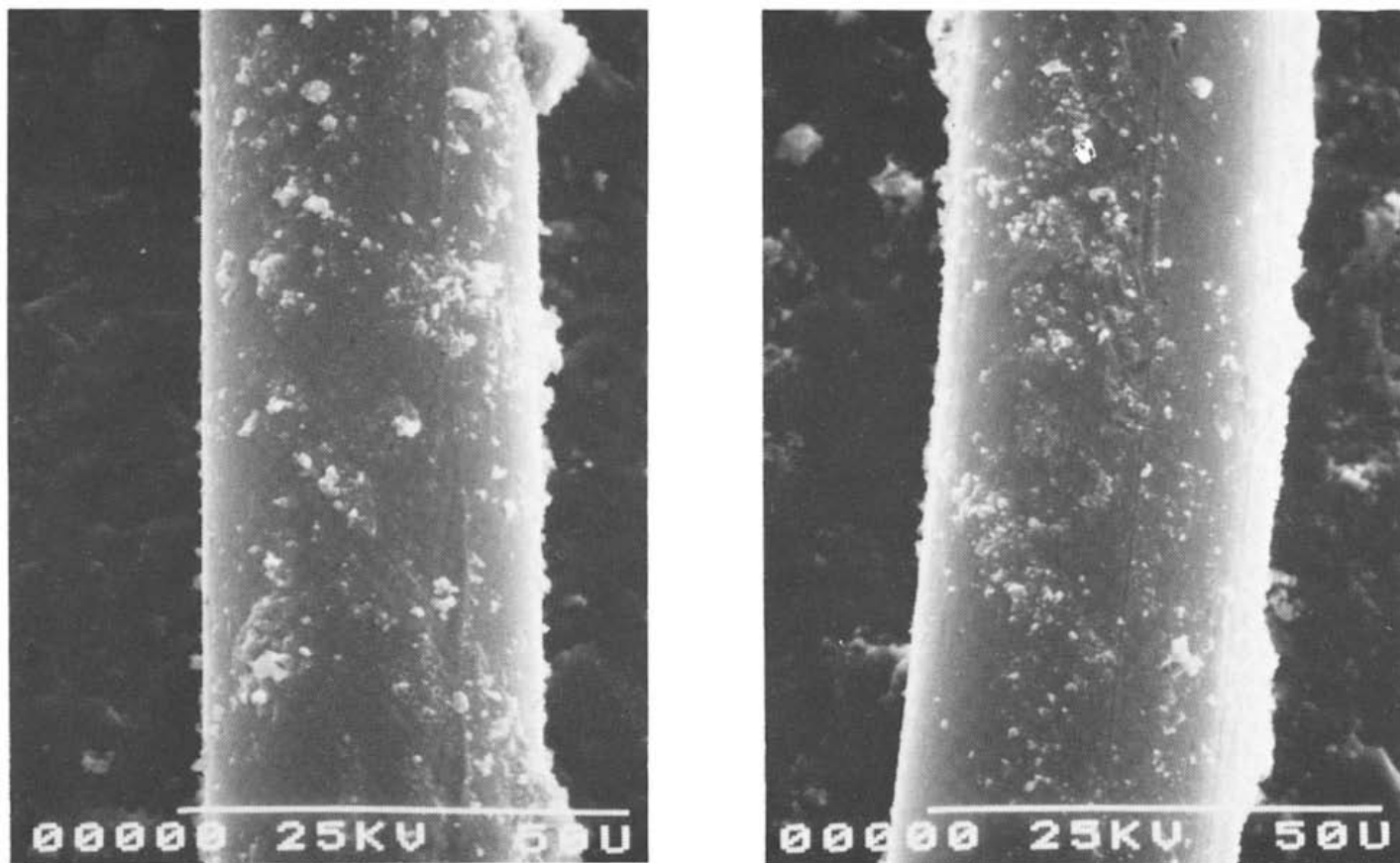
60°C/1078 days

120°C/1078 days

Fig. 8. SEM photomicrographs of Kovar pins in contact with CP

water predicted this result for high humidity conditions because a compound, inferred to be the chromate analog of CP precipitated stoichiometrically. Under normal humidity conditions (50 percent or less) and thermal environments, none of the chromate analog has been found.

The main screening technique for determining the compatibility of CP with other materials has been the isothermal DSC procedure previously described in the stability section. Figure 10 shows typical reaction rate plots for Arrhenius activation energy of copper powder mixed with CP, alumina mixed with CP and CP. No variations were observed in the activation energy reaction rate curves for the alumina mixed with CP compared to CP alone. For the copper mixed with CP sample a significant increase in the decomposition rate compared to CP was observed along with a decrease in the activation energy (Table 8). Follow-up studies utilizing copper wires pressed against CP powder have resulted in some corrosion of the copper wire when subjected to a 120°C



60°C/1078 days

120°C/1078 days

Fig. 9. SEM photomicrographs of Tophet A bridgewires in contact with CP

Table 8

Activation energy of CP compatibility samples

	Activation energy (kcal/mol)
CP lot 36164	41.7
CP lot 47344	42.9
CP plus Alumina (50/50 mix)	41.1
CP plus Copper (50/50 mix)	34.7

environment. Cobalt(II) analysis of equal mixtures of CP and copper powder which had been aged for two days at 120°C yielded values 3 to 4 times above pure CP similarly aged. CP has been found to be incompatible with copper and should not be considered for designs which contain copper. CP is considered compatible with alumina.

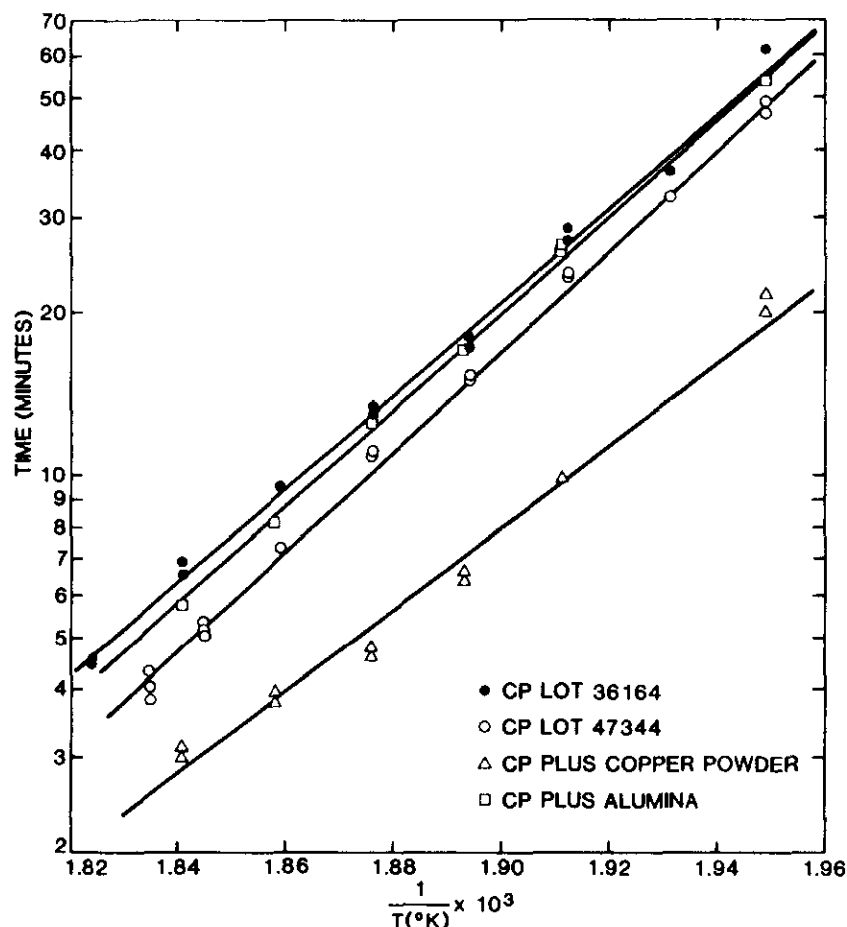


Fig. 10. Isothermal kinetic DSC analysis of CP compatibility studies

Amine and anhydride cured epoxy materials in the cured and uncured conditions have shown no compatibility problems with CP. This is in contrast with organic explosives and amine cured epoxy materials where numerous compatibility problems exist. The primary short term test for compatibility of CP with adhesives has been the chemical reactivity test (CRT) which measures the type and quantity of evolved gases due to reaction between the materials in question. Follow-up studies of these epoxy materials with CP for periods up to four months and temperatures up to 120°C have also revealed no compatibility problems occurring. Currently all uses of epoxy materials with CP have lifetime requirements of four months or less; therefore, no long term data have been generated.

#### CONCLUSIONS

Based upon the above data the following conclusions pertaining to CP stability and compatibility have been drawn.

1. CP has been shown to be thermally stable up to temperatures of 80°C for three years.
2. CP will undergo decomposition at 120°C.
3. Impurities and decomposition products in CP do not affect its decomposition.

4. Gaseous decomposition products such as ammonia shift the decomposition of CP to higher temperatures.
5. CP has been found compatible with most metallic, ceramic and epoxy materials used in typical detonator designs.
6. CP has been found incompatible with copper.
7. The isothermal DSC technique described has been shown to be a useful screening technique for compatibility testing of CP. It cannot be used to determine compatibility with materials that decompose at temperatures below the decomposition temperature of CP.

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