THE IDENTIFICATION AND SAFE LIFE PREDICTION OF HAZARDOUS MATERIALS

V. DAUGHERTY

Thiokol Corporation, Wasatch Division, Brigham City, Utah

ABSTRACT

   A suitable test for measuring the relative thermal stability of propellants containing nitrate esters is important not only for production controls, but also in defining the time and temperature at which this formulation can be safely stored. Over the years a number of tests have been developed for this purpose. However, most of these methods require either too much time or too sophisticated equipment to be implemented into inprocess control. This report explains an isothermal time to autoignition method which is presently being used to identify potentially hazardous materials, and the Ozawa method of predicting the half life of these substances. Other methods of identifying hazardous materials and predicting safe life are presented along with the reasons these techniques are not being utilized at Thiokol/Wasatch.

INTRODUCTION

   The potential hazards associated with the handling and processing of energy rich compounds require the development of tests that predict the relative stability as a function of time and temperature. Several incidents are recorded where either the autocatalytic decomposition as a function of time was not monitored (in some cases the test frequency was inadequate), or the particular analytical technique could not accurately predict the thermal properties of the substances. Although test techniques have been developed and generally the safety record in industry is very good, there have been materials that underwent unexpected rapid decomposition resulting in the loss of instruments, equipment, buildings, etc. Some of the methods used to analyze the variety of materials include: gas evolution, time-to-autoignition, stabilizer depletion, thermogravimetric, and several differential scanning calorimeter techniques.

   This report is divided into two general topics: (1) identification of the hazardous nature substances and mixtures and (2) methods of predicting the time and temperature of safe handling. Although several techniques have been evaluated, the two methods that best meet the requirements in terms of equipment cost,

sensitivity and analysis time are the time-to-autoignition for identification of hazardous materials and the Ozawa method of half life prediction for time and temperature of safe handling. These methods are described and the data showing the precision of the test presented. Other methods used at Thiokol/Wasatch Division are briefly outlined in the appendix.

OBJECTIVE

   The objective of this report is to present the techniques used for identifica-tion of hazardous material and safe life predicting and to indicate some of the advantages of these methods.

DISCUSSION

   There are several widely used methods to identify hazardous materials or the presence of substances that have altered the stability of known materials. The test technique used to accomplish this must be sensitive, yet easily adapted to a routine inprocess test. At the Thiokol/Wasatch Division, the method that best meets the requirements of not only identifying hazardous materials, but yields an indication to the degree of autocatalytic decomposition is the time-to-auto-ignition (or induction time). This method is presently being used as an inprocess control and has identified mixes of a nitrate ester propellant having signifi-cantly less time to ignition than normal for that formulation.

   After identifying mixes with less stability than normal, it is necessary to determine if these mixes can be safely processed then stored before using, which is the second topic of this report, methods of predicting the safe life. In our particular situation, the time between the identifying the relatively unstable material and when processing can be continued with no detrimental side effects is limited. This eliminates many of the generally accepted methods of safe life pre-diction. The method that best meets requirements at Thiokol/Wasatch Division is the variable heat rate method of Ozawa (ref. 1 and 2). The analysis time is approximately three hours at heating rates of 20, 10, 5 and 2.5 degrees per minute.

EXPERIMENTAL

Identification of Hazardous Materials or Stability Screening

   The information from the stability screening test outlined in this report should not be used to specify time-temperature storage parameters. One has a tendency to intuitively say that since compound A has the same "stability value" as B, and we have safely processed B for many years, we can use the same criteria to handle A. This type of approach is used throughout industry and generally no incident occurs. However, this hypothesis assumes that the slope of the time versus reaction temperature curve for A is identical to B and that rate controlling

step of the decomposition mechanism is also the same. The real value of the
stability screening tests discussed is derived from the comparison of mixes having
the same formula, or the effect that one substance has on the thermal properties
of another. This type of comparison has identified nitrate ester propellant
mixes contaminated with $CuCl_2$, NiCl, NaCl, $CuSO_4$ and $NaNO_3$ as being significantly
less stable than normal. This information indicated that the mixes should either
be discarded or processing suspended until additional tests could be run. Thus,
we can be certain that if A and B have the same formulation and relativity stability
they can be processed, handled and stored the same.

The time-to-ignition (or induction time) method is a simple yet sensitive
method of stability screening. This method measures the time required for a
substance or mixture to decompose at a given temperature. The experimental appa-
ratus consists of a constant temperature block, type K thermocouples, a strip
chart recorder and a temperature regulator capable of maintaining a temperature
within $\pm$ 0.1°C. The differential temperature between the sample and constant
temperature block is recorded on the strip chart recorder. The induction time is
measured from introduction of the sample to the peak of the decomposition exotherm.
The induction time is defined as the time required for a given sample weight to
decompose at a certain temperature. After this induction period is known for a
substance or mixture, any deviation from this norm indicates the presence of
materials which have altered the normal decomposition rate. The sensitivity of
the test was exemplified by a statistically significant decrease of induction
time on a nitrate ester propellant contaminated with 5 parts per million $CuCl_2$
(Table I).

The method has been implemented into the process control of propellants contain-
ing nitrate esters. The sample weight and temperature are chosen to allow enough
time for both identification of hazardous batches and some safe life testing
(usually a variable heating rate DSC test) before continuing the processing. It
is interesting to note that at the temperature selected the correlation between
induction times and stabilizer concentration is 0.95 (Table II). Thus, ·if the
safe life of the propellant is defined as the time required to deplete the stabi-
lizer at a certain temperature the time-to-ignition is a simple means of monitor-
ing the decomposition rate. There are, however, several substances that cannot
be evaluated with this method, i.e., a volatile liquid.

In choosing a method for stability screening, there are several factors that
should be considered. These should not only include the accuracy and precision
of the test, but if the analysis time, cost of equipment, and necessary qualifi-
cation of the operator are justified by the information. If we are interested
in relative numbers that may or may not correspond to real life conditions, then
the time-to-ignition method is the simplest and most easily adapted to process
control. This method does not require sophisticated equipment nor an extensive

TABLE I

Effect of Contaminants on Time-To-Autoignition

Contaminant	CuCl		$CuSO_4-2H_2O$		$NaNO_3$		Organic Acid	
	PPM	IT	PPM	IT	PPM	IT	PPM	IT
	0	116.3	0	115.6	0	115.6	0	115.3
	3.8	112.6	13.0	103.0	119	110.7	112	112.7
	5.6	106.1	38.9	87.9	113	110.2	207	111.9
	28.2	80.5	81.0	75.9	243	109.5	309	110.7
	67.2	65.4	61.9	70.3	301	108.1	446	109.7
	128.0	62.8	143.8	65.8	386	107.3	1082	108.2
	192.3	56.3	286.2	54.0	463	105.6		
	320.4	48.8	403.3	52.7				
	498.0	42.9	539.7	50.7				

All induction times are given in minutes

TABLE II

CORRELATION BETWEEN STABILIZER
CONTENT AND TIME-TO-AUTOIGNITION

Time (hrs) at 120°C	Induction Time @ 127.4°C	IT Standard Deviation	No. of Samples	% MNA	% NMNA	% MNA + % NMNA
0	114.57	2.11	6	.651	.022	.673
.5	113.27	2.05	6	.534	.090	.624
1.0	108.34	1.27	5	----	----	----
1.5	93.82	2.38	6	.282	.294	.576
2.0	80.42	2.46	6	.176	.377	.553
2.5	69.43	2.18	6	.100	.440	.540
3.0	44.88	1.88	6	.020	.536	.556
3.5	37.45	1.75	6	.021	.538	.559
4.0	43.60	2.03	6	.022	.511	.533
0	117.18	2.29	6	.637	.024	.656

$$r = 0.953$$

All induction times are given in minutes
MNA = N-Methyl p-nitroaniline
NMNA = N-Nitroso N-Methyl p-nitroaniline

training, yet has the sensitivity to identify potentially hazardous materials. The most critical parameter in this test is temperature. Studies have shown that the induction time changes approximately 22 minutes per degree centigrade with a typical nitrate ester propellant. Variations in weight also have an effect on the induction times. Using sample weights in the 0.3 to 1.0 gram range the induction time is inversely proportional to the sample weight. The safe life predicted with this method on propellant samples contaminated with sodium nitrate can be seen in Table III.

METHODS OF PREDICTING SAFE LIFE

After a known substance or mixture has been found to be significantly less stable than normal or any material with unknown thermal properties, it is necessary to determine if these materials can be safely processed and stored. This leads to the second and more difficult topic of predicting the time, temperature, and processing criteria at which the questionable material can be safely handled. The variety of techniques that has been used to answer this question are almost as numerous as the types of material being tested. Some of the methods were too specific to be used for the variety of material tested at Thiokol/Wasatch, while with others, the time required for the analysis was prohibitive. A few of the methods evaluated can be found in the appendix.

The most straight forward and generally accepted method of predicting the time-temperature relationship is based on the variable heat rate technique developed by Ozawa (ref. 1 and 2). This technique is the basis of the ASTM method of determining the Arrhenium kinetic constants for the screening of potentially hazardous materials. With this method, samples are placed in the Differential Scanning Calorimeter (DSC) and the temperature increased at a constant rate until decomposition occurs. The heating rate and peak temperature of the exotherm are recorded, then the procedure repeated with a different heat rate.

From Ozawa's derivation, the approximate activation energy (E) can be calculated from the slope of a plot of the log heating rate (B) versus 1/T, where T is the temperature of maximum reaction rate. The Arrhenium frequency factor (Z), rate constant (k), and half life times (t/2) are calculated from the following equations (Tables IV and V).

$$Z = \frac{B \; E \; e^{E/RT}}{R \; T^2}$$

$$k = Z \; e^{-E/RT}$$

$$t/2 = 0.693/k$$

TABLE III

THERMAL PROPERTIES OF PROPELLANT CONTAMINATED WITH SODIUM NITRATE
Calculated From Induction Times

PPM NaNO$_3$		0	119	248	301	386	463	133
Induction Time @ 120°C		286.7	272.5	274.5	269.7	265.3	260.7	272.8
Induction Time @ 124.8°C		160.2	154.75	150.7	150.05	148.85	147.75	153.3
Induction Time @ 127.4°C		115.6	110.7	109.5	108.1	107.33	105.55	110.2
Induction Time @ 129.8°C		87.35	84.25	82.45	82.12	80.45	80.0	83.2
Induction Time @ 135°C		55.2	53.7	52.9	52.75	52.55	52.2	53.35
Correlation Coefficient		0.9947	0.9958	0.9966	0.9966	0.9962	0.9962	0.9969
Slope		17790.5	17745.0	17769.3	17627.0	1.7544.7	17436.0	17655.1
Activation Energy(Kcal/mol°K)		35.35	35.26	35.31	35.02	34.86	34.64	35.08

Predicted

Safe Life @			0	119	248	301	386	463	133
383°K	230°F		15.0 hrs	14.4 hrs	14.2 hrs	13.9 hrs	13.6 hrs	13.3 hrs	14.15 hrs
373°K	212°F		52.2 hrs	50.0 hrs	49.4 hrs	47.7 hrs	46.5 hrs	45.1 hrs	48.7 hrs
355.22°K	180°F		23.7 days	22.6 days	22.3 days	21.2 days	20.4 days	19.5 days	21.2 days
344.11°K	160°F		119.4 days	113.2 days	112.3 days	105.1 days	100.5 days	95.1 days	108.0 days
333°K	140°F		1.84 yrs	1.73 yrs	1.72 yrs	1.59 yrs	1.51 yrs	1.46 yrs	1.64 yrs
310.78°K	100°F		83.7 yrs	78.3 yrs	78.2 yrs	70.0 yrs	65.3 yrs	59.7 yrs	72.6 yrs
298°K	77°F		974.4 yrs	906.5 yrs	908.5 yrs	797.4 yrs	734.8 yrs	662.2 yrs	829.5 yrs

TABLE IV

THERMAL PROPERTIES OF PROPELLANT CONTAMINATED WITH SODIUM NITRATE
Calculated by Ozawa Method

PPM NaNO$_3$		0	119	248	301	386	463	1100
Peak Exotherm @ 20°/min		466.0	467.5	466.5	467.5	467.0	469.0	464.3
Peak Exotherm @ 10°/min		460.3	459.0	457.3	460.0	459.0	460.0	457.3
Peak Exotherm @ 5°/min		451.5	451.5	448.0	448.6	446.2	447.5	440.0
Peak Exotherm @ 2.5°/min		441.5	441.3	440.0	441.3	439.5	440.5	437.5
Correlation Coefficient		0.9912	0.9971	0.9998	0.9960	0.9933	0.9953	0.9636
Slope		7401.5	7174.3	6953.8	6846.0	6395.0	6283.2	5801.5
Activation Energy(Kcal/mol°K)		32.21	31.22	30.26	29.79	27.83	27.34	25.24
Activation Energy (J/mol °K)		34764	130627	126613	124650	116438	114402	105632

Predicted

Half Life Time @		0	119	248	301	386	463	1100
383°K		15.8 hrs	13.3 hrs	9.6 hrs	9.8 hrs	6.2 hrs	6.3 hrs	3.2 hrs
373°K		49.0 hrs	38.5 hrs	27.7 hrs	27.8 hrs	16.3 hrs	16.2 hrs	7.6 hrs
355.22°K		17.8 days	13.4 days	8.8 days	8.5 days	4.3 days	4.2 days	1.7 days
344.11°K		76.9 days	55.2 days	34.5 days	32.8 days	15.2 days	14.2 days	5.2 days
333°K		367 days	251 days	149 days	138 days	58.0 days	53.0 days	17.4 days
310.73°K		32.1 yrs	19.6 yrs	10.5 yrs	9.2 yrs	3.1 yrs	2.7 yrs	0.7 yrs
298°K		297 yrs	168.9 yrs	84.0 yrs	71.4 yrs	20.7 yrs	17.3 yrs	3.8 yrs

TABLE V

THERMAL PROPERTIES OF PROPELLANT CONTAMINATED WITH ORGANIC ACID

PPM Organic Acid		0	112	207	309	446	1082
Induction Time @ 127.4°C		115.3	112.7	111.95	110.68	109.72	108.25
Peak Exotherm @ 20°/min		468.9	470.6	470.4	470.0	470.8	467.5
Peak Exotherm @ 10°/min		459.7	460.5	460.3	455.0	457.8	457.9
Peak Exotherm @ 5°/min		452.0	452.4	452.6	450.3	448.9	450.1
Peak Exotherm @ 2.5°/min		442.8	442.8	442.0	438.3	439.6	433.8
Correlation Coefficient		0.9992	0.9992	0.9978	0.9843	0.9974	0.9827
Slope		7257.0	6845.2	6709.4	6678.5	6042.4	5419.6
Activation Energy (Kcal/mol °K)		31.58	29.79	29.20	29.06	26.29	23.58
Activation Energy (J/mol°K)		132133	124635	122162	121599	110019	98678.9

Half Life Time @		0	112	207	309	446	1082
383°K	230°F	15.2 hrs	11.6 hrs	10.3 hrs	8.3 hrs	5.1 hrs	2.9 hrs
373°K	212°F	45.9 hrs	32.9 hrs	28.5 hrs	22.9 hrs	12.7 hrs	6.4 hrs
355.22°K	180°F	15.85 days	10.0 days	8.4 days	6.6 days	3.0 days	1.3 days
344.11°K	160°F	60.4 days	38.7 days	31.5 days	24.8 days	9.9 days	3.6 days
333°K	140°F	306.1 days	163.2 days	129.1 days	100.8 days	34.9 days	11.2 days
310.78°K	100°F	24.7 yrs	10.8 yrs	8.1 yrs	6.2 yrs	1.6 yrs	0.37 yrs
298°K	77°F	217.8 yrs	84.0 yrs	60.0 yrs	45.5 yrs	9.4 yrs	1.8 yrs

At slow heating rates the reaction occurs at lower temperatures and proceeds at much slower rates which makes it more difficult to accurately determine the maximum rate temperature. This slow heating rate data is particularly important, since the data are to be extrapolated to predict the decomposition at much lower temperatures and a zero heating rate. It should be noted that this method assumes a first order reaction, and the heat given off by the sample is immediately dissipated, with no loss of the products from the reaction. This procedure requires approximately three hours to analyze a sample at heating rates of 20, 10, 5 and 2.5 degrees per minute. The validity of the predicted half life times at the lower temperatures are somewhat questionable and seem to be on the conservative side. Samples of a propellant mix were held at 127.3°C for 0, 20, 40, 60 and 80 minutes, cooled to room temperature then the DSC run at three heating rates (20, 10 and 5°C/minute). The Ozawa treatment of the data showed that the predicted half life time at 25°C decreased from 222 years on the 0 time sample to 0.7 years for the samples heated for 80 minutes (Table VI). This same approach was also used on samples submitted for the time-to-ignition stability screening test and the induction times compared to those predicted with the Ozawa calculation (Table VII). It should be noted that the ratio of the induction time to predicted half life time is 1.7 for the 0, 20 and 40 minute samples, then decreases to 1.5 at 60 minutes and 1.1 at 80 minutes. This probably indicates a change in the reaction mechanism (in Table II, we can see that at induction times of approximately 40 minutes there is only 3% of the stabilizer remaining).

The precision of the Ozawa method on a propellant formulation was determined by making 10 replicate runs at heating rates of 20, 10, 5, 2.5 and 1.25 degrees per minute. The results showed that the peak temperature at the various heating rates had an average standard deviation of 1.15 degrees and coefficient of variation of 0.25% (Table VIII). The activation energy calculation showed an average of 35.6 Kcal/mol°K with a 3.1% coefficient of variation. At temperatures where most of the storage and handling occurs the variation in the predicted half life times is excessive, for example, at 100°F the times ranged from 87 to 587 years. This variation primarily comes from two sources, one of course, is the extrapolation error and the other is the nonhomogenity of the sample. It should be noted that the sample weight used in this investigation was 0.7 $\pm$ 0.1 milligrams, and the decomposition reaction is extremely complex and cannot be described by a single mechanism.

CONCLUSIONS

The stability screening test that has been outlined is a simple yet sensitive method of comparing the relative stability between different batches of the same substances or mixtures having the same formulations. This method has been implemented into the inprocess control of many of the energic compounds and

TABLE VI

Ozawa Half-Life Predictions

Sample No.	Decomposition Temperature			Eact KCal/mol	Predicted Half Life Times						
	20°C/min	10°C/min	5°C/min		383°K (230°F)	373°K (212°F)	344.1°K (160°F)	333°K (140°F)	321.0°K (120°F)	310.8°K (100°F)	298°K (77°F)
0 Time at 127.3°C	453°K	444°K	438°K	33.7	6.4h	20.9h	39.7d	205d	3.2y	21.3y	222y
20 Minutes at 127.3°C	451	441	436.5	33.4	4.9h	16.0h	29.3d	149d	2.3y	14.9y	152y
40 Minutes at 127.3°C	448	439	433	33.1	3.7h	11.9h	21.0d	106d	1.6y	10.3y	103y
60 Minutes at 127.3°C	446	436	430	30.5	2.0h	5.9h	7.6d	33.5d	163d	2.4y	20y
80 Minutes at 127.3°C	445	434	425	24.6	0.8h	1.8h	1.1d	3.7d	13.0d	50.2d	268d

h = hours   d = days   y = years

TABLE VII

Time-To-Autoignition Versus Predicted Half Life Times

Sample No.	Time-To-Ignition at 127.3°C	Ozawa Half Life at 127.3°C
0 Time at 127.3°C	99.1 Minutes	58.2 Minutes
20 Minutes @ 127.3°C	81.2 Minutes	46.3 Minutes
40 Minutes @ 127.3°C	61.8 Minutes	35.6 Minutes
60 Minutes @ 127.3°C	40.6 Minutes	26.5 Minutes
80 Minutes @ 127.3°C	22.0 Minutes	20.7 Minutes

R = 0.9907

TABLE VIII

Precision of the Ozawa Method

Heating Rates (°C per min.)					Activation Energy (Kcal/mol)	383°K, 230°F	373°K, 212°F	333°K, 140°F	310.8°K, 100°F	298°K, 77°F
20	10	5	2.5	1.25						
469°K	461°K	455°K	447°K	440°K	37.3	56.2 h	210 h	10.3 y	587 y	7921 y
471	461	455	447	440	35.4	40.5 h	141 h	5.0 y	228	2673 y
470	463	455	447	440	35.5	41.9 h	146 h	5.2	241	2850
470	462	455	447	440	35.8	44.0	155	5.9	284	2446
470	462	454	447	441	36.9	54.3	200	9.2	502	6586
472	464	455	447	440	33.4	29.6	95.7	2.4	87.0	880
472	461	455	448	440	34.9	38.1	130	4.2	182	2059
471	462	453	448	441	36.2	48.5	174	7.1	358	4463
471	464	455	448	441	34.7	37.8	128	4.0	167	1854
470	463	453	448	440	35.8	43.5	153	5.8	275	3319
$\bar{X}$ 470.6	462.3	454.5	447.4	440.2	35.6	43.4	153	5.6	291	3605
S 1.106	1.178	1.242	1.167	1.047	1.12	7.96	34.21	2.698	153.6	2178
% CV 0.235	0.255	0.273	0.261	0.230	3.136	18.31	22.32	48.26	52.76	60.40

mixtures of reactive chemicals manufactured today. There is, however, a hazard
in equating the data from a single point screening test to the thermal properties
of materials heated or stored for an extended time. This was exemplified by an
incident at a Dow Chemical factory in 1976 (ref. 2). A material (3,5-dinitro
ortho-tolumide) that had been designated stable by vacuum stability tests (samples
heated at 120°C for 28 hours evolved only 0.38 mls of gas), autoignition tests
(indicated the decomposition temperature between 216° and 300°C), and a conven-
tional differential scanning calorimeter analysis (which showed an exotherm at
273°C) exploded in a steam heated dryer after approximately 25 hours at 130° to
140°C. Later tests showed that this material would self heat to decomposition if
held under adiabatic conditions at 120 to 125°C for 24 hours.

   The validity of the calculated safe life values are somewhat questionable,
since no method can accurately simulate the conditions encountered in the storage
and handling of bulk quantities of energy rich compounds that are processed daily.
None of the techniques outlined in this report can measure the heat generated by
the autocatalytic decomposition reaction that occurs in bulk storage. In these
methods, any heat generated is immediately dissipated by the analytical apparatus,
thus the measured critical temperatures are much higher than "real life" conditions.
This point was verified by the initial decomposition temperature of ammonium
perchlorate as determined by the differential scanning calorimeter and thermogravi-
metric analysis techniques. These tests showed that decomposition occurred at 327
and 332°C respectively. This same material analyzed with the Accelerating Rate
Calorimeter (ARC) recorded an exotherm at 220°C. It should be noted that although
the ARC yields a better indication of "real life" the effects of long time storage
cannot be duplicated. Additional comparative data from the ARC and previously
described methods will be the topic of following reports.

REFERENCES
   1. T. Ozawa, J. Therm. Anal., 2,301 (1970).
   2. T. Ozawa, J. Therm. Anal., 9,369 (1976).

APPENDIX

OTHER METHODS OF STABILITY SCREENING

Gas Evolution

One of the most widely used methods of determining the relative stability and/
or compatibilities of propellants and explosives is the Taliana test. In this
method, the test material or equal amounts of a test material and propellant or
explosive are placed in a closed inert atmosphere and heated to $93.5° \pm .1°C$ for
23 hours. If the amount of gas evolved is less than a certain amount (usually 200 mm)
the material or mixture is considered safe for normal handling and processing. A
similar gas evolution method is the vacuum stability test where samples are placed
in a closed evacuated system and heated for a given time period. Again if the
amount of gas evolved is less than a certain amount the material is considered
"safe".

ThermoGravimetric Analysis

The thermogravimetric method of stability screening testing is to heat a known
weight of sample at a constant rate (usually 10°C per minute) and to record the
weight as a function of temperature. The initial decomposition temperature, as
indicated by the loss of weight and the temperature of maximum weight loss are used
for comparison. If these temperatures are within the statistical tolerance limits
for the material in question it is considered safe for continued processing. This
technique not only allows for comparative stability screening, but also yields an
insight to the rate of thermal reaction.

Differential Scanning Calorimeter and Differential Thermal Analysis

The last two methods of stability screening to be discussed are the differential
scanning calorimeter (DSC) and differential thermal analysis (DTA). In both
techniques a known weight of material is placed in the respective instrument and
heated at a constant rate (usually 10°C per minute) until the sample decomposes.
In the case of the DTA the differential temperature, between the sample and an
inert reference, as a function of the temperature is monitored. The DSC
measures the differential energy that is required to keep the sample and inert
reference at the same temperature. In both cases, the initial and peak decomposi-
tion temperatures are used to determine the relative stability of the particular
substance or mixture. If these temperatures are within the statistical tolerance
for that material then it is considered safe for continued processing. The data
from both the DSC and DTA can be used to further define the kinetic parameters of
the particular sample. Some of these methods of data interpretation will be
discussed in the next section.

METHODS OF PREDICTING SAFE LIFE

Stabilizer Depletion Rate

One of the selective methods that has been used to predict the safe life of propellants containing nitrate esters is the stabilizer depletion rate. With this technique, the propellant safe life is defined as the time required to deplete the stabilizer at a given temperature. The test procedure measures the concentration of stabilizer as a function of time and temperature by placing propellant samples in an oven (usually at 75°, 90°, 105° and 120°C) for various time periods (usually 0, 2, 4, 6 and 8 hours). The concentration of stabilizer is determined with a liquid chromatograph equipped with a silica gel column and a UV detector. From this information, it is possible to predict the time at any temperature (the correlation between stabilizer depletion and time-to-ignition can be found in Table II).

Time-To-Ignition

This is another method that is somewhat limited as far as number of materials that can be tested, but is one of the better techniques for those operating with a constrained budget. The equipment that is required for this test is a constant temperature block, thermocouples, a strip chart recorder or some other means of measuring time, and a temperature regulator capable of maintaining a temperature within $\pm$ 0.1°C (at our lab the only thing that was purchased specifically for this test was the temperature regulator for approximately $200.00). The time-to-ignition or induction time is defined as the time required for a given weight of sample to decompose at a certain temperature. The induction time is measured by monitoring the differential temperature between the constant temperature block and the sample and is generally determined at minimum of 5 different temperatures. The activation energy and safe life are found by plotting the log of the induction time (IT) versus the reciprocal temperature (T) (Table III and Figure 1) using the following equation.

$$E = R \ \frac{d \ln (IT)}{d \ (1/T)}$$

Where: E = activation energy

R = gas constant, 1.982 cal/mole degree

Isothermal Method

This method is often overlooked because of the time required for a complete analysis. This method directly measures the extent of the reaction as a function of time and temperature. The samples are held in the DSC at a set temperature for varying time periods, the samples are then temperature programmed through their decomposition and the exotherm recorded. The decrease in the exotherm area per unit sample weight as a function of the previous isothermal exposure time is a measure of the reaction rate at that temperature. From this relationship, the

specific reaction rate constant k can be calculated. For example, a first order
decomposition would yield a straight line whose slope equals k from the plot of
$-\ln a_i/a_o$ versus time (where a_i = exothermic area per unit weight after the
isothermal exposure time). If the procedure is repeated at different temperatures
the slope of the plot of R ln k versus 1/T yields the activation energy E. From
this information the safe life at any temperature can be predicted.