THE APPLICATION OF A CHEMILUMINESCENCE NOx ANALYSER TO STABILITY AND
COMPATIBILITY TESTING

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ABSTRACT

An experimental facility based on a chemiluminescence NOx analyser has been
employed to study various aspects of the thermal decomposition of nitrate ester
based propellants. A description of the facility and its use in determining
the decomposition characteristics of single, double and triple based propellants
as well as their nitrate ester ingredients are presented. The NOx evolution
profiles obtained at $60^{\circ}C$ are discussed and the results compared with those
obtained by traditional stability tests. Evidence is presented in support of a
mechanism for NOx production which explains the often poor correlation between
different test methods. The temperature dependence of the decomposition rate
for a wide range of propellants has also been determined and the implications of
these results for lifetime prediction are discussed.

The use of the technique as a method for determining incompatibility has been
investigated using mixtures of propellants with a wide range of materials. The
influence of temperature on the propellant-material interaction has also been
determined. The results illustrate the importance of knowing temperature dependence
before making judgements on in service compatibility.

The merits of a stability or compatibility test based on chemiluminescence are
discussed. It has been concluded that the main advantages of such a test are its
specificty and sensitivity. Consequences of the latter are that tests can be
carried out in a relatively short time and that realistic test temperatures can
be employed.

INTRODUCTION

Propellants containing nitrate esters can degrade to the extent where they
fail to meet their design specification. The failure may appear as a change in
mechanical properties, ballistic performance or chemical composition. The under-
lying reason for many such changes is the intrinsic instability of the nitrate
ester. Even at ambient temperatures these propellant ingredients can decompose

by a sequence of reactions beginning with the cleavage of the nitrate ester linkage (ref 1,2,3).

$$RO-NO_2 \longrightarrow RO\cdot + NO_2$$
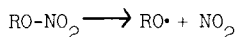
Both products from this initial step are reactive and undergo further reactions both with the nitrate esters themselves and with other constituents in the composition. A consequence of some of these secondary reactions is specific life limiting effects such as

(a) Gas evolution leading to crack formation in motors.

(b) Consumption of ballistic modifiers causing changes in ballistic performance.

(c) Consumption of stabilisers leading to a reduction in shelf life and, at worst, to autocatalytic decomposition.

If one is to predict any of these events an essential element in the predictive model is the rate of decomposition of the nitrate ester in its propellant environment. Of the several methods available for the determination of decomposition rate the most convenient one in practice is to measure the rate at which oxides of nitrogen are produced. This is the method which has been adopted by most of the traditional stability tests.

Most of these tests use relatively insensitive methods to detect nitrogen oxides and consequently to accumulate sufficient product to measure one is forced to adopt either long test times or high temperatures. Neither of these solutions is satisfactory; long tests mean that delays may occur in processing whilst waiting for a test result. High temperatures are likewise unpopular since a decomposition mechanism involved at the elevated test temperature may not necessarily dominate under normal storage conditions.

These shortcomings apply equally well to most compatibility tests since these are normally extensions of stability tests. The usual criterion adopted for compatibility is that the presence of the test material does not substantially increase the rate of decomposition of the propellant with which it is tested.

In recent years instrumentation sensitive to nitrogen oxides has become available. This is based on the chemiluminescence reaction between nitric oxide and ozone. Not surprisingly a number of workers (ref 4,5,6) have examined the application of this technique in studying various aspects of propellant decomposition. Several of these areas have been examined at PERME (ref 7,8,9) where the recent emphasis has been on compatibility and stability problems of double base compositions.

The present work describes the studies which have been carried out recently to examine the way in which the decomposition rate of the nitrate ester is influenced by its environment.

EXPERIMENTAL

The equipment used throughout this work centres around a chemiluminescence
NOx analyser. This instrument operates on the basis of a specific technique
for the detection of nitric oxide, namely the application of the chemiluminescence
reaction of nitric oxide with ozone. The reactions involved are

$$NO + O_3 \rightleftharpoons NO_2{}^* + O_2$$

$$NO_2{}^* + M \rightleftharpoons NO_2 + M$$

$$NO_2{}^* \rightleftharpoons NO_2 + h\nu$$
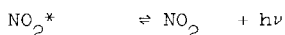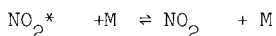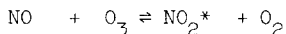
The excited nitrogen dioxide produced decays to its ground state emitting light
in the process. The intensity of this emitted radiation is measured by a
photomultiplier/electrometer system and is related to the nitric oxide concentration
by the expression

$$I = e^{-k/t} \frac{[NO][O_3]}{[M]}$$

where k = constant
t = temperature
[M] = total pressure

The elements of a typical analyser are arranged as shown in Figure 1. The central
feature of the instrument is the low pressure reaction chamber in which the
chemiluminescence reaction occurs. Air is passed through an ozone generator and
the partially ozonised air is then metered into the chamber where it reacts with
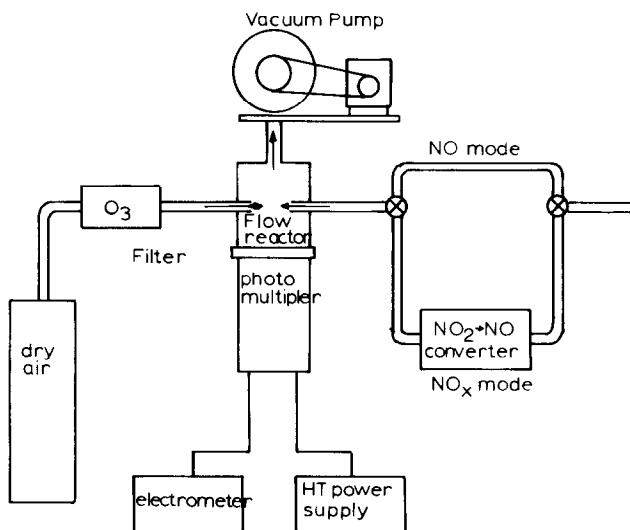the nitric oxide in the sample gas.

Fig. 1. Chemiluminescence Analyser Schematic

Oxides of nitrogen evolved from the samples of propellant are transferred to the reaction vessel using the system shown in Figure 2. The precision flow controller at the head of the sample train maintains a constant flow of carrier gas, usually oxygen-free nitrogen through the sample vessel. The vessel itself contains a coarse glass sinter which supports the ground propellant. A modified gas chromatograph oven is used to heat the sample whilst a glass coated thermocouple embedded in the propellant constantly monitors the temperature. The carrier gas passes through a solid CO_2/acetone trap to remove volatile species, which can seriously degrade the performance of the analyser. Finally, in order that nitrogen dioxide may be determined as well as nitric oxide, a high temperature ($650^{\circ}C$) catalytic, stainless steel converter is provided as an option to reduce any nitrogen dioxide in the sample. Both total oxides of nitrogen (NOx) and nitric oxide can be determined by a simple diversion of gas flow. Nitrogen dioxide can be calculated as the difference between the total oxide level and the nitric oxide concentration i.e. $[NO_x] - [NO] = [NO_2]$.
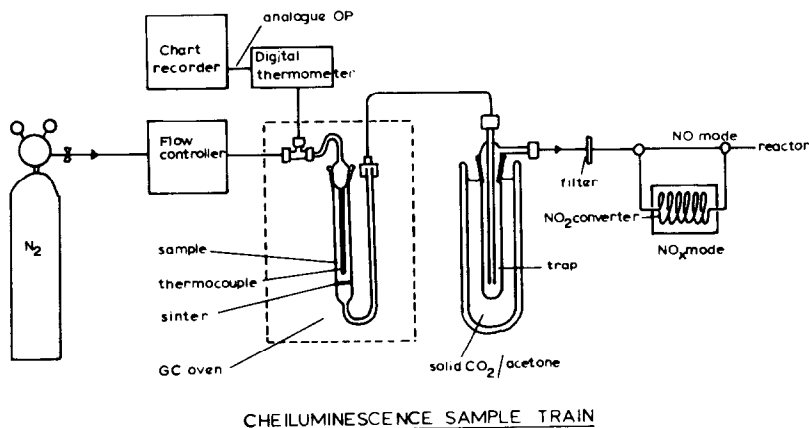

CHEILUMINESCENCE SAMPLE TRAIN

Fig. 2. Chemiluminescence Sample train.

During the current study experimental conditions have been standardised. A carrier gas flow rate of 25.0 ml min^{-1} is passed through a one gram sample of propellant which has been ground to heat test size. The concentration of oxides of nitrogen evolved is then related to the rate of evolution by the expression

$$\text{RATE} = \frac{N \times F \times 4.461 \times 10^{-5}}{W} \mu \text{ mol g}^{-1} \text{ min}^{-1}$$

where   N = NOx concentration in parts per million

        F = carrier gas flow rate ml min^{-1}

        W = sample weight in grams

RESULTS

NOx Evolution from Nitrate Esters

    The first task undertaken was that of characterising the decomposition behaviour of the major propellant nitrate esters, nitroglycerin and nitrocellulose Two main aspects of the decomposition were examined,

    (a)   The rate of NOx evolution at constant temperature.

    (b)   The effect of temperature on that rate.

    The rate of NOx evolution was determined with respect to time for samples of NC and NG at a temperature of 60°C. Figure 3 shows that in both cases a high level of evolution was observed in the early stages of heating. This fell with time and eventually levelled out to a constant value which persisted for several days. It is this constant value which has been taken as a measure of the rate of decomposition of the nitrate ester.
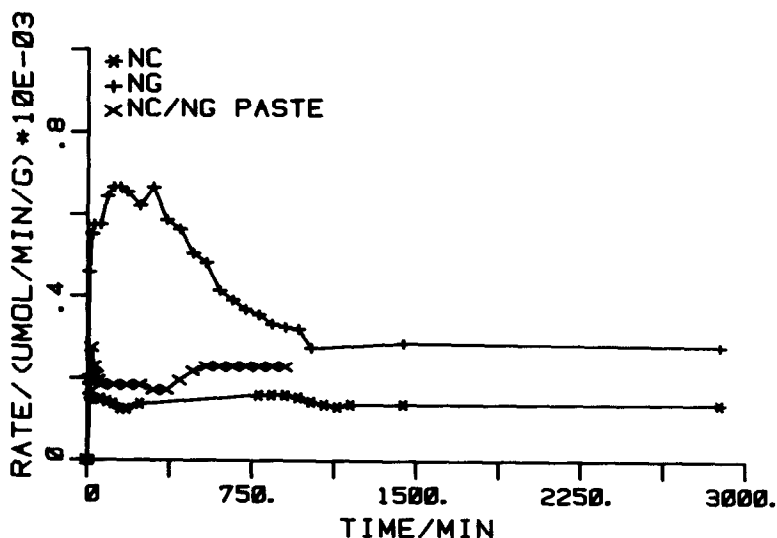

Fig. 3. NOx Evolution from Nitrate Esters

    When a 50:50 mixture of these nitrate esters, in the form of basic paste, was heated at the same temperature, the rate of NOx evolution showed a value which

was the sum of the contributions from the two separate ingredients. This implie
that these two nitrate esters are mutually compatible i.e. that neither effects
the decomposition rate of the other.

Once a steady rate of decomposition had been established the temperature was
varied and the effect of this on the NOx evolution was determined. The results
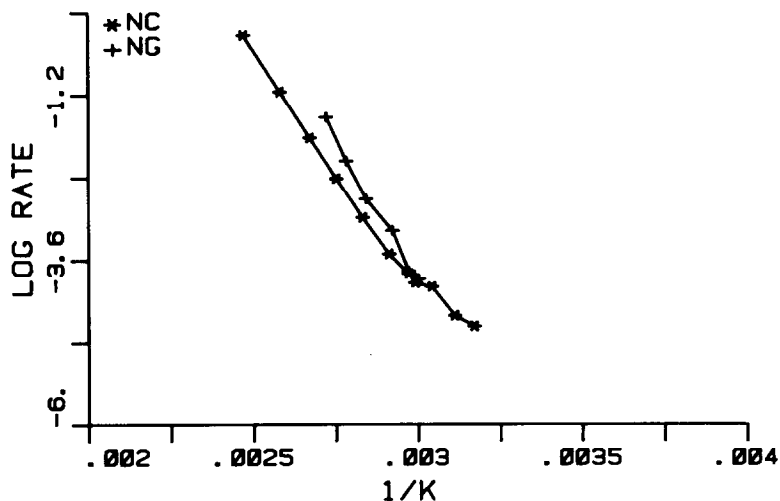are shown in the form of the Arrhenius plots in Figure 4.

Fig. 4.   Temperature Dependance of Nitrate Ester Decomposition

The plots can be seen to be linear over a range of 55-95°C for NG and from
50-135 for NC.   The activation energies calculated from this data are shown in
Table 1 and can be seen to lie well within the spread of results obtained by
other workers using a variety of techniques.

TABLE 1

Activation Energy kJ mol^{-1} K^{-1}		Method	Reference
Nitroglycerin	Nitrocellulose		
171.1	141.0	Chemiluminescence	This work
108.7 (80-90°)	104.5 (80-100°)	VAC Stability	Tranchant (18)
50.1 (70-80°)	160.9 (100-110°)		
	154.6-163.0	Mass Spec	Malchevskii (14)
172	155.0	Will Test	Blay (10)
		Infra-red	Krastins (3)
168.5		Gas Generation	Phillips (1)
	171.0		Volk (11)
121.2	113.7-143.0	Time to Autocatalsis	Frey (12)
146.3			Serbinov (15)

The main advantage of the chemiluminescence method over most of these other techniques is that of speed. A typical temperature dependence run can be carried out in about a day as against the many weeks often required by other methods.

The Compatibility of Nitrate Esters with Other Propellant Ingredients

Although the main emphasis on the work has been to examine the decomposition characteristics of in-service compositions an opportunity was taken to examine the way in which some materials, including common propellant ingredients influence the decomposition rate of a NG/NC paste.

In these experiments small additions (2% w/w) of finely ground materials were added to 1g lots of dry NG/NC paste. The mixture was then examined in the usual way by the chemiluminescence method although in this case, the slightly higher temperature of 80C was used. The histogram Figure 5 shows the way in which these additives influence the rate of decomposition.
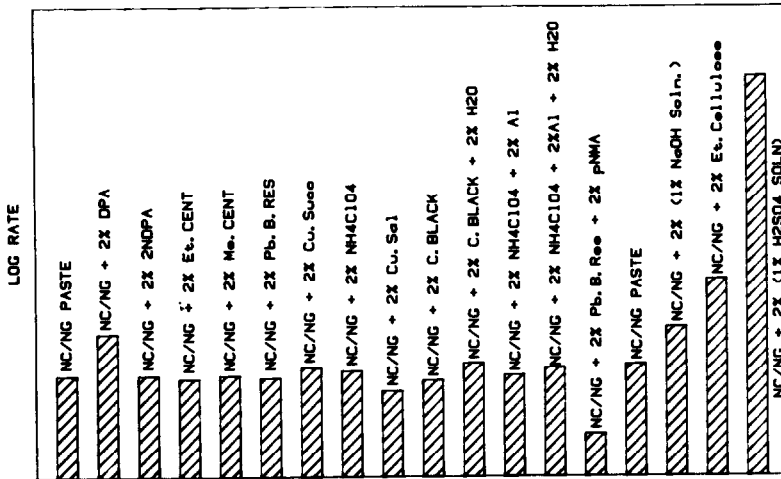
Fig. 5. The Effect of Additives on Nitrate Ester Decomposition.

In most cases the rate is little changed from that of the paste on its own. However in several instances significant changes in NOx evolution rate were observed indicating that the nitrate ester was decomposing at a faster rate. The most dramatic effect was noted when small additions of acid were made while less pronounced reactivity was observed when small additions of 1% Sodium Hydroxide, Diphenylamine and Ethyl Cellulose were made. Significantly change was also observed when small amounts of water were added to the paste. This last effect is of particular interest and it is hoped that further work can be carried out to quantify the effect.

NOx Evolution from Propellants

When nitrate esters are formulated into propellants the new environment undoubtedly influences their rate of decomposition and consequently the rate of NOx evolution. This can be seen in the NOx evolution profiles of two compositions Figure 6.
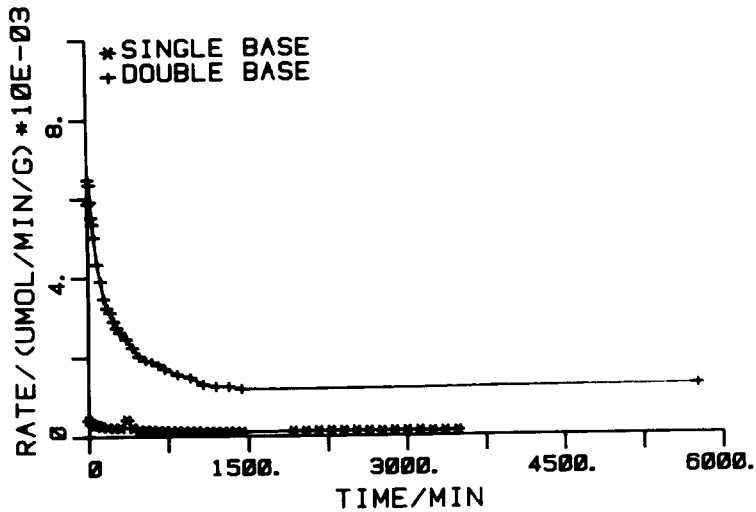
Fig. 6. NOx Evolution from Propellants

A distinctive feature of these NOx evolution profiles is the high initial value
of NOx which is observed in the early stages of heating. This high initial rate
which can be seen to decay exponentially to a final constant value was the subject
of a previous study (ref 9). It was confirmed in that study that the high initial
value was due to the decomposition of small amounts of nitrosamines in the propellant
These N-nitroso compounds are known to be thermally labile (ref 17) and to be
readily formed during earlier propellant decomposition. Even newly-manufactured
propellants have been found to contain sufficient nitrosamines to produce an
enhanced NOx evolution rate when the material is heated. This effect has some
interesting ramifications for some traditional tests. The high rate of NOx
production in the first minutes of heating has been shown to considerably influence
the results of short term test such as Abel's heat test. Once the finite amount
of N-nitroso compound has decomposed the NOx evolution rate adopts a value which
is presumed to be due to the nitrate ester decomposition in the propellant. It
is therefore this value which reflects the compatibility of the other propellant
ingredients with the nitrate ester. It can be seen Figure 7 that the decomposition
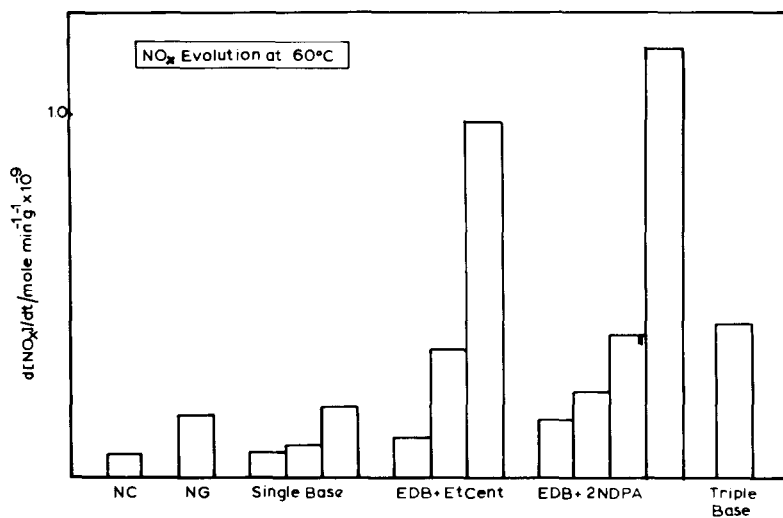rate varies considerably with composition.

Fig. 7. NOx Evolution from Propellants.

In addition to their behaviour at 60C the temperature dependence of the decomposition rate was also examined for these compositions. Significant differe were observed as can be seen in Figure 8.
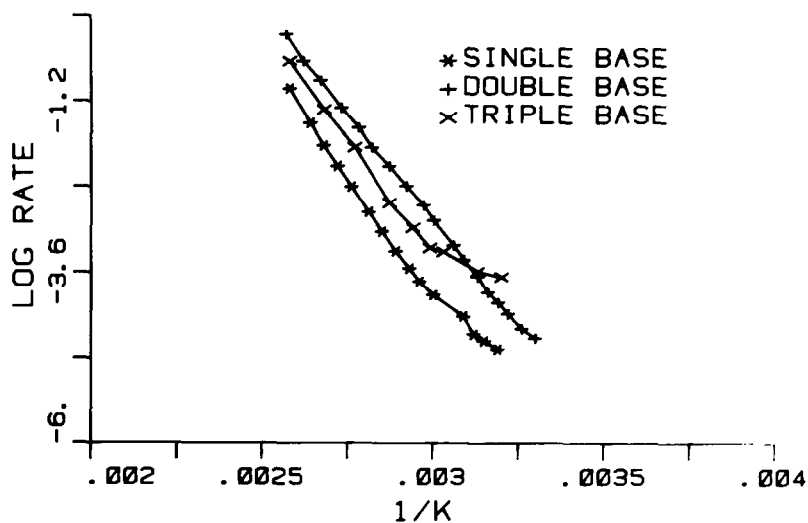

Fig. 8. Temperature Dependence of Propellant NOx Evolution.

Once again these differences are thought to reflect the influence of propellant ingredients and the decomposition behaviour of the nitrate ester. The different activation energies are of course important when it comes to making predictions on the shelf life of propellants. The following table illustrates the dramatic effect activation energy has on some specified event e.g. production of n mls of gas or the time to autocatalysis at a number of temperatures.

TABLE 2

$T^{o}C$	Activation Energy kJ mol^{-1} K^{-1}		
	180.0	140.0	100.0
100	40 hrs	40 hrs	40 hrs
80	44 days	21.5 days	10 days
60	60 months	12 months	2.6 months
40	311 years	26 years	2.2 years
20	35,000 years	1033 years	30 years

The practice in several countries, including the UK, is to make predictions about low temperature behaviour on the basis of higher temperature tests. To make such a prediction the same time honoured, temperature dependence "factor" is used for all compositions. In view of the significant differences observed in the activation energies of different compositions it would seem wise to take account of these differences if reliable predictions are to be made.

Perhaps the reason why little account has been taken of the differences in temperature dependence is that reliable low temperature data has been lacking. The high sensitivity of the chemiluminescence method means that not only can temperature dependence data be easily obtained but that temperatures little above normal storage temperatures can be examined.

Compatibility of Propellant with Other Materials

Once a propellant has been manufactured with satisfactory stability one has to ensure that the stability is not adversely affected by contact with other processing materials. For this reason compatibility tests are usually carried out with the whole range of materials with which the propellant may come into contact.

This aspect of compatibility has been examined in the past for single base compositions (ref 5). The following results illustrate the use of chemiluminescence to determine the effect of a second material on the decomposition rate of a well-characterised, double base composition.

Mixtures (50:50) of the propellant with some common production materials were heated in the usual way at 80C. The profile, Figure 9 shows the distinctive decay which was observed in all cases where an interaction occurred.
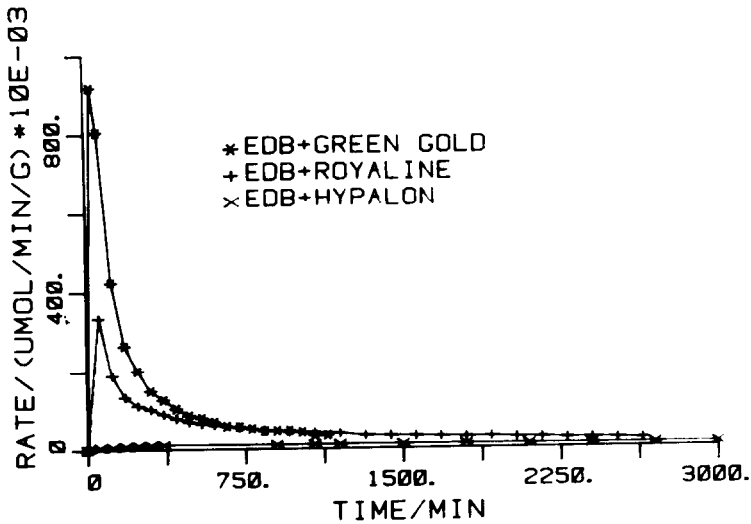
Fig. 9. NOx Evolution from Propellant/Rubber Mixture.

Despite the similarity in appearance with the decay curve due to nitroso decomposition the cause of this decay was quite different. Integration of the decay in rate revealed that the quantity of material involved was too great to be accounted for by a small amount of nitroso compound. One alternative explanation is that nitrate ester on the surface of the propellant grain decomposes rapidly because of contact with the incompatible material. Once the surface material has been degraded the NOx evolution will be dominated by decomposition of the bulk material.

Whatever the reason the fact remains that a second material can have an effect on the NOx production. The most appropriate way to quantify this effect was to integrate the rate curve over a specified period. The histogram Figure 10 shows the integral of the rate curve over the first 24 hours of heating. These results agree, qualitatively at least, with vacuum stability measurements on the same mixture and in several cases indicate significant incompatibility.
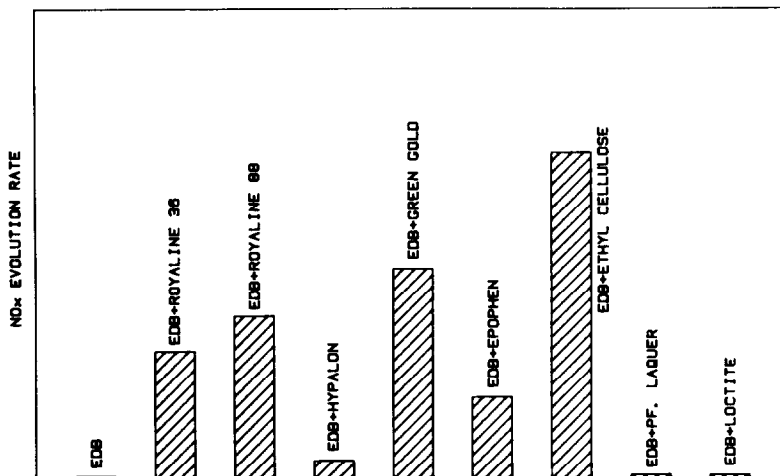
Fig. 10. NOx Evolution from Mixtures of Propellant with Other Materials.

As in previous sections the temperature dependence of the decomposition rate was determined for the mixtures. The results shown in Figure 11 illustrate the way in which the second material can influence the decomposition of the propellant
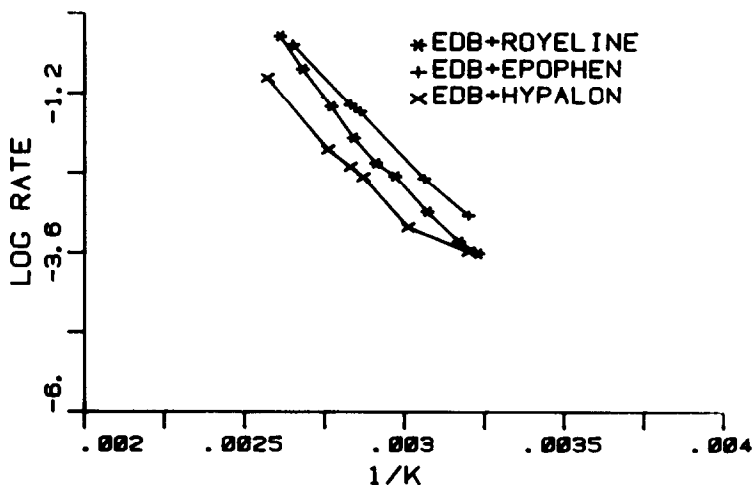
Fig. 11. Temperature Dependence of NOx Evolution from Mixtures.

CONCLUSIONS

Chemiluminescence provides a specific and highly sensitive method of determining the decomposition behaviour of nitrate esters and propellants. The current study has illustrated a number of specific applications of the technique. These are

(a) To rapidly determine the decomposition rate of nitrate esters over a wide range of temperatures.

(b) To determine the influence of individual and combinations of other propellant ingredients over the same temperature range.

(c) Single, double, triple and even composite modified propellant can be likewise characterised even at temperatures little above their normal storage conditions. Information on temperature dependence can be readily and rapidly acquired so that more meaningful data can be provided for lifetime prediction.

(d) The effect of other materials on decomposition behaviour of a well-characterised propellant can be easily determined again over a wide temperature range.

REFERENCES

1　L. Phillips, Nature 160(1947)755.
2　L. Phillips, Nature 165(1950)564.
3　G. Krastins, PhD Thesis, University of Connecticut, (1957).
4　R.D. Suart, E Ahad and G. Perrault, Proc. Conference on "Standardisation of Safety and Performance Tests for Energetic Materials", Dover NJ, June 21-23, 1977, US Arradcom.
5　D.E. Ayer, M.T. Tari, R.P. Keller, Proc. Symp. Compatibility of Plastics and Other Materials with Explosives, Propellants, and Pyrotechnics, Naval Ordnance Station, Indian Head MD. April 27-29, 1976, ADPA.
6　R.W. Dalton, C.D. Chandler, W.T. Bolleter. Proc 11th INT ICT Conference on Testing Methods for Propellants and Explosives. Karlsruhe, W. Germany, 25-27 June, 1980.
7　I.G. Wallace, R.J. Powell and B.J. Downes, Proc. 5th Symp Chemical Problems Related to the Stability of Explosives, Bastad, Sweden, May 28-30, 1979.
8　I.G. Wallace, R.J. Powell, Proc. Conference. Nitrocellulose Characterisation and Double-Base Propellant Structure, Waltham Abbey, England, 7-9 May, 1980.
9　I.G. Wallace, R.J. Powell, Proc. 11th INT Conference. Testing Methods for Propellants and Explosives. Karlsruhe, W. Germany, 25-27 June, 1980.
10 N.J. Blay, Proc. Conference. Nitrocellulose Characterisation and Double-Base Propellant Structure. Waltham Abbey, England, 7-9 May, 1980.
11 F. Volk, Proc. 2nd INT ICT Conference, Karlsruhe, W. Germany, 1971.
12 M. Frey, Explosivstoffe 15(1967)97.
13 J. Thanchant, Mem. Poudres Annex 44(1962)11.
14 V.A. Malchevskii, O.F. Pozdryakov, V.R. Regel, M.G. Falkovskii, Vysokomal. Soedin, Ser A. 13(9), (1971)207.8; CA 76:15879m.
15 A.I. Serbinov, Zhir. Fiz. Khim 33(1959), 2641.
16 F. Volk, Propellants and Explosives, 1(1976), 59
17 D.H. Fine, F. Rufeh and B. Gunther, Anal. Lett 6(1973)731.