UNCLASSIFIED

AD NUMBER
AD467495
LIMITATION CHANGES
TO: **Approved for public release; distribution is unlimited.**
FROM: **Distribution authorized to U.S. Gov't. agencies and their contractors; Foreign Government Information; 12 APR 1965. Other requests shall be referred to British Embassy, 3100 Massachusetts Avenue, NW, Washington, DC 20008.**
AUTHORITY
DSTL, AVIA 37/1146, 8 Dec 2008

THIS PAGE IS UNCLASSIFIED

7 SEP 1965

UNCLASSIFIED

BRL

E.R.D.E. ~~13/R/65~~
R-13/R/65

Copy No. 45

Forwarded by:
US ARMY STANDARDIZATION GROUP
UNITED KINGDOM
FPO, New York,

20080731 069

MINISTRY OF AVIATION

EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT

AD-467 495 65-18 7A

REPORT No. 13/R/65

The Pyrolysis of Some Composite Propellant Fuel Binders

TECHNICAL LIBRARY
BLDG. 313
ABERDEEN PROVING GROUND MD.
STEAP-TL

B.C. Howard

COUNTED IN

THE RECIPIENT IS WARNED THAT INFORMATION CONTAINED IN THIS DOCUMENT MAY BE SUBJECT TO PRIVATELY-OWNED RIGHTS.

ERDE
R-13/R/65

WALTHAM ABBEY
ESSEX

UNCLASSIFIED

AD-467495

MINISTRY OF AVIATION

EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT

REPORT NO. 13/R/65

The Pyrolysis of Some Composite Propellant Fuel Binders

by

B.C. Howard

1. Propellants, composite
2. Binders, fuel.

Approved: P.R. FREEMAN
S.P.2

Approved for Circulation: G.H.S. YOUNG
P.S.(D)

12th April, 1965

WALTHAM ABBEY
ESSEX

TECHNICAL LIBRARY
BLDG 313
ABERDEEN PROVING GROUND MD.
STEAP-TL

CONTENTS

		Page No.
1.	Summary	1
2.	Introduction	1
3.	Experimental	2
4.	Results	2
5.	Comparison of Results	5
6.	Discussion	7
6.1	Mechanism of Depolymerisation	7
6.2	Polyisobutene	8
6.3	Polyester-Polyurethane Rubber	9
6.4	Polyether-Polyurethane Rubber	11
6.5	Future Work	13
7.	References	13
	Appendix	14
	Figures 1 - 5	

Reference: WAC/167/08

1. SUMMARY

Over the temperature range examined (350° to 475°C) polyether-polyurethane rubbers gasify more readily than polyisobutene which, in turn, gasifies at a faster rate than polyester-polyurethane rubbers. Prepolymers gasify at a slower rate than the corresponding polyurethane rubbers. At 350°C all of the polymers examined give first order reactions but increasing the temperature to 475°C produces deviation from first order behaviour. There is evidence that at the higher temperatures free-radical breakdown is responsible for the rapid rate of gas production.

Polyisobutene gives a high monomer yield at lower temperatures but at 475°C methane and ethylene are also formed. The polyurethane rubbers produce acetaldehyde, methane, ethylene, and carbon monoxide; the polyethers, in addition, give propylene and the polyesters carbon dioxide. Not all of the polymer pyrolysed can be accounted for by these simple gases; the other products probably consist of a mixture of higher molecular weight hydrocarbons.

2. INTRODUCTION

At low pressures (say, below 100 p.s.i.g.) and constant heat of explosion the burning rate of ammonium perchlorate-based composite propellants is usually independent of the precise chemical nature of the fuel binder but in the high pressure region (say, above 1000 p.s.i.g.) individual fuels have markedly different effects upon propellant burning rate and pressure exponent (1).

No studies, other than some limited pyrolysis measurements, have been made to ascertain those characteristics of fuel-binder pyrolysis which are likely to be important as far as rate of burning control is concerned. The present work has set out to measure the relative rates of gasification of practical fuel-binders at temperatures as near as possible to those which are likely to be encountered at the gas-solid interface of a burning propellant.

The types of fuel examined were polyester-and polyether-polyurethane rubbers, the corresponding polyesters and polyethers, and a polyhydrocarbon. A typical polyester-polyurethane rubber would be formulated from a long-chain ester (e.g., poly(diethylene adipate)) crosslinked via a 'triol' (e.g., hexane,-1,2,6-triol) and tolylene di-isocyanate. Formulations of the materials studied are given in the Appendix and details of the rubbers, and propellants in which they are used, may be found in references (2) (3) (the same numbers are used).

/Measurements .....

Measurements of the surface temperature of the fuels burning in oxygen have been made at atmospheric pressure (4) when all of the binders appeared to decompose in the temperature range 490° ± 20°C. The degradation of the polymers was therefore studied at temperatures as near to this as was compatible with reasonably accurate measurements of rate of gas production.

3. EXPERIMENTAL

The rates of gasification of the polymers were studied at temperatures in the range 350° to 475°C in the Pyrex glass apparatus shown in Figure 1. The reaction vessel was pressurised to approximately 500 mm Hg with nitrogen to prevent distillation of the pyrolysates. A weighed piece of polymer was dropped into the 250 ml reaction vessel and the progress of the reaction measured by noting the pressure indicated by the spiral gauge at regular intervals. When the reaction was complete the products in the reaction vessel were expanded into a 10-cm-long gas cell fitted with NaCl windows. The pressure in the cell was measured, the cell pressurised to 400 mm Hg with nitrogen, and the infrared spectrum recorded. The gases present were identified and from calibration curves the partial pressures of the components found.

4. RESULTS

In view of the complex nature of the fuel-binders the study has been limited to the determination of the rate of gasification of the polymers, the nature of the gaseous pyrolysis products, and the elements of the overall kinetic processes.

Graphs of the volume of gas (reduced to n.t.p.) liberated per gram of polymer against time have been plotted for polyisobutene and the polyester- and polyether-polyurethane rubbers at 400° and 450° (Figures 2a and b). A comparison of the rates of gasification of the rubbers and their precursors at the same two temperatures is made in Figures 3a and b. The gas volumes were reduced to n.t.p. to correct for small temperature variations between the pyrolyses. The final volumes of gas evolved (at n.t.p.) per gram of polymer are shown in Table 1.

/TABLE 1 .....

TABLE 1

Polymer	350°C Volume at n.t.p. (ml/gm)	400°C Volume at n.t.p. (ml/gm)	450°C Volume at n.t.p. (ml/gm)	475°C Volume at n.t.p. (ml/gm)
Polyester-polyurethane rubbers				
L77	very slow reaction	435	481	628
HPEL 74	-	449	-	-
HPEL 71	-	367	-	-
Formulation 1	-	338	428	-
Polyester				
Polydiethylene adipate (Formulation 1 prepolymer)	very slow reaction	236	279	461
Polyether-polyurethane rubbers				
Formulation 6	-	590	-	-
Formulation 13	412	616	624	very fast reaction
Polyether				
Polypropylene glycol (Formulation 13 prepolymer)	243	476	457	very fast reaction
Polyisobutene				
(1×10^6 poise at 25°C)	295	393	391	519

/The .....

The polyether rubbers produce a greater volume of gas than the polyester rubbers at any given temperature and the rubbers give greater final volumes of gas than the corresponding prepolymers. It can be seen in Figures 2a and b that polyether-polyurethanes degrade faster than polyester-polyurethanes while polyisobutene produces gas at an intermediate rate. The initial lag in gas generation for polyisobutene may be due, in part, to the heating-up of the fragment of glass on which this viscous liquid is handled in the system. In Figures 3a and 3b it can be seen that the prepolymers follow the behaviour of the rubbers in that the polyether breaks down at a greater rate than the polyester, and both types of rubber degrade faster than the corresponding prepolymers.

The infrared analysis of the gaseous products is given in Table 2 for the rubbers, and their precursors. The sum of the partial pressures of the various gases identified accounts for all of the gases in the cell within the limits of experimental error. However, a calculation of the weight of the products compared with the weight of original polymer shows that at 400°C only 40 to 70 per cent of the products are gases at room temperature in the gas cell. Formaldehyde was detected among the gaseous products of the polyether and its precursor by using analytical reagents. The same test applied to the gaseous pyrolysates of the polyester and its precursor showed no formaldehyde to be present.

TABLE 2

Products	Polyester-PU rubber (Formulation 1) % w/w	P.D.E.A.* Polyester % w/w		Polyether-PU rubber (Formulation 13) % w/w	Polypropylene glycol % w/w
CO_2	10.2	7.8	8.4	nil	nil
CO	11.2	12.6	12.0	24.9	28.9
CH_4	2.3	3.6	3.6	7.4	9.7
C_2H_4	2.8	3.6	3.7	2.5	3.5
CH_3CHO	10.8	7.1	9.9	8.7	8.9
$CH_3CH{:}CH_2$	nil	nil	nil	12.4	9.2
CH_2O	nil	nil	nil	present	present
% Unidentified	62.7	72.1	70.6	44.1 (less CH_2O)	39.8 (less CH_2O)
Temperature °C	400°	400°	450°	400° and 450°	400° and 450°

*Poly(diethylene adipate)

/5. .....

5. COMPARISON OF RESULTS

The results in Figures 2a and b show that at 400° and 450°C the order of increasing rate of gasification is: polyester-polyurethane rubbers, polyisobutene, polyether-polyurethane rubbers. Figures 3a and b show that at the same two temperatures the polyurethane rubbers degrade faster than the corresponding prepolymers, and the order of stability is preserved in that the polyester prepolymer gasifies at a slower rate than the polyether prepolymer.

These observations indicate that the urethane crosslinks are the most important points of scission for both rubbers but the structure of the precursor from which the rubber is made is probably the main factor which determines the relative rate of degradation.

The gas analysis of the products accounts for only 60 per cent of the pyrolysates at the most (Table 2). The formaldehyde produced by the polyethers probably forms a proportion of the products equal to that of the acetaldehyde, but this still leaves 20 to 70 per cent of the products unaccounted for. In all cases, the main bulk of the unidentified pyrolysates condense at room temperature to form a viscous liquid. The analysis of polyisobutene degradation products shows a high yield of monomer at 400°C in agreement with other workers (5); methane and ethylene were produced in addition to isobutene at 475°C.

Using the pressure of the gaseous products (x) as a measure of the extent of reaction at time (t), and the final gas pressure as a measure of initial concentration (a), it can be seen from the linear plots of log (a-x) against t (Figures 4a to f) that at 350°C a first order reaction describes the breakdown of all the materials examined. At 400°C there is a deviation from first order for the polyether rubbers and polyisobutene, while the prepolymers and the polyester rubbers retain first order characteristics, and only show signs of departure from this at 450°C. At 475°C all the substances investigated have changed from first order, indicating there is a different mechanism controlling breakdown at the higher temperatures. The values of the rate constants from the slopes of the lines, or from initial gradients (where non-linear plots were obtained in Figure 4a to f) are given in Table 3.

/TABLE 3 .....

TABLE 3

L77 Polyester - PU Rubber	Temperature °C		408°	445°	477°
	k min^{-1}		0.172	0.451*	1.40*
Formulation 1. Polyester - PU Rubber	Temperature °C	350°	400°	450°	475°
	k min^{-1}	slow rate	0.472	0.687*	0.764*
Poly(diethylene adipate) Polyester (Formulation 1 Precursor)	Temperature °C	350°	400°	450°	475°
	k min^{-1}	slow rate	0.065	0.156*	0.469*
Formulation 13 Polyether - PU Rubber	Temperature °C	350°	400°	450°	475°
	k min^{-1}	0.076	0.677*	1.49*	fast rate
Polypropylene Glycol (Formulation 13 Precursor)	Temperature °C	350°	400°	450°	475°
	k min^{-1}	0.069	0.132	0.480	fast rate
Polyisobutene	Temperature °C	547°	412°	445°	475°
	k min^{-1}	0.187	1.09*	2.68*	4.21*

*Approximate first order reaction assumed. Rate constants obtained by measuring the average slope of the graph for the first minute.

The activation energies are not consistent because of the departure from first order behaviour, and have therefore been omitted.

A series of graphs showing rate of volatilisation against percentage reaction has been drawn, (Figures 5a, b and c). These are of interest particularly with regard to the decompositions at the higher temperatures since Simha and Wall (6) have shown that the breakdown mechanism is indicated by the type of curve produced. An initial low rate followed by a maximum and a subsequent fall shows that the maximum number of free-radical chain-ends occurs late in the reaction, while a continuous fall in the rate of reaction indicates a maximum number of radical chain-ends early in the pyrolysis. It has been suggested by Oakes and Richards (7) that this second type of curve (initial maximum rate) is a modified "late maximum" curve but that the number of chain-ends builds up very rapidly due to a fast initial reaction.

From the curves in Figures 4a to c (first order plots) and the rate/percentage reaction graphs Figures 5a, b and c, it would appear that the fuel-binders examined all undergo a change in pyrolysis mechanism within the temperature range studied. For each polymer a transition-temperature range exists at which the breakdown mechanism changes from apparent first order to a radical chain mechanism. At the temperature of combustion processes the radical-chain process will be dominant.

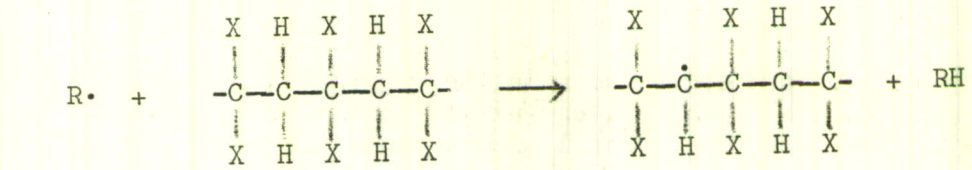
/6. .....

6. DISCUSSION

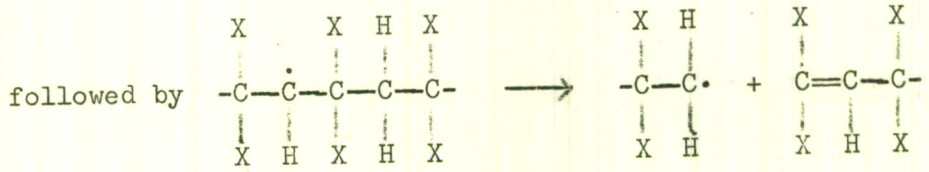
6.1 Mechanism of Depolymerisation

A polymeric molecule degrades by scissions in the chain, each break producing either two smaller stable chains, one stable chain and one free-radical chain, or two free-radical chains. Which of these processes is dominant in a given polymer depends upon factors such as chemical composition, stearic hindrance, and temperature of pyrolysis (8), (9).

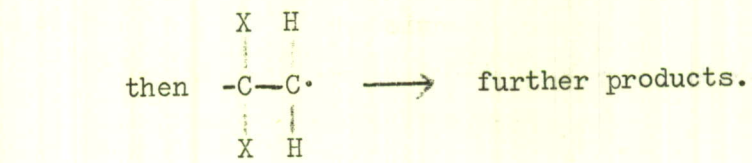
In general terms there can be hydrogen abstraction by a free-radical:



followed by

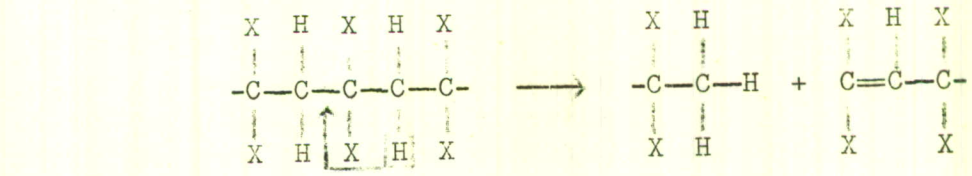


then



i.e., an olefinic end-group is produced together with a free-radical chain.

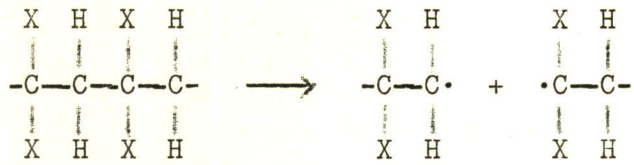
Another type of degradation process can occur by a hydrogen atom migrating without free-radical initiation:



i.e., two smaller molecules are formed per scission without the immediate possibility of further breakdown.

/A .....

A third type of rupture produces two free-radical chains:

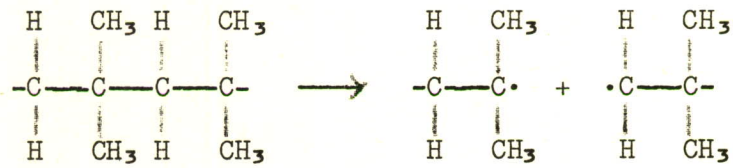


This will give rise to a higher rate of gasification than the production of one free-radical chain which, in turn, will give faster gas production than hydrogen transfer.

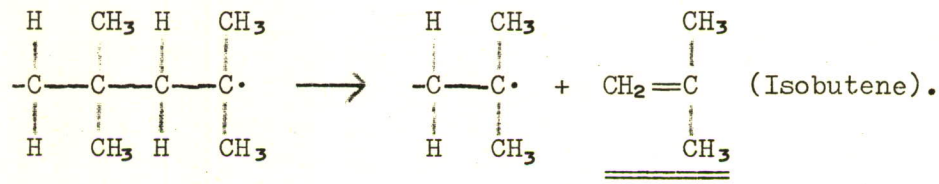
The pyrolysis of fuel binders in the region 450° to 500°C, and during burning, probably relies to a large extent on the production of two free-radical chains per scission. The other two mechanisms are subsidiary at high temperatures, although they may be dominant at lower temperatures (350° - 400°C). The different types of binder are now considered in the light of the foregoing general remarks.

6.2 Polyisobutene

The initiating reaction at 475°C is suggested to be the following:



followed by:



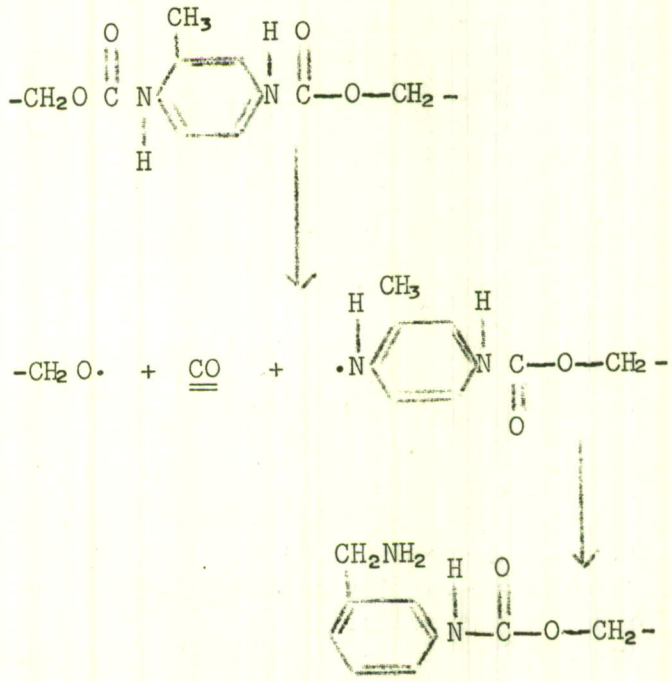
In this instance two free-radical chains are produced by the original scission which then produces monomer units until the entire chain has degraded, or radical transfer to another chain has taken place. The other two methods of depolymerisation can only occur to a limited extent at 475°C, but are probably important at much lower temperatures. The high monomer yield rules out any major contribution to breakdown being made by either hydrogen transfer, or extensive free-radical attack.

/6.3 .....

6.3 Polyester-Polyurethane Rubber

From the results (Figure 2a) it is concluded that the polyester-polyurethane rubbers (Formulation 1, HPEL 74 and L77) all break down in a similar manner; therefore the mechanism of only one polyester rubber (Formulation 1) is considered.

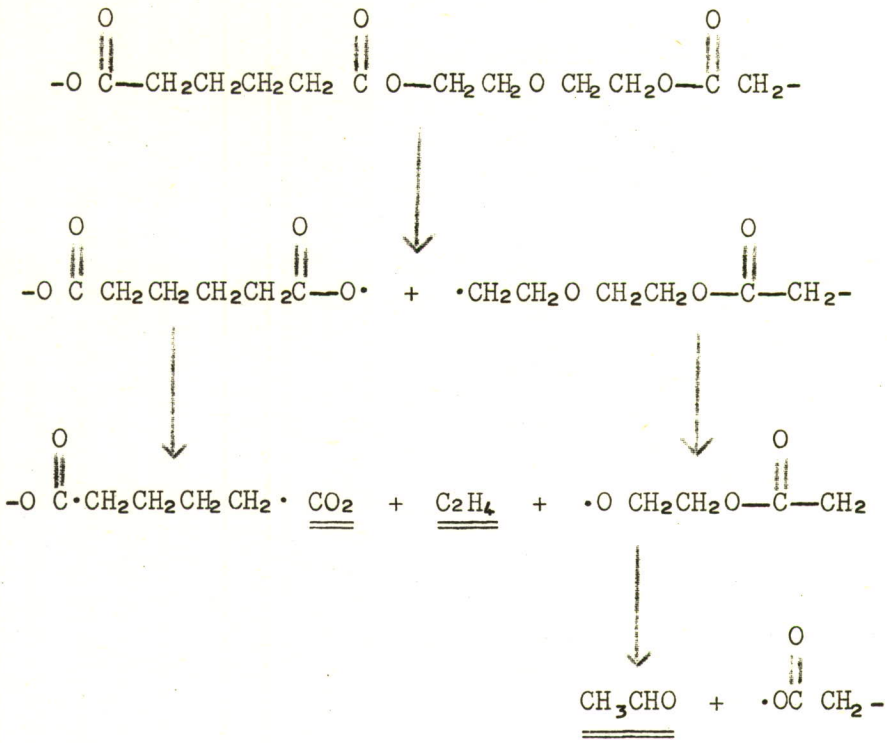
The points of chain scission to be considered are the polyester chain and the urethane crosslinks. The evidence for the urethane links being points of scission is that the rubber degrades at a faster rate than its prepolymer (Figures 3a and b). No nitrogen-containing compounds were detected in the gas analysis and no work appears to have been done on the pyrolysis of simple urethanes so the mechanism proposed is tentative but could explain the formation of some of the liquid products.



i.e., a stable amine and a free-radical chain per scission.

The degradation of the main polyester chains of Formulation 1 is probably initiated at one of the -C—O- linkages. Pohl (8) has shown that replacement of ethylene glycol by diethylene glycol in a polyester chain leads to faster breakdown (more ether linkages). The following mechanism is proposed in the light of the gaseous products found, the absence of formaldehyde, and the observations on chain stability by Pohl (8).

/Formulae .....



The pyrolysis of acetaldehyde would account for the production of methane and carbon monoxide:

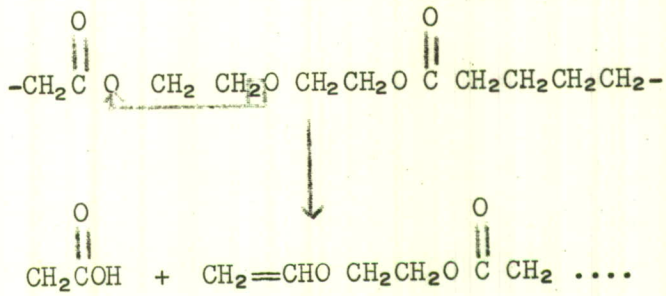
$$CH_3CHO \longrightarrow CH_4 + CO$$

The mechanism proposed would lead to complete degradation of the chains but this is probably a rare occurence even at 475°C since analysis only accounts for a small percentage of low molecular weight products. The slower rate of breakdown of the polyester chains compared with the polyethers and polyisobutene probably lies in the stability of the acid chain which has a $-CH_2 \cdot CH_2-$ structure with no preferential points of chain scission as in polyisobutene. (Polyethylene is much more stable than polyisobutene for this reason.)

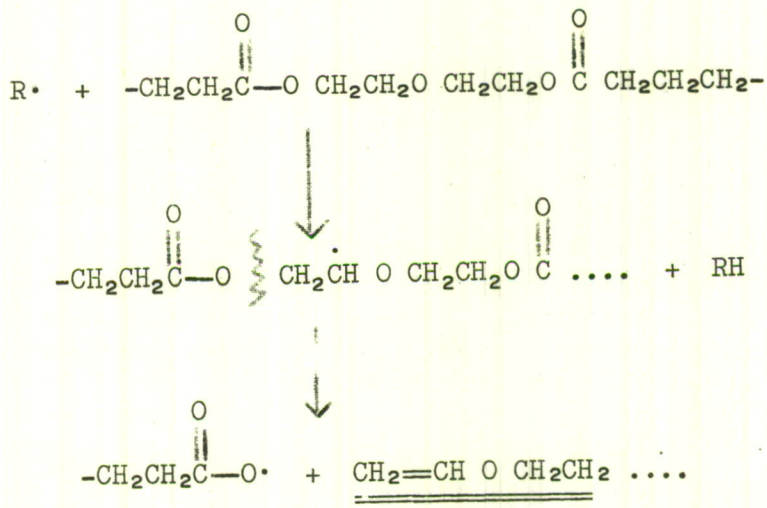
Other competitive reactions in the degradation of the polyester chains are hydrogen transfer and free-radical attack:

/Hydrogen transfer .....

Hydrogen transfer



Free-radical attack (hydrogen abstraction) would give

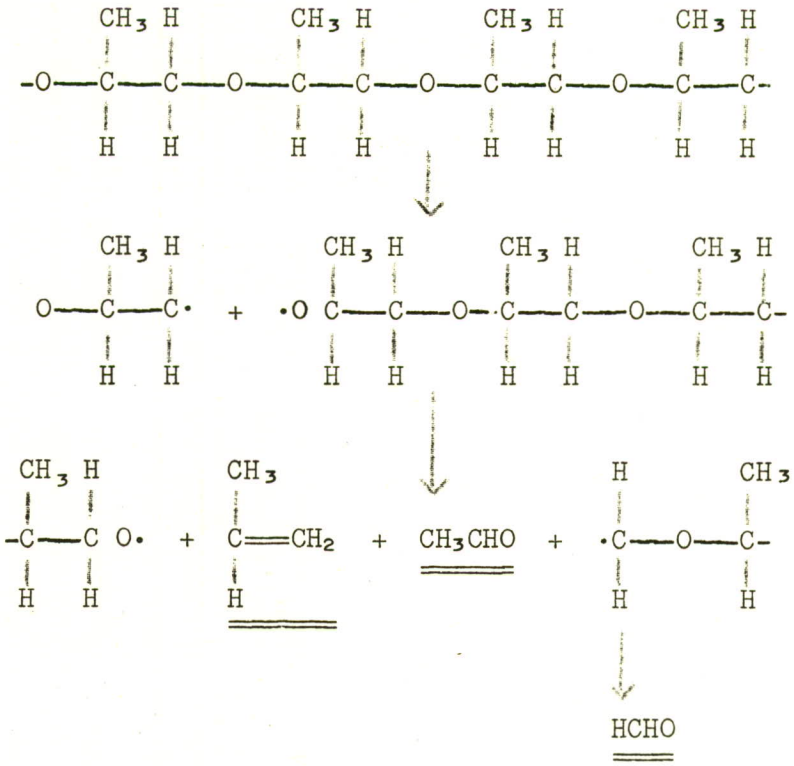


a stable end group and a free-radical chain. These reactions are probably important at the lower temperatures.

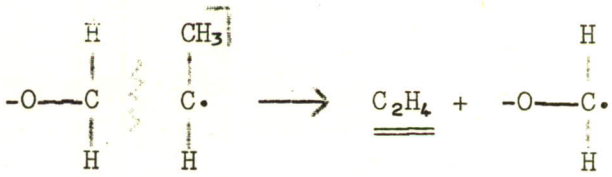
6.4 Polyether-Polyurethane Rubber

The foregoing remarks on the lowering of stability by the inclusion of ether linkages in the chain is further substantiated by the breakdown of polypropylene glycol polyurethane rubber. The urethane links are points of scission as in the polyester rubber but comparison of polyether with polyester prepolymer shows that the main cause of the difference in the rates of gasification lies in the structure of the polymer chains. Thus for the polyether at the higher temperatures:

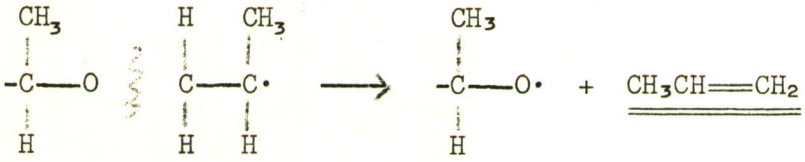
/Formulae .....



The degradation products of the polypropylene chain are therefore propylene, acetaldehyde and formaldehyde. Methane and carbon monoxide are produced from the decomposition of acetaldehyde. If the mechanism is correct then the quantity of formaldehyde produced should be the same as the propylene. The production of ethylene is not explained by the mechanism but could be due to the chain degrading thus:



instead of:



/6.5 .....

6.5 Future Work

The present investigation has shown that at temperatures just below the surface temperatures of burning propellants the rate of bulk pyrolysis of the fuel binders examined is increasingly rapid in the order: polyester-polyurethane rubber, polyisobutene, polyether-polyurethane rubber. It would be desirable now to relate fuel pyrolysis characteristics to the burning rates of composite propellants based on these fuels. For this purpose a logical extension of the present work would be a direct comparison of the burning rates of composite propellants with those of the fuels pyrolysing at temperatures and pressures encountered in rocket motors.

7. REFERENCES

1. G.K. Adams, B.H. Newman, and A.B. Robins, E.R.D.E. Report No. 16/R/54.
2. E.M.G. Cooke, F.H. Doe, B.H. Newman, and J. Scrivener, E.R.D.E. Report No. 27/R/62.
3. J. Scrivener and A.J.B. Thomas Unpublished Work on Polyurethane Rubbers.
4. J. Powling and W.A.W. Smith, Combustion and Flame, 1962, 6, 173.
5. S.L. Madorsky, S. Strauss, D. Thompson and L. Williamson, J. Res. Nat. Bur. Stand. 1949, 42, 499.
6. R. Simha and L.A. Wall, 1962, J. Phys, Chem., 56, 707.
7. W.G. Oakes and R.B. Richards, 1949, J. Chem. Soc., 2929.
8. H.A. Pohl, J. Amer. Chem. Soc., 1951, 73, 5660.
9. "High Temperature Resistance and Thermal Degradation of Polymers" S.C.I. Monograph No. 13, p.65.

/APPENDIX .....

APPENDIX

Polymer Compositions

L77 Polyester

14.5	moles	Diethylene glycol
13.0	moles	Isosebacic acid†
0.5	mole	Trimethylolpropane
2.2	moles	Suprasec S.F.*

Formulation I Polyester

1.0	mole	Poly(diethylene adipate)
0.7	mole	Hexane-1,2,6,-triol
2.05	moles	2,4-Tolylene di-isocyanate

HPEL 71 Polyester

14.5	moles	Neopentyl glycol
13.0	moles	Isosebacic acid†
0.3	mole	Pentaerythritol
2.2	moles	Suprasec S.F.*

HPEL 74 Polyester

14.5	moles	Diethylene glycol
13.0	moles	Isosebacic acid (methyl ester)†
0.5	mole	Trimethylolpropane
2.2	moles	Tolylene di-isocyanate*

Formulation 13 Polyether

1.0	mole	Shell 2000 Polypropylene glycol
0.07	mole	Shell Triol G 4000
1.05	moles	Suprasec S.F.*
Trace		Ferric acetyl acetonate
Small amount		Phenyl-β-naphthylamine

/Formulation 6 .....

Formulation 6

1.0	mole	Polypropylene glycol
0.15	mole	L.H.T. 2025 Triol
0.017	mole	Phenyl-β-napthylamine
Trace		Ferric acetyl acetonate
0.26	mole	Suprasec S.F.*

---

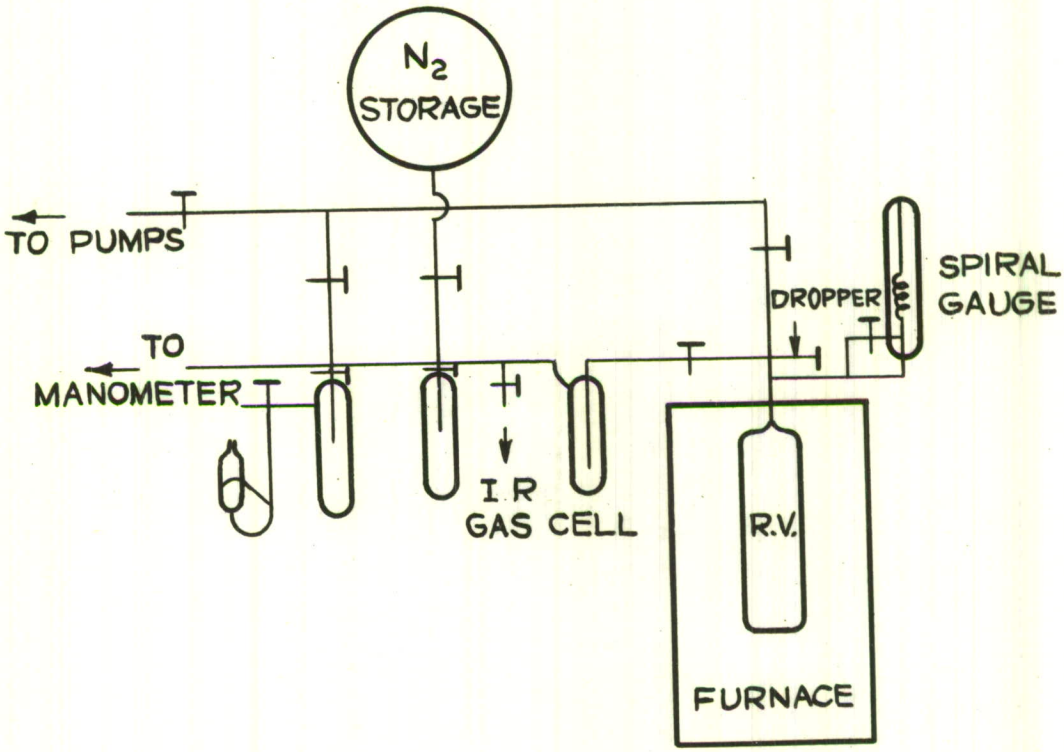
†Isosebacic acid is a mixture of:

72 to 80 per cent 2 Ethyl suberic acid
12 to 18 per cent 2,5 Diethyl adipic acid
6 to 10 per cent Sebacic acid

*Suprasec S.F. is a mixture of 2,4- and 2,6-Tolylene di-isocyanate.

S. No. 907/65/RA

TECHNICAL LIBRARY
BLDG. 313
ABERDEEN PROVING GROUND MD.
STEAP-TL



PYROLYSIS APPARATUS

FIG. 1.

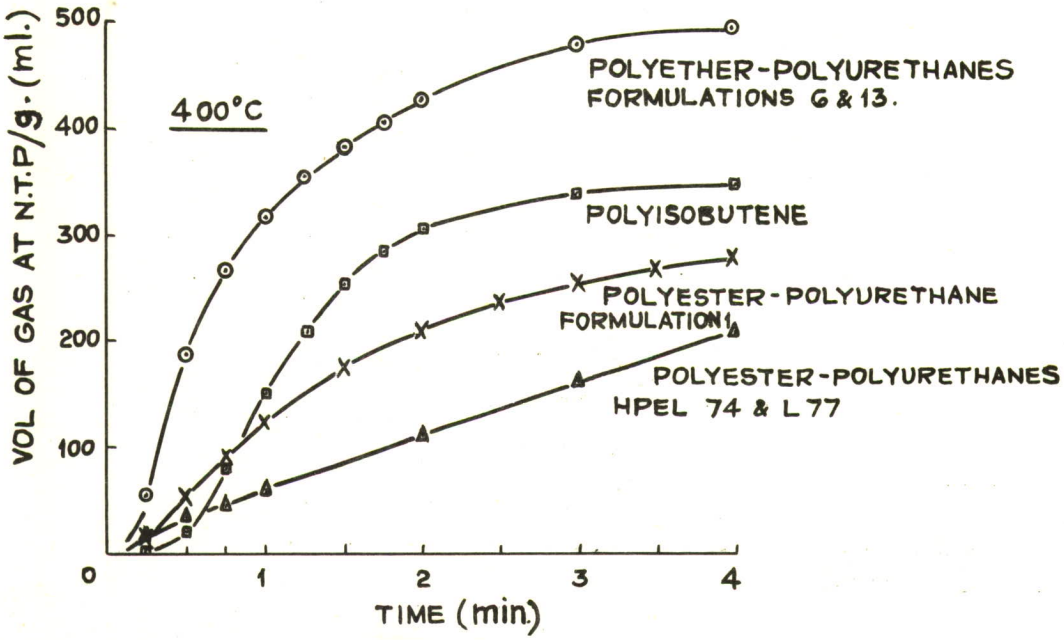

VOL OF GAS AT N.T.P/g. (ml.)
500
400
300
200
100
0
1
2
3
4
TIME (min.)
400°C
POLYETHER-POLYURETHANES
FORMULATIONS 6 & 13.
POLYISOBUTENE
POLYESTER-POLYURETHANE
FORMULATION 1
POLYESTER-POLYURETHANES
HPEL 74 & L77

FIG. 2 a.

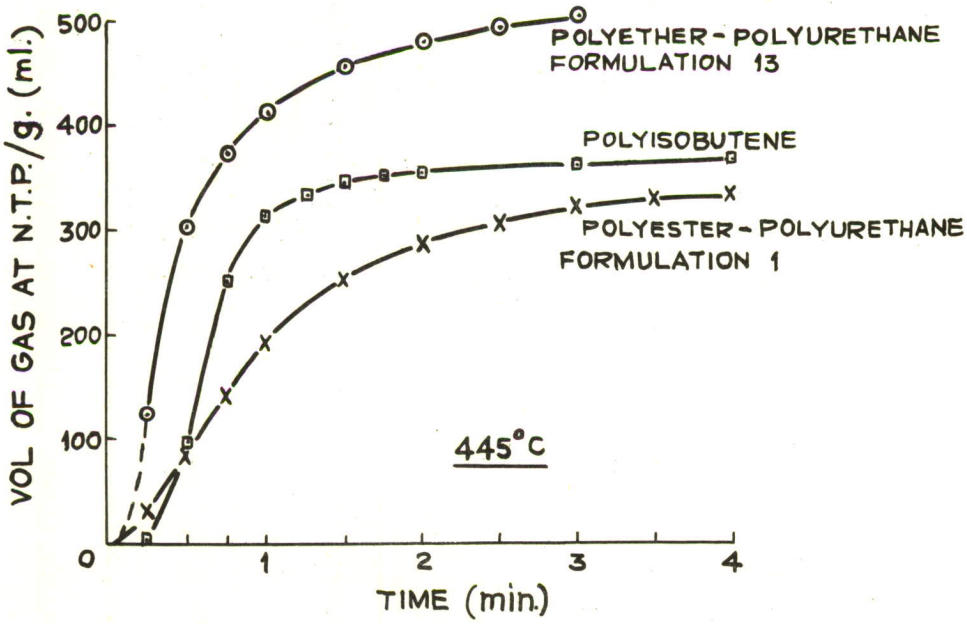

VOL OF GAS AT N.T.P./g. (ml.)
500
400
300
200
100
0
1
2
3
4
TIME (min.)
POLYETHER-POLYURETHANE
FORMULATION 13
POLYISOBUTENE
POLYESTER-POLYURETHANE
FORMULATION 1
445°C

FIG. 2 b.

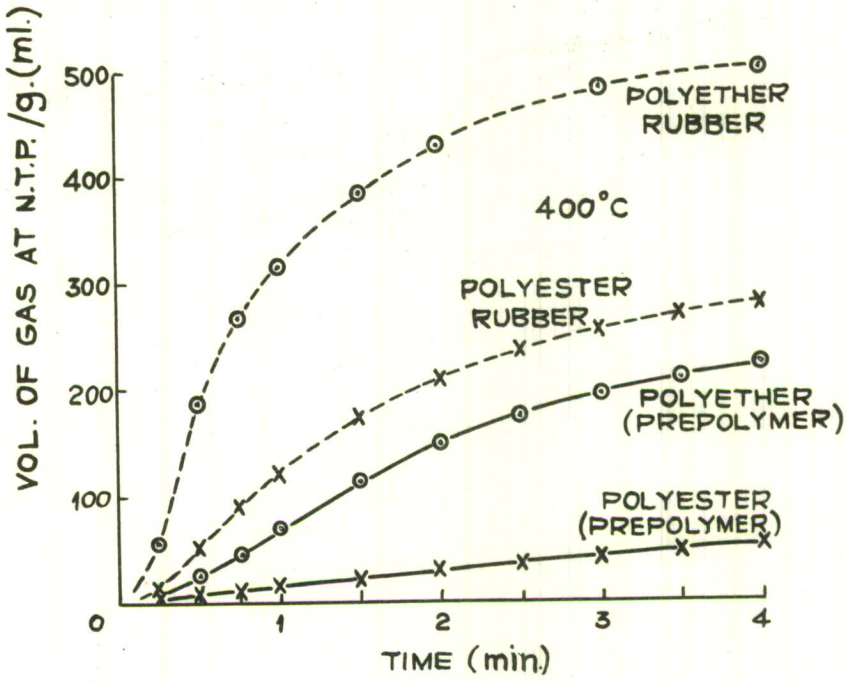

VOL. OF GAS AT N.T.P. /g.(ml.)
500
400
300
200
100
0
1
2
3
4
TIME (min.)
POLYETHER RUBBER
400°C
POLYESTER RUBBER
POLYETHER (PREPOLYMER)
POLYESTER (PREPOLYMER)

FIG. 3 a.

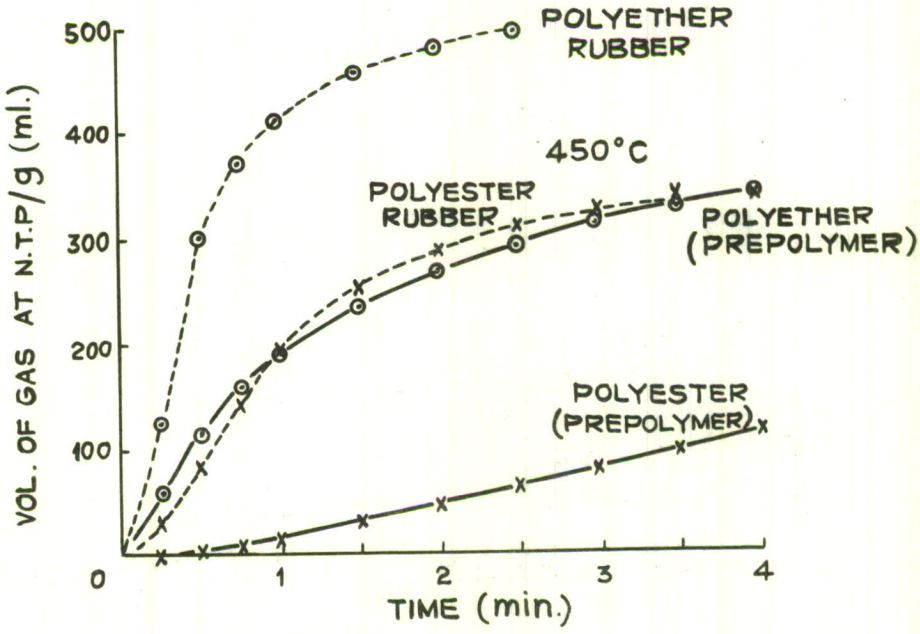

VOL. OF GAS AT N.T.P/g (ml.)
500
400
300
200
100
0
1
2
3
4
TIME (min.)
POLYETHER RUBBER
450°C
POLYESTER RUBBER
POLYETHER (PREPOLYMER)
POLYESTER (PREPOLYMER)

FIG. 3 b.

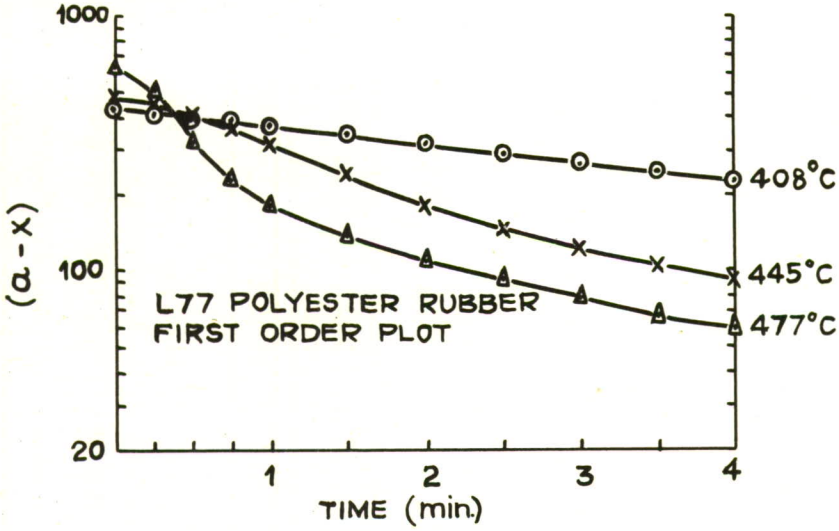


FIG. 4 a

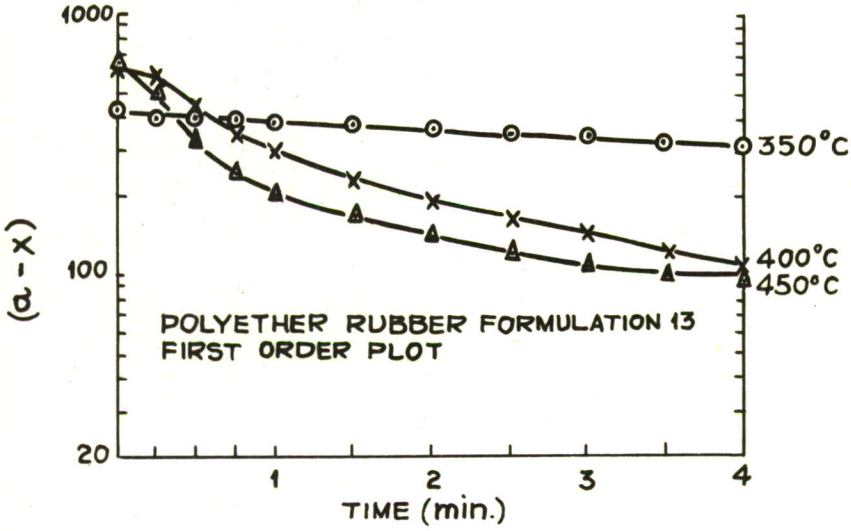


FIG. 4 b

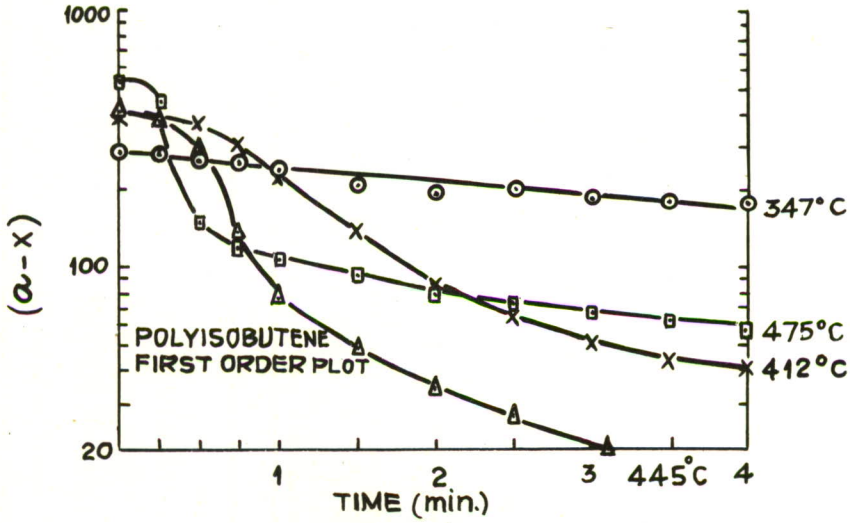


FIG. 4 c

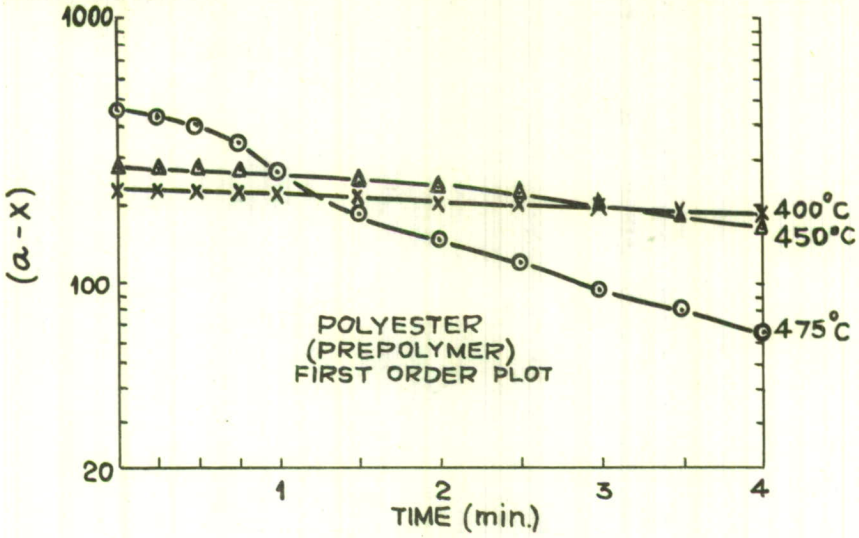


FIG. 4 d.

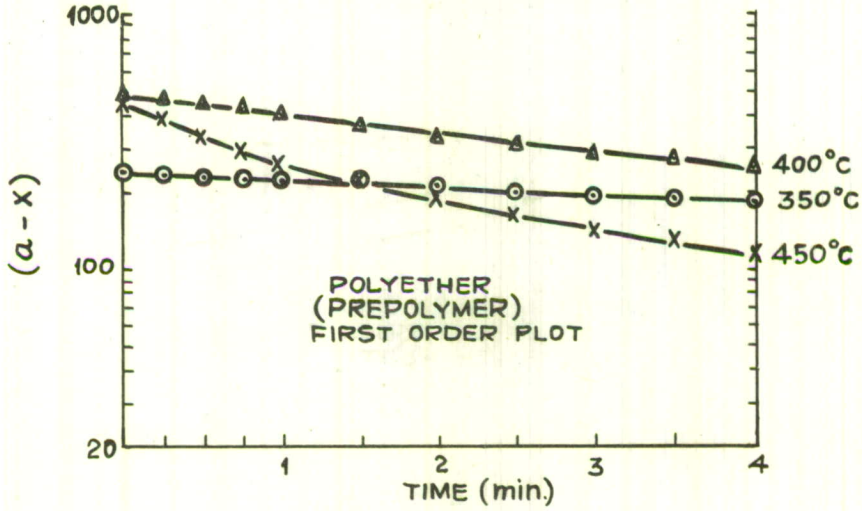


FIG. 4 e

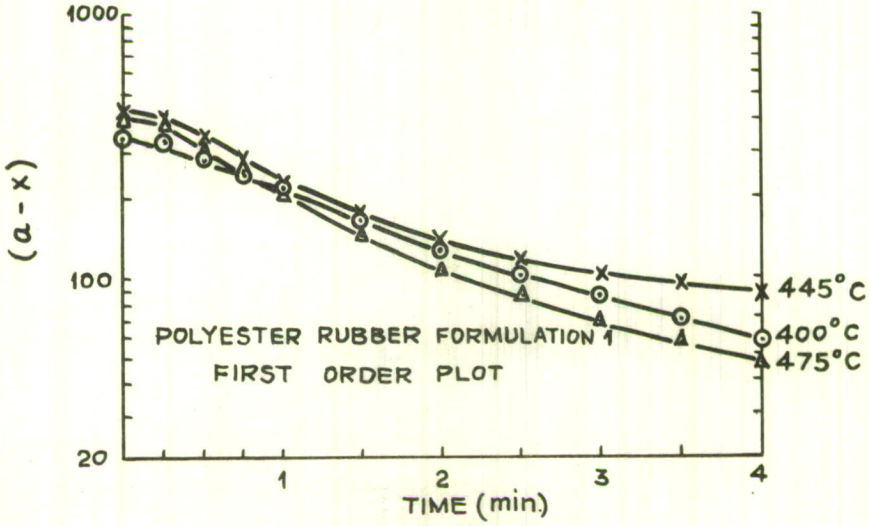


FIG. 4 f

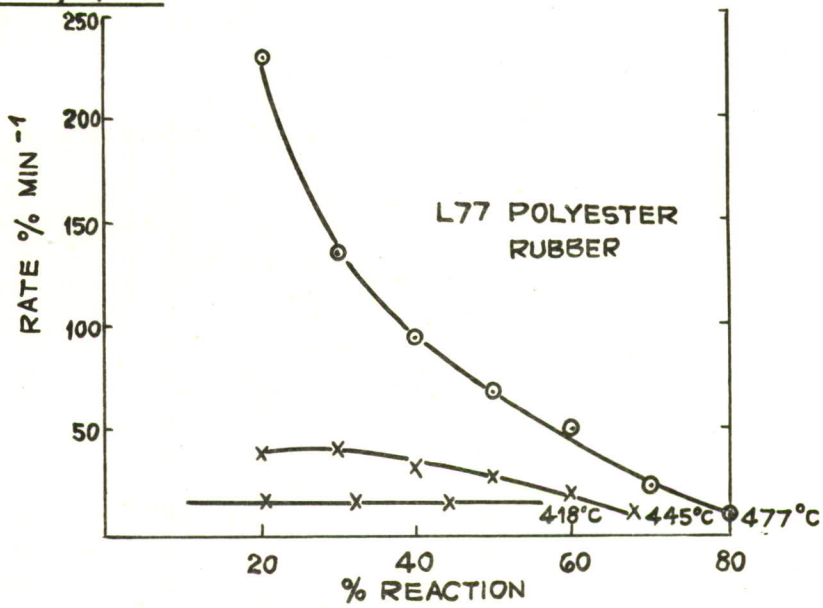


FIG. 5 a

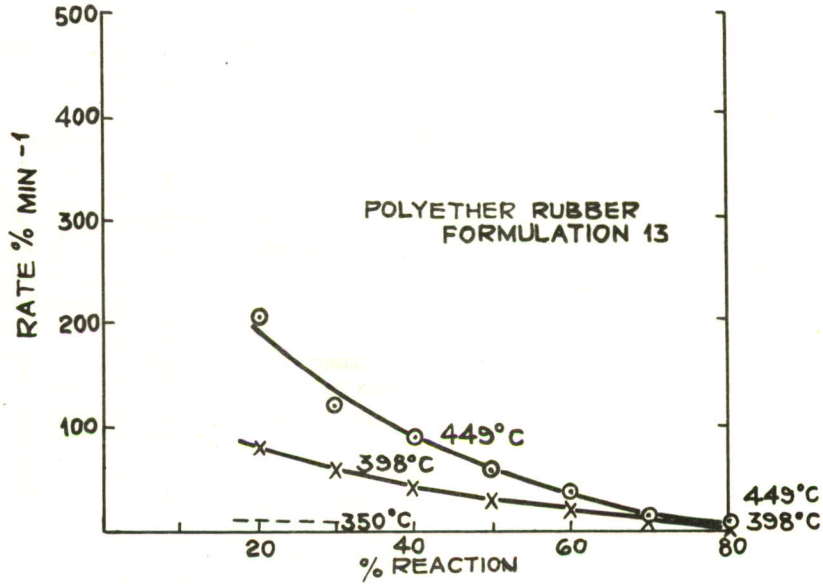


FIG. 5 b.

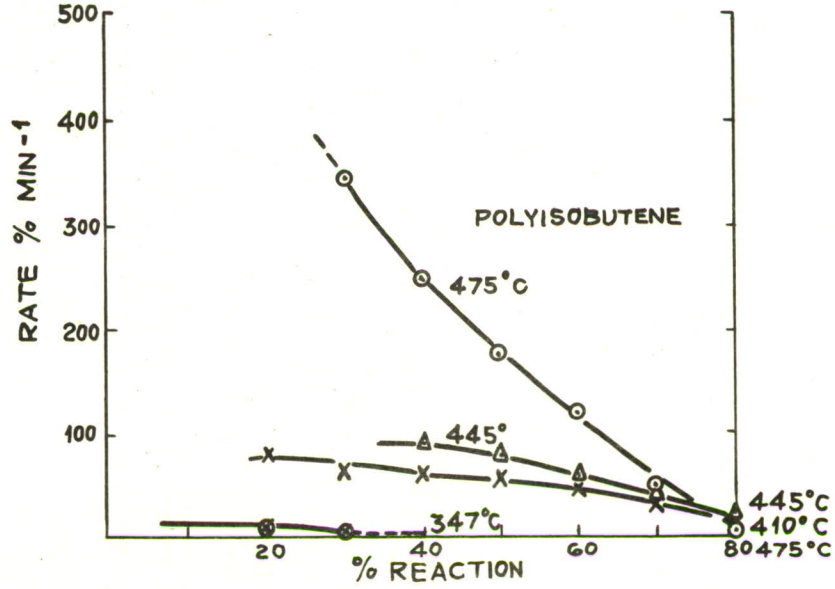


FIG. 5 c.

[dstl]
Information Centre
Knowledge Services
[dstl] Porton Down
Salisbury
Wilts
SP4 0JQ
[illegible]
Tel: 01980-613753
Fax 01980-613970

Defense Technical Information Center (DTIC)
8725 John J. Kingman Road, Suit 0944
Fort Belvoir, VA 22060-6218
U.S.A.

AD#: AD467495

Date of Search: 8 December 2008

Record Summary: AVIA 37/1146
Title: Pyrolysis of some composite propellant fuel binders
Availability Open Document, Open Description, Normal Closure before FOI Act: 30 years
Former reference (Department) ERDE 13/R/65
Held by The National Archives, Kew

This document is now available at the National Archives, Kew, Surrey, United Kingdom.

DTIC has checked the National Archives Catalogue website (http://www.nationalarchives.gov.uk) and found the document is available and releasable to the public.

Access to UK public records is governed by statute, namely the Public Records Act, 1958, and the Public Records Act, 1967.
The document has been released under the 30 year rule.
(The vast majority of records selected for permanent preservation are made available to the public when they are 30 years old. This is commonly referred to as the 30 year rule and was established by the Public Records Act of 1967).

This document may be treated as UNLIMITED.