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## COMPOSITE PROPELLANT DEVELOPMENT

Parts I, II and III

by

*L.A. Dickinson*



DEFENCE RESEARCH BOARD

CANADIAN ARMAMENT RESEARCH AND DEVELOPMENT ESTABLISHMENT

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Parts I, II and III

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L.A. Dickinson

Propellant Development Group

Explosives Wing

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ABSTRACT

The considerations leading to the selection of case bonded composite rocket propellants as a main field for research in support of the Canadian Armed Forces are described. The type of composite propellants selected had to be suitable for casting and had to possess adequate processing, physical and ballistic properties. It was considered that polyurethane binders were a promising field for applied research and an initial survey of this type of elastomer was carried out.

While many useful research leads developed from the survey, it was found that many factors affected the superficially simple preparation of polyurethane elastomers. In spite of these initial problems propellants with adequate properties are now being satisfactorily prepared.

Future avenues for research are in the fields of partially crystallizable elastomers and high energy propellants utilizing reactive aluminum alloy powders.




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ACKNOWLEDGEMENTS

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COMPOSITE PROPELLANT DEVELOPMENT

## PART I

INTRODUCTION TO THE PROGRAMMEINTRODUCTION

The advent of guided missiles in the last decade has led to large scale development of rocket power plants since they offer a convenient means of rapidly obtaining the supersonic speeds which military operations now call for. It is generally accepted that solid propellants have an increasing role to play in the evolution of guided missiles and that the crash development programmes of existing propellants, while often giving temporary solutions, have often served only to reveal the limitations of these propellants.

Although the conditions to be met by a satisfactory solid propellant will be described in detail subsequently, it is pertinent to outline the main requirements of the Canadian Armed Services. Any propellant must preferably be:

- (i) serviceable over the temperature range  $-50^{\circ}$  to  $+70^{\circ}$ C,
- (ii) based on non-strategic materials indigenous to Canada and relatively inexpensive to manufacture,
- (iii) adaptable to the manufacture of both large and small rocket engines, and
- (iv) capable of use in engines which are subject to accelerations of up to 100 g.

In an attempt to fulfill these requirements as closely as possible, CARDE is currently involved in the development of elastomeric case-bondable composite propellants which are to be known as "CARDEPLEX Propellants".

A wide variety of solid propellants has been considered for use in rocket engines. The two chief groups are:

- (i) double-base propellants containing nitrocellulose and nitroglycerine or other nitric esters, and
- (ii) composite propellants consisting of an inorganic oxidizer with an organic fuel which frequently serves to bind the oxidizer crystals together by formation of a complex polymer matrix.

The extensive experience with single and double-base gun propellants over the last century led to the selection of these propellants for rocket use prior to, and during, World War II. Large volume production of double-base rocket charges up to 5 in. calibre was common practice in the United Kingdom, United States and U.S.S.R. by 1945. Even during this period the relative high price of double-base propellants had initiated research into alternative propellants. In the U.K. plastic propellants based on a mixture of polystyrene and poly- $\alpha$ -methylstyrene with crystalline oxidizers were being developed; in the U.S. Galcit propellants consisting of asphalt and inorganic perchlorates were used in Service JATO's for aircraft; there is no reason to suggest that the U.S.S.R. lagged in this field.

In the decade from 1945, double-base propellants have carried the main burden of guided missile development work although the composites have made an important contribution. This period has indicated the limitations of double-base propellants which may be summarized as follows:

- (a) they cannot be readily case-bonded and must, therefore, be rigid enough to withstand, over the extremes of temperature, the compression loading which appears during acceleration. The nature of the material is such that a propellant which is acceptable at elevated temperatures is too brittle at low temperatures (Fig. 1.1),
- (b) large grain cross-sections are prone to cracking on temperature cycling, because of unequal thermal expansion arising from poor thermal conductivity and associated rheological factors, and
- (c) the chemical instability of nitric esters tends to preclude long storage of large grains since the decomposition products cannot readily diffuse out; consequently, an internal pressure builds up which ultimately cracks the grain.

Both the case-bonded and loose-filled composite propellant grains have been investigated. The main contenders in the first class are Thiokol propellants which use a polymerizable polysulphide binder and the U.K. plastic propellant which now uses polyisobutylene as a 'tack' binder. The U.K. propellant is satisfactory for small grains but very large grains deform too readily under their own weight at elevated temperatures. Thiokol propellants are still being improved but the main objections to their universal acceptance have been the poor properties of elongation at low temperatures and the tendency to form an incombustible surface skin on prolonged storage. In these case-bonded systems, the engine case takes out the loads induced by acceleration and there is no accumulative stress build-up down the grain.

In the second class there are the cast and extruded grains. Foremost among cast grains has been Aeroplex using a polystyrene binder diluted with a polyester prepolymer while extruded grains are made using the Phillips butadiene/methylvinylpyridine copolymer or oil-modified butyl rubbers. These latter types of binder have used ammonium nitrate as oxidizer and, since mixing involves mastication of a stiff dough, it is not surprising that ignitions (leading to detonation) have been reported by several contractors.

From these considerations of the various types of propellant, it appears that case-bonded composite propellants are not likely to suffer from defects associated with double-base propellants and hence they present the most promising propellant field for investigation. In the succeeding sections, various aspects of composite propellant formulation and processing are discussed to indicate the factors to be considered.

## PROPELLANT REQUIREMENTS

### Composite Propellants

This investigation has aimed at developing easily processable case-bonded propellants based on a cross-linked organic binder associated with an inorganic oxidizer. Experience with composite propellants had indicated that certain characteristics are desirable in the propellant in both its cured and uncured state. While the desired properties of the cured propellant should tend to be static, variations in the raw propellant may be permitted since handling methods can vary. Accordingly, note of this was taken in setting down the suggested properties and the associated flow sheet for processing rocket propellants (Fig. 1.2).

The experimental programme has been confined to propellants based on ammonium perchlorate. Ammonium nitrate is a low cost oxidizer but its use presents some difficulty due to poor moisture resistance, caking tendency, and crystal phase change; ballistically it gives propellants with low burning rates and low specific impulses. Methods exist for overcoming some of these defects and ammonium nitrate may be investigated in future work.

### Manufacture of Composite Propellants

Two methods exist for filling propellant into rocket engine tubes. The first is based on a casting technique in which a slurry of binder intermediates and oxidizer is poured into an engine tube which contains a shaped former to fix the conduit. In the other method a non-pourable viscous dough is extruded by a screw press (pug mill) into the engine tube where it is subsequently consolidated and formed under pressure by forcing in a shaped former.



The first method offers more scope for large scale production since a slurry can be more easily handled and the casting of large engines poses no major problems. Care must be taken to prevent settling out of the oxidizer or crystals during handling and vibration casting. Another advantage of slurry mixing is that little or no abrasion of the crystals occurs. Increase of raw propellant viscosity into the dough region means that more energy is dissipated in the mixing process causing crystal abrasion and increasing the ignition hazard. Furthermore, doughs may pose severe handling problems and the chance of obtaining voids in forming the grain is increased.

Factors Affecting Fluidity of the Propellant Mix

The two main factors controlling the fluidity of the raw propellant are the particle size distribution of the oxidizer and the viscosity of the resin binder. The use of coarse particles means that the surface to be wetted by the binder decreases and the amount of voids to be filled with binder increases. These two effects work against each other but, by using a bimodal coarse and fine particle size distribution, considerable gains in fluidity can be made. The fine particles serve to fill the voids. Since particle size distribution also affects the ballistic behaviour of the cured propellant, strict control is necessary. This involves specification of the particle size of the materials as crystallized from the mother liquor and control of the types of mill or grinder used in subsequent size reduction.

The percentage of binder used exerts a controlling effect on viscosity although the thermo-chemical nature of the binder determines its optimum concentration in relation to the oxidizer used. Where the binder is a carbonaceous fuel, worthwhile propellants must have an oxidizer content in the region of 70 to 80 per cent; fortunately it is possible to produce fluid mixes at this level. If high energy binders are used the oxidizer content may be considerably reduced, possibly as low as 50 per cent; unfortunately, high energy binders are often nitro-compounds or nitrate esters and, besides having a high glass point, suffer from chemical instability. Experience has shown that binders should possess viscosities in the region 100 to 1000 centipoises (15 to 30°C) if manageable slurries are to be obtained. Some improvement of mix viscosity may be made by incorporating surfactants.

Polymerization

It is an obvious requirement that the binder used should neither liberate a large amount of heat nor exhibit a large volume shrinkage during polymerization. This condition can be met by using high molecular weight prepolymers but an upper limit is fixed by the maximum viscosity which can be accepted in the mixing process.

To obtain a satisfactory propellant the polymerization reaction should proceed to completion at the curing temperature. If not, there is a danger that the product will harden at high temperatures or on long storage. For this reason it may be that the peak temperature reached during curing should exceed the normal upper working or storage temperature; if the reaction can be made to go to completion at a lower temperature, so much the better. A very high curing temperature should be avoided since it tends to cause excessive thermal shrinkage and cracking.

Handling considerations necessitate that the reaction should not proceed with appreciable velocity at room temperature and this suggests that a curing temperature of 40° to 70°C should be aimed at; any exothermic reaction will take the propellant up to a higher temperature which would vary with the binder and 100° to 150°C could be accepted. Ammonium nitrate propellants must be cured at temperatures below 100°C to obviate any chance of decomposition.

High temperature exotherms may be overcome by curing at a lower temperature with cooled cores, or using a two-stage cure consisting of one slow step at room temperature and a fast step at a higher temperature. Long cures at elevated temperatures must be avoided since they involve an uneconomic tie-up of plant and facilities. The possibility of two-stage cures using different active groups which react at definite temperatures may be feasible as a means of controlling physical properties. For instance, chain extension might be promoted at 40°C while the cross-linking of these chains could be carried out at 75°C. Competition between the various reacting groups could thus be avoided.

In addition to the points outlined above, two other points are relevant. Firstly, systems which generate gas during curing and systems which are unstable to traces of water should be avoided since traces of water may be difficult to exclude during large scale manufacture. Secondly, the intermediates should be of low toxicity or alternatively be handled satisfactorily by mechanical means under remote control.

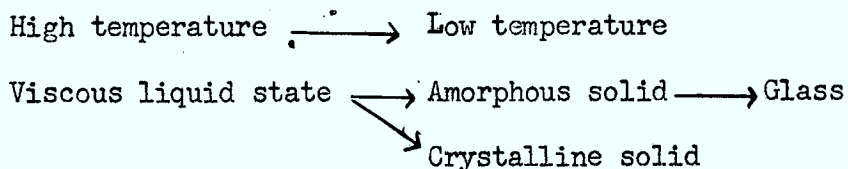
#### Rheology of the Cured Propellant

It is assumed that all acceleration loading will be transmitted from the propellant to the engine case wall and that column loading of the propellant will not occur. The propellant should possess a low modulus of elasticity, a high elongation to break and high strength to accommodate the stresses induced by temperature cycling. Under all conditions it is thought that the following minimum requirements should be met:

	<u>Cured Binder</u>	<u>Cured Propellant</u>
Elongation to Maximum Stress, per cent	300 - 400	15 - 20
Young's Modulus, psi	30 - 600	750 - 10,000
Maximum Stress, psi	100 - 300	60 - 150

Adequate elasticity must be maintained down to low temperatures and it is thought that the 'brittle point' of the propellant should be in the region of  $-60^{\circ}\text{C}$ . The definition of the term is arbitrary and it is probably best described as that point at which, with a particular design, the elongation is insufficient to accommodate the stresses induced by temperature change. The glass point of the polymer will be  $20^{\circ}$  to  $30^{\circ}\text{C}$  below this.

A further factor to be considered is crystallization; during cooling an elastomer enters temperature zones in which one particular type of structure predominates, e.g.



There is little difference between the liquid and amorphous solid state since both are in considerable disorder but, at a certain temperature, it is possible for an ordered (i.e. crystalline) state to exist in equilibrium with the liquid. Owing to the nature of polymers, the transition point is generally diffuse and may extend over a broad temperature band. Crystallinity need not embrace the whole macromolecule but only those segments of it which contain small repeating units. The rate of interchange between the states varies with temperature; at high temperatures the molecular segments have high thermal energy and are able to resist the forces promoting order, while at low temperatures the probability of escape from the ordered state decreases. Since the rate of crystallization varies with temperature, rapid supercooling can result in the preservation of a metastable amorphous state in a temperature zone where it is thermodynamically unstable. Frequently a polymer consists of amorphous regions in which small crystalline pockets are embedded. On further cooling the amorphous state changes into a rigid glass, at a temperature denoted by  $T_g$ , in which the kinetic motion of the individual segments of the molecule virtually ceases. The crystalline structure undergoes no further major change of state with decrease in temperature. It is possible to cause irreversible crystallization of the metastable amorphous state by increasing the order in the structure by application of mechanical stress; for this reason elastomers which appear to be serviceable can become useless due to embrittlement when slightly stressed.

It is obvious that the most useful elastomer is one that has a low glass point ( $T_g$ ) and is not prone to crystallization. However, the requirement for high strength demands that crystallization should take place reversibly on application of stress and it is sometimes necessary to compromise between a polymer with adequate low temperature properties and one with adequate strength. Plasticizers can play a role in improving the low temperature properties in a polymer based on such a compromise. At elevated temperatures the polymer may soften but the propellant must be capable of withstanding the shear stresses induced by accelerations of up to  $100\text{ g}$  at temperatures up to  $70^{\circ}\text{C}$  and must not suffer cold flow under gravitational forces when stored for long periods of time at the upper temperatures.

Since the propellant takes out the locally induced acceleration loadings onto the engine case, the bond strength at the interface must be equivalent to the propellant shear strength. The case may be coated to facilitate bonding.

### Propellant Ballistic Properties

A diversity of propulsion requirements exists and, consequently, propellants with a wide range of burning rate should be capable of formulation. Burning rates in the range 0.1 to 1.5 in. per sec at 800 to 2000 psi pressure are required. Blends of oxidizers and burning rate catalysts can be used to meet these requirements.

### Chemical Stability

A storage life of 5 to 10 years should be obtained under magazine conditions without the occurrence of excessive physical or chemical degradation. Special care must be taken in the selection of surfactants and burning rate catalysts to avoid the introduction of de-stabilising influences. The addition of antioxidants may be necessary to prevent degradation of the polymers themselves by air oxidation.

## PROGRAMME OF RESEARCH AND DEVELOPMENT

An applied research programme was initiated with the aim of meeting the functional requirements which would enable the operational needs of the Canadian Armed Services to be fulfilled.

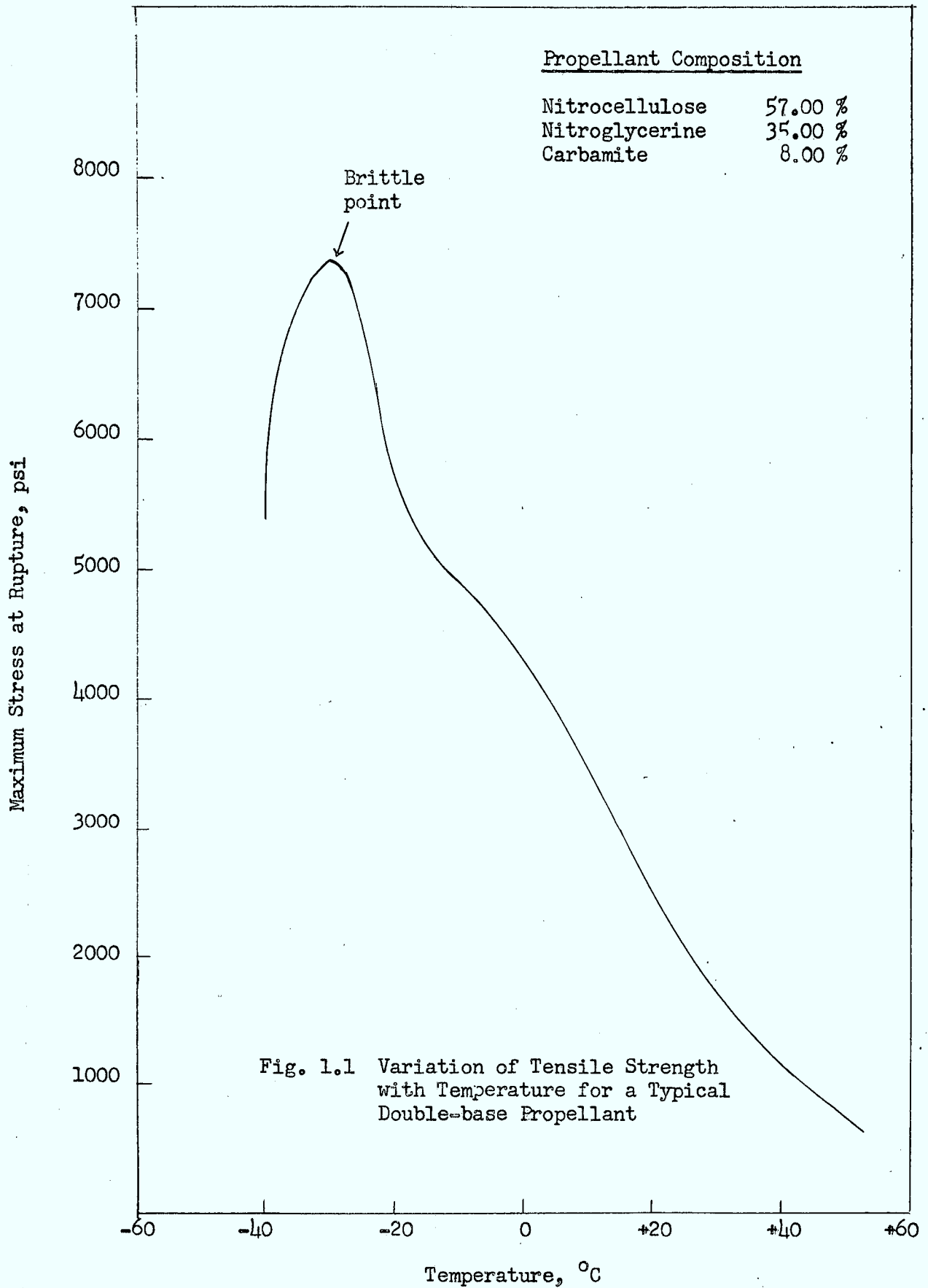
This programme was divided into four main parts:

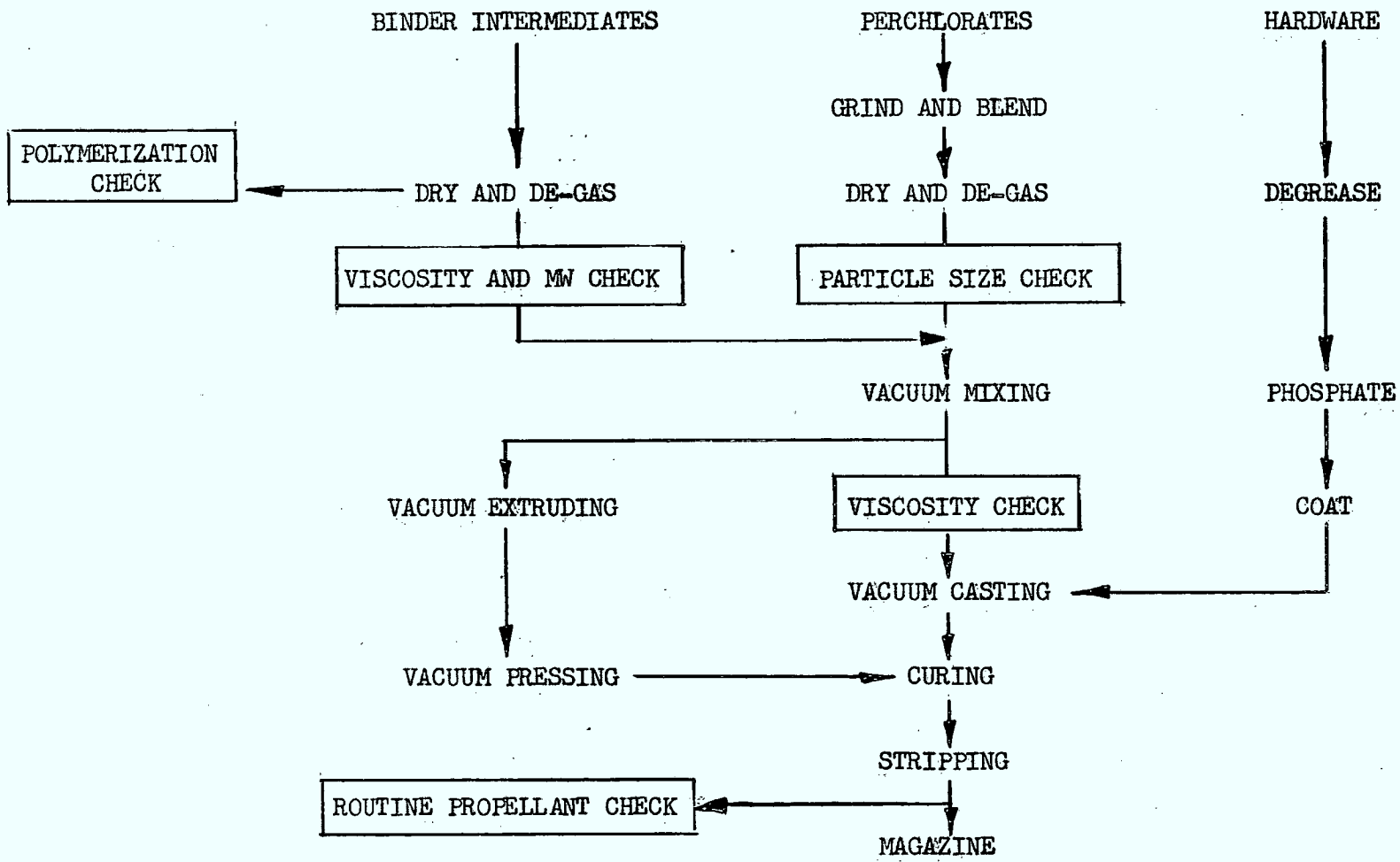
- (i) development of elastomeric binders and propellant formulations on a laboratory scale,
- (ii) provision of an experimental plant for the manufacture of large rocket engines,
- (iii) the establishment of static and environmental testing facilities for large rocket engines, and
- (iv) a research programme with the long term aim of producing new polymeric organic binders which would enable superior propellants to be formulated.

A survey of the systems available for use in polymerizable propellants, within the limitations previously outlined, indicated that the diisocyanate addition of prepolymers offered many advantages, amongst which are the following:

- (1) many fluid diisocyanates are available which can be associated with a range of fluid prepolymers,
- (2) the versatility of isocyanate chemistry allows unlimited scope for the polymer chemist to develop new polymer backbones with novel properties, and
- (3) the polymerization can be carried out at moderate temperatures.

This report is, accordingly, an interim progress statement to outline the achievements to date and sign-post the route for future development programmes.



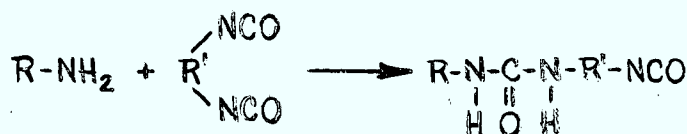
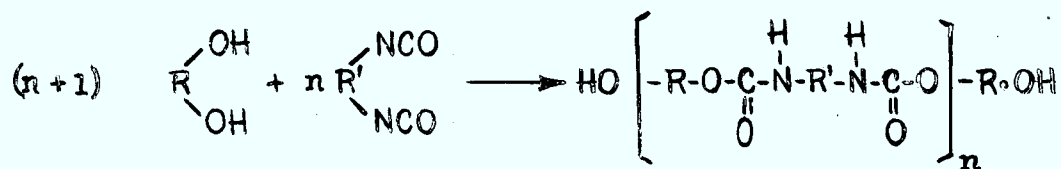


Composite Propellant Processes

Fig. 1.2.

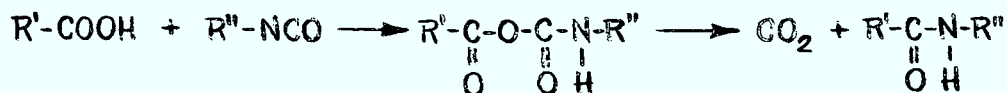
PART IITHE SELECTION OF INGREDIENTS FOR  
CASTABLE ISOCYANATE-BASED ELASTOMERSINTRODUCTION

The isocyanate-based elastomers are polymers formed by reacting di- and trifunctional isocyanates with mixtures of monomers and prepolymers containing a plurality of reactive hydrogen atoms. Typical reactions leading to chain extension are:



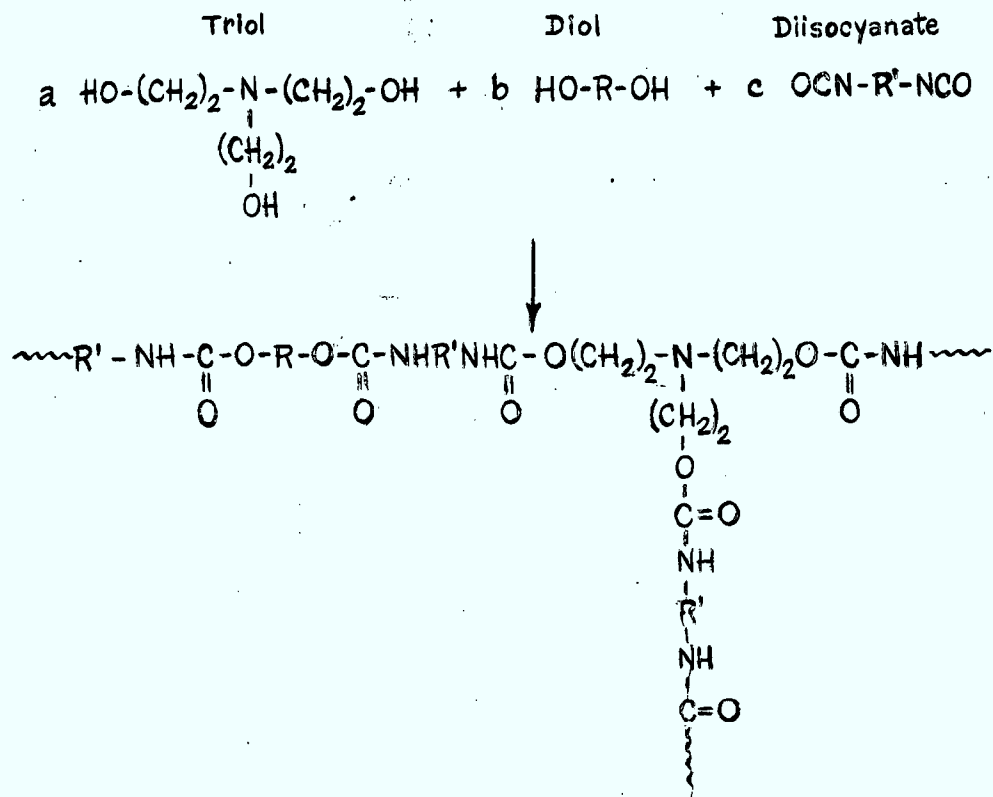
To obtain castable elastomers it is desirable to use only liquid ingredients and this considerably restricts the range of isocyanates and other reactants which can be used. For the production of gum stocks suitable for calendaring and working by conventional rubber technology, the range of ingredients is of course extended. This report will not, however, more than briefly touch on these aspects of isocyanate elastomers.

The most suitable isocyanates currently available in commercial and development quantities are the tolylene diisocyanates, hexamethylene diisocyanates, and sym-diphenylmethane diisocyanate. The other reactants available are those containing, -OH, -NH<sub>2</sub>, -NH and -SH groups; typical examples are the -OH terminated polyesters, di- and tri-esters of polyols containing -OH groups in the acid side chains (e.g. castor oil), diols and triols, the polyether diols formed by polymerizing ethylene and propylene oxides, diamines, polyamines and mercaptans. Other groups will react with the isocyanates but often undesirable side reactions occur as with the carboxylic group which gives an unstable derivative ultimately decomposing to form carbon dioxide. This reaction is useful if a foamed rubber is required, i.e.





As with all polymers, the physical properties are considerably enhanced by cross-linking the linear polymers. The build-up of a three dimensional network is easily facilitated in isocyanate polymers by incorporating a small proportion of a trifunctional isocyanate, a triol or diamine as shown below. Since the triisocyanates are more expensive than triols, diamines or other suitable reactants, they are not normally used in formulations. Cross-linking is also reported to occur through the reactions of isocyanate groups with the urethane hydrogen formed in the primary reaction. Considerable doubt appears to have been cast on this mechanism and work by Boivin<sup>(1)</sup> indicates that the diisocyanate dimers may be a factor at moderate temperatures whereas Bedard and MacDonald<sup>(2)</sup> have shown that the diisocyanate trimers may be formed under certain reaction conditions. This latter view is confirmed by work published by Kane et al<sup>(3)</sup>.



PRELIMINARY SURVEYRaw Materials

Bearing in mind both the need to investigate elastomers suitable for use in castable propellants and the necessity of determining the influence of the polymer backbone on the physical properties over the Service temperature range, a wide variety of diols and polyols was considered as ingredients. Representative homopolymeric diols are listed in Table 2.1.

TABLE 2.1Physical Properties of Diols

Homopolymers	Pouring Point, °C	Melting Point, °C	Viscosity at 100°F (cps)	Remarks on Active Groups
Polyoxyethylene Glycol:				
PEG 200	-	supercools	23	2 primary
PEG 400	-	4-8	37	2 primary
PEG 600	-	23	60	2 primary
Polyoxypropylene Glycol:				
PG-F 750 (Dow Chem)	-44	-	54	60-80% secondary
PG-F 2000 (Dow Chem)	-32	-45	175	50-80% secondary
PPG 1025 (Carbide Chem)	-39	-50	75	50-80% secondary
PPG 2025 (Carbide Chem)	-32	-45	175	50-80% secondary
Polyoxytetramethylene Glycol:				
Teracol 30 (du Pont) (Mol. wt. 3000)	-	35	5000	2 primary

A number of polyols prepared by copolymerization of alkylene oxides were also studied; typical materials are listed in Table 2.2.

TABLE 2.2

Physical Properties of Polyols

Copolymers	Pouring Point, °C	Melting Point, °C	Viscosity at 100°F (cps)	Remarks on Active Groups
Ethylene and Propylene Oxide Copolymers:				
Polyglycol 15-200 (Dow Chem) (trifunctional M.W. 2500)	-40	-	206	60-80% secondary
UCON 65-H-660 (Carbide Chem) (Random 65% C <sub>2</sub> H <sub>4</sub> O, M.W. 1600)	-	-	150	2 primary
UCON 65-H-1670 (Carbide Chem) (Random 65% C <sub>2</sub> H <sub>4</sub> O, M.W. 2870)	-	-	350	2 primary
Pluronic E61 (Wyandotte Chem) (Block 10% C <sub>2</sub> H <sub>4</sub> O, M.W. 1900)	-29	-	≈150	2 primary
1,2- and 2,3-Epoxy Butylene Copolymers:				
Polyglycol B-500 (Dow Chem)	-23	-	49	2 secondary
B-1000 (Dow Chem)	-20	-	93	2 secondary
B-1500 (Dow Chem)	-20	-	118	2 secondary
B-2000 (Dow Chem)	-17.8	-	223	2 secondary

Several fluid diisocyanates were available at the time of the initial survey and these are detailed in Table 2.3. It must be noted that mixed isomers of tolylene diisocyanate were also available but these were not considered since it was thought unwise to complicate the bulk polymerization to be carried out. A wide range of formulations was investigated.

TABLE 2.3

Physical Properties of Diisocyanates

Diisocyanates	Pouring Point, °C	Melting Point, °C	Viscosity at 100°F (cps)	Remarks on Active Groups
Hexamethylene diisocyanate	-	supercools	-	2 equivalent
2,4-Tolylene diisocyanate	-	21	-	1 de-activated
Diphenylmethane diisocyanate	-	37.2	-	2 equivalent

### Elastomer Formulations

Formulations incorporating polyoxypropylene glycols and polyoxyethylene glycols are detailed in Table 2.4.

TABLE 2.4

#### Comparison of Diols

Ingredients	Elastomer Formulation in Molecular Proportions					
	1	2	3	4	5	6
PG-P 2000	1	-	-	-	-	-
PPG 2025	-	1	1	4	-	-
PG-P 750	-	-	-	-	4	-
PEG 600	-	-	-	-	-	4
Triethylene glycol	-	-	1	-	-	-
1,2,6-Hexanetriol	1	1	1	1	1	1
2,4-Tolylene diisocyanate <sup>(1)</sup>	10	10	10	5	5	-
Remarks	B	B	A	A	A	B
Shore Hardness	39	42	31	10	-	60

A = passable elastomer; B = poor tear resistance; (1) Per cent excess over reactive groups

The use of various butylene glycols was investigated using the formulations outlined in Table 2.5.

TABLE 2.5

Comparison of Various Polymer Backbones

Ingredients	Elastomer Formulation in Molecular Proportions					
	5	7	8	9	19	20
PPG 2025	-	-	5	4	-	-
PG-P 750	4	-	-	-	-	-
PG-B 1500	-	-	-	-	4	-
PPG 1025	-	-	-	-	-	2
PG-B 1000	-	-	-	-	-	2
Teracol 30	-	4	5	2	-	-
1,2,6-Hexanetriol	1	1	2	1	1	1
2,4-Tolylene diisocyanate (1)	5	5	5	5	10	5
Remarks	A	A	A	A	D	A
Shore Hardness	-	35	20	10	5	15

A = passable elastomer; D = tacky polymer; (1) = Per cent excess over reactive groups

The cross-linking of molecules was also considered; Table 2.6 details typical formulations based on low molecular weight amino compounds while Table 2.7 details formulations using high molecular weight compounds.

TABLE 2.6

Comparison of Polyols and Cross-linking Molecules

Ingredients	Elastomer Formulation in Molecular Proportions						
	12	13	14	15	16	17	18
PPG 2025	1	1	1	1	1	4	2
PEG 200	-	-	-	-	-	4	2
Triethylene glycol	1	1	1	-	-	-	-
2,4-Tolylene diisocyanate (1)	10	10	10	10	10	10	10
Dipropylene glycol	-	-	-	1	1	-	-
Trimethylol nitromethane	1	-	-	1	-	-	-
Triethanolamine	-	1	-	-	1	-	-
Triisopropanolamine	-	-	1	-	-	-	-
2-Amino propanol	-	-	-	-	-	-	1
2-Methyl-2-amino propanediol	-	-	-	-	1	1	-
Remarks	A	A	cheesy	A	A	A	A
Shore Hardness	41	25	49	52	39	40	30

A = passable elastomer; (1) Per cent excess over reactive groups

TABLE 2.7

Formulations Using Large Cross-Linking Triols

Ingredients	Elastomer Formulation in Molecular Proportions			
	29	30	31	32
PPG 2025	4	-	-	-
Teracol 30	-	-	2	-
PEG 1540	-	-	-	3
Triethylene glycol	-	1.5	-	-
Pentanediol	-	-	2	-
Glyceryl monoricinoleate	1	-	-	-
Phosphoric acid/PPG 1025 triester	-	1	-	-
1,2,6-Hexanetriol	-	-	1	-
Ethylene oxide adduct of hexanetriol	-	-	-	1
2,4-Tolylene diisocyanate <sup>(1)</sup>	10	10	5	5

(1) = Per cent excess over reactive groups.

Table 2.8 shows the results of preliminary experiments with the three diisocyanates previously mentioned.

TABLE 2.8

Comparison of Diisocyanates

Ingredients	Elastomer Formulation in Molecular Proportions		
	4	10	11
PPG 2025	4	-	4
PG-P 750	-	4	-
1,2,6-Hexanetriol	1	1	1
2,4-Tolylene diisocyanate <sup>(1)</sup>	5	-	-
Hexamethylene diisocyanate <sup>(1)</sup>	-	5	-
Diphenylmethane diisocyanate <sup>(1)</sup>	-	-	5
Remarks	A	-	A
Shore Hardness	10	5	D

A = passable elastomer; D = tacky polymer

(1) = Per cent excess over reactive groups

The physical properties of promising formulations were evaluated more extensively over the temperature range. In the initial stages the Clash-Berg stiffness tester (ASTM D 1043-51) was used but this method was later abandoned in favour of the multi-bank Gehman tester (ASTM 1053-54T). The tensile test data were obtained by elongating rotating bands on an Instron Tester<sup>(4)</sup>. The physical test data are summarized in Table 2.9. The cold hardening of many polymers is illustrated in Fig. 2.2 and the influence of blending of prepolymers is shown in Fig. 2.1.

TABLE 2.9

## Physical Test Data of Formulations 1 Through 20

Formulation	Stiffness Temp. Clash-Berg (45,000 psi value)	Tensile Test Data					
		-40°F (-40°C)		77°F (25°C)		140°F (60°C)	
		Elong. %	Ultimate T.S. psi	Elong. %	Ultimate T.S. psi	Elong. %	Ultimate T.S. psi
1	-42	-	-	118	83	-	-
2	-42	225	1600	100	136	39	75
3	-42	230	2340	173	200	126	111
4	-48	490	560	273	41	522	26
5	-16	-	-	-	-	-	-
6	-22 <sup>‡</sup>	-	-	156	339	-	-
7	-72 <sup>‡</sup>	stress crystal- lized		730	290	802	153
8	-64 <sup>‡</sup>	555	3800	1045	184	430	184
9	-63	450	1830	396	28	219	15
10	-46	-	-	-	-	-	-
11	-50	490	527	220	27	106	14
12	-39	297	4270	226	473	105	90
13	-45	-	-	-	-	-	-
14	-38	-	-	-	-	-	-
15	-28	-	-	182	405	-	-
16	-25	-	-	212	410	-	-
17	-44	405	3900	467	245	347	176
18	-44	415	2700	765	155	966	169
19	-46	-	-	606	16	-	-
20	-29	-	-	480	44	256	20

Note: Tensile test data were obtained by elongating bands between pulleys on an Instron Tester.

<sup>‡</sup> Tendency to crystallize .

### Experimental Methods

Elastomers were prepared in sheet form by casting a 200-gram batch on a plate coated with Kel F or polyethylene wax and curing under a dry nitrogen blanket at 70°C for 24 hours. The ingredients were carefully dried and their functionality checked before compounding. Drying was carried out by using Linde Molecular Sieves or by heating under a vacuum of 6 to 8 mm of mercury for two hours. The latter is often preferable since it also removes other low molecular weight impurities which may be monofunctional. A 5 to 10 per cent excess of diisocyanate was used and the catalyst, ferric acetylacetonate, was preblended into the diols at a level of 0.06 per cent by weight on the final elastomer.

Polymers containing propylene oxide are known to be subject to terminal unsaturation possibly originating from dehydration of secondary hydroxyl groups. These polymers were analyzed for the presence of unsaturation which was believed to be a measure of monofunctionality. Typical data are given in Table 2.10; only the prepolymers with low unsaturation were selected for investigation.

TABLE 2.10

Comparison of Terminal Unsaturation for  
Several Polyether Glycols

Diol	Source	Terminal Unsaturation (m. eq/g)
PG-P 2000	Dow	0.192
PG-P 3000	Dow	0.024
PG-P 4000	Dow	0.040
PPG 2025	Carbide	0.026
UCON 25-H-2005	Carbide	0.015
UCON 50-H-1100 (M.W. 2600)	Carbide	0.009

### Initial Conclusions

A study of the data obtained in the initial survey indicated several points which were interesting fields for further investigation. These were:

- (i) low temperature properties improved with increasing prepolymer molecular weight (Fig. 2.3),



- (ii) substitution of the aliphatic hexamethylene diisocyanate for 2,4-tolylene diisocyanate improved the low temperature properties,
- (iii) low temperature properties appeared to be improved when a high molecular weight cross-linking molecule was used e.g. glyceryl monoricinoleate, and
- (iv) polyoxytetramethylene glycol gave very promising high strength elastomers but, unfortunately, they were prone to crystallization as were the polyethylene glycol-based products.

A pertinent observation during sample preparation was that, when reactive low molecular weight ingredients were present, they often prereacted to yield a gel and an inhomogeneous polymer resulted.

#### SELECTION OF INGREDIENTS FOR IMPROVED POLYMERS

It has been noted that the low temperature properties of polymers improved as the prepolymer molecular weight increased. This is caused, in part, by the increase in length of the polymer kinetic segments<sup>(5)</sup> but, equally well, it leads to a decrease in the diisocyanate content which will considerably reduce the mean molecular cohesion. However, the substitution of hexamethylene diisocyanate for 2,4-tolylene diisocyanate improves the low temperature properties also and it is thought that this is caused by the aliphatic diisocyanate increasing the effective kinetic segment rather than acting as a bulky segment termination point, as with 2,4-tolylene diisocyanate. It has not proved possible to assess these effects quantitatively but it is apparent that the prepolymer molecular weight should be increased as far as it is compatible with processing equipment and the aliphatic diisocyanate should be preferred. However, there is some evidence that elastomers containing the aliphatic diisocyanate are not stable on prolonged storage and they have not yet been investigated extensively.

The improvements sought through the use of specially selected high molecular weight cross-linking molecules were:

- (i) the prevention of cross-linking centre bunching,
- (ii) compatibility of the cross-liner with the diol, and
- (iii) control of the end group reactivity.

The preparation of propylene oxide adducts of hexanetriol was requested of one manufacturer<sup>(6)</sup> and, when an acceptable one eventually came to hand, it was tested in a variety of formulations. An improvement in the low temperature properties was found when it was used in place of hexanetriol in comparable elastomers, the Gehman freeze point being some 10°C lower. The chief problem with large molecular weight triols is the probability of intramolecular ring

closures and, accordingly, this triol has generally been prereacted to form the triisocyanate adduct before mixing it with the balance of the ingredients. In preparing the adduct, a small percentage of plasticizer, such as di-2-ethylhexyl azelate, is added to maintain the adduct at a low level of viscosity. Typical formulations are listed in Table 2.11 and representative physical properties are shown in Table 2.12.

TABLE 2.11

Variation of Cross-linking Density

Ingredients	Formulation		
	A	B	C
PFG 2025	6	3	1.5
NIAx Triol, LHT 112*	1	1	1
Di-2-ethylhexyl azelate (1)	5	5	5
2,4-Tolylene diisocyanate (2)	7.5	7.5	7.5
Phenyl- $\beta$ -naphthylamine (1)	1	1	1

\* 1,2,6-tris( $\omega$ -hydroxy polyoxypropylene) hexane 1500

(1) Per cent by weight

(2) Per cent excess over reactive groups

TABLE 2.12

Effect of Cross-linking Density on Physical Properties

Physical Data	Formulation		
	A	B	C
Cross-linking Ratio (After 20 hr curing at 70°C)	6	3	1.5
Molecular Weight per Cross-link	13,000	7,000	4,000
Ultimate Tensile Strength, psi, at 25°C	1149	99	55
Elongation at break, per cent	1243	332	290
Theoretical Elongation, per cent	1500 <sup>‡</sup>	1100	800

<sup>‡</sup> Certain formulations have achieved elongation slightly in excess of this value.

It will be noted that good physical properties are only obtained at a low cross-link density and, accordingly, formulation A has been investigated for use in propellant formulations.

The upgrading of elastomers by copolymerizing crystallizable and non-crystallizable molecular groups was investigated in the group of compounds known as 'UCON'(7) fluids which are copolymers of ethylene and propylene oxides. Table 2.13 details the fluids investigated and the results are summarized in Fig. 2.4.

TABLE 2.13

UCON Copolymers of Ethylene and Propylene Oxides

Per Cent C <sub>2</sub> H <sub>4</sub> O	Molecular Weight	Manufacturer's Code
0	2025	PPG-2025
25	2180	25-HEG-56
50	2600	50-H-1100
65	1729	65-H-660
75	2160	75-H-1400

These UCON fluids are attractive since the viscosity of the copolymer does not increase until the percentage of ethylene oxide is above 65 per cent. Unfortunately, they have not yet been successfully evaluated in propellants since it appears that ammonium salts are soluble in the ethylene oxide chain fragments(8). This solubility leads to an increase both in mix viscosity and low temperature stiffness, possibly due to ionic or hydrogen bonding.

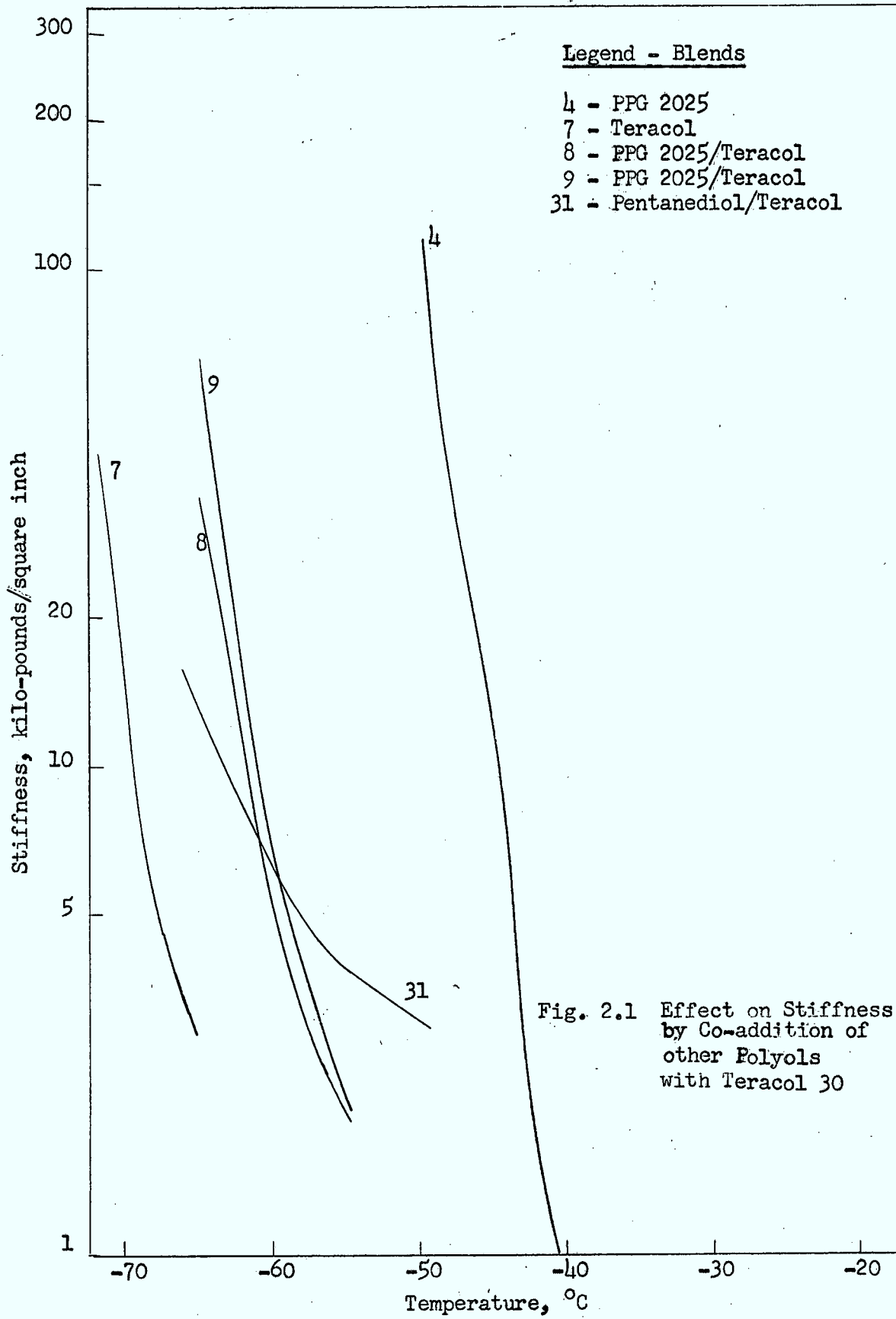
CONCLUSIONS

The most important conclusions from the experimental work carried out were:

- (1) Cross-linking molecules of low molecular weight were often immiscible with the diol prepolymer and reacted too rapidly with the diisocyanate.
- (2) Cross-linking molecules of high molecular weight and similar polymer backbone obviated some of the formulation problems.

- (3) High strength elastomers could be obtained with crystallizable backbones which on storing at low temperatures often hardened.
- (4) Random copolymers of propylene oxide and ethylene oxide gave promising high strength elastomers, which were found to interact with the propellant oxidant to degrade low temperature properties.
- (5) A 6:1 diol/triol ratio enabled optimum polymer properties to be obtained with PPG 2025 and the Niax Triol LHT 112.

These conclusions suggest that copolymers of propylene oxide and n-butylene oxide (tetrahydrofuran) might be promising binder materials. In future work block and random copolymers of these materials will be investigated.



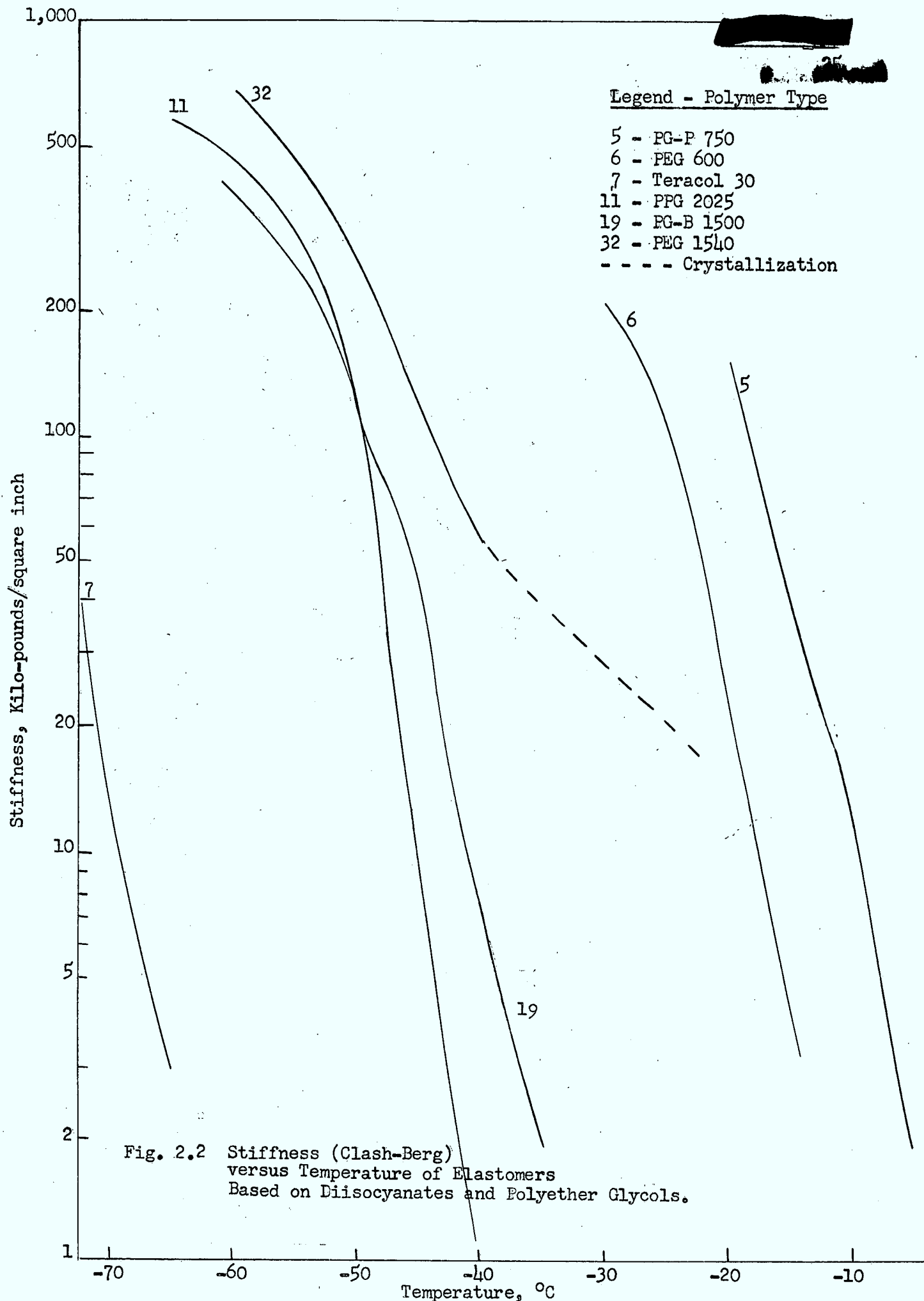


Fig. 2.2 Stiffness (Clash-Berg) versus Temperature of Elastomers Based on Diisocyanates and Polyether Glycols.

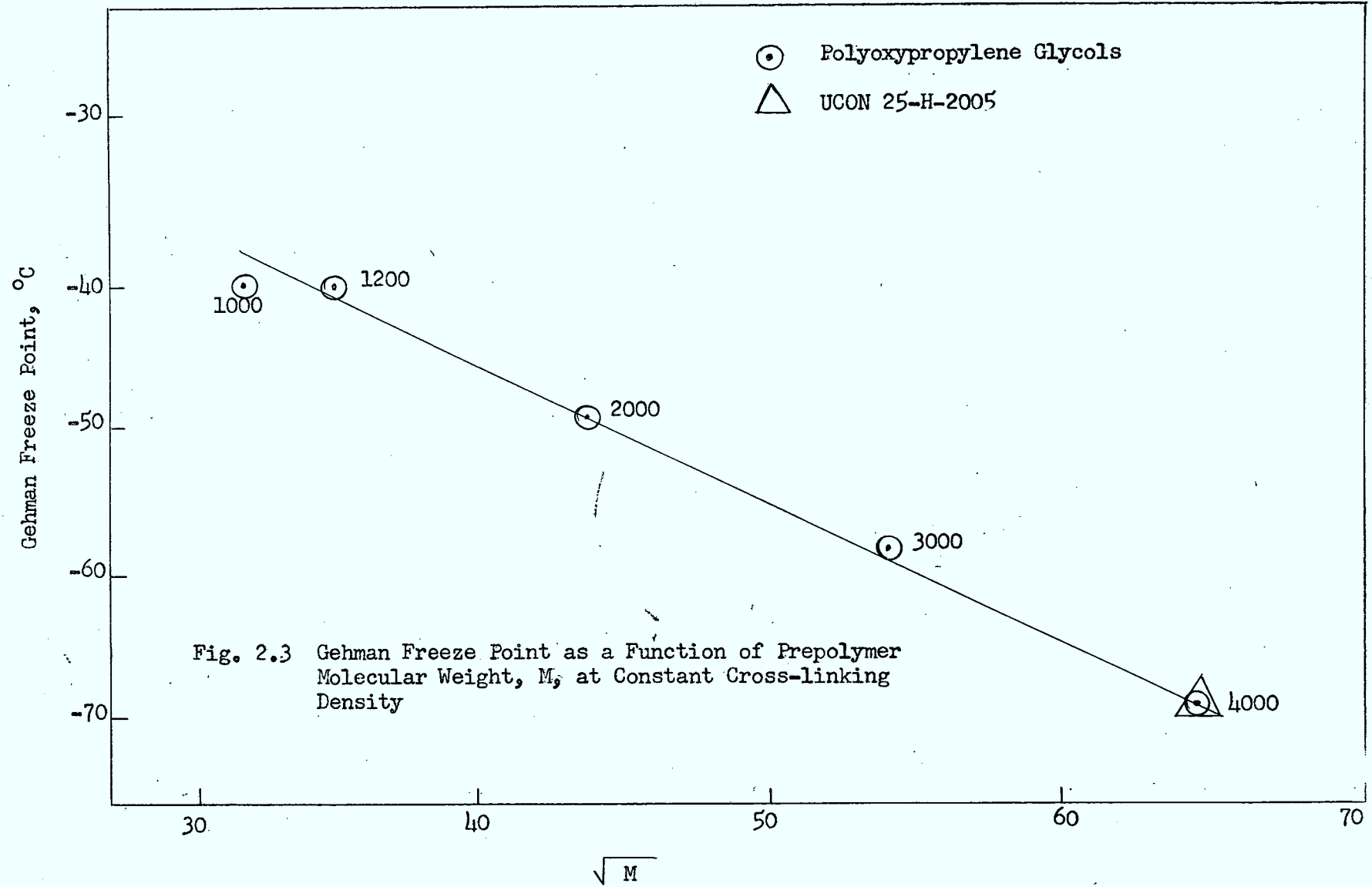


Fig. 2.3 Gehman Freeze Point as a Function of Prepolymer Molecular Weight,  $M$ , at Constant Cross-linking Density

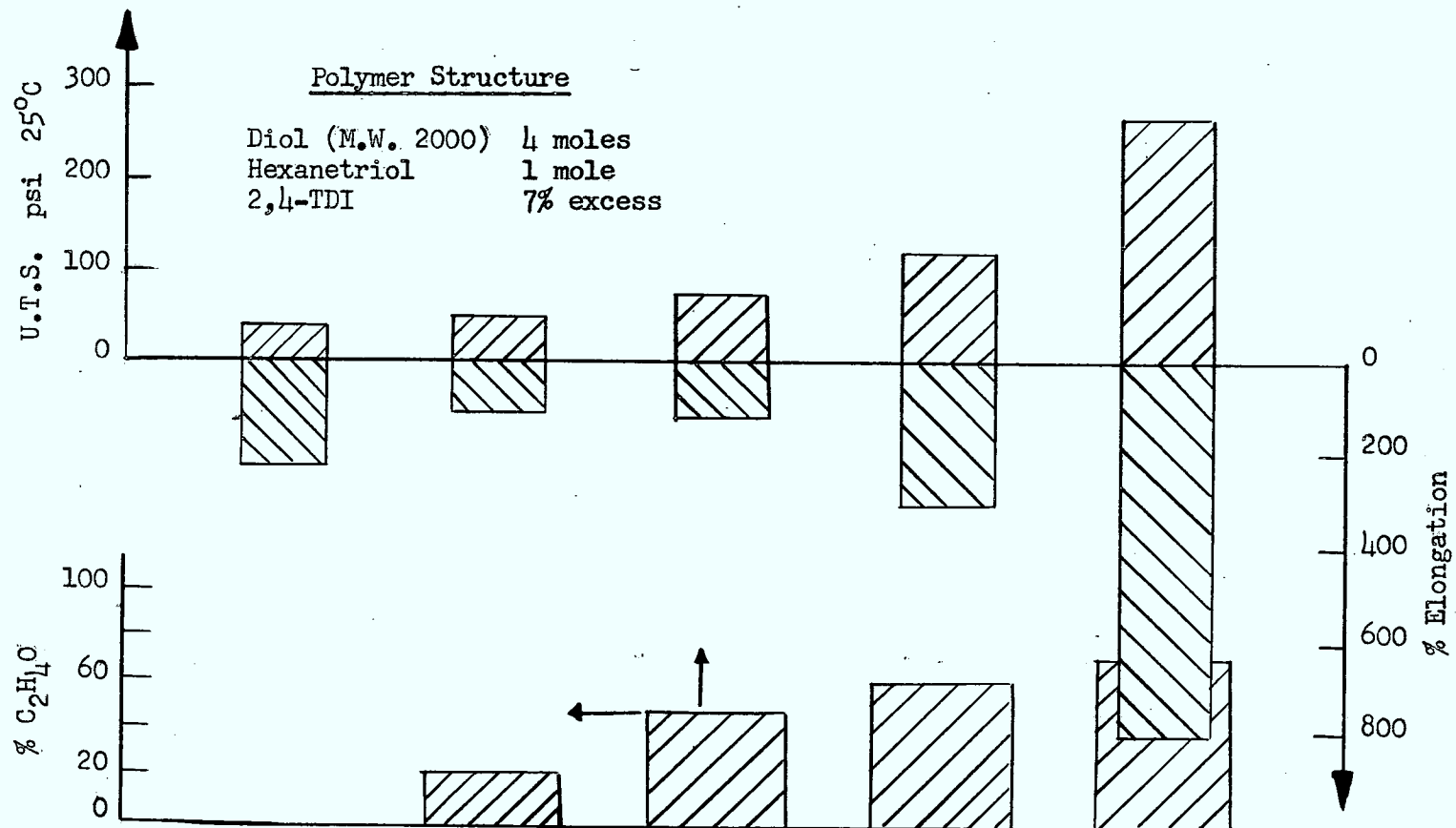


Fig. 2.4 Tensile Data on Elastomers Based on UCON Fluids



PART III  
DEVELOPMENT OF PROPELLANT FORMULATIONS

INTRODUCTION

A composite propellant based on a polymerizable elastomer and an inorganic oxidizer contains other ingredients. A typical composition of a polyurethane propellant is given in Table 3.1.

TABLE 3.1

<u>Ingredient</u>	<u>Purpose</u>
Inorganic oxidizer	Source of oxygen
Castable elastomer	Fuel and binder - based on diols or amines and diisocyanates
Catalyst	To aid the polymerization of the elastomer
Inhibitor	To control the polymerization of the elastomer
Antioxidant	To prevent degradation of the polymer by oxidation on storage
Burning rate modifiers	To control the ballistic properties
Plasticizers	To improve the physical properties at low temperatures
Surfactants	To control the filler/binder interaction in order to modify the physical properties

The main requirement has been for relatively slow-burning propellants and the investigation has been in the field of fuel-rich propellants. It is of course possible to increase the oxidizer content of a propellant up to 85 per cent by weight depending on the chemical nature of the binder so that, on combustion, the maximum heat release and, consequently, the maximum performance is obtained. Unfortunately, it is generally found that the following difficulties arise:

- (1) the viscosity of the propellant slurry may become excessive, and

- (2) the physical properties of the cured propellant are degraded and the amount of binder may be inadequate to fill the interstices between the oxidizer crystals under all environments. (When the propellant is cooled or strained a porous propellant prone to detonation could result).

It is fortunate that the loss in performance encountered on departing from stoichiometric mixtures is slight and it is possible to formulate very useful propellants with oxidizer levels between 75 and 80 per cent. Performance can be considerably enhanced by adding aluminum powder which will give propellants with a performance of 245 lb sec/lb (260 lb sec/lb theoretical).

#### LABORATORY METHODS

The preparation of small batches of polyurethane-based composite propellants has been carried out in a small six-pound vertical ribbon mixer operating at a vacuum of 1 to 2 mm of mercury. The design permits the blades to be withdrawn from the mixing pot while still under vacuum so that entrainment of air during removal of the pot is minimized. A dumping valve has been fitted to one pot so that the propellant can be transferred to the mould or test engine more readily. The mixer and casting bell are shown in Fig. 3.1, 3.1A and 3.2.

Two main techniques have been used to prepare propellant mixes. The first one used was the one-shot method in which the oxidizer is slurried with the diols and cross-linking triol, after which the diisocyanate is mixed in. With the advent of the preferred high molecular weight cross-linking agents, intra-molecular ring closures of the triol had to be prevented and, accordingly, a new technique was developed. In this new process the triol was prereacted with the tolylene diisocyanate, which is of course present in excess since the diol prepolymer is absent, and this isocyanate-rich adduct mixture is added after the oxidizer has been slurried with the diol. Since the adduct technique is preferred to the one-shot process, the detailed description of the propellant mixing procedure given below relates to the former method.

#### Ingredient Preparation

All ingredients are subjected to routine analysis to determine their suitability for use. The principle tests for diisocyanates are diisocyanate equivalent, hydrolyzable chlorine, presence of dimers and trimers and possible monofunctionality. The diols and triols, dried to less than 0.03 per cent water, are checked for effective molecular weight. The polyglycol ethers, which are principally used, are tested for unsaturation, believed to be mainly terminal, and for the peroxide content which is known to be a specific catalyst for diisocyanate trimerization. The method of drying is quite important and it has been found desirable to add the antioxidant before drying at 90°C for two hours at 2 mm mercury\*. Furthermore drying must not be done in steel equipment but

\* Recently the time has been increased to three hours.

carried out in glass apparatus because metals degrade the polyglycols. The oxidizer is dried to less than 0.03 per cent moisture and ground to the correct bimodal grist sizes. The blended oxidizer is stabilized against agglomeration with an anti-caking agent, generally tricalcium phosphate. All minor constituents such as surfactants and catalysts are tested for purity and dryness.

### Mixing Procedure

The first step carried out is the formation of the prepolymer by prereacting the cross-linking triol with the diisocyanate in the presence of the plasticizer. On mixing, the prepolymer ingredients are heated at 60°C until the initial exotherm is over, after which the product is cooled. As prepared with 2,4-tolylene diisocyanate, the prepolymer (containing 0.02 per cent hydrolyzable chlorine) is stable for a maximum period of seven days. If the hydrolyzable chlorine is omitted the prepolymer is unstable and a gel is rapidly formed; the instability is believed to be due to the presence in the triol of peroxide impurities which catalyze diisocyanate homopolymerization at high pH levels.

During the prepolymer preparation, the curing catalyst, ferric acetylacetonate, is dissolved in the diol, usually polyoxypropylene glycol 2025, by heating at 80°C and stirring for 30 minutes. Experience has shown that aldehydic impurities reduce the  $Fe^{+++}$  to  $Fe^{++}$  leading to catalyst degradation and consequently this operation is carried out immediately before mixing the propellant.

The mixing cycle is commenced by pouring the diol into the mixer and then adding the oxidizer, after which mixing continues for 30 minutes under a vacuum of 2 mm of mercury. At the end of this period the vacuum is broken, the prepolymer is added and mixing continued under vacuum for 20 minutes.

After completion of the mixing schedule the blades are elevated before breaking the vacuum and the mix, still in the pot, is transferred to the casting bell. The propellant is admitted to the bell through an air-lock and it is extruded as a thin ribbon into the vacuum (2 mm mercury) where it is degassed as it drops into the test engine or strip mould. After casting, the propellant is transferred to the curing oven where it is cured for a period of 24 to 72 hours at associated temperatures of 75 to 50°C.

### EXPERIMENTAL RESULTS

The first propellant made was based on polyoxypropylene glycol 2025, 1,2,6-hexanetriol and 2,4-tolylene diisocyanate and was mixed by the one-shot technique; its detailed composition is given in Table 3.2.

TABLE 3.2

Propellant Composition 4760/A1

Ingredients	Parts by weight	Moles (active species)
PPG 2025	26.2	4
1,2,6-hexanetriol	0.416	1
2,4-tolylene diisocyanate	3.0	5.775
Ionol	0.099	-
Ammonium perchlorate	70.20	-
Ferric acetylacetonate	0.065	-

The physical properties of this propellant, after curing for 48 hours at 70°C, were measured over the temperature range -40°F (-40°C) to +140°F (+60°C). These data, which are given in Table 3.3, indicate that firings should not be carried out below -25°F because of the high modulus below this temperature.

TABLE 3.3

Physical Test Data Propellant 4760/A1

Temperature °C	$S_m$	$\gamma_m$	$\gamma_b$
+ 60	66	0.12	0.23
+ 25	83	0.15	0.52
- 10	248	0.30	2.03
- 25	419	0.25	2.56
- 40	1309	0.025	0.016
<u>Gehman Data</u>			
Freeze Point - 40°C (- 40°F)			
RM 10 Point - 32°C (- 26°F)			
rel to 25°C			

$S_m$  = max stress (psi);  $\gamma_m$  = strain at max stress

$\gamma_b$  = strain at break; RM 10 point = tenfold relative modulus.

Sample performance curves obtained with the 3.5 in. test motor are given in Fig. 3.3. It must be emphasized that in the early firings the case-bonding of polyurethane propellants was of doubtful reliability and the planned interrupted burning firings later revealed some bonding deficiencies. A layout of the test motor is shown in Fig. 3.4.

As indicated elsewhere, the development of elastomers had shown that the use of high molecular weight triols was advantageous and they were consequently tested in propellants. The analog of 4760/A1, containing 70 per cent ammonium perchlorate, was first formulated and designated as 4760/A2; its composition is detailed in Table 3.4.

TABLE 3.4

Propellant 4760/A2 - Detailed Composition

Ingredients	Parts by weight	Moles (active species)
PPG 2025	22.79	6
NIAX Triol LHT 112 <sup>HE</sup>	2.8	1
2,4-Tolylene diisocyanate <sup>HE</sup>	2.69	7.875
Di-2-ethylhexyl azelate	1.42	-
Ammonium perchlorate <sup>HEHE</sup>	70.00	-
Phenyl- $\beta$ -naphthylamine	0.29	-
Ferric acetylacetonate	0.06	-

- <sup>HE</sup> 1,2,6-tris( $\omega$ -hydroxy polyoxypropylene) hexane 1500  
<sup>HEH</sup> Contains 0.02 per cent hydrolyzable chlorine  
<sup>HEHE</sup> Bimodal grist (10  $\mu$  to 100  $\mu$ )

Physical test data for this formulation are shown in Table 3.5; it will be noted that the ultimate elongation of the propellant was considerably enhanced.

TABLE 3.5

Physical Test Data Propellant 4760/A2

Temperature °C	S <sub>m</sub>	$\gamma$ <sub>m</sub>	$\gamma$ <sub>b</sub>
+ 60	53	0.40	0.60
+ 25	71	0.60	3.21
- 10	137	0.80	2.34
- 40	349	0.325	2.39
- 50	995	0.05	0.42
<u>Gehman Data</u>			
Freeze Point - 53°C (- 63°F)			
RM 10 Point - 38°C (- 36°F) rel to 25°C			

S<sub>m</sub> = max stress (psi);  $\gamma$ <sub>m</sub> = strain at max stress  
 $\gamma$ <sub>b</sub> = strain at break; RM 10 point = tenfold relative modulus

In this investigation it was considered that propellants containing 75 per cent oxidizer would be interesting performance-wise and, accordingly, propellant 4760/A3 was formulated; its composition is detailed in Table 3.6.

TABLE 3.6

Propellant 4760/A3 - Detailed Composition

Ingredients	Parts by weight	Moles (active species)
PPG 2025	19.02	6
NIAX Triol 1500	2.32	1
2,4-Tolylene diisocyanate	2.25	7.875
Di-2-ethylhexyl azelate	1.18	-
Phenyl- $\beta$ -naphthylamine	0.25	-
Ammonium perchlorate	75.00	-
Ferric acetylacetonate	0.06	-

The physical test data for this propellant are shown in Table 3.7.

TABLE 3.7

Physical Test Data Propellant 4760/A3

Temperature $^{\circ}\text{C}$	$S_m$	$\epsilon_m$	$\epsilon_b$
+ 60	66	0.30	0.48
+ 25	93	0.40	0.98
- 10	159	0.60	1.14
- 40	408	0.225	0.76
- 50	1300	0.04	0.18
<u>Gehman Data</u>			
Freeze Point - $54^{\circ}\text{C}$ ( $-65^{\circ}\text{F}$ )			
RM 10 Point - $39^{\circ}\text{C}$ ( $-38^{\circ}\text{F}$ ) rel to $25^{\circ}\text{C}$			

$S_m$  = max stress (psi);  $\epsilon_m$  = strain at max stress;

$\epsilon_b$  = strain at break; RM 10 point = tenfold relative modulus.

COMPARATIVE PHYSICAL PROPERTIES AND ENGINE REQUIREMENTS

In selecting the best type of propellant for use in a rocket engine, it is pertinent to evaluate the minimum properties necessary to withstand temperature cycling. To determine the requirements in the limiting case, a longitudinal section of an infinitely long, case-bonded cylindrical grain, shown in Fig. 3.5, is considered and assumed to be cured at the upper temperature limit of +60°C. It is thus fully relaxed at this temperature and, on cooling, neglecting the low shrinkage of the engine casing, a strain is induced at the inner surface of the grain by the thermal contraction of the propellant. The strain may be evaluated by assuming that no longitudinal relief occurs and thus the thermal change in volume per unit length,

$$\Delta V = \Delta T \gamma \pi (R_2^2 - R_1^2)$$

where  $R_1$  = internal radius of grain

$R_2$  = external radius of grain

$\Delta T$  = change in temperature

$\gamma$  = cubical coefficient of thermal expansion

causes an increase in the inner radius,  $\Delta R$ , such that

$$\Delta R = \frac{\Delta T \gamma}{2} \frac{(R_2^2 - R_1^2)}{R_1}$$

and the associated strain is

$$\epsilon = \frac{\Delta T \gamma}{2} \left[ \left( \frac{R_2}{R_1} \right)^2 - 1 \right]$$

Data for elementary cylindrical grains of various internal/external diameter ratios are given in Fig. 3.6 and show that, for this type of grain, the strain increases rapidly with increase of loading density. The more complex grains, such as the star-centre, Fig. 3.7, are not so amenable to interpretation however; if the unrealistic extreme case of linear radial retreat to the engine casing is assumed with no relief, it may be deduced that maximum strain will occur at the radii on the root of the star points and will be equal to the radial retreat divided by the initial radius of the root, Fig. 3.8. Since the degree of sliver burning is partially dependent on this radius, it is obviously desirable that a propellant should have a high working strain so that this radius may be minimized.

Looking at the propellants developed, it is apparent that the formulation 4760/A2 is more acceptable over the temperature range than formulation 4760/A1, for comparable oxidizer loading. Increasing the oxidizer level from 70 to 75 per cent with formulation 4760/A3 does not materially reduce the desirable properties of the new binder system.

During flight projection of a rocket engine, longitudinal shear stresses are induced in the propellant grain; these are by no means excessive and it may be shown to be a maximum at the wall where

$$S_m = g \frac{W}{2 \pi R_2}$$

(where W is the weight per inch of length), and

it is generally in the range of 10 to 20 psi. In view of this, most propellants are acceptable to meet the functional requirement of withstanding flight firing conditions.

A word of caution must be stated in interpreting comparative physical test data which are normally carried out at the standard rate of one inch per minute per inch in contrast to the temperature cycling rate which generally approximates to a zero rate of strain. It is known that the physical properties of propellant fall off with decreasing strain rate, Fig. 3.9, and hence some measure of a propellant's ability to withstand a very low rate of strain is needed. The formulations currently under investigation are, consequently, being subjected to stresses within their elastic limit and will be classified in order of the time to failure.

In assessing the low temperature limit of propellants, comparison of the Gehman freeze point and the tenfold modulus point are listed. It must be realized that this low limit is entirely governed by the brittleness of the propellant in relation to the rate of strain to which it is subjected. Temperature cycling strains are of low rate but ignition shock may well induce a very high rate strain unless precautions are taken to avoid a brisant igniter and a rapid build-up of the chamber pressure. Work is in hand to determine the brittle temperature of propellant 4760/A3 at various strain rates and to correlate this with various ignition systems for a given grain design.

#### BALLISTIC PROPERTIES

Little ballistic data were obtained with propellant 4760/A1 other than the firing of the 3.5 in. test motor previously referred to. Propellants 4760/A2 and 4760/A3 have been investigated in the strand burner, the latter over the temperature range  $-25^{\circ}$  to  $+50^{\circ}\text{C}$ . The burning rate data and associated computed restriction ratio curves are shown in Fig. 3.10. General ballistic data are given in Table 3.8.



TABLE 3.8

Thermochemical Properties of Typical Polyurethane  
Propellants (Frozen Flow)

Propellant No.	Composition % wt.		T <sub>c</sub> °K	$\bar{\gamma}$	$\bar{M}$ g/mole	c <sup>#</sup> fps	I <sub>sp</sub> , sec at psi			Cal. Val. cal/g
	NH <sub>4</sub> ClO <sub>4</sub>	Fuel					700	1000	1400	
4760/A2	70	30	1980	1.263	20.882	4413	209.7	215.1	220.0	685
4760/A3	75	25	2150	1.253	21.537	4542	215.9	221.7	227.2	755

Fuels of slightly differing compositions based on polyoxypropylene glycol and tolylene diisocyanate were used but this fact does not materially affect comparison of the data.

Theoretical computations of the gas composition of the propellants referred to have given the data listed in Table 3.9.

TABLE 3.9

Gas Compositions

Propellant No.	Compositon, moles/g					
	HCl	CO <sub>2</sub>	CO	H <sub>2</sub> O	H <sub>2</sub>	N <sub>2</sub>
4760/A2	0.005943	0.002444	0.012996	0.010982	0.012360	0.003174
4760/A3	0.006398	0.002529	0.011394	0.012410	0.010443	0.003271

STORAGE PROPERTIES

Long term storage of propellants at elevated temperature is important although only limited data have been accumulated to date. The accelerated degradation of the polyglycols is also being followed and experiments indicate that a number of facts need to be more thoroughly explained. Data shown in

Table 3.10 indicates that a high level of antioxidant is beneficial with propellant 4760/A1. Propellant 4760/A3 has been studied over a relatively shorter

TABLE 3.10

Propellant 4760/A1 - Aging Data  
with Various Antioxidants

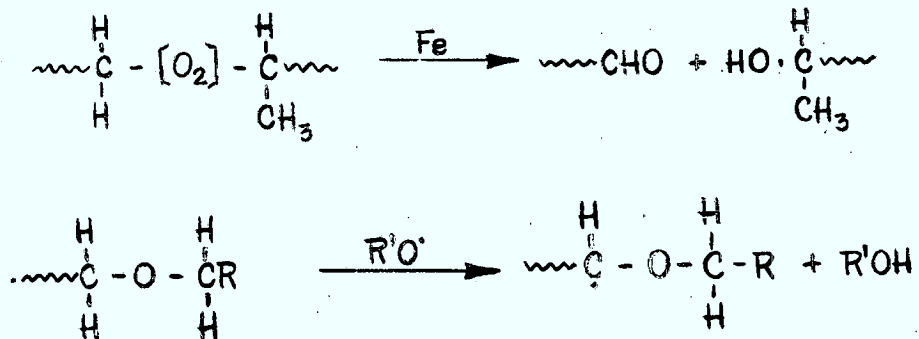
Antioxidant Concentration Based on Binder	Time in months at 60°C							
	0		3		6		9	
	S <sub>m</sub>	γ <sub>m</sub>	S <sub>m</sub>	γ <sub>m</sub>	S <sub>m</sub>	γ <sub>m</sub>	S <sub>m</sub>	γ <sub>m</sub>
1.00 % Ionol	78	0.13	114	0.40	89	0.475	81	0.52
0.33 % PBNA	80	0.14	102	0.46	91	0.52	72	0.55
1.00 % PBNA	61	0.12	107	0.37	106	0.40	-	-
0.33 % 2246 <sup>NE</sup>	70	0.16	94	0.37	88	0.35	77	0.35
1.00 % 2246 <sup>NE</sup>	76	0.14	95	0.35	90	0.325	77	0.35

<sup>NE</sup> North American Cyanamid Limited antioxidant

S<sub>m</sub> = max stress (psi); γ<sub>m</sub> = strain at max stress

period with a number of antioxidants; results are shown in Fig. 3.11. During the routine investigation of this latter propellant, it became the practice to add the antioxidant to the polyglycol which, it was assumed, would protect it from degradation. Routine analytical investigation revealed that the polyglycol used for development work had a higher carbonyl content than that used on the pilot plant. It transpired that the inferior material was dried in a stainless steel kettle and held in steel drums whereas the better material was processed in glass-lined apparatus. On changing over to glass-stored material, a significant increase in tensile strength of the propellant was found.

Amongst other explanations, it is possible that various metals and ions promote the auto-oxidation of the polyglycol by internally combined peroxides or its attack by the peroxide radical formed by atmospheric oxygen.



The second process is a possible chain reaction which should be stopped by conventional antioxidants.

Whilst it appears possible to improve the overall properties of the polyglycol-type propellants, the existing formulation, as typified by propellant 4760/A3, is quite adequate for use in rocket engines.

#### CURING OF PROPELLANTS

The use of propellants in large rocket engines poses many problems, the two main ones being adequate pot life of the uncured propellant and the volume change occurring on raising the filled engine to the curing temperature. To minimize the thermal expansion, curing should be done at a low temperature using an active catalyst although this will tend to reduce the ambient pot life.

Dilatometric studies have been carried out at various temperatures and typical cures are shown in Fig. 3.12. Most of the propellant evaluation has been carried out at 70°C at which temperature an expansion of about 1.5 per cent occurs. This is obviously undesirable on a big engine since it would have to be accommodated at the ends, where considerable longitudinal distortion of the grain would occur.

At the present time 50°C appears to be a feasible curing temperature using ferric acetylacetonate but the dilatometric experiments suggest that this may be lowered by at least another 10°C. Curing data for 4760/A3 indicate differences in behaviour at 50°C and 70°C for, at the lower temperature, the propellant develops its strength earlier in the curing cycle.

Another aspect yet to be fully investigated is the side reaction of residual moisture to form carbon dioxide but it is believed that this is rendered less probable by curing at low temperatures.

### CONCLUSIONS

This preliminary work has shown that it is feasible to formulate castable polyurethane based propellants with adequate ballistic and physical properties for use in very large rocket engines.

The experience gained has demonstrated that, in common with other propellants, the polyurethane system has its own special problems to be solved if very good reproducibility is to be obtained in large scale production. Many of these problems are concerned with analytical control and bulk manufacture and these will be reported on separately.

Future work will be aimed at improving the physical properties of the propellants over the temperature ranges concerned by studying novel copolymer backbones. In addition, the use of metallic high energy additives based on pyrophoric alloys in conjunction with high energy plasticizers will be investigated in an attempt to obtain a workable propellant with a specific impulse in the region of 250 - 260 lb-sec/lb.

### ACKNOWLEDGEMENTS

The assistance obtained from Mr. J.L. Myers in the analytical field, Mr. B.J. Holsgrove on equipment design and Mr. I.R. Cameron on general problems, is gratefully acknowledged.

Mention must be made of the valuable interchange of ideas with the Jet Propulsion Laboratory, California Institute of Technology, whose detailed reports have often materially assisted the CARDE programme.

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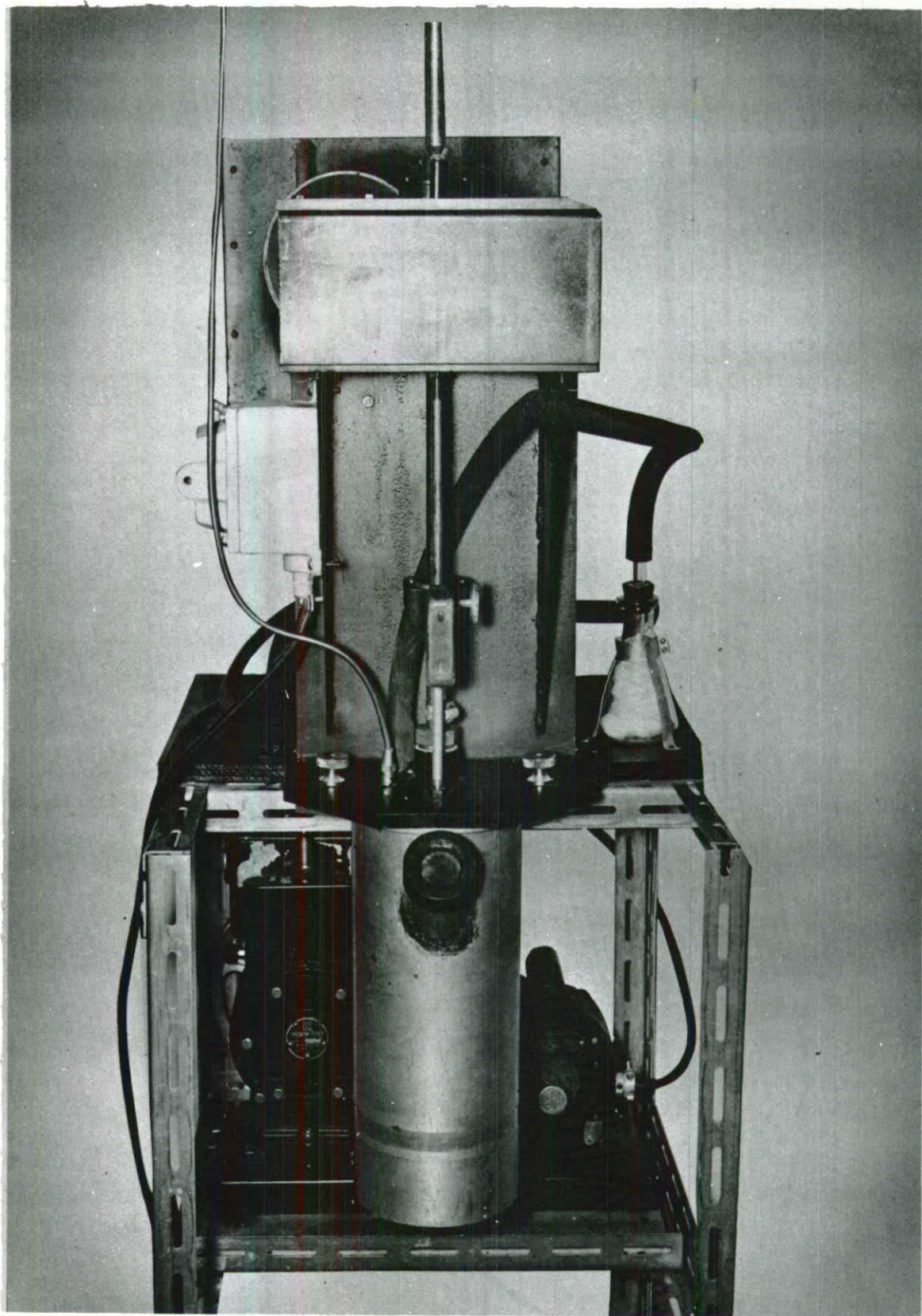


Fig. 3.1 Six Pound Vertical Ribbon Mixer

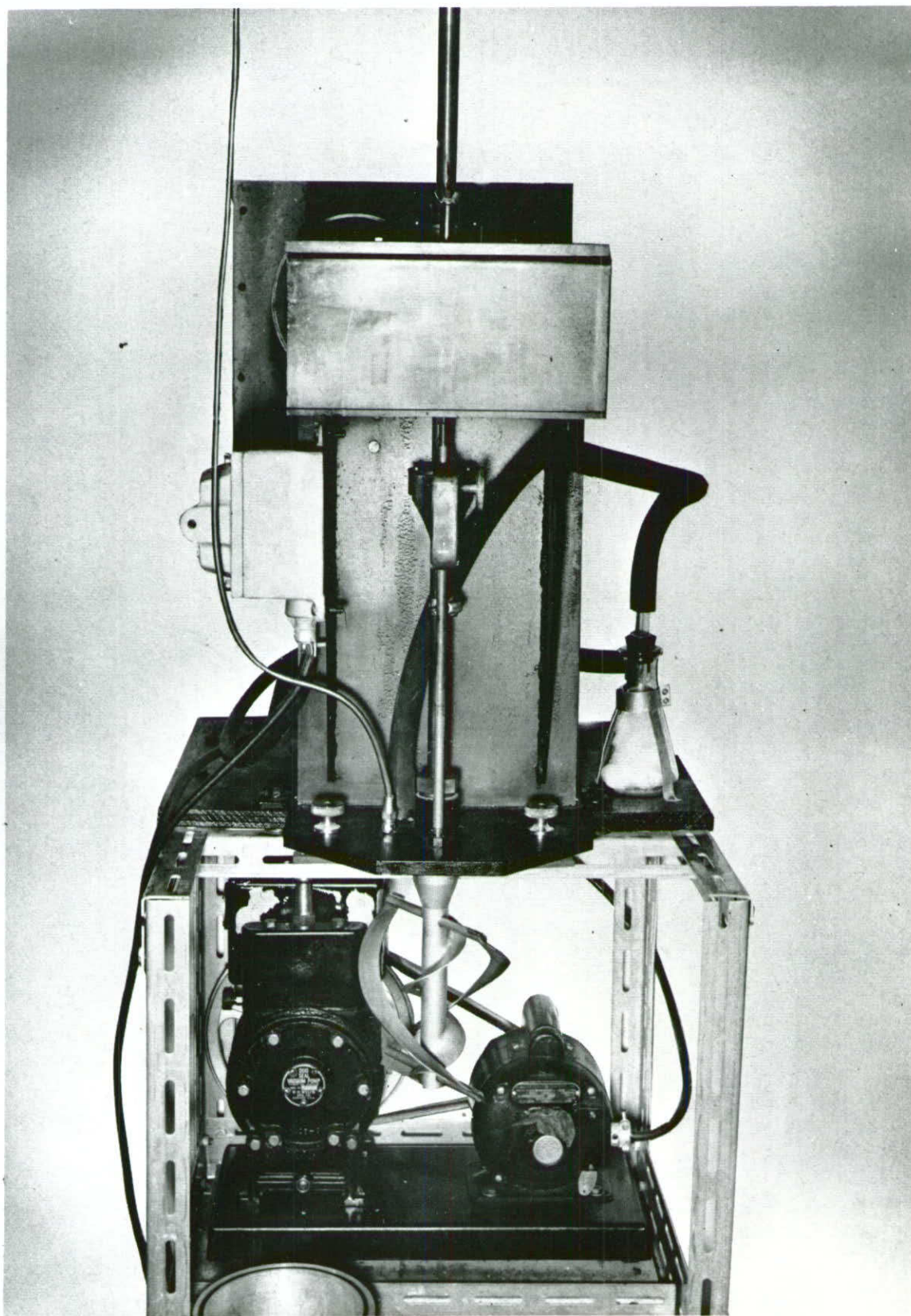


Fig. 3.1A Six Pound Vertical Ribbon Mixer Showing Ribbon Blades

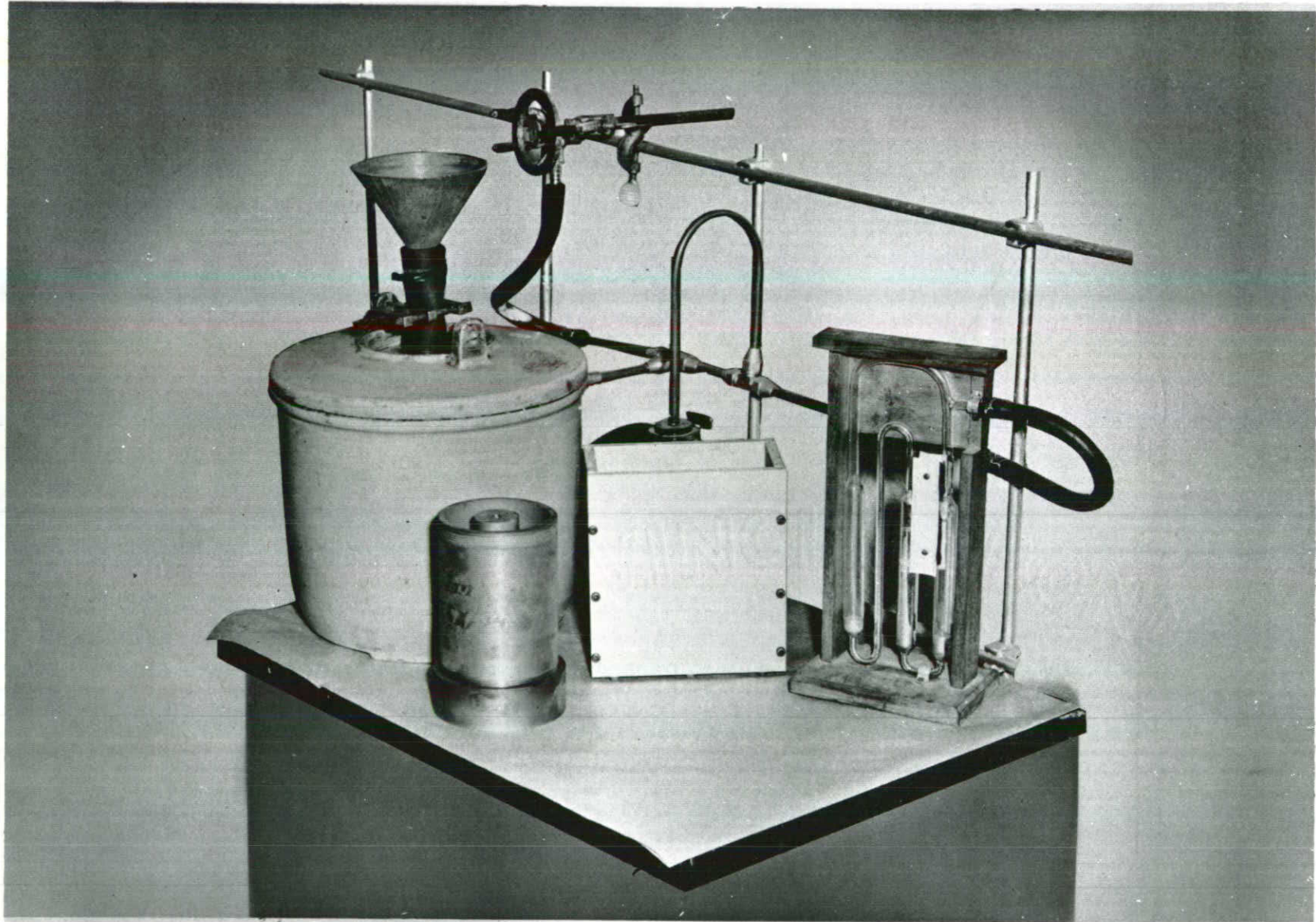


Fig. 3.2 Casting Bell



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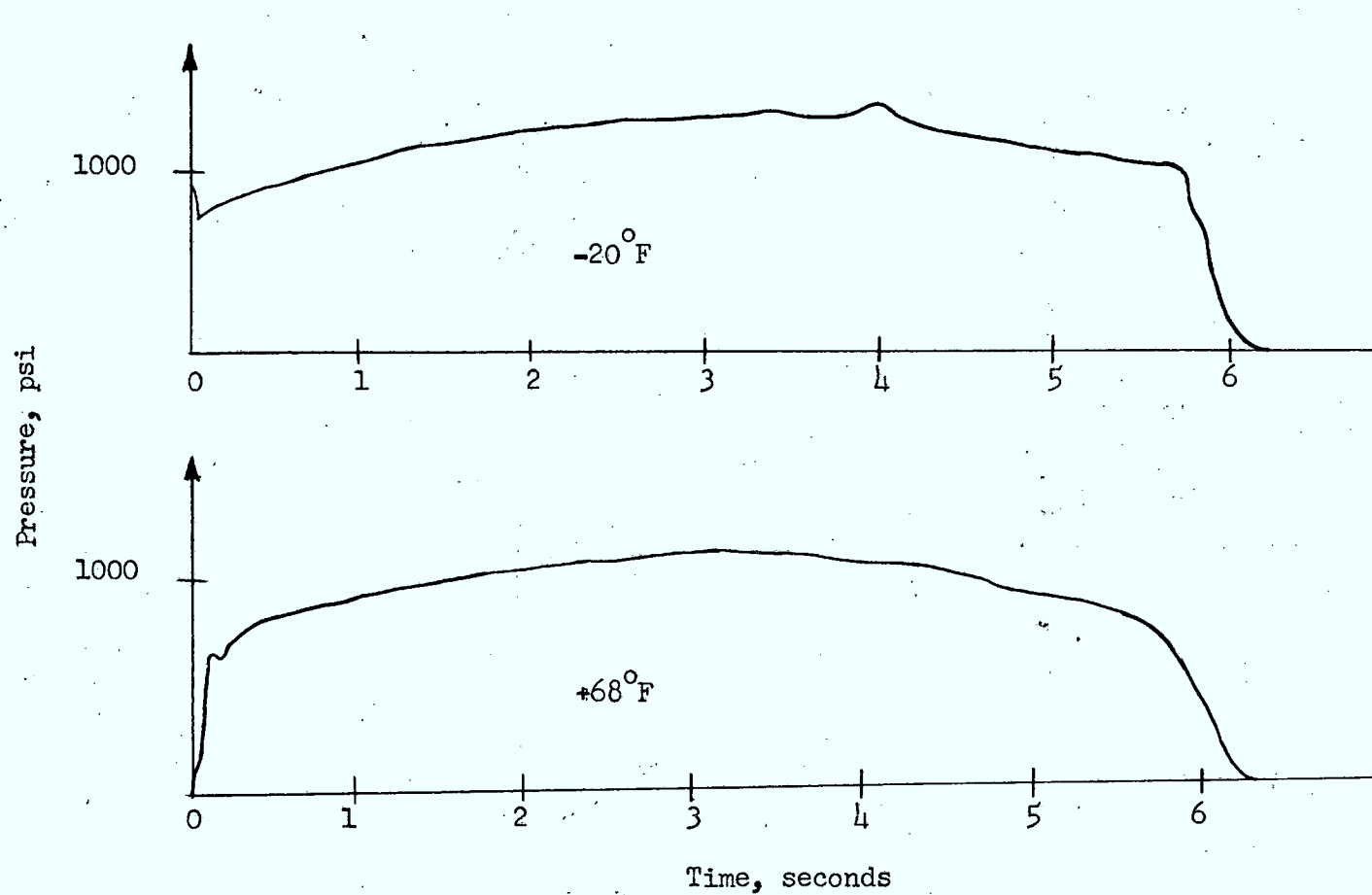


Fig. 3.3 Performance of 3.5 in. Test Motor Filled Propellant 4760/A1

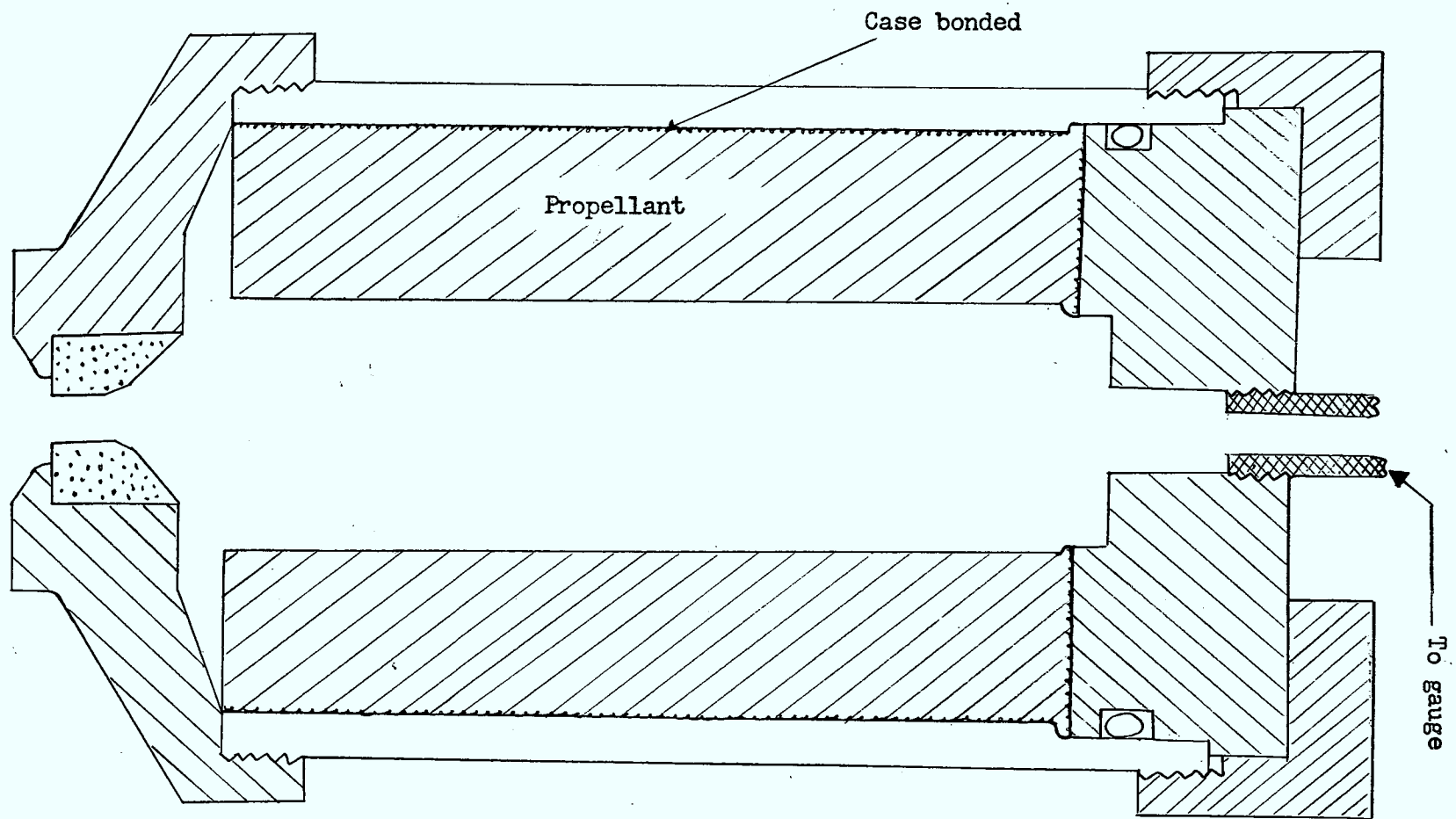


Fig. 3.4 3.5 in. Test Motor

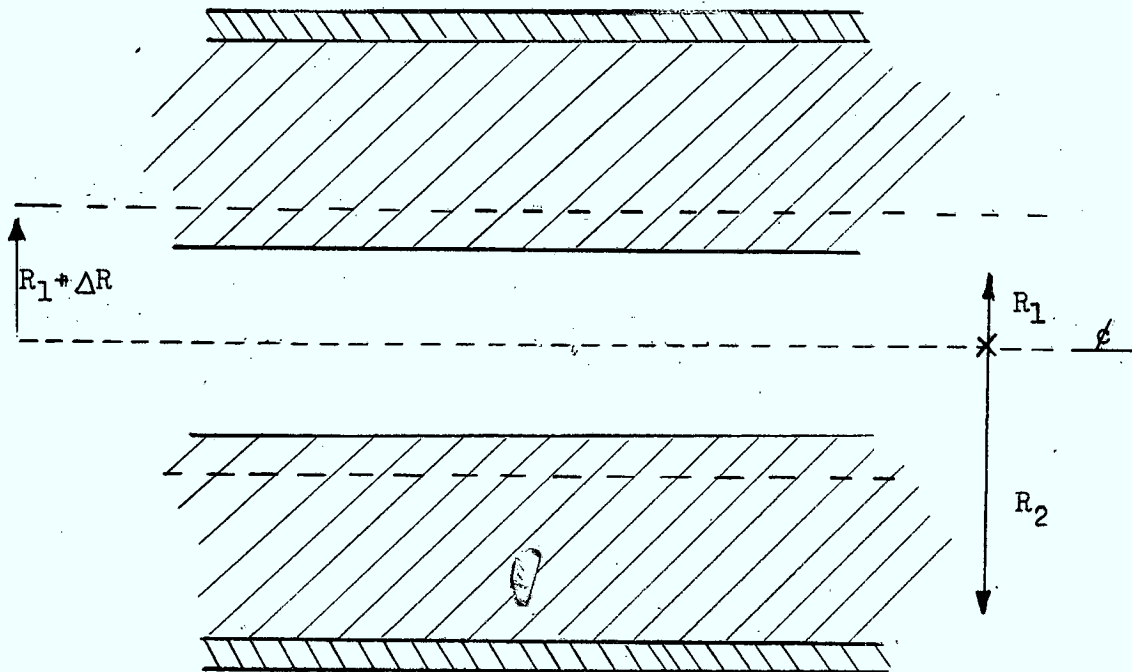


Fig. 3.5 Infinite Tubular Case-bonded Grain

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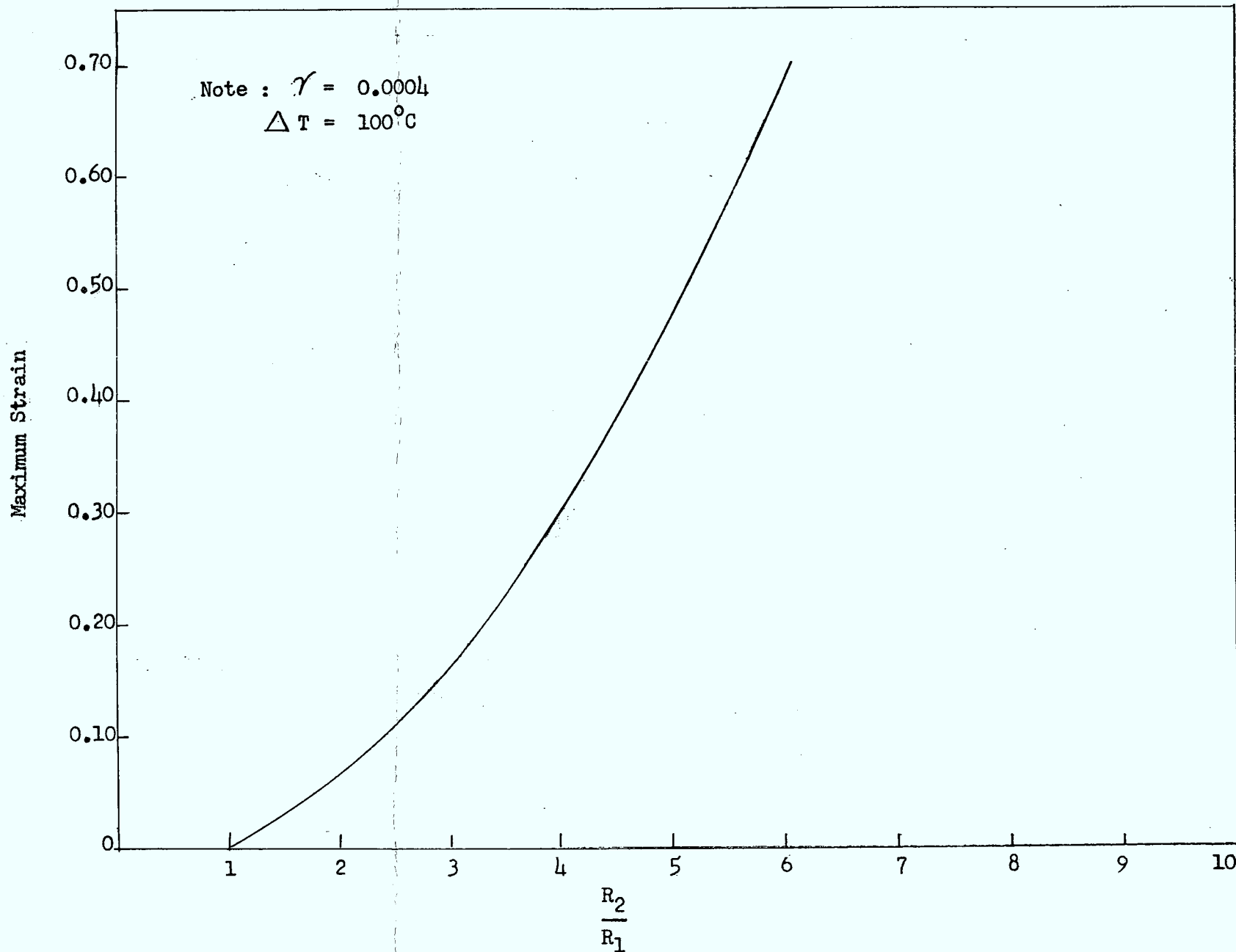


Fig. 3.6 Variation of Maximum Strain with Radius Ratio

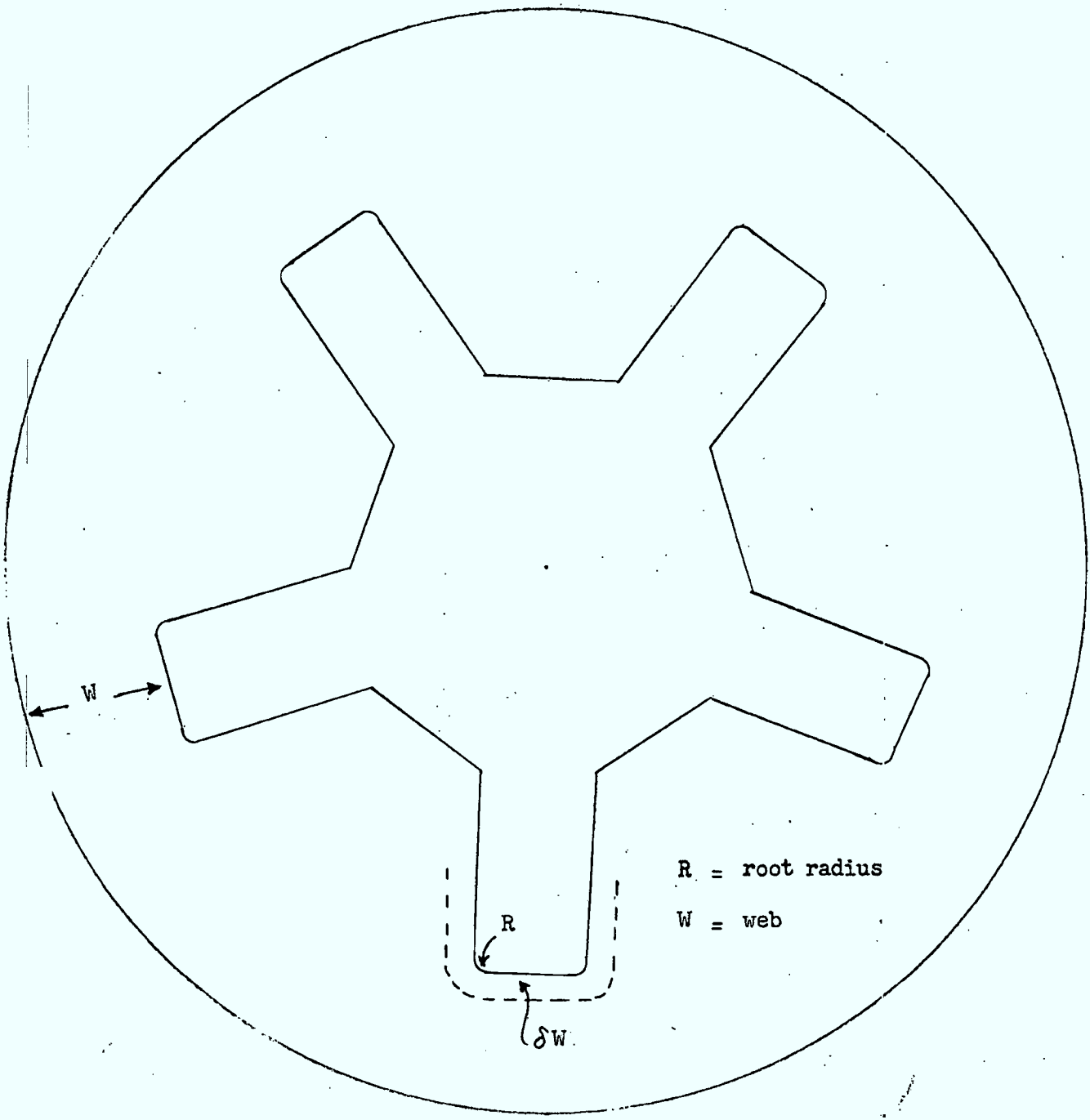


Fig. 3.7 Star Centre Grain Showing Region of Stress

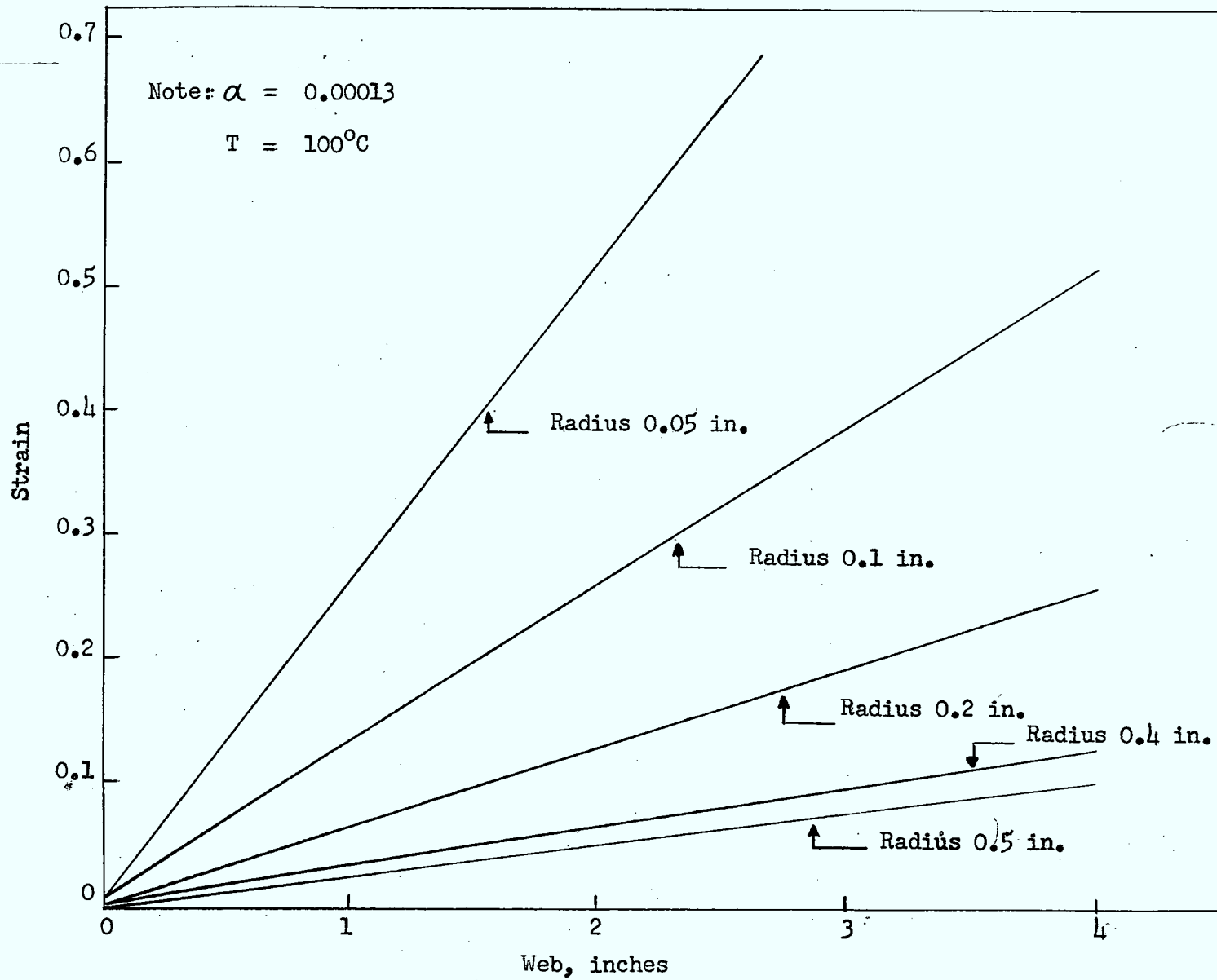


Fig. 3.8 Variation of Max Strain at Root with Corner Radius

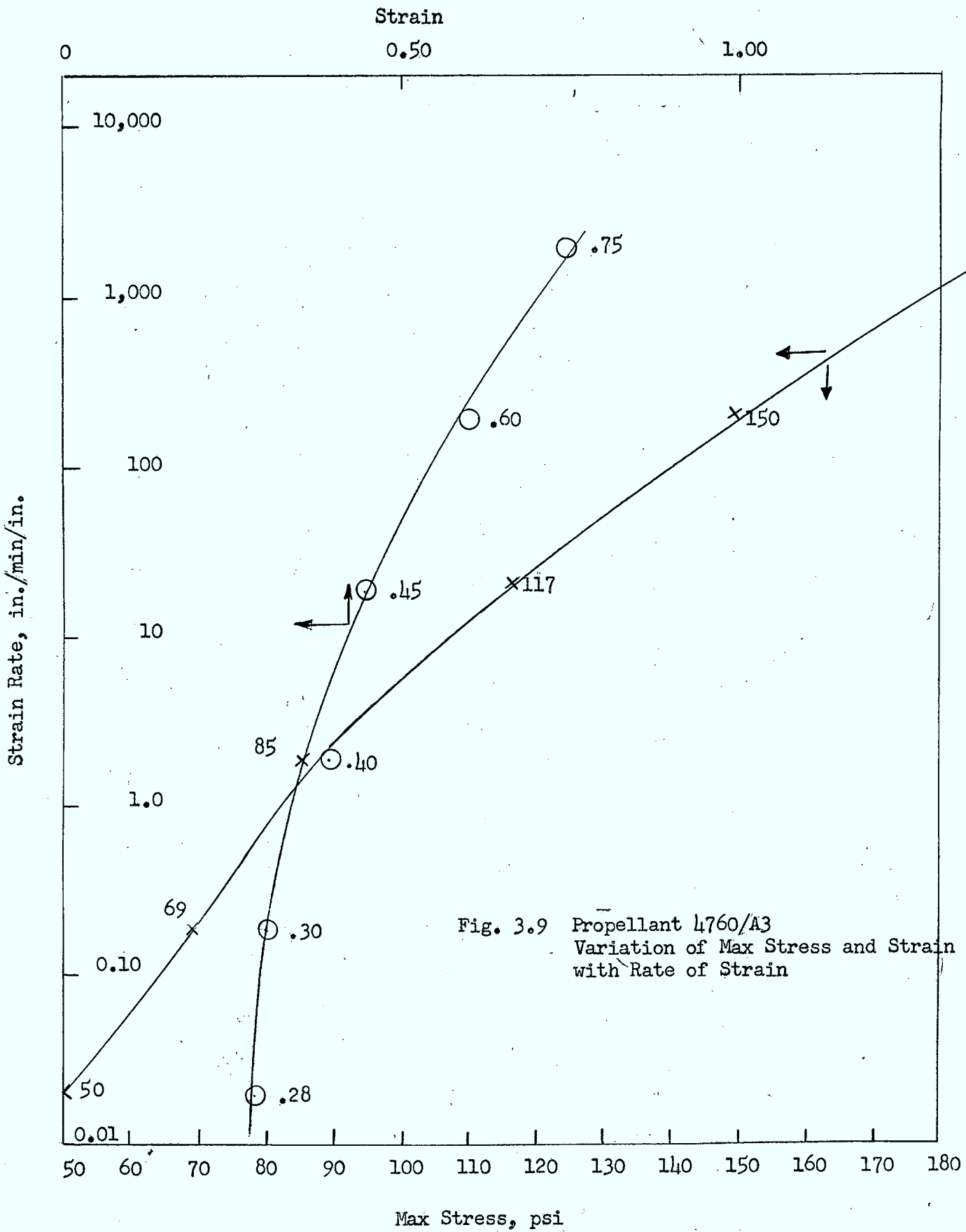


Fig. 3.9 Propellant 4760/A3  
Variation of Max Stress and Strain  
with Rate of Strain

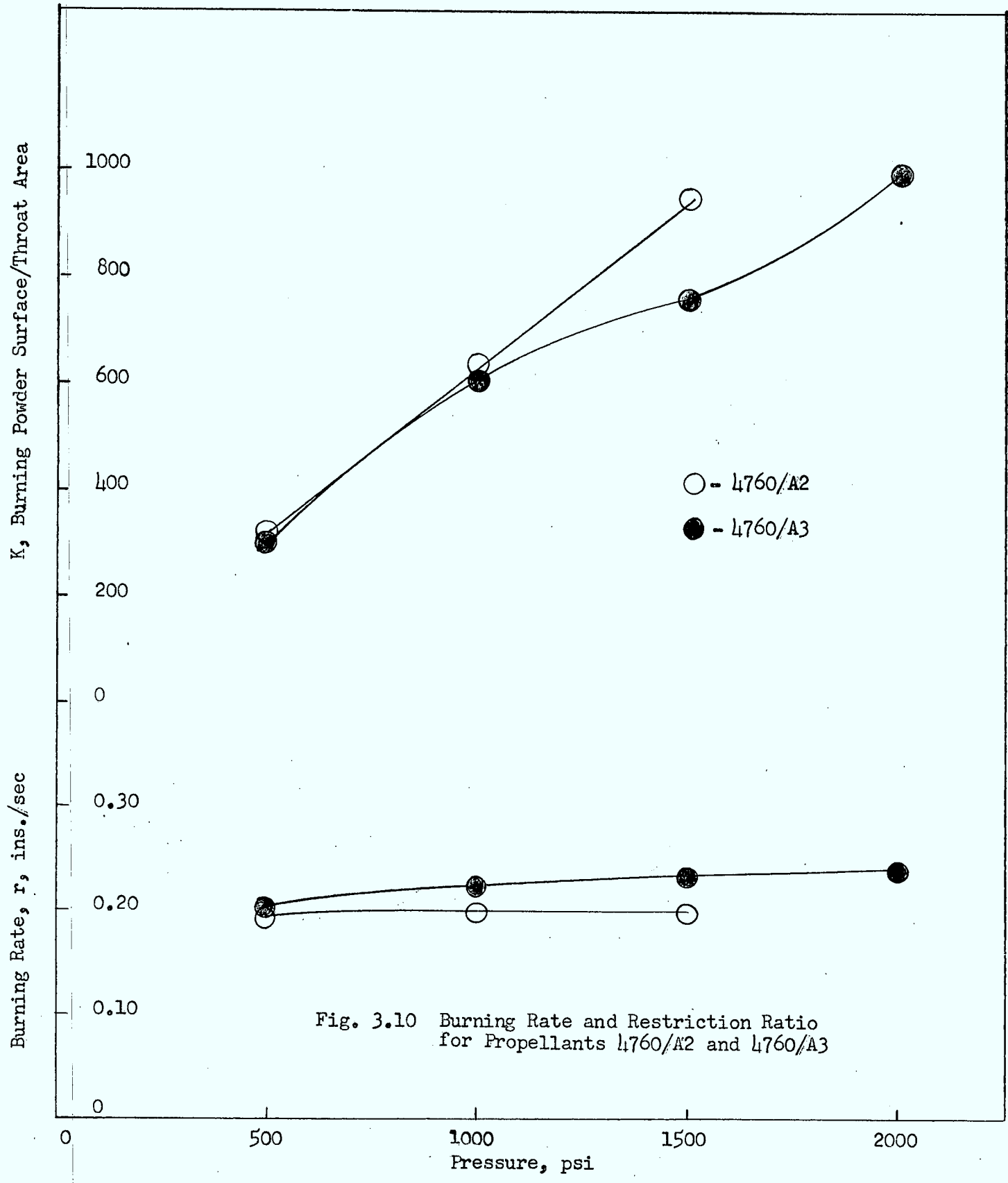


Fig. 3.10 Burning Rate and Restriction Ratio for Propellants 4760/A2 and 4760/A3



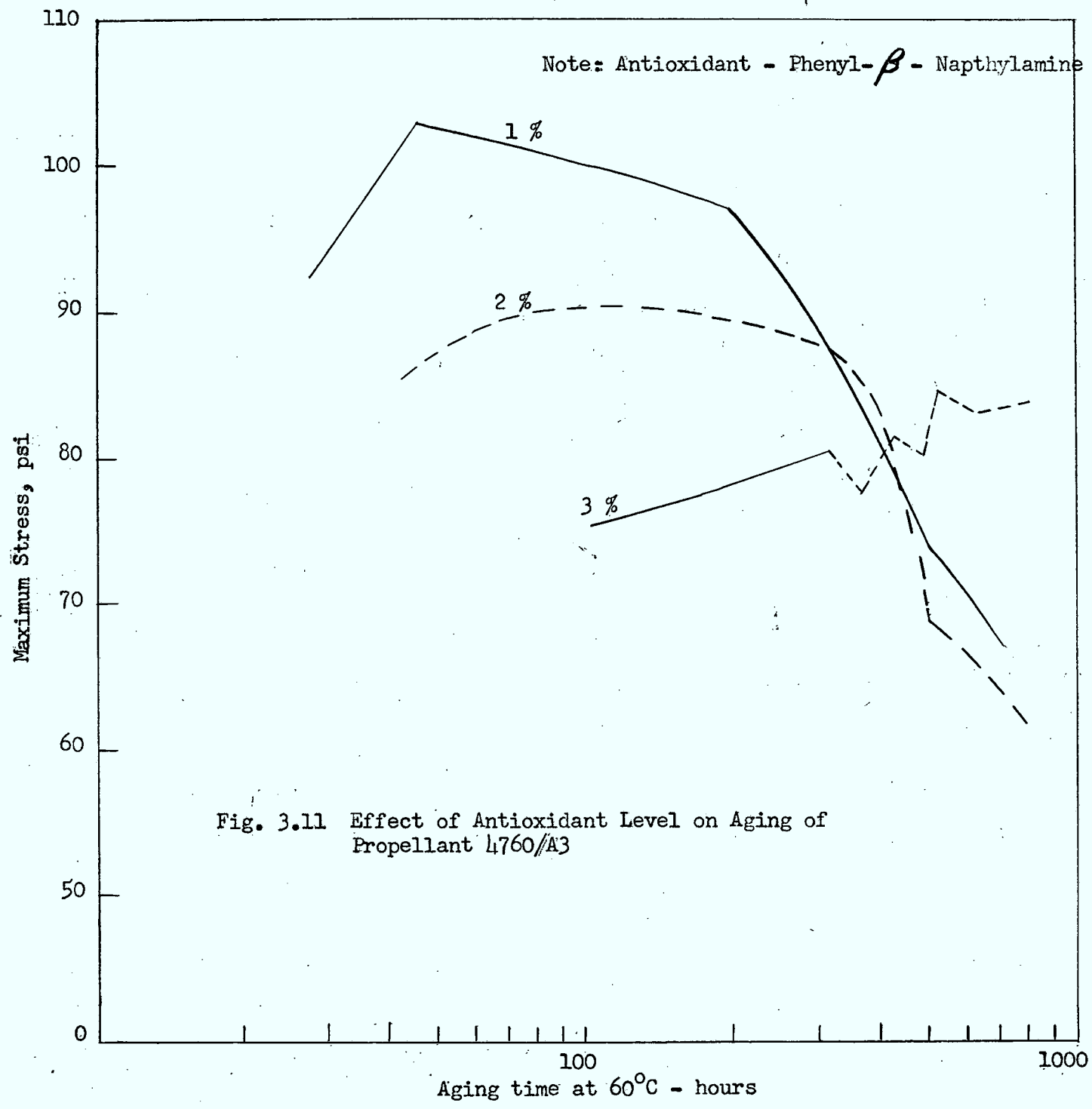
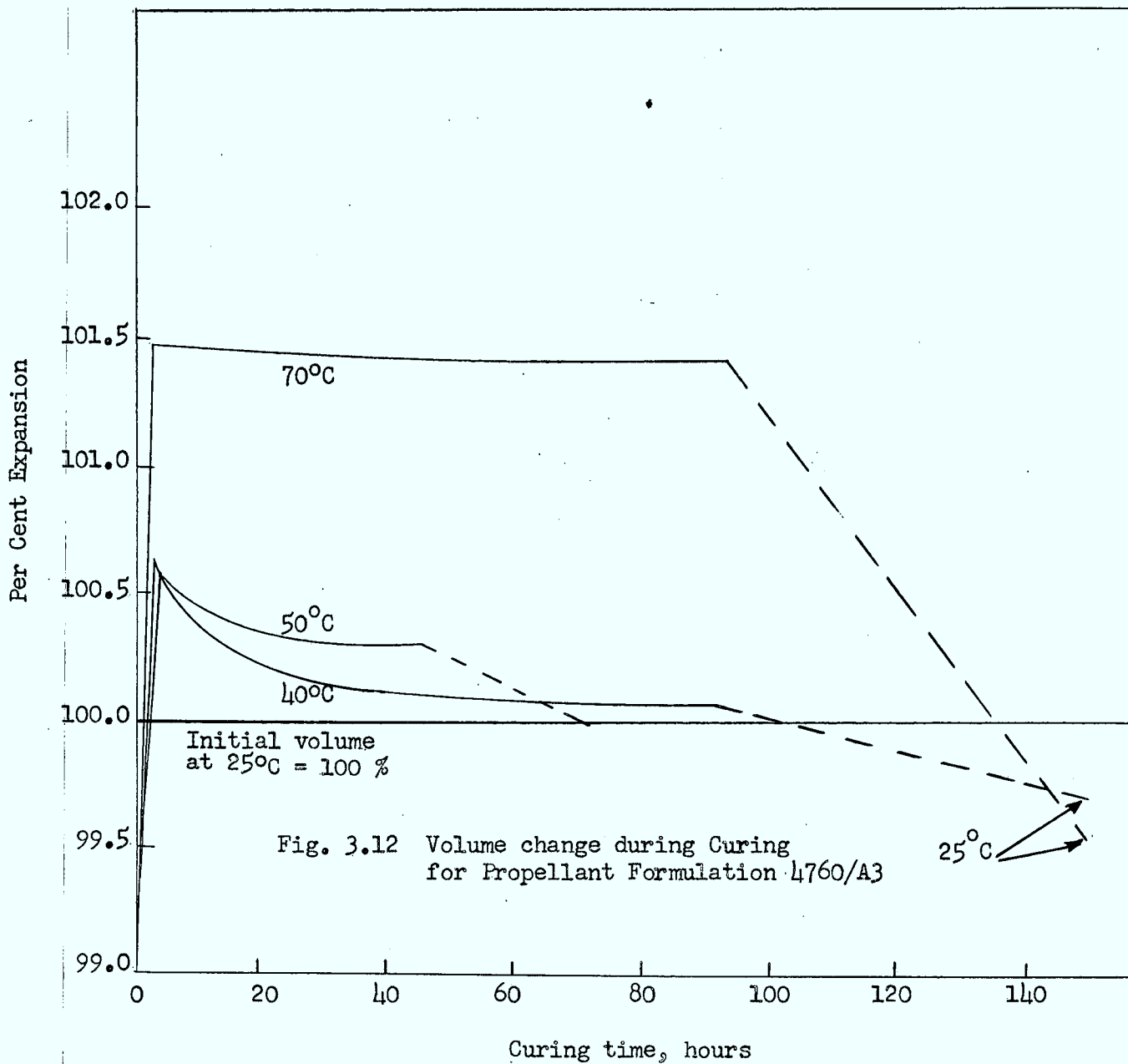


Fig. 3.11 Effect of Antioxidant Level on Aging of Propellant 4760/A3



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