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THE DURABILITY OF HIGH TEMPERATURE THERMOPLASTICS

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The Durability of High Temperature Thermoplastics

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A comprehensive investigation undertaken by RAPRA to provide characterisation and design data.

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A few words of explanation about the format of this report.

There is a number of materials which has been examined and the individual results are recorded, separately, in the appropriate sub-sections of Section 3. As a consequence, Table and Figure numbering throughout the report has been done on a section or sub-section basis. Thus all figures pertaining to Polyphenylene sulphide for instance, in Section 3.3, are numbered 3.3.1, 3.3.2 et seq. and are contained, collectively, in the report at the end of the appropriate sub-section. However, in Sections 4 and 5, 'Discussion of Results' and 'Summary', the various Tables and Figures have been included in the text as they arise in discussion.

The 'Colour-change' photographs are contained in transparent wallets at the beginning of Section 3.

In due course the work described in this report will form the basis of a number of papers which will be submitted for publication in appropriate Plastics journals.

CONTENTS

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OBJECTIVES

The objectives of this project were threefold:

1. To determine the long term durability of a number of selected polymers, at elevated temperatures, in terms of integrity and toughness as well as basic form stability.
2. To examine the response of these polymers, when subjected to externally applied loads, at 20°C and at elevated temperatures.
3. Throughout the investigation, a study would be made of the phenomenological response of the materials.

TIMESCALE

From 1st January 1981 to end of 1983.

1. INTRODUCTION

1.1 General

At the time of inception of the project, although there was a certain amount of information available concerning the behaviour of reputedly high temperature polymers at elevated temperatures, it was still considered that the Plastics Industry would benefit from a formalised study of such materials. This view was, subsequently, reinforced by the committee administering the project, when it was formed and first met in July 1981. The composition of this committee, by selection, was such that it embraced as wide a range of interests and views within the industry as was possible. Its constitution throughout the major part of its lifetime was as follows:

Laporte Industries Ltd./Solvay et Cie – Raw Materials manufacturer
Phillips Petroleum Chemicals UK Ltd. – Raw Materials manufacturer
Imperial Chemical Industries PLC – Raw Materials manufacturer
Lucas Group Research Centre – User
Standard Telecommunications Laboratories Ltd. – User
Ford Motor Company – User
Pilkington Bros. PLC – Glass fibre manufacturer

The committee was chaired by RAPRA who also acted as secretariat. Throughout the project, the committee met eight times, not only to establish the scope of the project but also to progress and discuss the results as they became available. In the event, the system worked very well and the project overall benefited from supervision.

1.2 The Programme

The general format of the programme agreed upon was as follows. Some eleven materials were to be examined, and although there was a heavy bias towards reinforced grades, this was not wholly to the exclusion of some of their unreinforced counterparts. It was agreed that examination should cover both heat ageing and performance aspects. In view of the effort available and duration of the project it was decided to run the programme, essentially, in three stages.

The first stage was concerned with injection moulding of appropriate samples. It was agreed that RAPRA would be responsible for this, the aim being to produce mouldings having optimum physical/mechanical properties. To achieve this, advice, guidance and in fact direct supervision of the injection moulding trials was made available by the raw materials manufacturers who also supplied the materials. It was accepted that with the reinforced grades in particular, mouldings could be strongly anisotropic in their properties. However, with the straightforward objective of assessing the effects of heat ageing upon properties, anisotropy was considered to be of secondary importance at this stage and an ASTM tensile bar (D618, Type I) was selected. In conjunction with this, at least in the earlier part of the investigation, a thick (12.5 × 12.5 mm) cross section bar was also moulded. This was to be used for fracture toughness measurements.

The second stage of the programme was concerned solely with the effect that ageing at elevated temperatures had upon selected mechanical and physical properties. In view of the fairly wide range of polymers agreed upon, the range of temperature selected was 20°C to 200°C with a sampling time, initially, of up to six months but this was later extended to one year. One particular elevated temperature was selected as a reference datum, + 120°C. The reason for this choice stems from the requirements of the auto industry. A temperature of 120°C is considered to represent the upper limit for 'under-bonnet' temperatures. In the same vein, one material in particular viz. a glass reinforced Nylon 66 was included because over the years it has been used in such applications and as a consequence, a significant amount of field experience etc. has accrued. From this standpoint, it would serve as a very useful practical reference material.

The third stage of the programme was scheduled to examine certain performance properties, creep response and fatigue under cyclic loading. Both were to be evaluated at 20°C and 120°C, but additional creep tests at elevated temperatures in excess of 120°C were envisaged.

The format of this report of the work is a simple and straightforward one. In discussion of the various data obtained, Section 3 is concerned with the materials tested, individually, in their own right, whereas Section 4 considers the characterisation of the materials as a whole and as such provides a comparison between materials from various criteria.

2. EXPERIMENTAL

2.1 Materials

The materials examined during the course of the programme are listed in Table 2.1 below.

Table 2.1 Materials

Plastic	Prog Code	Standard Abbreviation	Glass Content wt/wt %	Manufacturer	Grade
Polyarylate	A	PAr	Nil	Solvay et Cie Brussels	ARYLEF U100
Polyamide	B	PA	33	Imperial Chemical Industries PLC	MARANYL A190
Polyphenylene sulphide	C	PPS	40	Phillips Petroleum Company (USA)	RYTON R4
Polyvinylidene fluoride	D	PVDF	Nil	Solvay et Cie Brussels	SOLEF 1008
Polyvinylidene fluoride	E	PVDF	Carbon fibre 10	Solvay et Cie Brussels	SOLEF 8808
Polyether sulphone	F	PES	Nil	Imperial Chemical Industries PLC	VICTREX 200P
Polyether sulphone	G	PES	30	Imperial Chemical Industries PLC	VICTREX 430P
Polyether ether ketone	H	PEEK	Nil	Imperial Chemical Industries PLC	VICTREX 45G
Polyether ether ketone	J	PEEK	30	Imperial Chemical Industries PLC	VICTREX 4530 GL
Polybutylene terephthalate	K	PBTP	30	Akzo Chemie	ARNITE TV4 261
Polyphenylene sulphide	L	PPS	40	Phillips Petroleum Company (USA)	RYTON A100

2.2 Test Conditions and Equipment

(1) The tensile, flexural and fracture toughness tests were performed on an Instron Model 1115 – 100 KN capacity.

The majority of the tests were done at 23°C but a few were done at 120°C.

(2) Uniaxial tensile creep was carried out at 20°C/50% rh; and at 120°C with air drawn into the oven from the standard laboratory atmosphere (20°C/50% rh). The force is applied by a dead weight lever loading system at a 5x arm ratio. Creep response is followed using the RAPRA Moiré fringe extensometer (1). Photographs of the equipment; room temperature

and high temperature are shown in Figures 2.1 and 2.2 respectively. At elevated temperatures, only short term equilibrium between the specimen and the environment, was established before a creep test was begun. This condition was achieved after 1 hour.

(3) Uniaxial fatigue was effected by direct loading through pneumatically energised, double acting cylinders fitted with low friction filled PTFE seals. The system is based upon an original ICI design (2). A photograph of the actuator used at room temperature (23 ± 3°C) is shown in Figure 2.3 and the high temperature assembly is shown in Figure 2.4.

2.3 Characterisation Tests/Ageing Trials

(1) *Sample form.* In the early part of the programme viz for materials coded A, B, C, D and E, see Table 2.1, two mouldings were produced; an ASTM D638, Type I tensile bar and an Izod unnotched impact bar with a 12.5 × 12.5 mm cross section. See Figures 2.5 and 2.6. Both these mouldings were end gated and were processed on a Stubbe SKM 76–110 machine.

The optimum moulding conditions recommended by the raw materials manufacturers were used, and the individual details are recorded under the respective sub-sections 3.1 to 3.11.

(2) *Ageing schedule.* Although, initially, a maximum period for ageing had been set at 6 months, this figure was revised and a target of 12 months set with a maximum temperature of 200°C.

The ageing schedule agreed upon was as follows:

Ageing period (days) 1, 5, 10, 40, 160, 365
Ageing temperatures (°C) 20, 120, 150, 175, 200

Ageing at elevated temperatures was carried out in electrically heated ovens, with the specimens simply supported upon open grill shelves. It was not possible, on grounds of cost, to segregate materials generically. After the appropriate period of ageing had elapsed, samples were removed from the various ovens, wrapped immediately in paper, and then stored in a large open mouth Dewar to cool slowly.

Currently, thermoplastics are graded with regard to ageing by what is termed – their UL rating – determined by the Underwriters Laboratories USA (3). There is a number of these 'Relative Thermal Indices' according to property; impact strength, dielectric strength, tensile strength. The rating is based upon a time/temperature relationship at which the property has fallen to 50% of its unaged value. In the absence of data for a control material, the commonly accepted duration of ageing is 100,000 hours.

Thus, 'The UL rating is that temperature at which the property value has fallen to 50% of its unaged value after 100,000 hours'.

(3) *Characterisation tests.* Changes in mechanical performance caused by ageing have been monitored using two tests.

(a) *Tensile test.* This was the main test and was done on a standard ASTM D638, Type 1 tensile bar. Specimens were loaded at a constant rate of crosshead movement of 5 mm min^{-1}.

This gives an initial straining rate within the extensometer gauge length of 0.17% s^{-1}. Strain measurements were made thoughout using an Instron extensometer type 2630/017. Force/strain curves were recorded by X/Y plotter and the usual force/elongation curves were produced by the Instron. From these curves, parameters such as yield stress, brittle strength, yield strain, modulus etc. were calculated.

(b) *Fracture toughness.* This property provides a measure of the resistance to crack propagation of a material. It is made using a very sharply notched specimen. The notch is first introduced by making a saw cut, a further small cut is made by razor blade (new). Two specimen geometries were used. For materials A–E the single edge notched bend (SENB) specimen was used. The complete Izod bar, a prismatic beam, proved ideal for this test. Because of difficulties, experienced with this moulding, in producing void free specimens, it was decided to use the tensile specimen instead for the remaining materials F,G,H,J,K and L. This was notched in one edge only to give a single edge notched tensile specimen (SENT). Where applicable the test geometry was in accordance with Reference 4. The rate of loading was the same in both cases with a crosshead speed of 50 mm min^{-1}.

2.4 Performance Tests

(1) *Sample form.* Again two mouldings were used, as a source for test specimens. They were: the ASTM tensile bar, previously described, and a square plaque, film gated, measuring 100 mm × 100 mm × 6 mm thick. This is illustrated in Figure 2.7 which details not only the geometry but also defines the two orthogonal directions, within the plaque, with respect to direction of injection. The mould was kindly loaned to RAPRA by Brunel University. It provided a useful sample for fatigue and impact specimens.

(2) Creep. Creep response was measured at three stress levels and at two temperatures 20°C and 120°C. Duration of the creep tests was of the order of 10^6 seconds.

Procedure, specimen geometry, extensometer accuracy etc. were in accordance with Reference 5. Two general guidelines were followed with regard to the level of applied stress. These were laid down in order to facilitate easy inter and intra materials comparison. The first guideline was that the highest stress applied should generate a strain in the region of 1% for the unreinforced and 0.5% for the reinforced materials. In some cases, e.g. the heavily reinforced polyphenylene sulphide Ryton R4, the load necessary to achieve this was outside the limits of the creep equipment. The second guideline was that the stress applied, be selected from a rational sequence of stresses, e.g. 5, 7.5, 10. 15, 20, 30 et seq. This particular rule presented no real problem except in the case of SOLEF 1008 (PVDF) at 120°C under which conditions, 5 MN/m^2 was the maximum stress that could be applied.

The geometry of the creep specimen is shown in Figure 2.8. In the case of the glass fibre reinforced materials, the dimension at the pin load ends was increased to prevent 'pull-through'.

The data are presented as strain (%) vs log time(s) plots, from which various other informative cross plots such as isometric curves, modulus as a function of strain level and time etc. can be generated. Data reported for times in excess of 10^6 seconds, have been generated using simple extrapolation techniques.

(3) *Fatigue*. Resistance to fatigue was evaluated at two temperatures, room and 120°C. The conditions under which these measurements were made were as follows:

Mode — Uniaxial tensile
Force — Constant — applied between + tension and zero (T/O). $\sigma_{mean} \neq 0$
Specimen — A waisted tensile dumb-bell
Waveform shape — Square
Frequency — 0.5 Hz

The data are plotted as S/Nf curves, that is applied stress vs/Log number of cycles required to cause failure. These data can be transformed to complementary initial strain/Log number of cycles to failure cures (€/Nf) using appropriate stress/strain relationships. The strain recorded is 'initial strain' because no account, with this equipment, can be taken of background creep c time of exposure to the applied load increases. The initial strain, however, is considered to be a practical parameter useful for design purposes.

Specimen geometry is illustrated ir 2.9. Specimen selection for test was random.

(4) *Impact*. This part of the investigation was carried out for the project team by Pilkington Bros. PLC., using an instrumented falling weight ...... The specimen geometry 48 × 10 × 6 mm enabled seventeen specimens to be cut in directions parallel (0°) and transverse (90°) to the mould filling direction and according to the plan shown in Figure 2.10 which gives the precise location of each specimen.

Details of the geometry of the impact test are shown in Figure 2.11. A specimen is freely supported across the 40 mm span and a mass of 4.8 kg is allowed to fall on it from a height of 300 mm. Force values throughout the impact event are obtained by means of a force transducer inserted between the tup and the falling mass. Values of deflection and energy corresponding to each pair of force and time co-ordinates can be computed. A full account of both the equipment and experiment recorded elsewhere (6,7).

(5) *Colour Change*. In a number of instances, it has been possible to see the effects ageing has upon the colour of a sample. This is particularly true for agein[illegible] peratures. These changes in colour are attributed to chemical changes. the eleven samples examined, only Solef 8808 the carbon fibre filled both samples of PPS, Ryton R4 and A100 did not exhibit changes bec[illegible] utural very dark brown colour. Those colour photographs which have been tak[illegible] corporated in the report between Sections 2 and 3.

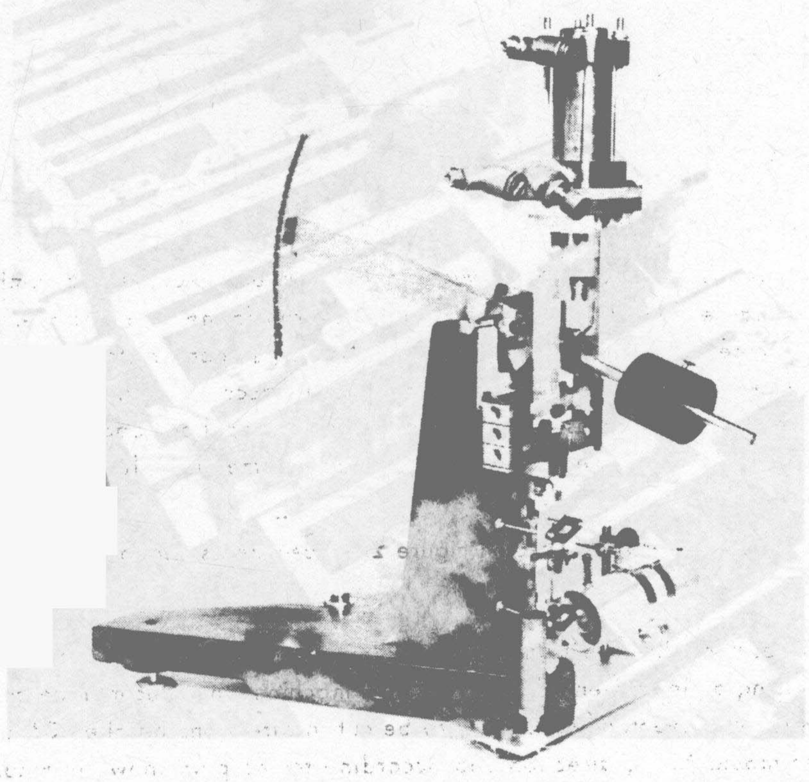


Figure 2.1 RAPRA tensile creep machine – 20°C

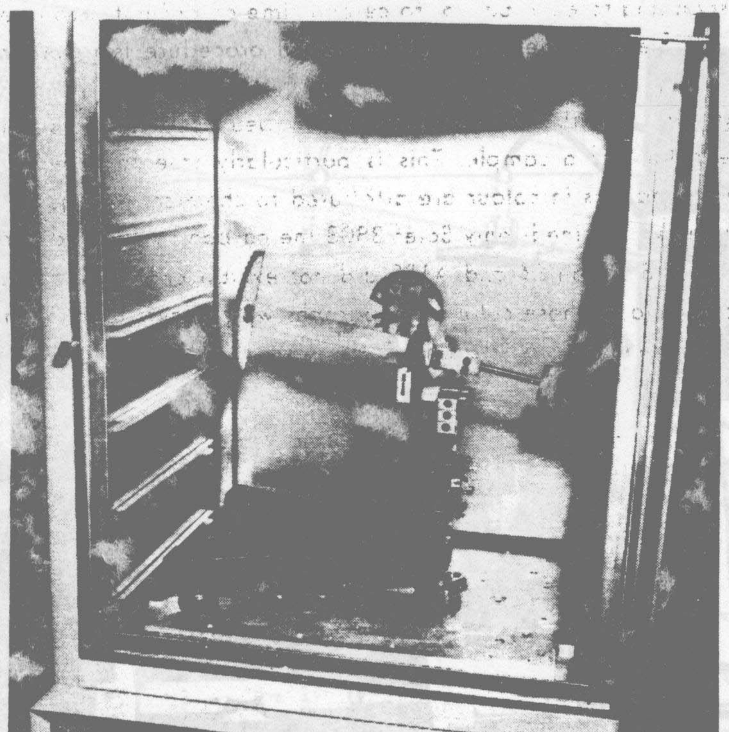


Figure 2.2 Elevated temperature creep equipment

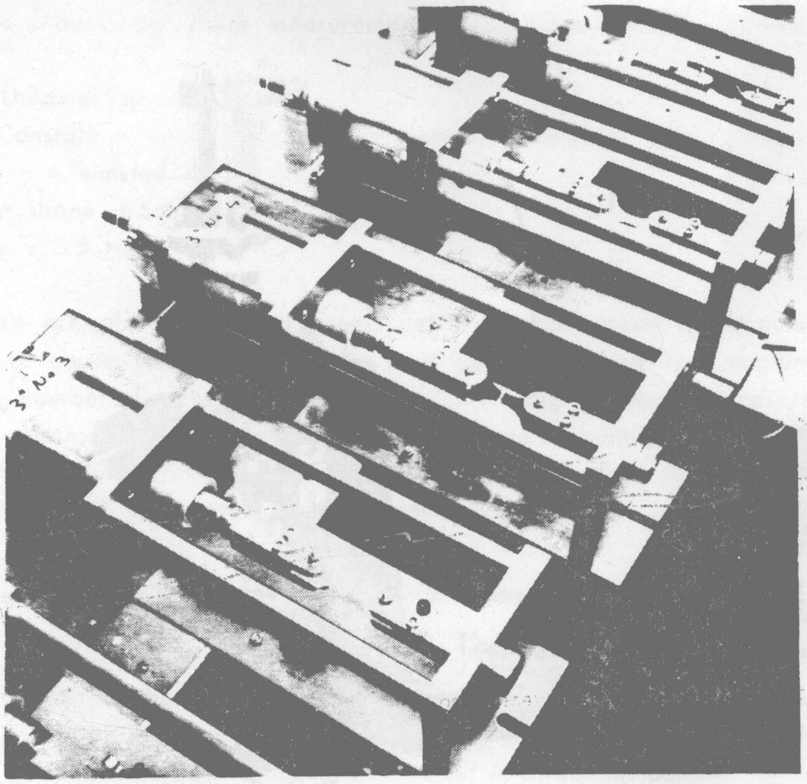


Figure 2.3 Fatigue equipment – 20°C

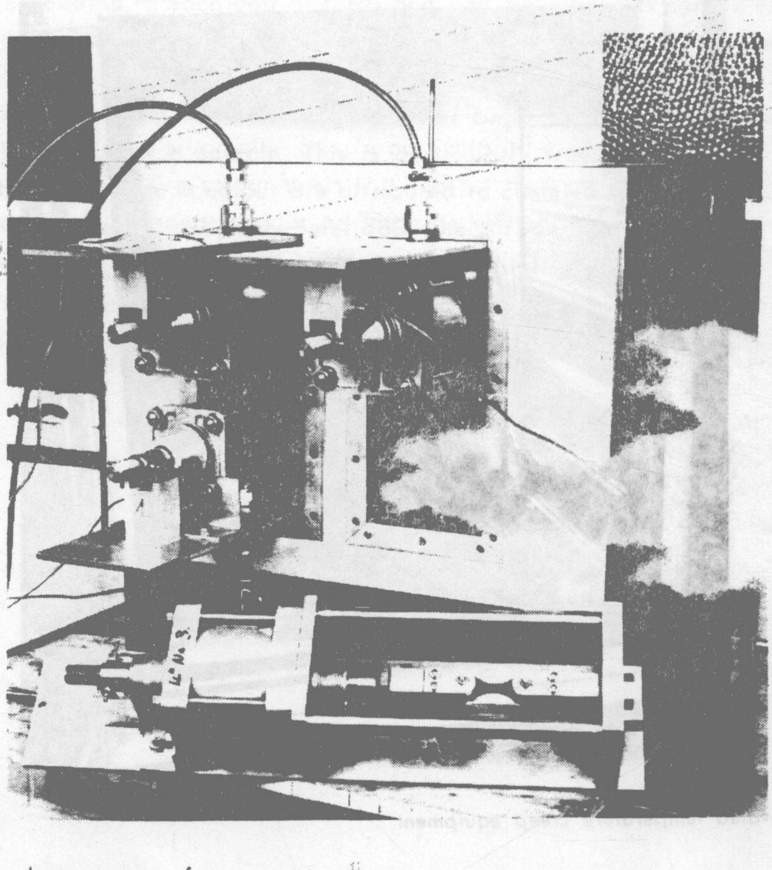


Figure 2.4 Elevated temperature fatigue equipment

Figure 2.5 ASTM D638, Type I tensile bar

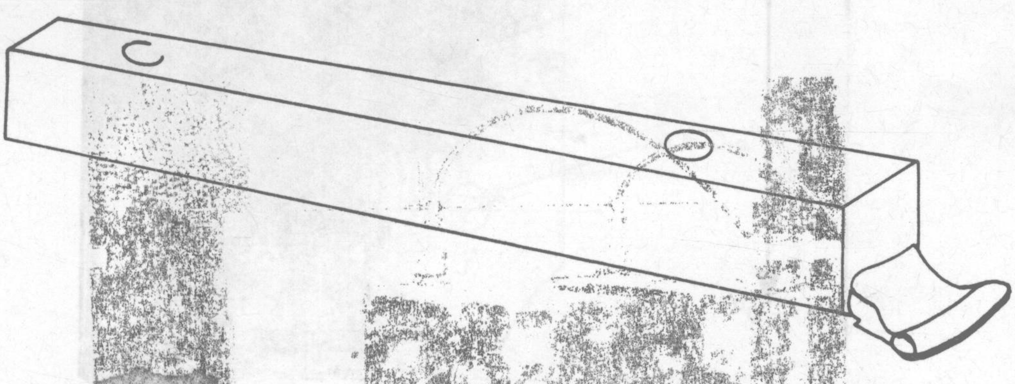


Figure 2.6 I [illegible] bar

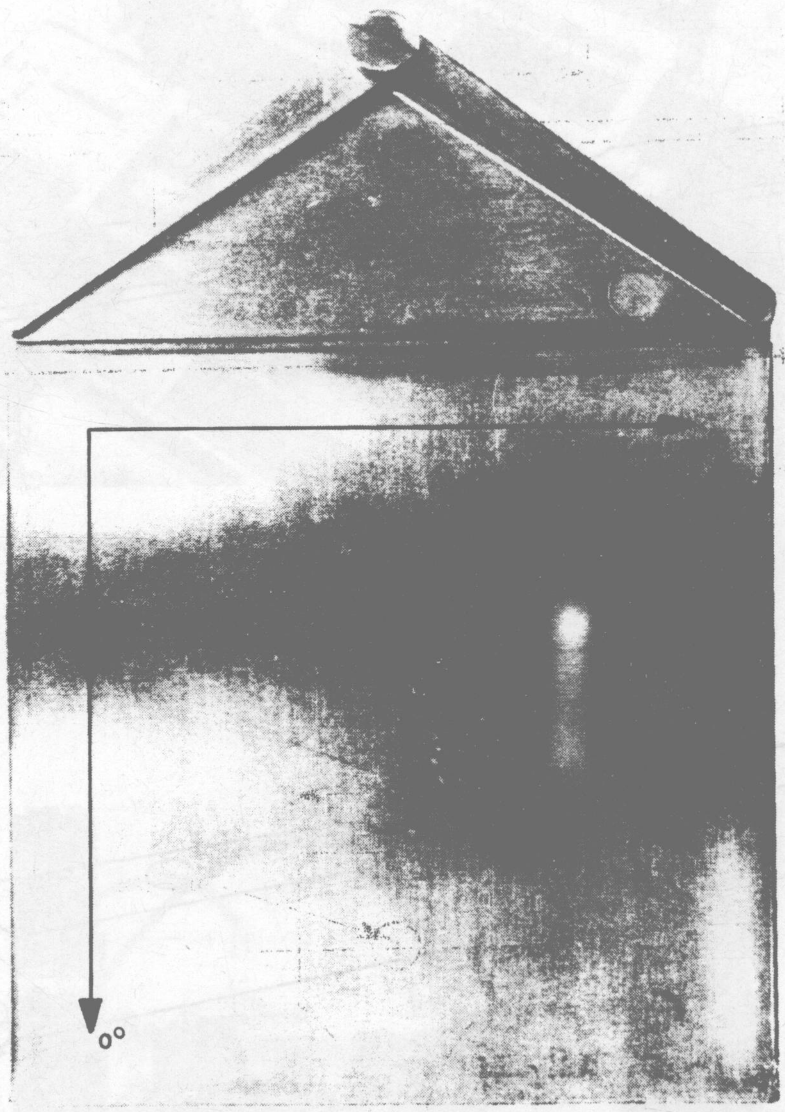


Figure 2.7 Fatigue and impact plaque

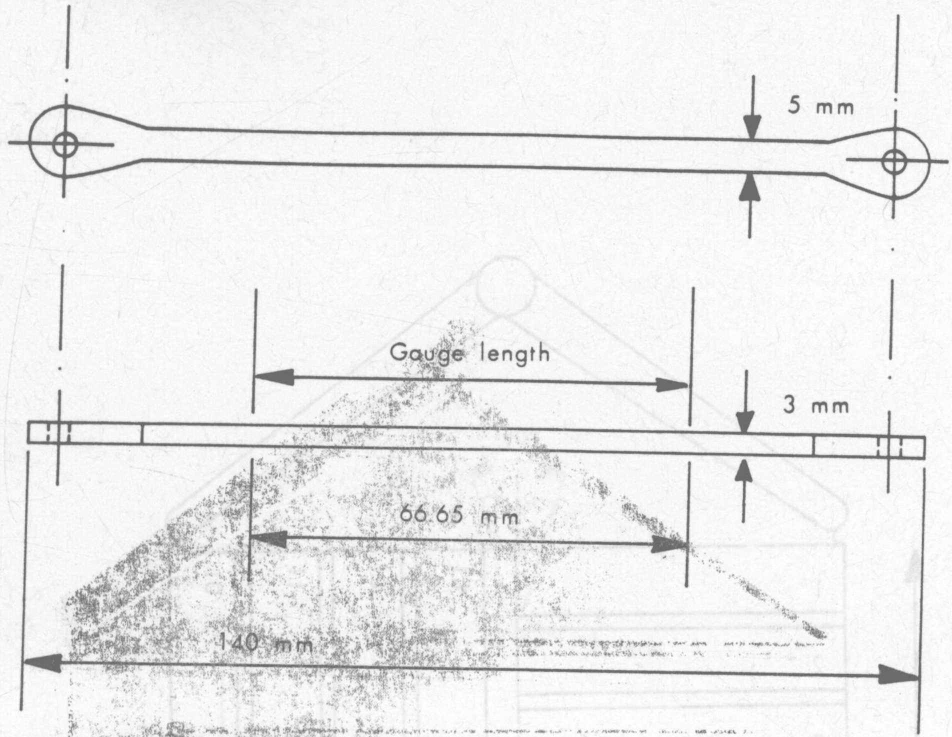


Figure 2.8 Tensile creep specimen

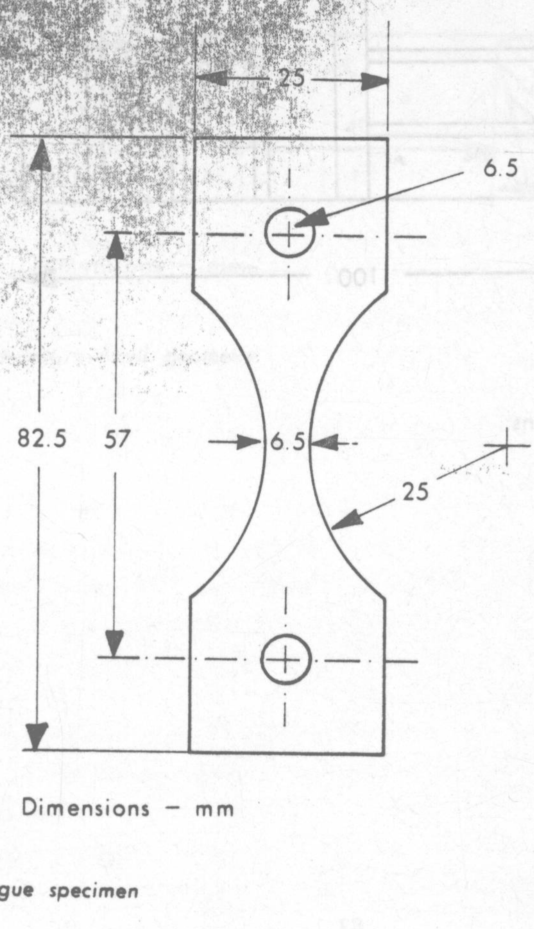
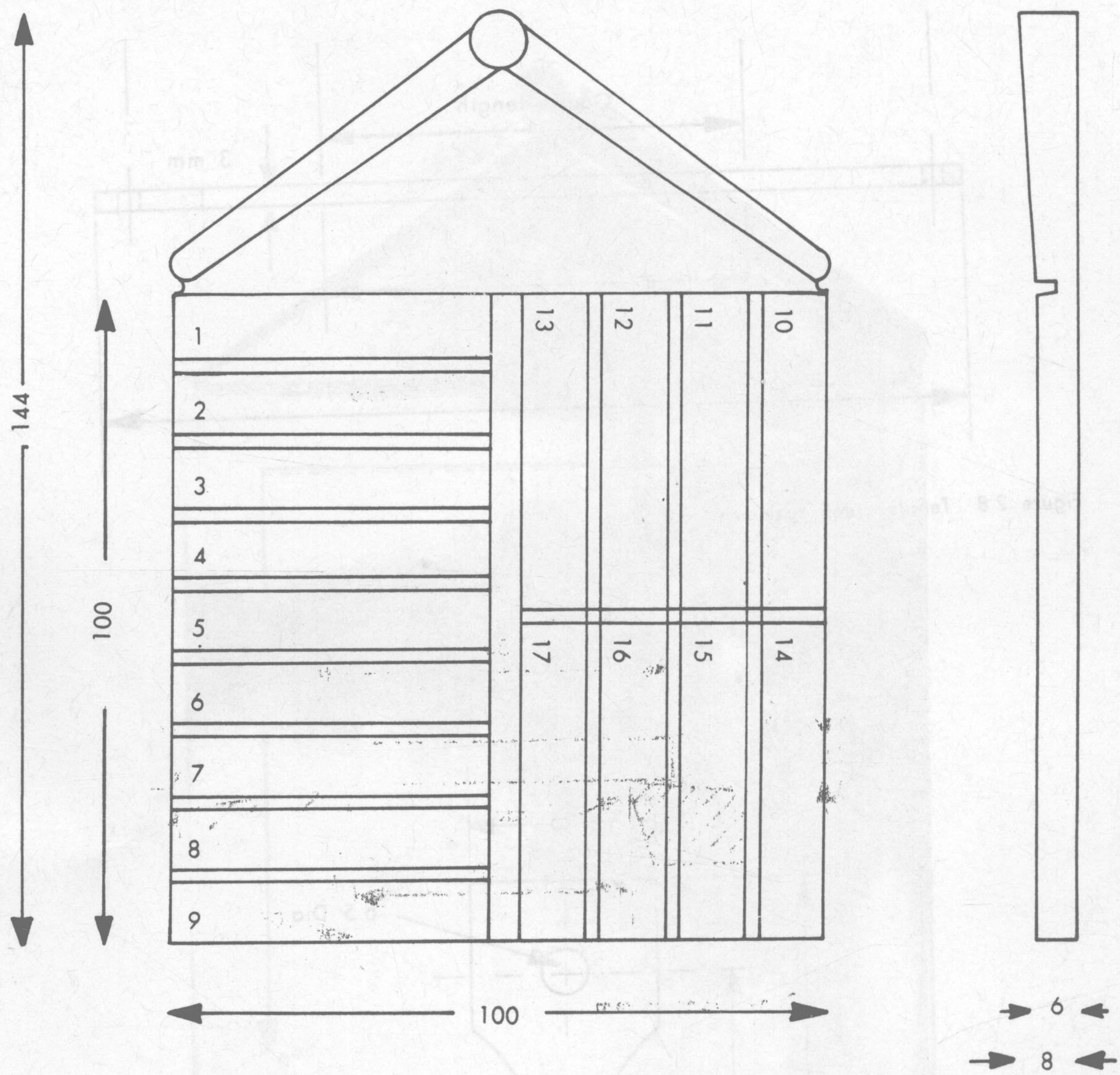


Figure 2.9 Dynamic fatigue specimen



Cutting plan for specimens

Dimensions – mm

Figure 2.10 Plaque moulding

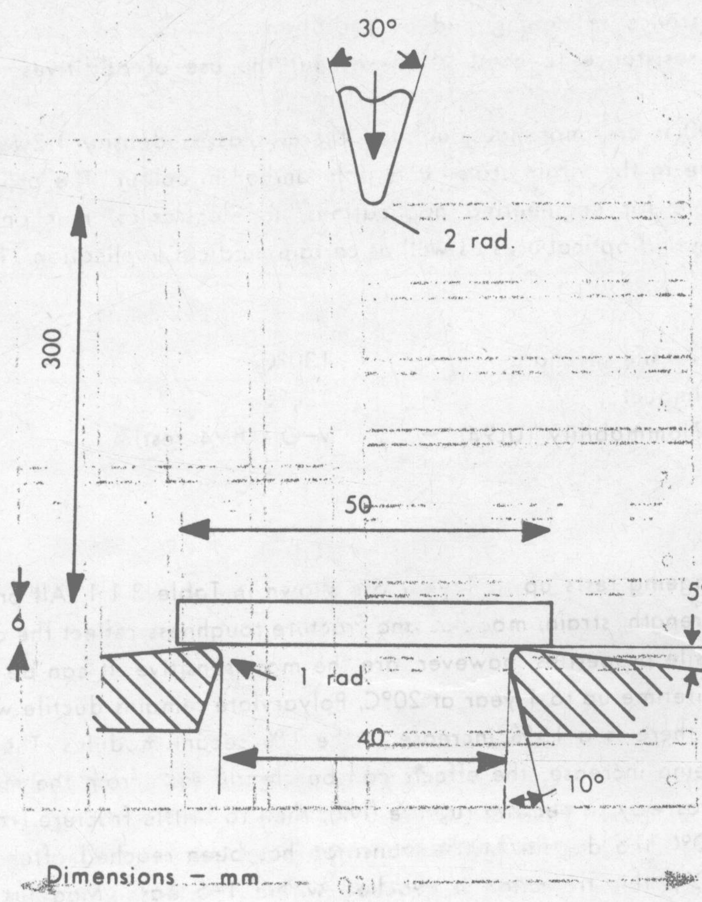


Figure 2.11 Impact test — Anvil geometry