THE SELECTION OF ADHESIVES AND COMPOSITE MATRIX RESINS FOR AIRCRAFT REPAIRS

by

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CONTENTS

ABSTRACT

This Thesis studies various aspects of the selection of adhesives for aircraft repairs. It was undertaken because of the need to repair a number of different aircraft types with a limited range of adhesives to minimise stockholdings and wastage of materials which have shelf-life limitations. The aspects studied were tensile strength, tensile modulus, elongation at failure, fracture energy, compression strength, compression modulus, water uptake, Tg dry and wet and diffusion coefficient. A computer programme written at Leicester Polytechnic was adapted to suit an IBM PC and this allowed water uptake within a lap joint to be related to time, diffusion coefficient and solubility coefficient.

Later in the project attempts were made to relate the tensile properties to lap joint strength. They were partially successful and led to a number of wedge tests to obtain fracture energy data. From this fracture toughness was calculated and this gave the best correlation with lap joint strength. It was finally concluded that good lap joint strength required an optimum combination of tensile strength, modulus, elongation to failure and fracture energy to achieve a fracture toughness of at least 3 $MN.m^{-3/2}$

The fracture energy data clearly separated the brittle composite "matrix resins" from the tougher "adhesives". It was concluded that matrix resins and adhesives can be more easily and effectively compared using the fundamental properties of the resins themselves than by using the limited data normally supplied by the Manufacturers on their data sheets.

It was also considered that the simpler tensile, compression and wedge tests used in this programme could obtain more data, more quickly and more cheaply than the thick adherend or napkin ring tests usually advocated.

From the results obtained it was possible to suggest specifications for both composite matrix resins and adhesives for making bonded metal or composite joints. These should lead to the development of better matrix resins and adhesives.

CHAPTER ONE INTRODUCTION

The objective of this work was to obtain the mechanical properties and some physical properties of a range of resins, used for the repair of metal and composite aircraft parts in order to be able to compare them more effectively and to make better substitutions for one another where necessary.

It was carried out in essentially two phases, see Armstrong (1987) and (1989a), and it became clear during the second phase of the work that two distinct classes of materials could be discerned. Those resins which were tough, of high viscosity when molten (or immediately after mixing in the case of pastes) and of moderate or low modulus were called "Adhesives" and those which were brittle, of low viscosity when molten (or freshly mixed) and with a high modulus were called "Matrix resins". It is accepted that some older "adhesives" can be rather brittle and that some newer "matrix resins" have improved toughness so that the borderline between the two types is not sharply defined. As the work progressed it was found that the properties required of a good adhesive could be fairly well defined and the work of Palmer (1981) showed that the properties of a good matrix resin could be listed in a very similar way.

The choice of adhesives and matrix resins for the repair of composites, and of adhesives for the repair of bonded metal parts, needs careful consideration. Baker (1987), Baker and Jones (1988), Mahoney (1986a) (1986b). It may be argued that ideally repairs should be carried out using the same adhesive as that used for the original construction. In support of this it may also be argued that occasionally it is found that some epoxies are not compatible with others. A close match of properties is

important because harder and more brittle resins have lower impact resistance and give lower joint strengths than tougher resins. When used as composite matrices harder resins result in a greater area of damage from a given impact. McQuillen et al (1976), Palmer (1981). The elongation at break of the original material under repair needs to be matched by the elongation at break of the resin. The need for this in the case of composites is emphasised by Konur & Matthews (1989) who stated in a review paper entitled 'Effect of the properties of the constituents on the fatigue performance of composites', "It appears that the fatigue properties are determined by matrix properties in composites which have larger static failure strains than the matrix fatigue strain limit, whereas composites which have lower failure strains than the matrix fatigue strain limit have fatigue properties independent of the matrix properties". Fibres with a high elongation to failure need resin matrices with a high elongation. This paper shows that generalisations are not reliable and that interfacial properties and processing are also important.

A high modulus material can use a higher modulus adhesive than a low modulus material, Armstrong (1983). However, original manufacture commonly involves film adhesives, or pre-preg matrices which, for curing, require elevated ($120^{o}C$-$180^{o}C$) temperatures and in some cases increased pressures. (30 psi or 2 atmospheres is common for epoxies and 100 psi or 7 atmospheres is required for some phenolics).

If these are to be used for repairs, problems arise both in the techniques of carrying out the work, sometimes under somewhat primitive conditions in the field, and in the storage of materials for reasonable periods at $-18^{o}C$ when refrigerated storage is called for.

An Airline, or Air Force, usually uses several types of aircraft. These will almost certainly be supplied by different manufacturers and the likelihood of each of them selecting the same adhesives and pre-pregs is virtually zero. Additionally it is becoming increasingly common for airframe manufacturers to subcontract the design or manufacture, or both, of composite or bonded parts. If composites or bonded metal parts from several different sub-contractors are involved then even a single aircraft type may be made using a range of adhesive and pre-preg materials.

The question then arises, can all be repaired using the same materials? This problem is further compounded by the fact that fabrics of different materials, weaves and weights may have been employed. This has led some users to consider stocking one film adhesive for each cure temperature and to interleave these between layers of dry fabric of the type required for each repair rather than buying and using a variety of pre-preg materials.

It offers the advantage that the same adhesive can then be used for composite and bonded metal repairs, avoiding the need to keep a wide range of materials, perhaps under refrigerated storage. However, it does not resolve the question of how the properties of the chosen film adhesive compare with the properties of the resin systems used in the various composites. In general film adhesives are likely to be tougher and of lower modulus. It will be seen later that the use of film adhesives in this way may be acceptable but that, because they generally have lower moduli than matrix resins, additional fabric layers may be required. Fig 7 (page 31).

Unfortunately, manufacturers do not commonly quote all the relevant properties either for composite matrix resins or for film adhesives. The provision of more data would be very helpful and is to be most warmly encouraged.

Comprehensive data should include for each fully cured material:-

1. Ultimate tensile strength
2. Tensile modulus
3. Ultimate compression strength
4. Compression modulus
5. Shear strength
6. Shear modulus
7. Poisson's ratio
8. Elongation at failure
9. Fracture energy
10. Creep properties
11. Fatigue properties
12. Water diffusion coefficient
13. Water solubility coefficient

Ideally all this data should cover the whole range of service temperature.

Additionally it would be useful to know -

14. Glass transition temperature after cure at various temperatures

15. Glass transition temperature at various water uptake levels.

16. Coefficient of thermal expansion.

There is an urgent need to develop comprehensive Specifications and Data Sheets for a fairly wide range of Adhesive and Pre-Preg materials, which might most usefully be done through the International Standards Organisation (I.S.O). This has been recommended by an I.A.T.A. (International Air Transport Association) Task Force charged with producing a document on the Standardisation of Composite Repairs. (IATA 1990) Standard Data sheets for adhesives and pre-pregs have been proposed in the IATA document entitled "Guidance material for the Design, Maintenance and Repair of thermosetting epoxy matrix composite aircraft structures".

Items 1 to 11 are very dependent on testing technique, specimen shape and testing speed and it is important to use standard test methods and specimens so that results from different laboratories may be compared with confidence. One variable, very difficult to cover in the laboratory, is the range of strain rates experienced in service. For aircraft these can vary from very slow creep rates, possibly while parked in hot sun, to very high rates due to gust loading in turbulent air perhaps occurring at low temperatures. Hence, it is important to specify and control temperatures at which all testing is carried out.

The modulus values, in particular, will affect the behaviour of a composite, as a whole, in bending or compression buckling. Strength is considerably reduced at temperatures above the glass transition temperature of the resin and Tg can be reduced by as much as 20°C for each 1% of water absorbed in hot-curing resins, Delmonte J (1981) and Wright W W (1979). However, the tests carried out in the second phase of this work showed that the reduction of Tg with water uptake is not so bad for two-part, cold-setting epoxies. This is fortunate as their Tg, after

room temperature cure, is lower and their water uptake can be higher than the hot-curing versions.
In some cases the Tg of cold-setting epoxies can be increased by warm curing, say at 50°C or 80°C. Table 1 (courtesy RAE) (Page 12).

Table 1B (page 15) derived from Table 1A (pages 13 and 14) shows that in some cases Tg can actually be higher after saturation! The presence of water could allow further cure to proceed.

In the case of Redux 408 and 501 higher water uptake seems to give very little Tg loss whereas for the acrylic adhesive high uptake and high Tg loss go together.

In the case of Epikote 828 + RTU a low water uptake produces a high loss. It would seem that a more detailed study of these effects is required. Post-curing seems to have a negative effect in some cases and actually makes Tg loss worse. Fig 1 is very much a "worst case" figure and a generalisation. Precise data needs to be supplied by each manufacturer for each material. As mentioned again later, cold-setting epoxies suffer a smaller reduction of Tg with water uptake than hot-sets.

In practical situations it is often difficult to carry out a repair at the original cure temperature. To do so would mean extensive tooling. It is also necessary to carry out hot curing at a fairly precise and controlled temperature. Overheating one area to achieve the minimum temperature in another may make the hotter area too brittle. Conversely, to limit the highest temperature in one area to the recommended value could mean that the minimum temperature for an adequate cure would not be achieved in a cooler area.

TABLE 1
Tg Dry & Wet After Various Cure Temperatures

ADHESIVE	Tg DRY & WET AFTER VARIOUS CURE TEMPERATURES					
	After RT Cure Dry	After RT Cure Wet	After 50°C Dry	After 50°C Wet	After 80°C Dry	After 80°C Wet
EA 9330	11°C	NR	NR	NR	27°C	NR
EPIKOTE 815+RTU	48°C	NR	61°C	52°C	69°C	47°C
EPIKOTE 828 + VERSAMID 125	47°C	NR	51°C	37°C	47°C	NR
EC 2216	NR	NR	--	NR	NR	NR
EC 3524	NR	NR	--	64°C	NR	NR
EA 9321	--	53°C	--	47°C	NR	NR
AF 163 *	--	--	--	--	108°C	NR
EC 3559	--	50°C	--	NR	71°C	49°C
EA 9330 + 20% MICROBALLOONS	--	NR	--	NR	--	NR
EC 3568	--	NR	--	--	--	--
EC 3578	--	NR	--	NR	NR	NR
PERMABOND E34	119°C **	NR	--	NR	NR	NR

NR means tested but no satisfactory result obtained by DSC
-- means that no test carried out
* AF 163-2M film adhesive cured at 120°C for 1 hour
** figure from Permabond Adhesives
None of the wet specimens tested gave a clear cut result
The figures quoted should be viewed with caution
All data obtained on Perkin-Elmer DSC-2 at RAE Farnborough at a rate of temperature rise of 10°C/minute. Some polymers scanned between 40°C and 280°C, others between 0°C and 280°C. Results indicate that some tests should have been started at lower temperatures.

TABLE 1A
Phase II Additional Work
Tg Dry & Wet After Various Cure Temperatures

ADHESIVE	Tg DRY & WET AFTER VARIOUS CURE TEMPERATURES					
	RT Cure Dry	RT Cure Wet	50°C Dry	50°C Wet	80°C Dry	80°C Wet
REDUX 308A *	--	--	--	--	90°C + 4	NR 4
REDUX 408	61°C	NR	56°C	51°C	NR	NR
REDUX 408 + 20% REDUX 410NA	54°C	55°C	--	--	--	--
REDUX 408 + 40% REDUX 410NA	54°C	57°C	--	--	--	--
REDUX 410NA	46°C	48°C	47°C +	52°C	49°C +	52°C
REDUX 501	60°C	50°C	65°C	58°C	NR	51°C
REDUX 501 + 20% REDUX 410NA	58°C	51°C	--	--	--	--
REDUX 501 + 40% REDUX 410NA	57°C	52°C	--	--	--	--
EC 9323	42°C	49°C	60°C	50°C	54°C	50°C
BOSTIK 5435+TM2	50°C	-1°C	--	--	--	--
EA 9309.3NA	47°C	47°C	56°C	51°C	65°C	50°C
PERMABOND E37	119°C **	61°C	--	--	--	--
PERMABOND E38	--	--	NR		--	--
EPIKOTE 815+RTU	--	--	--	--	80°C 1	NR

TABLE 1A
Phase II Additional Work
Tg Dry & Wet After Various Cure Temperatures

ADHESIVE	Tg DRY & WET AFTER VARIOUS CURE TEMPERATURES					
	RT Cure Dry	RT Cure Wet	50°C Dry	50°C Wet	80°C Dry	80°C Wet
EPIKOTE 828+RTU	93°C +	58°C	106°C + 3	NR	116°C 2	NR
FR 7020	NR	49°C	NR	46°C	NR	47°C
REDUX 775 Cured 100 psi	--	--	--	--	--	NR 4
REDUX 775 Cured Zero psi	--	--	--	--	--	NR 4

* Redux 308A film adhesive cured at 170°C for 1 hour
** Permabond result
\+ Clear cut result - All other results should be treated with caution
NR Tested but no useful result obtained
1 120°C Cure
2 100°C Cure
3 60°C Cure
4 170°C Cure
-- Means no test carried out

TABLE 1B

Adhesive	Tg loss at saturation			Solubility Coeff.			Tg loss °C for each 1% water absorbed		
	RT cure	50°C postcure	80°C postcure	RT	50°	80°	RT	50°C	80°C
815+ RTU	NR	9°C	22°C	7.35	5.2	3.68	-	1.7	6
828+V125	NR	14°C	NR	6.25	6.6	7	-	2	-
EC 3559	NR	NR	22°C	5.15	5.4	4.76	-	-	4.5
Redux 408	NR	5°C	NR	13	12.4	7.9	-	0.4	-
Redux 410NA	-2°C	-3°C	-3°C	4.8	4.8	4.95	-0.4	-0.6	-0.6
Redux 501	10°C	7°C	NR	14.2	19.9	13.4	0.7	0.35	-
501 + 20% 410NA	7°C	-	-	15.1	-	-	0.46	-	-
501 + 40% 410NA	5°C	-	-	15.36	-	-	0.32	-	-
EA.9323	-7°C	10°C	4°C	9.1	8.2	6.8	-0.77	1.2	0.6
Bostik 5435/TM2	51°C	-	-	10.6	-	-	4.8	-	-
EA 9309.3NA	NIL	5°C	15°C	5	4.6	4.4	-	1.1	3.5
828+RTU	35°C	NR	NR	4.6	3.6	2.3	7.6	-	-

NR = tested but no result obtained

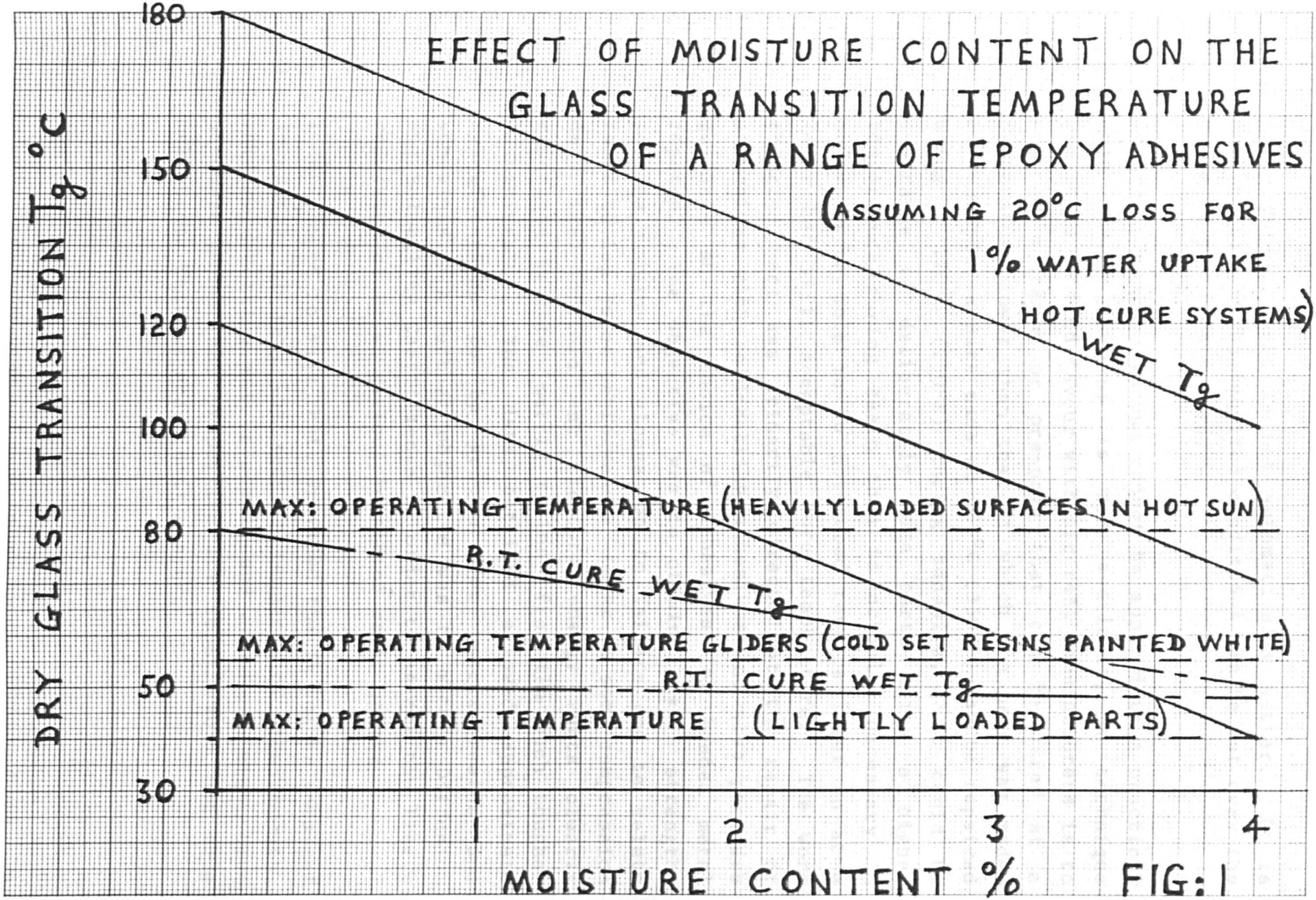

EFFECT OF MOISTURE CONTENT ON THE GLASS TRANSITION TEMPERATURE OF A RANGE OF EPOXY ADHESIVES
(ASSUMING 20°C LOSS FOR 1% WATER UPTAKE
HOT CURE SYSTEMS)
WET Tg
MAX: OPERATING TEMPERATURE (HEAVILY LOADED SURFACES IN HOT SUN)
R.T. CURE WET Tg
MAX: OPERATING TEMPERATURE GLIDERS (COLD SET RESINS PAINTED WHITE)
R.T. CURE WET Tg
MAX: OPERATING TEMPERATURE (LIGHTLY LOADED PARTS)
DRY GLASS TRANSITION Tg °C
180
150
120
100
80
50
30
1
2
3
4
MOISTURE CONTENT %

FIG: 1

A hot-cured repair is not automatically better. It is only better if the required conditions can be met over the whole of the repair area.

If pressure above vacuum cannot be applied in a practical case and/or tooling is not available, a technique beginning to find favour with aircraft manufacturers is to use an adhesive or pre-preg that can be cured at a temperature lower than that at which the part was made. For example, a part made at 180°C (350°F) can be repaired using a 120°C (250°F) curing adhesive. It could be desirable to deliberately make parts using a higher temperature curing resin than is actually necessary in order to be able to do hot-cured repairs later on at a lower but still acceptable cure temperature. The work reported here was primarily directed at the repair of composites with cold-setting adhesives and also provides guidance on the choice of adhesives for bonded metal repairs. The objective was to obtain tensile strength, tensile modulus and elongation to failure and to relate these to lap joint performance. Later on some compression data was obtained and fracture energy tests clearly separated brittle "matrix resins" from the much tougher "adhesives". The data obtained allowed approximate specifications to be written for matrix resins and adhesives. A further objective was to obtain Diffusion and Solubility Coefficients in order to assess the likely reduction of Tg at various levels of water uptake.

It was hoped to show that, provided the Tg values remained acceptable to meet the service temperature requirements, some cold-setting matrix resins and adhesives might have adequate mechanical properties for repair work and thus make these tasks a great deal easier.

Since this work was started some new two-part resins have come on the market for composite repairs. They claim a Tg of about 120°C from a room temperature cure. If their equilibrium water uptake can be limited to 4% or less then they should be quite suitable for permanent repairs to subsonic aircraft and also to supersonic aircraft where the skin temperature does not exceed 80°C. This assumes that they can also provide the required mechanical properties.

Cold-setting repairs can often be done with very little tooling and require no more than vacuum pressure. Also radiant lamp or heater mat curing is sufficient to improve both Tg values and the speed of the repair. The repair of contaminated composites may also need to be considered, Parker (1986) and (1989). The size of parts needing to be repaired may create a problem and the need for in-situ repair. Armstrong (1985) (1989b) and (1989c).

NOTE: Adhesive bonding is a truly International subject and for this reason both S.I. and Imperial units have been used in most of the figures.

The conversion factors used were:-

1,000 psi = 6.8944 MPa
1 lb = 4.448 Newtons

The figures in Tables 3 to 11 are as calculated. They are not intended to imply a high level of accuracy because this cannot be achieved in this type of work.

CHAPTER TWO LITERATURE SURVEY

2.1 Relationship of adhesive mechanical properties to joint strength.

In about 1984, when the first work was done, two situations were observed. Firstly, manufacturers' data sheets for adhesives and resins gave only results from standard tests such as lap shear strength, climbing drum peel strength, 'T' peel or floating roller peel strength, service temperature range, mix ratio and curing conditions. Basic mechanical properties such as tensile strength, tensile modulus and elongation were not mentioned and neither was the important property of fracture energy.

Water uptake was seldom given but even if it was it was the weight gain after 24 hours or some similar and very short period. As the results of this work will show, some adhesives have a high diffusion coefficient initially and a low solubility coefficient and others show the reverse behaviour. Water uptake data was therefore at its best of little value and at its worst possibly deceptive.

Very few data sheets mention the probability that adhesives can actually assist corrosion of the adherends they are bonding. Aluminium alloys suffer in particular as many aircraft parts have shown. Only a small number of the many adhesives on the market actually contain corrosion inhibitors.

Strangely more attention seems to be being paid to this in the electronic microchip field than in the design of aircraft structures. Adhesive specifications for aircraft use do not normally mention the subject. However, an interesting paper by Bolger et al (1985) shows that it has

been found necessary to control adhesive chemistry in order to drastically reduce microchip faults caused by corrosion to an acceptable level.

A new Specification, MIL-A-87172 (for type 1 electrically conductive adhesives) has been produced and Licari et al (1981) have suggested limits for the release of Chlorine, Potassium and Sodium. Ammonia and Ammonium ions may also be released but are very difficult to detect in p.p.m. quantities. MIL-A-87172 requires the following -

Extractable	Cl^-	<	300 ppm
	Na^+	<	50 ppm
	K^+	<	50 ppm
	NH_4^+		report for information

Other ions if present above 5 ppm, report for information

Tegg (1979) mentions that the most common epoxy resin, the di-glycidyl ether of Bis-phenol 'A' (DGEBA) is produced commercially by the reaction of Bis-phenol 'A' and Epichlorohydrin heated together with aqueous sodium hydroxide at 100°C for 3½ hrs. The crude product is contaminated by epichlorohydrin and sodium chloride. Residual epichlorohydrin is removed by distillation under reduced pressure. The sodium chloride is separated by the addition of Toluene followed by filtration and distillation to remove the toluene. The product obtained contains about 0.5% Chlorine.

Epoxy chemistry includes corrosive ions by its very nature and the thoroughness of purification is therefore very important.

Curing agents will need to be chosen with care as they can be an even greater problem.

Corrosion in aircraft parts becomes more understandable as Bolger et al (1985) point out that several first generation one-component epoxies were cured with a Lewis acid, which generates Boron tri-fluoride (BF_3) as a by product of cure. BF_3 gas is a strong acid and when combined with water vapour can attack aluminium and other metals. They also state that epoxies cured with Di-cyandiamide give off ammonia for long periods after cure. This may explain the distinctive smell observed when carrying out climbing drum peel tests on honeycomb test panels and also the corrosion of honeycomb in aircraft parts, especially when moisture enters at the edges through the adhesive or interface and through bolt inserts in the panels.

On the positive side some adhesive data sheets do state that the material contains chromate inhibitor. This is now going out of favour on health grounds so it is fortunate that Matienzo et al (1986) have studied the use of organic corrosion inhibitors. There seems to be a need for a great deal of work to provide good corrosion inhibitors for adhesives because the presence of corrosive ions in small quantities appears to be almost inevitable with the chemicals used in the production of adhesives, especially epoxies.

Clearly, specifications for aircraft adhesives need to call for the minimisation of the presence of corrosive ions and the use of suitable inhibitors as additives to the adhesives themselves or to primers for the preparation of surfaces prior to bonding. The difference between inhibited primers and non-inhibited primers is mentioned by Politi (1989).
Data sheets from each company were all laid out differently and comparison was difficult even between the products of a single manufacturer. Good properties were

mentioned, poor properties were omitted. Secondly, such references as there were to the mechanical properties of the resins themselves suggested that the thin layer properties of the adhesive in a bond line were so different from those of the bulk, that any attempt to relate them was hardly worth the effort!

At that stage, therefore, attempts to find literature relating adhesive mechanical properties to joint performance met with limited success. A paper by Bascom & Cottington (1976) shows that such criticisms were not without foundation. They found that the Mode 1 fracture energy ($G1_c$) was strongly dependent on bond line thickness and showed that the adhesive $G1_c$ is a maximum and equal to the bulk value when the crack tip deformation zone diameter, $2r_c$ and the bond thickness are equal. They also found that as the bond thickness is reduced to less than $2r_c$, there was a precipitous decrease in fracture toughness. In addition they observed a decline in adhesive $G1_c$when the bond thickness increased above $2r_c$. See findings of Kreiger (1973). Similar effects are found with composite materials which have a very thin resin layer between the fibre layers. In this case also the composite fracture toughness increases much less than expected when the matrix toughness is increased.

Variations of $G1_c$ with bond thickness were also found in this work but some adhesives, showed more variation than others.

Lark & Mays (1984) also doubted the value of basic resin mechanical properties. They studied the effect of epoxy formulation on mechanical properties but decided in favour of tests on joints except for flexure and shear tests on bulk adhesive, because they found that tensile tests and bulk adhesive fracture toughness tests were unreliable due

to the difficulty of producing flaw free specimens. Surprisingly they also found compression testing unreliable. In this work tensile testing did suffer from the same problem, but compression testing was found to be very consistent. However, flaw free bonds are also difficult to produce during component manufacture and it may be that tests on flawed specimens are, in fact, nearer to reality. These authors showed a relation between chemical formulation and mechanical and physical properties and that there was a need for suppliers to provide data on appropriate material properties.

Morgan (1985) showed a similar relationship between chemical formulation and mechanical properties for composite matrix resins.

For these reasons the test programme began with little foundation on previous work but rather in the intuitive belief that a relationship had to exist, even if it was not a direct relationship but rather some more complex function of the resin properties. As often happens in scientific research, several people work in parallel, for a time, not knowing of each other's work. In this case more recent literature has shown that Kreiger (1984) and (1988) of the American Cyanamid Company has produced a special extensometer to measure the shear strength and modulus of adhesives and Jeandrau (1986) has also worked on relating adhesive properties to joint performance. Findlater (1985) and (1987) in an extensive programme of work for the Production Engineering Research Association (PERA) also identified some important mechanical properties but he worked mainly with steel adherends and did not investigate fracture energy of his adhesives. He found that elongation to failure was important and also pointed out that improved elongation often results in a loss of tensile strength and modulus. One of the great

difficulties of adhesive and resin development is the improvement of elongation and fracture energy with the minimum loss of tensile modulus and strength.

As the work progressed it became clear that a study of the relationship between the mechanical performance of composites and the properties of their resin matrices would also be necessary.

Fortunately an excellent paper prepared by R J Palmer of the Douglas Aircraft Co. under a NASA contract was found, Palmer (1981) and this provided the mechanical properties required of a resin matrix material in a similar way to the work of this thesis to provide the mechanical properties required of an adhesive to make a strong joint. In his work Palmer used 23 toughened resin systems having a wide range of mechanical properties and from Figs 2 - 6 (pages 26 - 30) the optimum properties of the resin required to make a good composite can be deduced. The results of both programmes show that resin properties significantly affect performance and that material data sheets should provide enough basic material property data to allow effective comparison of one material with another. A considerable number of other references for composite materials were studied where the influence of material properties was mentioned, e.g. Beaumont and Wells (1984), Berry et al (1975), Bradley and Cohen (1985), Chai (1984), Chaudhari (1986), Corten (1968) El-Senussi and Webber (1989), Sela et al (1989a) (1989b), Garrett and Bailey (1977), Guha and Epel (1979), Hamoush and Ahmad (1989), Hewitt et al (1986), Hunston and Dehl (1986) (1987), Lee F.et al (1989) Lee L.H (1985) (1986a) (1986b) (1986c) (1987), Lee S et al (1984), Weinberg (1987), Whitney (1983) (1988), Lees W.A (1989), Mall and Ramamurthy (1989), Piggott and Harris (1980).

Many authors have shown, Wake (1976) Adams & Wake (1984) Adams (1986) Hartshorn (1986) Lees (1986) Adams & Harris (1987) that careful joint design, tapering either at the bond line or on the outer face, the forming of fillets and glue line thickness control can all make their improvements to the strength of an adhesively bonded joint.

However, while all these ideas are sound and should be adopted whenever it is practical to do so, the fact remains that the mechanical properties of the adhesive need to be in some optimum band to give the highest joint strengths. It became one of the objectives of this work to define those properties as accurately as possible.

(Text continues on Page 32)

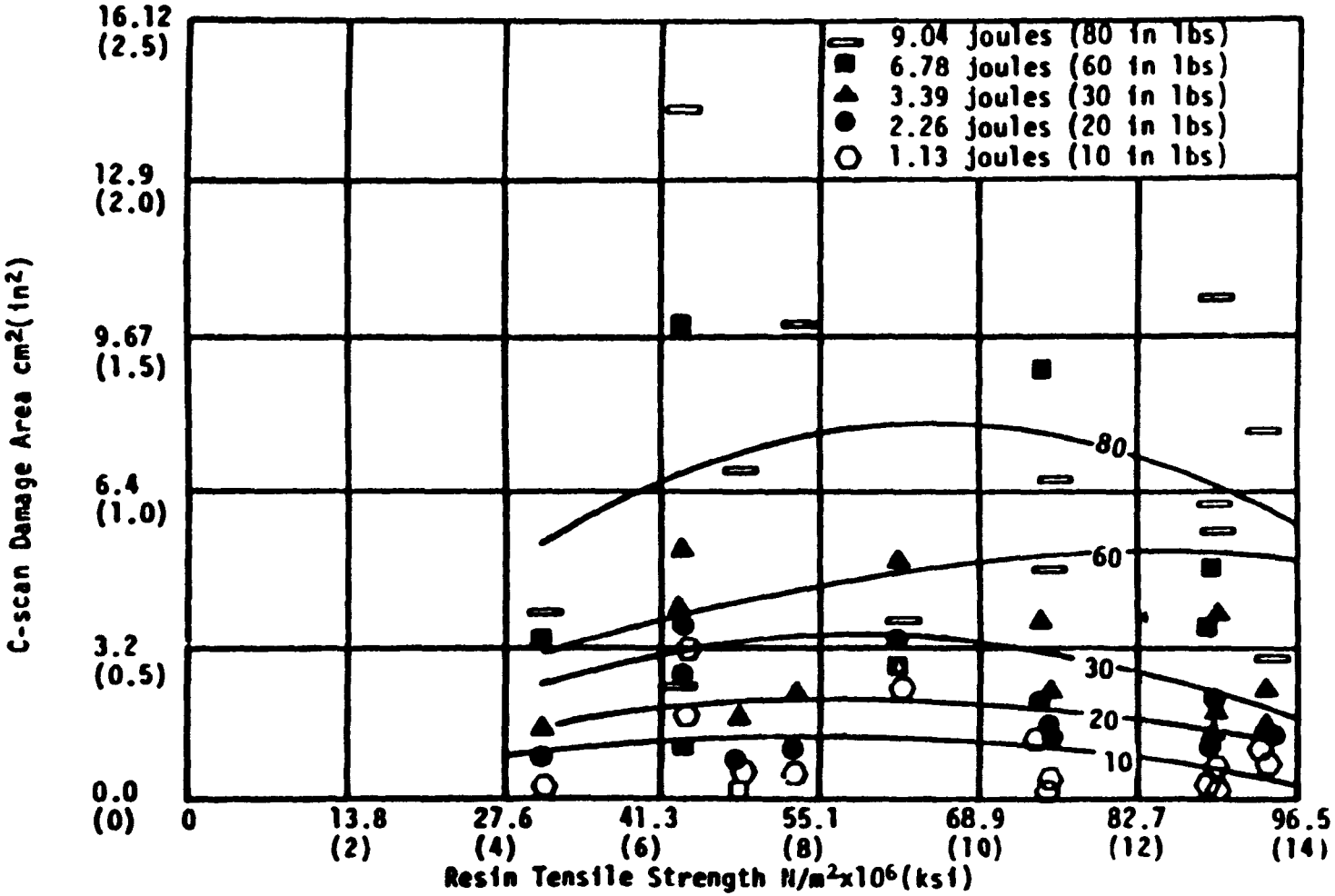


FIGURE 2. NEAT RESIN TENSILE STRENGTH VS IMPACT DAMAGE AREA

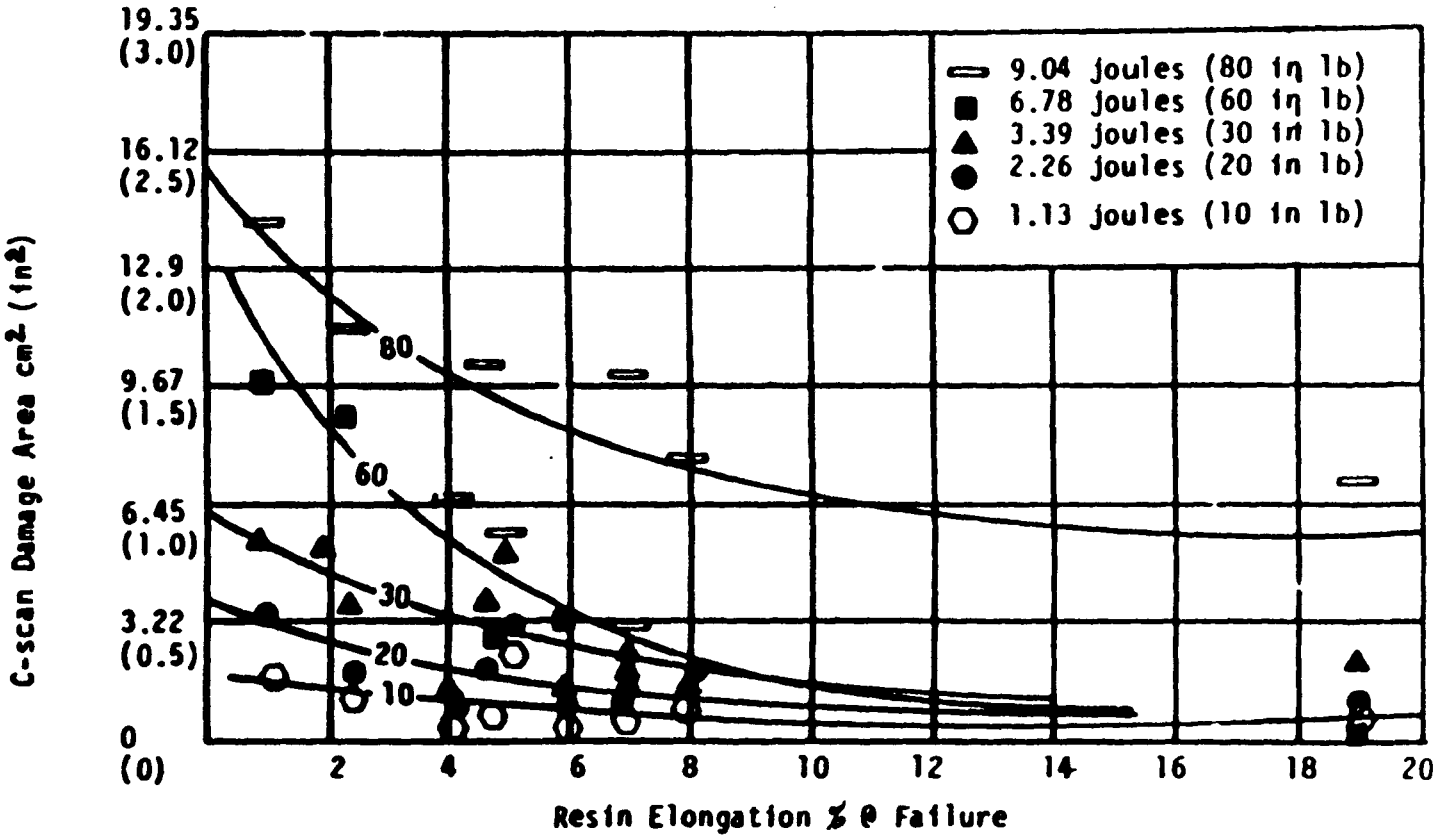


FIGURE 3. NEAT RESIN % ELONGATION AT FAILURE VS. IMPACT DAMAGE AREA

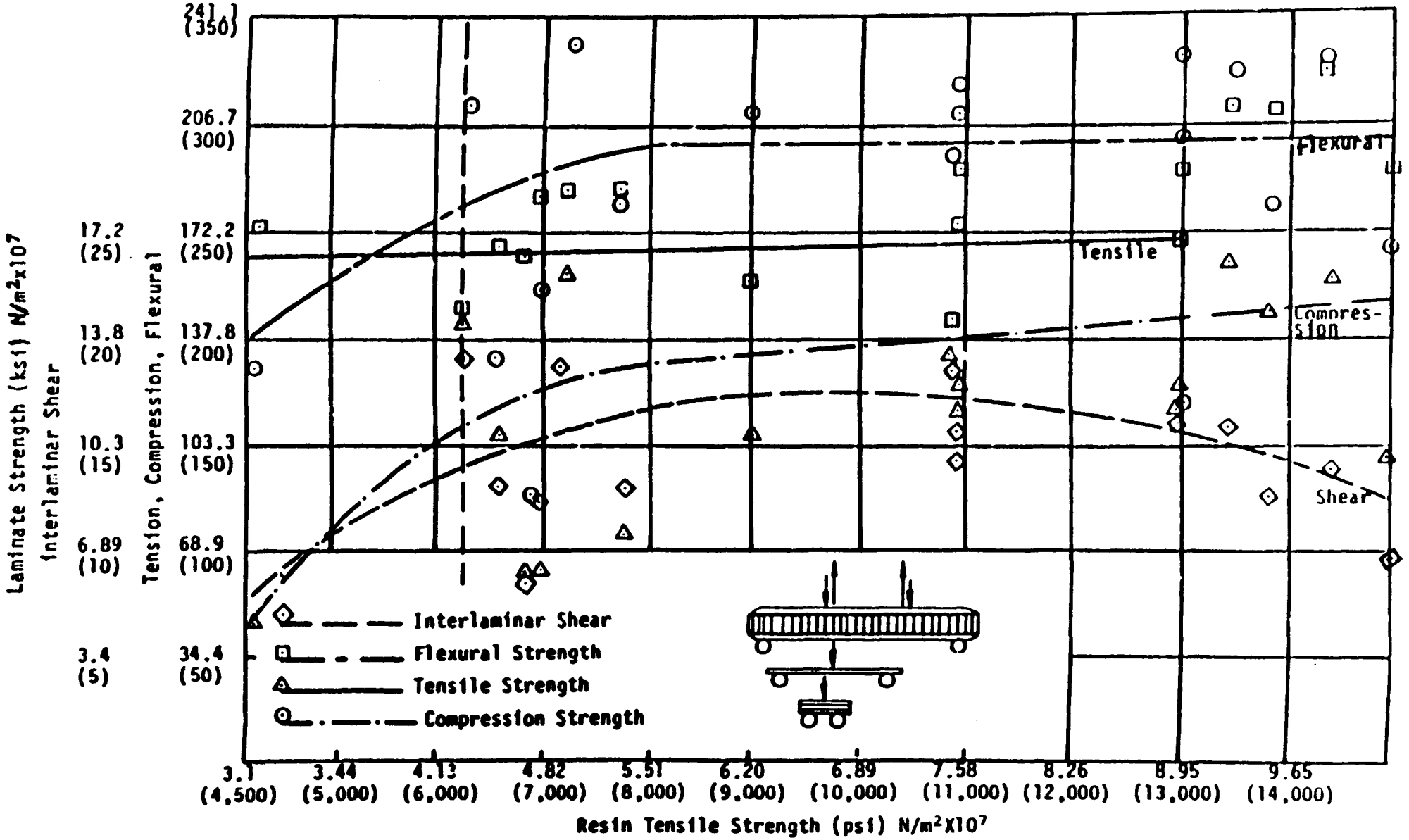


FIGURE 4. RESIN TENSILE STRENGTH VS LAMINATE MECHANICAL PROPERTIES

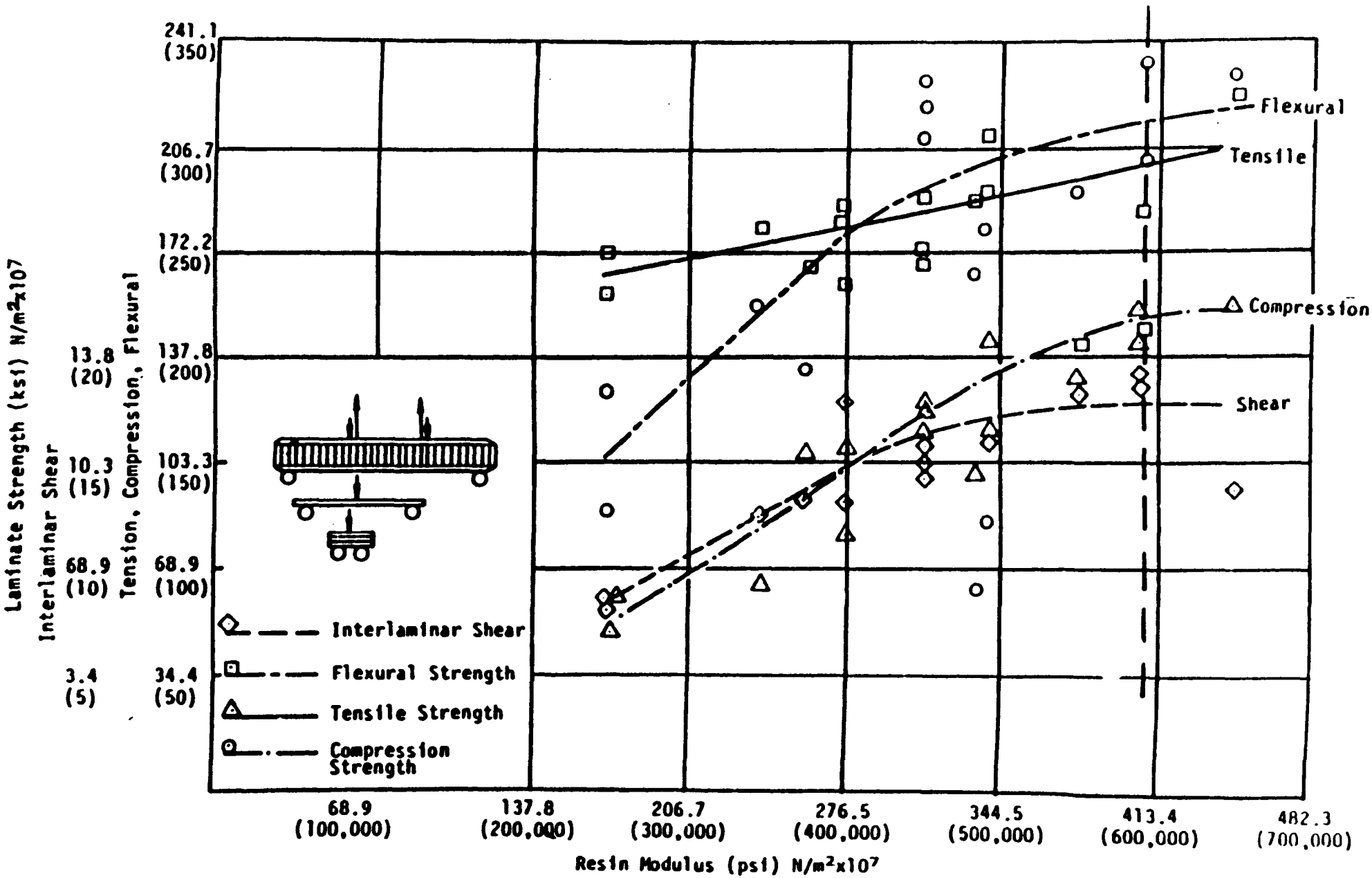


FIGURE 5. RESIN TENSILE MODULUS VS LAMINATE MECHANICAL PROPERTIES

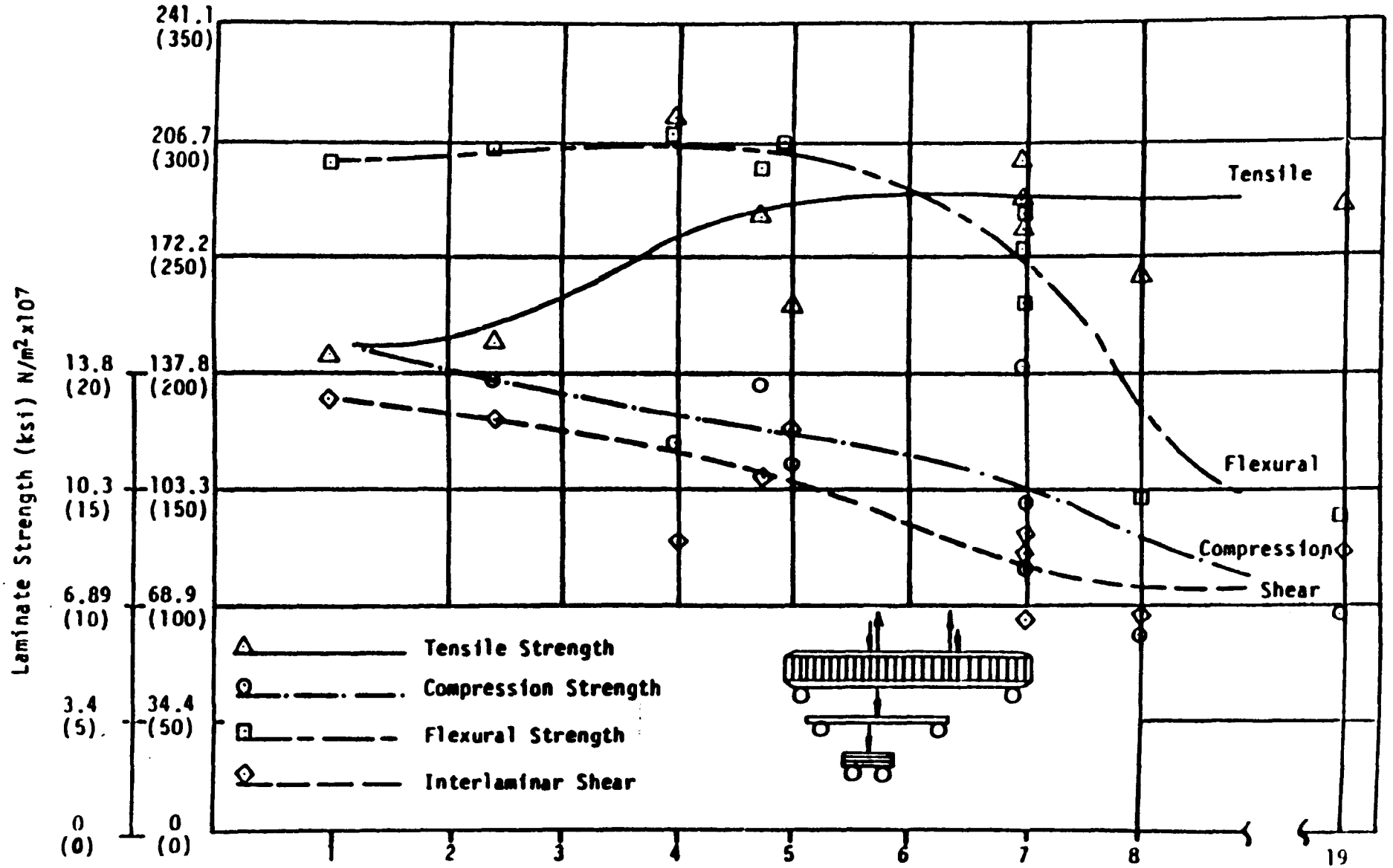


FIGURE 6. RESIN TENSILE ELONGATION VS LAMINATE MECHANICAL PROPERTIES

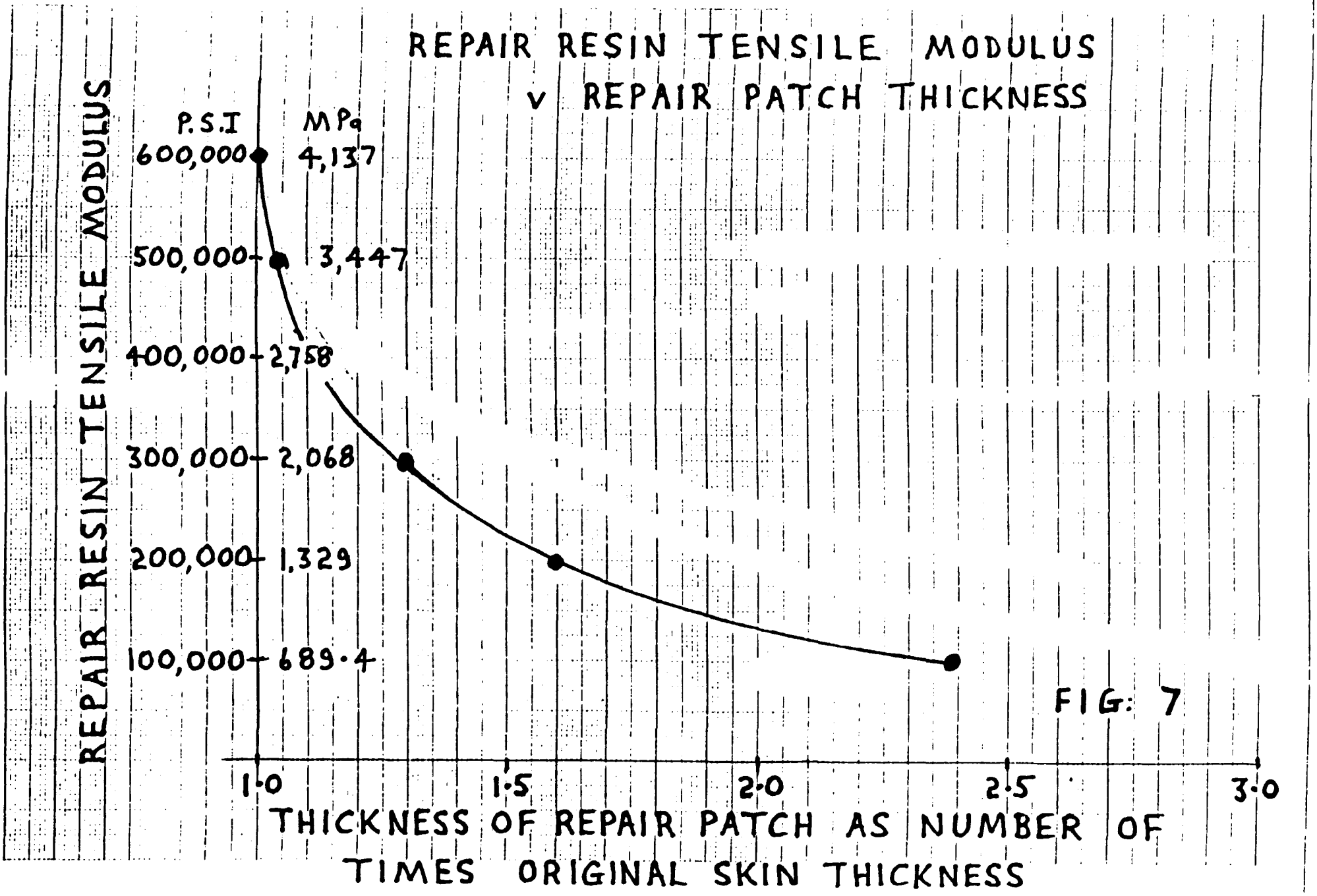

REPAIR RESIN TENSILE MODULUS
v REPAIR PATCH THICKNESS
REPAIR RESIN TENSILE MODULUS
P.S.I
MPa
600,000
4,137
500,000
3,447
400,000
2,758
300,000
2,068
200,000
1,329
100,000
689·4
1·0
1·5
2·0
2·5
3·0
THICKNESS OF REPAIR PATCH AS NUMBER OF TIMES ORIGINAL SKIN THICKNESS

FIG: 7

2.2 Moisture uptake of adhesives

In the area of moisture uptake the situation was very much better and a considerable amount of work had been done at Leicester Polytechnic under Comyn, Brewis and Cope and the Ph.D Theses of Tegg (1979) and Shalash (1979) were found particularly useful. It was found possible to adapt the computer programme used by Brewis et al (1979) to suit an IBM PC and from this Figs 8 - 11 (pages 33 - 36) were obtained. The standard method of obtaining the Diffusion Coefficient quoted by Tegg was used successfully. Reference was also made to Fujita (1968), Brewis et al (1979) Wright (1979), Ezell (1972) Ishai (1975) Shirrell (1988), Danieley (1981), Long (1979) Shen and Springer (1976) but most of the adhesives for which data was required had not been tested.

Later in the work other references became available Collings (1986) Brewis et al (1987). Most of the data tabulated in this work for adhesives other than those tested was obtained from Wright (1979).

This data is listed in Tables 2A - 2F (pages 37 - 46)

2.3 Testing plan as a result of the literature survey

Following this survey three lines of work were decided upon.

(Text continues on page 47)

FRACTIONAL UPTAKE OF WATER AT THE CENTRE OF A 38 MM X 250 MM LAP JOINT v LOG TIME FOR VARIOUS DIFFUSION COEFFICIENTS

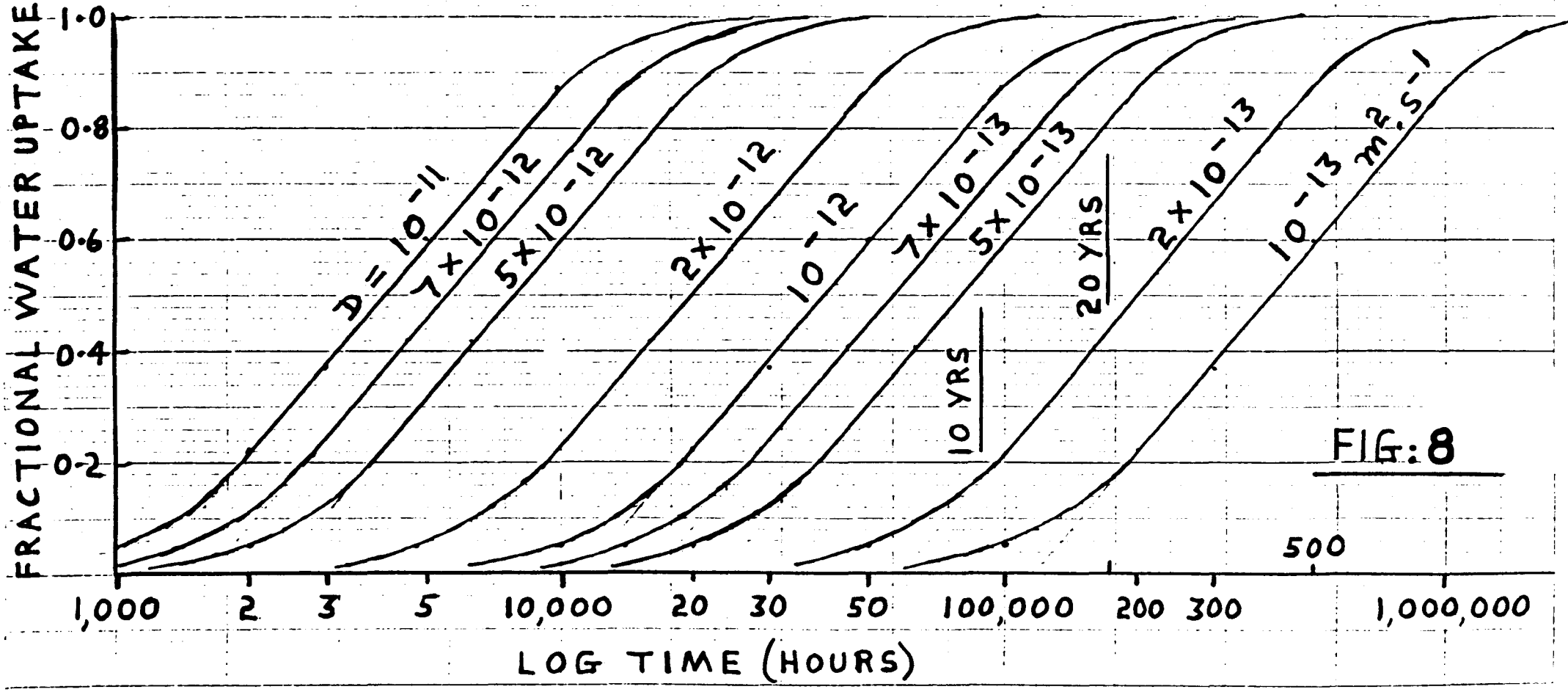


FIG: 8

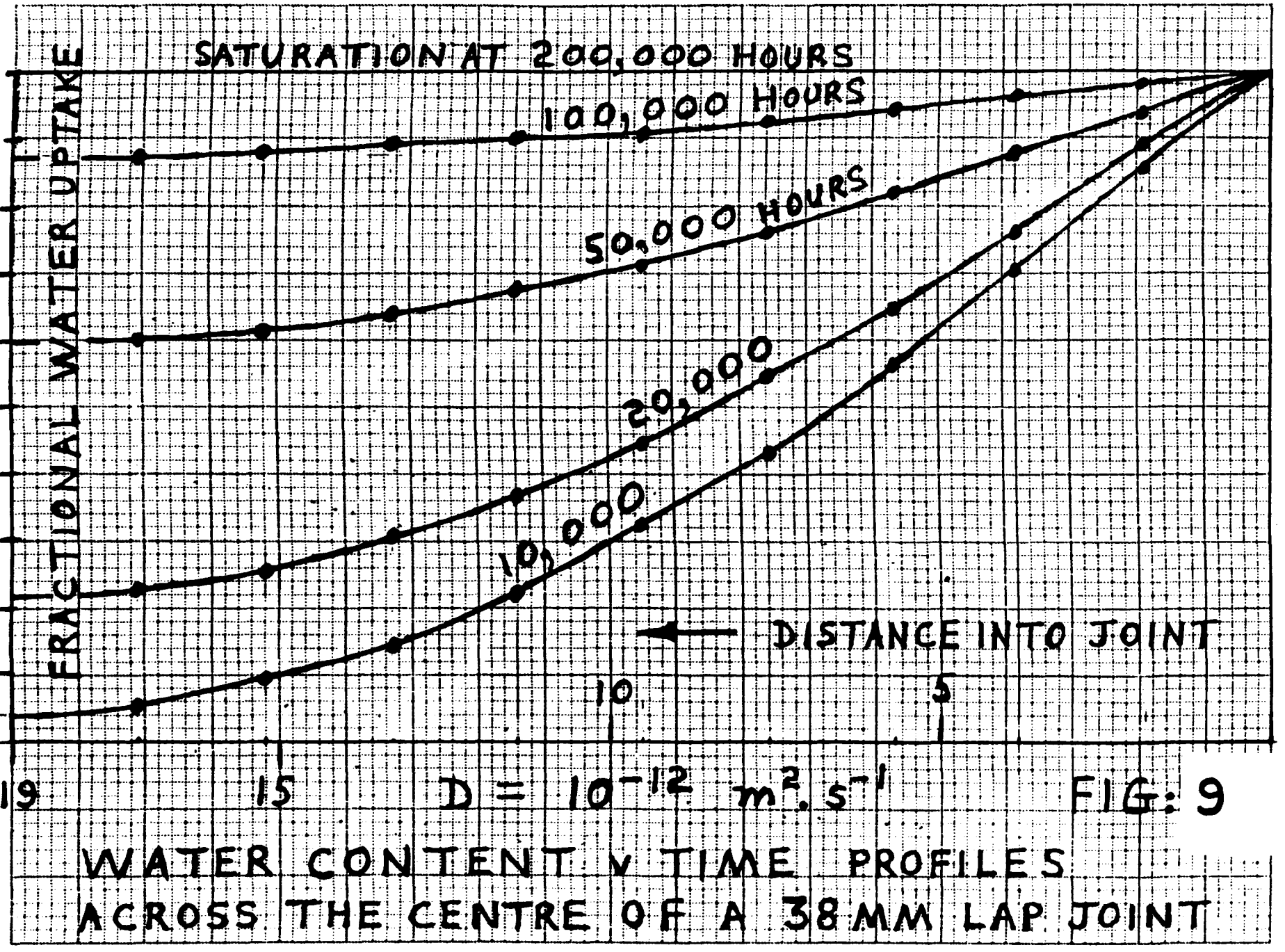


FIG: 9

WATER CONTENT v TIME PROFILES ACROSS THE CENTRE OF A 38 MM LAP JOINT

FRACTIONAL UPTAKE OF WATER AT THE CENTRE OF A 12·5 × 25 MM LAP JOINT v LOG TIME FOR VARIOUS DIFFUSION COEFFICIENTS

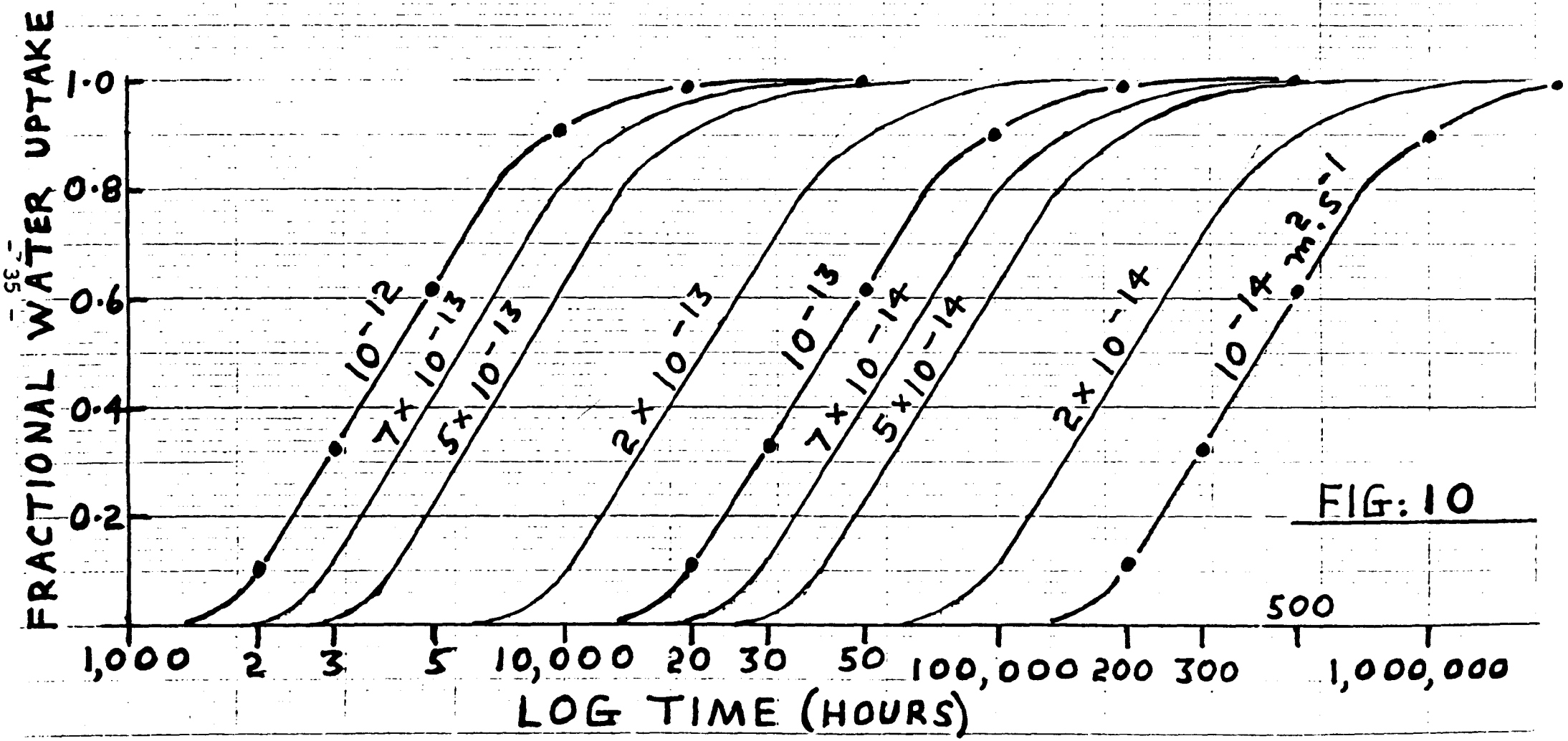
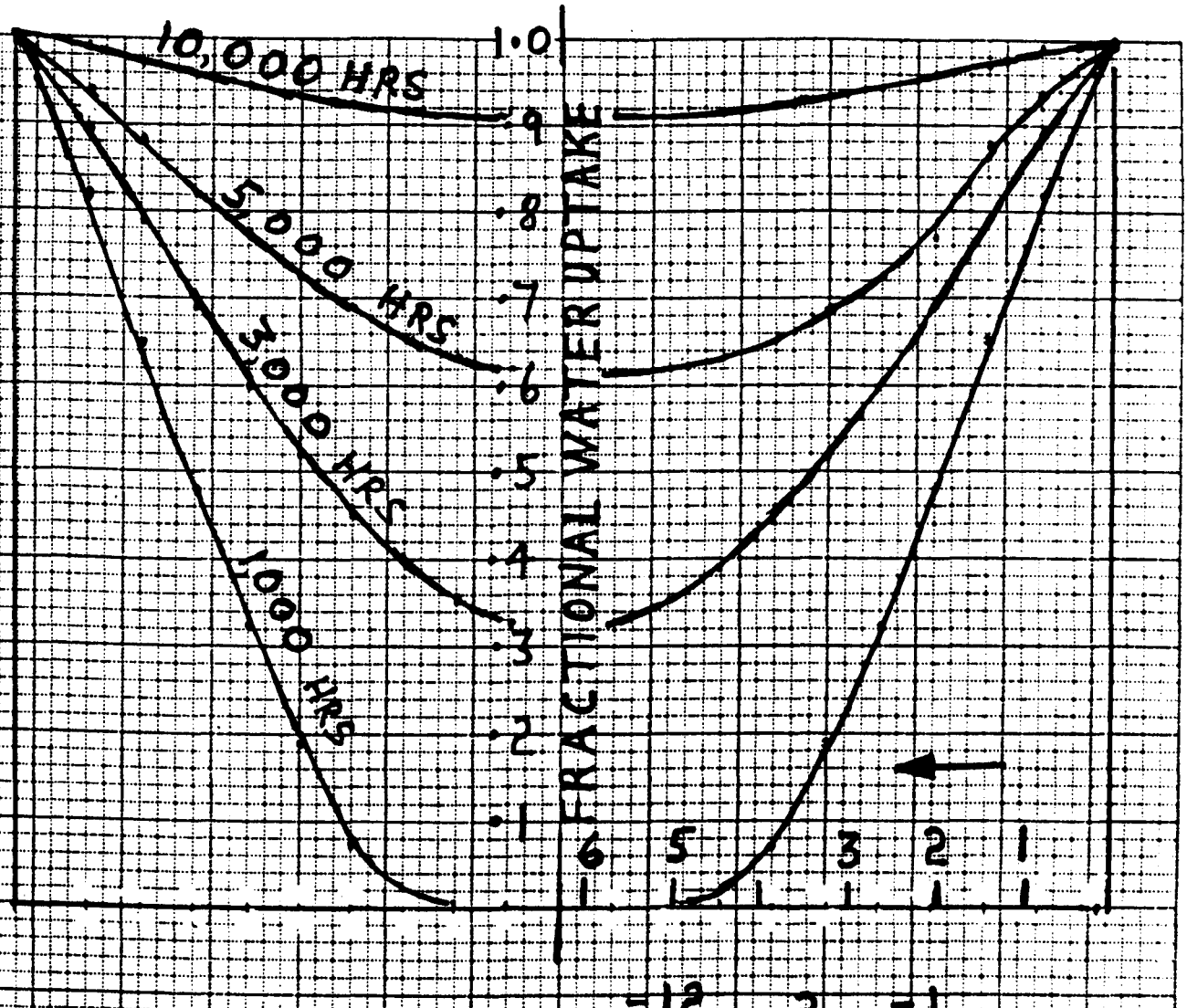


FIG: 10



$D = 10^{-12}\ m^2.s^{-1}$

FOR LOWER OR HIGHER DIFFUSION COEFFICIENTS MULTIPLY OR DIVIDE TIME IN THE SAME PROPORTION

FIG: 11

WATER CONTENT v TIME PROFILES ACROSS CENTRE OF 12·5 MM LAP JOINT

TABLE 2A

ADHESIVE	DIFFUSION COEFFICIENT "D" $m^2.s^{-1}$ SOLUBILITY COEFFICIENT "S"					
	After RT Cure "D"	After RT Cure "S"	After 50°C Cure "D"	After 50°C Cure "S"	After 80°C Cure "D"	After 80°C Cure "S"
EA 9330	1.63^{-13}	13%	1.63^{-13}	**18%	1.63^{-13}	10.4%
EPIKOTE 815 + RTU	4.74^{-14}	7.35%	3.51^{-14}	5.2%	4.31^{-14}	3.68%
EPIKOTE 828 + VERSAMID 125	4.43^{-14}	6.25%	4.43^{-14}	6.6%	4.43^{-14}	7%
EC 2216	1.575^{-14}	5.7%	9.07^{-14}	6.0%	9.07^{-14}	5.47%
EC 3524	1.194^{-13}	35%	1.194^{-13}	32.9%	1.194^{-13}	34.4%
EA 9321	9.34^{-14}	7.88%	3.46^{-14}	4.89%	4.33^{-14}	4.28%
AF 163 *	---	---	---	---	8.04^{-14}	1.89%
EC 3559	8.81^{-14}	5.15%	4.33^{-14}	5.4%	6.38^{-14}	4.76%
EA 9330 + 20% MICROBALLOONS	7.22^{-14}	79.7%	2.83^{-14}	67%	8.72^{-14}	102%
EC 3568	NR	18.7%	---	---	---	---
EC 3578	NR	9.7%	NR	18.1%	NR	9.5%
PERMABOND E34	NR	1.9%	NR	1.9%	NR	2.15%

* AF 163-2M film adhesive cured at 120°C for 1 hour
** Suspect mix.

NR = No result. These materials gave a sigmoidal uptake curve from which no normal diffusion coefficient could be obtained.

TABLE 2B

ADHESIVE & TEMPERATURE	"D" m^2s^{-1}	"S" %	REMARKS
CIBA GEIGY			Hot setting film
BSL 312 50°C	3.0×10^{-13}	2.2	120°C
25°C	1.4×10^{-13}	2.1	
1°C	1.3×10^{-14}	2.6	
AMERICAN CYANAMID			Hot setting film
FM1000 50°C	3.2×10^{-12}	15	120°C
25°C	1.1×10^{-12}	16	
1°C	7.5×10^{-14}	21	
AMERICAN CYANAMID			Hot setting film
FM73 60°C	1.37×10^{-12}	2.7	120°C
100°C		12.0	
CIBA GEIGY			Farnborough result .6mm
BSL 312 50°C	12.5×10^{-13}	2.8	thick sample
CIBA GEIGY			Two-part R.T. cure 1.9mm
Redux 410 50°C	16×10^{-13}	4.4	thick Farnborough result
CIBA GEIGY			1.3mm thick Farnborough
Redux 410 50°C	10×10^{-13}	5.2	result
CIBA GEIGY			.3mm thick Farnborough
Redux 410 50°C	7×10^{-13}	3.6	result
HYSOL			Two-part R.T. cure .8mm
EA 9309.2 50°C	6.2×10^{-13}	4.1	thick Farnborough result
ARALDITE MY790 + HY951			Cured 3 hours at 60°C
84°C	1.0×10^{-12}	5	")
60°C	7.0×10^{-13}	3.9	")
40°C	4.4×10^{-13}	3.1	") Two Part Mix
21°C	1.0×10^{-13}	2.4	")
3°C	5.0×10^{-14}	1.8	")
			From p190 Int.Journal of Adhesion & Adhesives Oct 1983

MOISTURE ABSORPTION PROPERTIES OF COMPOSITE MATRIX RESINS

(FROM REF. 5)

ADHESIVE & CURING AGENT	MANUFACTURER	TEMP °C	ABSORPTION D $m^2.s^{-1} \times 10^{14}$	S%	RH %
EPIKOTE 828 +TETA		23	-	3.92	Immersion
		45	-	3.90	Immersion
		75	-	4.12	Immersion
MY 750 + DDM	CIBA GEIGY	0.2	2.67	2.59	100
		25	20.9	2.51	100
		37	40.9	2.36	100
		50	102	2.47	100
		60	179	2.44	100
		70	316	2.45	100
		80	411	2.57	100
		90	630	2.77	100
MY 750 + PA	CIBA GEIGY	37	13.2	1.35	100
5208	NARMCO	30	-	5.93	100
		75	-	6.10	100
		100	-	5.98	100

TABLE 2C

ADHESIVE & CURING AGENT	MANUFACTURER	TEMP °C	ABSORPTION D $m^2.s^{-1} \times 10^{14}$	S%	RH %
EPON 1031/BDMA	SHELL	30	-	1.67	80
DER 332 + DDS		30	-	2.84	80
		45	-	2.61	80
		60	-	2.48	80
		75	-	2.07	80
X-904 + ANHYDRIDE	FIBERITE	25	113	1.1	70
X-915	FIBERITE	25	-	3.8	70
X-934 + AMINE	FIBERITE	25	-	4.8	75
E-293 + ANHYDRIDE	FERRO	25	47.7	0.9	75
E350 + AROMATIC AMINE	FERRO	25	7.44	3.1	75
E450 + AROMATIC AMINE	FERRO	25	-	4.6	75
X-2003 + AMINE	HERCULES	25	-	1.6	75
3002 + AMINE	HERCULES	25	3.53	7.7	75
SR-10500	WHITTAKER	25	-	2.3	75
1004	WHITTAKER	25	-	2.8	75
MY720 DDS/BF_3-MEA	CIBA GEIGY	70	-	5.6	100

ADHESIVE & CURING AGENT	MANUFACTURER	TEMP °C	ABSORPTION D $m^2 s^{-1} \times 10^{14}$	S%	RH %
3501-5 + AMINE	HERCULES	NOT GIVEN		6.2	100
3501-6 + AMINE	HERCULES	NOT GIVEN		6.2	100
3502	HERCULES	NOT GIVEN		6.3	100
934	FIBERITE	NOT GIVEN		6.5	100
NMD 2373		NOT GIVEN		9.9	100
5208	NARMCO	NOT GIVEN		6.3	100
5208	NARMCO	71		7.0	IMMERSION
3501-5 + AMINE	HERCULES	49		5.9	IMMERSION
		71		5.9	IMMERSION
5208	NARMCO	49		6.4	IMMERSION
5209	NARMCO	25		3.17	99
		51		4.53	92
		64		4.55	97
DER 332 + DDS		RT		4.14	95
934	FIBERITE	RT		4.69	95

ADHESIVE & CURING AGENT	MANUFACTURER	TEMP °C	ABSORPTION D $m^2.s^{-1} \times 10^{14}$	S%	RH %
X80 + MNA		RT		3.48	95
XD7342 + DDS		RT		5.4	95
5208	NARMCO	RT		6.4	95
X801 + TONOX		RT		7.31	95
X801 + DDS		RT		7.15	95
904	FIBERITE	RT		1.71	95
EPON 1031 + MNA	SHELL	RT		2.98	95

DIFFUSION COEFFICIENTS FOR VARIOUS COMPOSITE MATRIX RESINS AT 100% RH OR IMMERSION (FROM REF. 5)

ADHESIVE & CURING AGENT	MANUFACTURER	TEMP °C	D $m^2.s^{-1} \times 10^{14}$
MY750 + DDM	CIBA GEIGY	0.2	2.67
		25	20.9
		37	40.9
		50	102
MY750 + PA	CIBA GEIGY	37	13.2
3501-5 + DDS	HERCULES	23	7.65
		49	31.0
3501-6 + DDS	HERCULES	23	4.59
		60	36.1
3502	HERCULES	23	4.96
		60	37.3

DIFFUSION COEFFICIENTS FOR VARIOUS COMPOSITE MATRIX RESINS AT 100% RH OR IMMERSION (FROM REF. 5)

ADHESIVE & CURING AGENT	MANUFACTURER	TEMP °C	D $m^2 s^{-1} \times 10^{14}$
5208 + DDS	NARMCO	23	3.61
		60	36.9
934 + DDS	FIBERITE	23	3.01
		60	20.8
NMD 2373		23	2.18
NMD 2373		60	36.3
3501-5 + DDS	HERCULES	49	31.8
5208 + DDS	NARMCO	49	43.3
		30	15.0

Where several results are quoted for the same resin they came from different sources.

TABLE 2E

MOISTURE ABSORPTION PROPERTIES OF SOME HOT-CURED FILM ADHESIVES

ADHESIVE	MANUFACTURER	TEST TEMP °C	ABSORPTION "D" $m^2.s^{-1} \times 10^{14}$	"S"	RH %
BSL 312	CIBA GEIGY	50	30	2.2	IMMERSION
		25	14	2.1	IMMERSION
		1	1.3	2.1	IMMERSION
FM 1000	AMERICAN CYANAMID	50	320	15	IMMERSION
		25	110	16	IMMERSION
		1	7.5	21	IMMERSION
FM 73	AMERICAN CYANAMID	100	-	12	100
		65	137	2.7	100

TABLE 2F

MOISTURE ABSORPTION PROPERTIES OF SOME TWO-PART COLD-SETTING ADHESIVES

ADHESIVE	MANUFACTURER	TEST TEMP °C	ABSORPTION "D" $m^2.s^{-1} \times 10^{14}$	"S"	RH %
REDUX 410	CIBA GEIGY	50	160	4.4	96
EA 9309.2	HYSOL	50	62.0	4.1	96
EA 9330	HYSOL	RT	16.32	13	IMMERSION
EPIKOTE 815 +RTU	SHELL	RT	3.88	7.35	IMMERSION
EPIKOTE 828 + VERSAMID 125	SHELL GENERAL MILLS	RT	3.88	7.35	IMMERSION
EC 2216	3M	RT	16.32	5.7	IMMERSION
EC 3524	3M	RT	13	35	IMMERSION

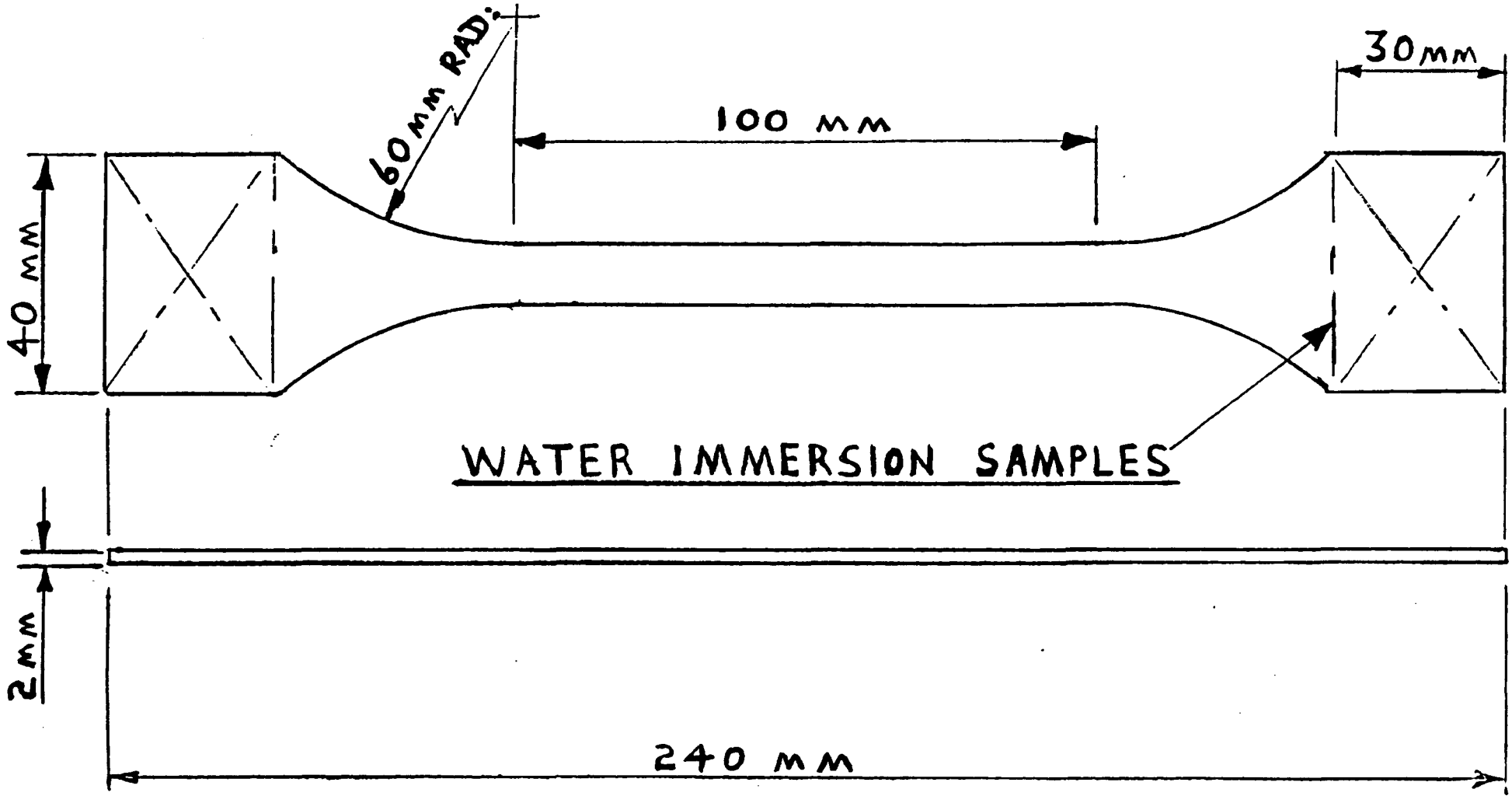
2.3.1 Mechanical testing to obtain tensile strength, tensile modulus, elongation at failure, compression strength and compression modulus.

Drawings were made of the test pieces required Figs 12A - 12C (pages 48 - 50) and a mould designed for casting the tensile test pieces Fig. 12D (page 51).

It was decided to carry out tensile testing to ASTM-D-638 except that no extensometer was available and compression testing to ASTM-D-695 but without a compressometer.

At a later stage, when correlation of the simpler mechanical properties with lap shear strength proved difficult it was decided to carry out a range of wedge tests to ASTM-D-3762. This method was originally developed by the Boeing Aircraft Co. as a quality control test for various surface preparation methods and in particular to act as a simple routine check on the quality of their new Phosphoric Acid Anodising process. (Boeing Spec. BAC 5555). See Marceau et al (1977).

The mathematics quoted below were originally developed by Mostovoy and Ripling and were obtained from Stone & Peet (1980). This formula is the simplified version and gives the fracture energy within 1% of the value obtained from the more precise and complicated formula, provided that the total crack length is at least 50 mm. The much shorter crack lengths achieved with good surface preparations and tough adhesives (in the region of 25-30 mm) result in only slightly greater errors of the order of 2%. Below a crack length of 25 mm the error increases quite rapidly but crack lengths much shorter than this are not achieved in practice.



TENSILE TEST PIECE

TEST AT 1 MM/MIN: CROSSHEAD SPEED

FIG: 12A

REMOVE ALL SHARP EDGES — REPORT ANY ERRORS TO ORIGINATING ENGINEERING OFFICE — DEVIATIONS MUST HAVE PRIOR DESIGN APPROVAL

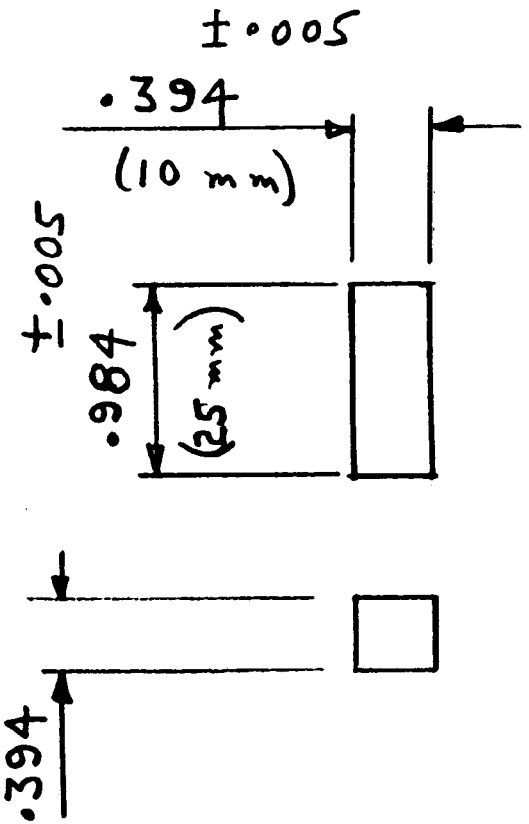
DRG. No.	SHT.	OF	A/C TYPE
4-43497	1	1	/

DESIGN REFERENCE DATA

PROJECTION ◎

DO NOT SCALE

ISSUE	A					
DATE						
CHECKED	/					
STRESS						



NOTE! ENDS TO BE FLAT AND PARALLEL AND SQUARE TO AXIS.

TEST TO A.S.T.M. D-695 EXCEPT THAT MACHINE CROSSHEAD SPEED TO BE 0·25 MM PER MINUTE TO ALLOW DIRECT COMPARISON WITH TENSILE TESTS TO DRG 4-43218.

COMPRESSION TEST PIECE FOR COMPARISON OF ADHESIVES.

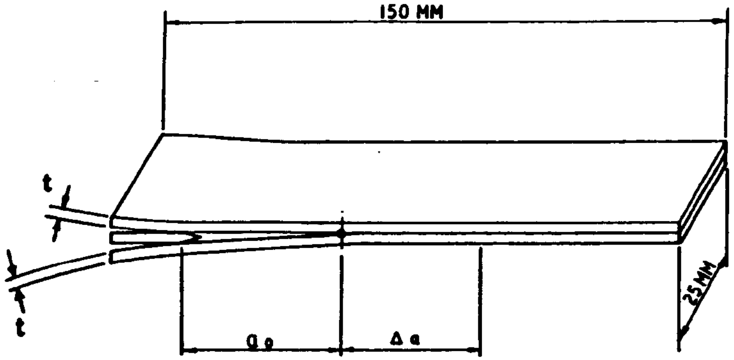
WEIGHT Kg	TOLERANCES UNLESS SPECIFIED	GEN. MACH. ± ·010"/·25mm; PLATE WORK ± ·030"/·75mm; ANGLES ± ½°	IDENTIFY METHOD:-	No.	MATERIAL	AS REQUESTED
					SPEC.	

CALLED FOR ON		SCALE	1/1	DRAWN	KBQ	17/2/87	BONDED STRUCTURES
MOD. REPAIR No.		DIMENSIONS	INCHES/mm	TRACED			COMPRESSION TEST PIECE
AIRWORTHINESS ITEM (DELETE AS REQUIRED)		FINISH		CHECKED			British airways
		HEAT TREAT		APPROVED			DRG. No. 4-43497 SHT. 1 OF 1

Form No. DC 14682-1

MT 106157 R

FIG: 12 B

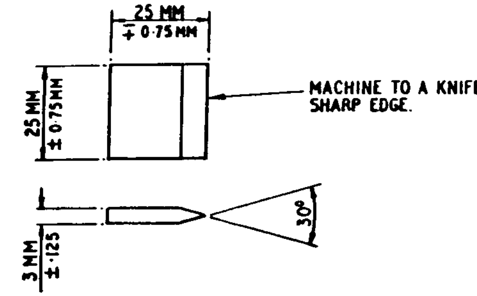


FRACTURE MECHANICS SPECIMEN

THIN ADHEREND

ao = DISTANCE FROM LOAD POINT TO INITIAL CRACK TIP.

Δa = GROWTH IN CRACK DURING ENVIRONMENTAL EXPOSURE.



WEDGE DIMENSIONS

MAKE FROM 7075 -T6
OR STAINLESS STEEL

NOTE:-
SPECIMENS TO BE PREPARED AT THE SAME TIME AND IN THE SAME WAY AS THE ASSOCIATED REPAIR.
SPECIMENS ARE TO BE MADE FROM MATERIAL TO THE SAME SPECIFICATION AS THAT USED FOR THE REPAIR OR RE-BUILD.
INSERT WEDGE USING SEVERAL TAPS WITH A HAMMER. USE THE SAME SIZED WEDGE FOR ALL MATERIALS.
MEASURE AND RECORD INITIAL CRACK LENGTH AND MARK ITS END ON SPECIMEN WITH A SCRIBER. USE A MAGNIFYING GLASS OR MICROSCOPE IF NECESSARY.
PLACE SPECIMEN IN A BEAKER OF WATER AT A CONTROLLED TEMPERATURE (SEE TABLE) FOR THE SPECIFIED PERIOD OF TIME (SEE TABLE).
IMMEDIATELY AFTER EXPOSURE FOR THE CORRECT TIME, MEASURE AND RECORD CRACK GROWTH AND MARK THE POSITION OF THE NEW CRACK END WITH A SCRIBER.
SPLIT SPECIMEN COMPLETELY TO CHECK THAT THE FAILURE IS COHESIVE WITHIN THE ADHESIVE LAYER.
REFER ANY QUERIES CONCERNING THIS TEST TO THE STRESS OFFICE.
SEE ALSO ASTM. D-3762.

MATERIAL USED FOR REPAIR	WATER TEMPERATURE	EXPOSURE TIME	PERMITTED CRACK GROWTH Δa MAX:	MATERIAL THICKNESS t	BOEING PROCESS SPECIFICATION
ALUMINIUM ALLOY	23°C ±1°C	1 HOUR	12·5 MM 0·5 INCH	3MM ±·125 ·12 INCH ±·005	BAC 5555
TITANIUM ALLOY	23°C ±1°C	1 HOUR	12·5 MM 0·5 INCH	1·25MM ±·1 ·05 INCH ±·004	BAC 5890
STAINLESS STEEL	23°C ±1°C	1 HOUR	12·5 MM 0·5 INCH	3·0MM ±·075 ·12 INCH ±·003	*

FIG: 12 C

SEE ALSO BOEING DOCUMENT D6-16925.

* SEE 'HANDBOOK OF SURFACE PREPARATION' BY R.C. SNOGREN PUBLISHED BY PALMERTON PUBLISHING CO. INC.

D	C	B	A	ISSUE
26-1-82	18-8-80	11-6-80	—	AMEND No

REMOVE ALL SHARP EDGES
DO NOT SCALE DIMENSIONS
REPORT ANY ERROR OR OMISSION TO ENGINEERING OFFICE

DRAWN K.B.A. 15-5-80
TRACED I.M.J. 19-1-82

BONDED STRUCTURE REPAIRS
BOEING WEDGE TEST
SPECIMEN AND TEST DETAILS

British airways

2-BA.19884

REMOVE ALL SHARP EDGES | REPORT ANY ERRORS TO ORIGINATING ENGINEERING OFFICE | DEVIATIONS MUST HAVE PRIOR DESIGN APPROVAL

DRG. No. 3-43322 SHT. 1 OF 1 | A/C TYPE | PROJECTION | DO NOT SCALE | IDENTIFY No METHOD -

DESIGN REFERENCE DATA

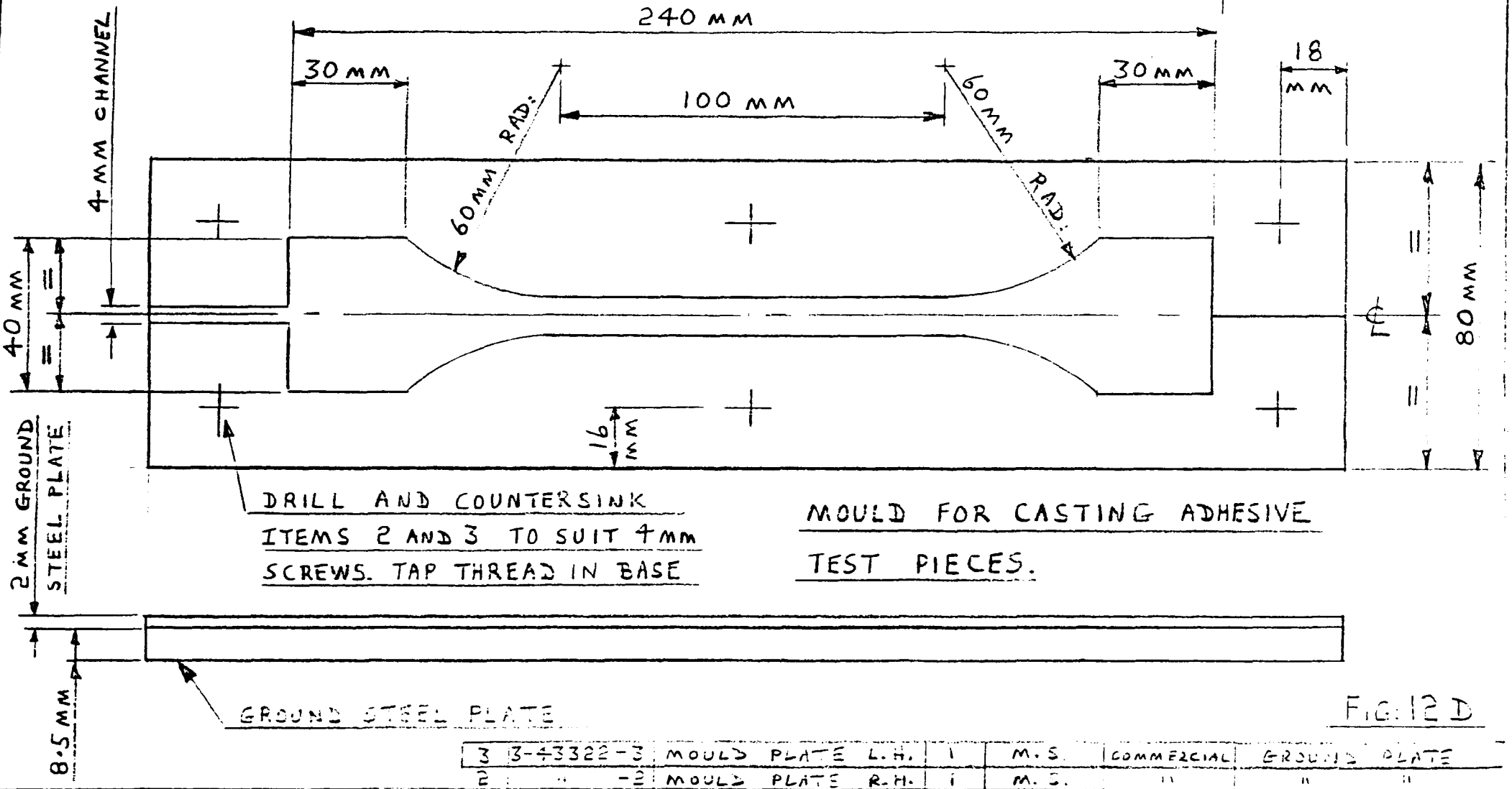


FIG: 12 D

3	3-43322-3	MOULD PLATE L.H.	1	M.S.	COMMERCIAL	GROUND PLATE
2	" -2	MOULD PLATE R.H.	1	M.S.	"	"
1	3-43322-1	BASE PLATE	1	M.S	"	"

ISSUE A | FULL SIZE | KBA 11/9/84 | BONDED STRUCTURES

STRESS | DIMENSIONS mm/in | TRACED

WEIGHT | TOLERANCES UNLESS SPECIFIED | AIRWORTHINESS ITEM | MOULD - TENSILE TEST PIECE

BRITISH AIRWAYS | 3-43322

2.3.1.1 Mathematics for Wedge Test - Fracture Energy

The approximate formula is

$$G_1 = 3 E d^2 h^3 / 16 (a + 0.6h)^4$$

where G_1 is the Mode 1 fracture energy

E is the Young's Modulus of Aluminium ($70.5 GP_a$)

d is the displacement of the load point (thickness of wedge = 3 mm)

h is the specimen thickness (3mm)

a is the crack length and

0.6 is a geometric correction factor for rotation about the crack tip.

2.3.1.2 Mathematics for calculation of Fracture Toughness

Fracture toughness can be calculated from fracture energy using the formula

$$K_1^2 = E.G \text{ for plane stress}$$

$$\text{or } K_1^2 = \frac{E.G}{(1-\nu^2)} \text{ for plane strain}$$

Where E = Young's modulus (MN/m^2)

G = Fracture energy (MJ/m^2)

ν = Poissons ratio

K_1 is in units of $MN.m^{-3/2}$

Formulae can be found in Ashbee (1989) and Adams & Wake (1984).

The plane strain formula was used.

The value of ν was taken as 0.4 for most adhesives but 0.45 was used for the softer materials 3M-EC2216 and Bostik 5435/TM2.

2.3.1.3 Adhesive maximum shear stress formula and formula for length of doubler required (Kreiger)

Kreiger (1975) (1976) gives the following

Maximum shear stress in Adhesive

$$f_a = \frac{K P}{\sqrt{\frac{t.ta.\ E}{G}}}$$

Where E = Young's Modulus of adherend
G = Shear modulus of adhesive
P = Applied load
K = A constant (Kreiger 1975)
t = adherend thickness
ta = adhesive thickness

$$L = k\sqrt{\frac{t.\ ta.\ E}{G}}$$

where L = length of doubler at which the tension stress in the doubler equals that in the skin and load transfer has been completed
k = a constant related to K

K also depends on ratio of doubler thickness to skin thickness. Graphs from which K and k may be read can be found in Kreiger (1976).

2.3.2 Water uptake testing was undertaken to obtain the diffusion and solubility coefficients of a number of adhesives for comparison purposes using distilled water at room temperature. For economy and simplicity and also to ensure that the mechanical properties and water uptake characteristics were obtained from the same mix of resin, it was decided to cut the ends from tensile test pieces after testing and use these for the water immersion tests. These pieces were 40 mm x 30 mm x 2 mm approx and were stored in glass jars containing distilled water. Plastic screwed caps were used to seal the jars which were kept in the temperature controlled Chemistry laboratory.

2.3.2.1 Theoretical basis for water uptake testing

2.3.2.1.1 Water sorption is similar to the sorption of other solvents. Sorption is a generalised term used to describe the penetration and dispersal of the molecules of a fluid onto and throughout a polymeric solid to form a mixture.

The absorption of a solvent by a polymer involves two processes. Firstly the solvent dissolves in the polymer at the surface, and secondly, the solvent is transported through the polymer by the process of diffusion, which is discussed in detail below. These processes continue until the solvent is at a uniform concentration throughout the polymer, that is the system has reached equilibrium.

For the sorption of water by polar polymers, polar groups such as -OH, -COOH and $-NH_2$ may act as specific sorption sites, and equilibrium sorption may depend not only on the quantity and nature of the polar groups, but also on their positions in the polymer chain.

2.3.2.1.2 Diffusion

Diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motions. Diffusion as a physical process closely resembles thermal conduction in which heat is transported by random molecular motions. The similarity between these two processes was first recognised by Fick (1855) who derived the fundamental laws of diffusion by analogy with the laws of thermal conduction established by Fourier (1822).

2.3.2.1.3 Fick's laws of diffusion

Fick's first law of diffusion states that the rate of transfer of diffusing substance through unit area of a section is proportional to the concentration gradient measured normal to the section, i.e.

$$F = -D \partial c / \partial x \qquad (2.1)$$

where F = flux, or rate of transfer per unit area of section
C = concentration
x = space co-ordinate measured normal to the section
D = Diffusion coefficient

Fick's first law is only applicable to steady state conditions, that is when the concentration of the diffusing substance is neither building up nor decaying.

Fick's second law of diffusion applies to non-steady state conditions when $\partial c / \partial t \neq 0$, and may be derived from Fick's first law by consideration of the mass balance of an element of volume. Crank (1967)

The second law is in the form of a differential equation

$$\frac{\partial c}{\partial t} = D\left\{\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right\} \quad (2.2)$$

where y and z are the new space co-ordinates and t is time.

When diffusion occurs only along the "x" axis then equation (2.2) reduces to

$$\frac{\partial c}{\partial t} = D\left\{\frac{\partial^2 C}{\partial x^2}\right\} \quad (2.3)$$

In many polymer-solvent systems, D is concentration dependent Fujita (1961), and equations 2.2 and 2.3 become 2.4 and 2.5 respectively.

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left\{D.\frac{\partial c}{\partial x}\right\} + \frac{\partial}{\partial y}\left\{D.\frac{\partial c}{\partial y}\right\} + \frac{\partial}{\partial z}\left\{D.\frac{\partial c}{\partial z}\right\} \quad (2.4)$$

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left\{D.\frac{\partial c}{\partial x}\right\} \quad (2.5)$$

Mathematical solutions to Fick's equations for various experimental boundary conditions have been reported by Crank (1967), and one such solution of value to the work reported here is described below.

Solution to Fick's second law for sorption by a semi-infinite film from an infinite bath.

Although the plates used in this work were much thicker than the films used by Tegg (0.35 mm thick), it was considered that they met the definition of a thin film for practical purposes as length and width were much greater than thickness and may be regarded as semi-infinite plates, i.e. ones in which edge diffusion can be neglected and diffusion is restricted to the x - direction only which is perpendicular to the plane of the plate.
Thus the appropriate form of Fick's second law is -

$$\frac{\partial c}{\partial t} = D \left\{ \frac{\partial^2 c}{\partial x^2} \right\} \qquad (2.6)$$

The source of water used in the experimental work may be regarded as an infinite bath, that is, one which is infinitely larger than the plate under investigation, and whose concentration does not vary during the experiment.

For a semi-infinite film in an infinite bath, the solution to Fick's second law is -

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{ -\frac{(2n+1)^2 \pi^2 D t}{L^2} \right\} \qquad (2.7)$$

where M_t = mass of diffusant taken up at time t
M_∞ = mass of diffusant taken up at equilibrium
L = film thickness
n = integer over which the series is summed

At short times this equation simplifies to -

$$\frac{M_t}{M_\infty} = \frac{4}{L}\left\{\frac{Dt}{\pi}\right\}^{\frac{1}{2}} \qquad (2.8)$$

This is the simplified equation used in this work. Uptake data can be plotted as fractional uptake

$$\frac{M_t}{M_\infty} \text{ against } t^{\frac{1}{2}} \text{ or } \frac{t^{\frac{1}{2}}}{L}$$

If diffusion is Fickian (see para 2.3.2.1.4.1) then the sorption curve is initially linear up to about $\frac{M_t}{M_\infty} = 0.6$ as shown in Fig: 13 (page 59),from Tegg and D may be obtained from the gradient of the linear portion of the curve.

When D is a function of the penetrant concentration the value of D obtained from equation (2.8) is an average over the penetrant concentration range zero to the equilibrium concentration, the mean value of the diffusion coefficient is represented by D.

Fickian diffusion is usually exhibited by polymers in the leathery state (that is above the glass transition temperature) when D is a function of penetrant concentration only. Fujita (1968). For polymers in the glassy state, D may be a function of time, Fujita (1961) as well as penetrant concentration, and the absorption curve is sigmoidal. See Fig. 14 (page 62).

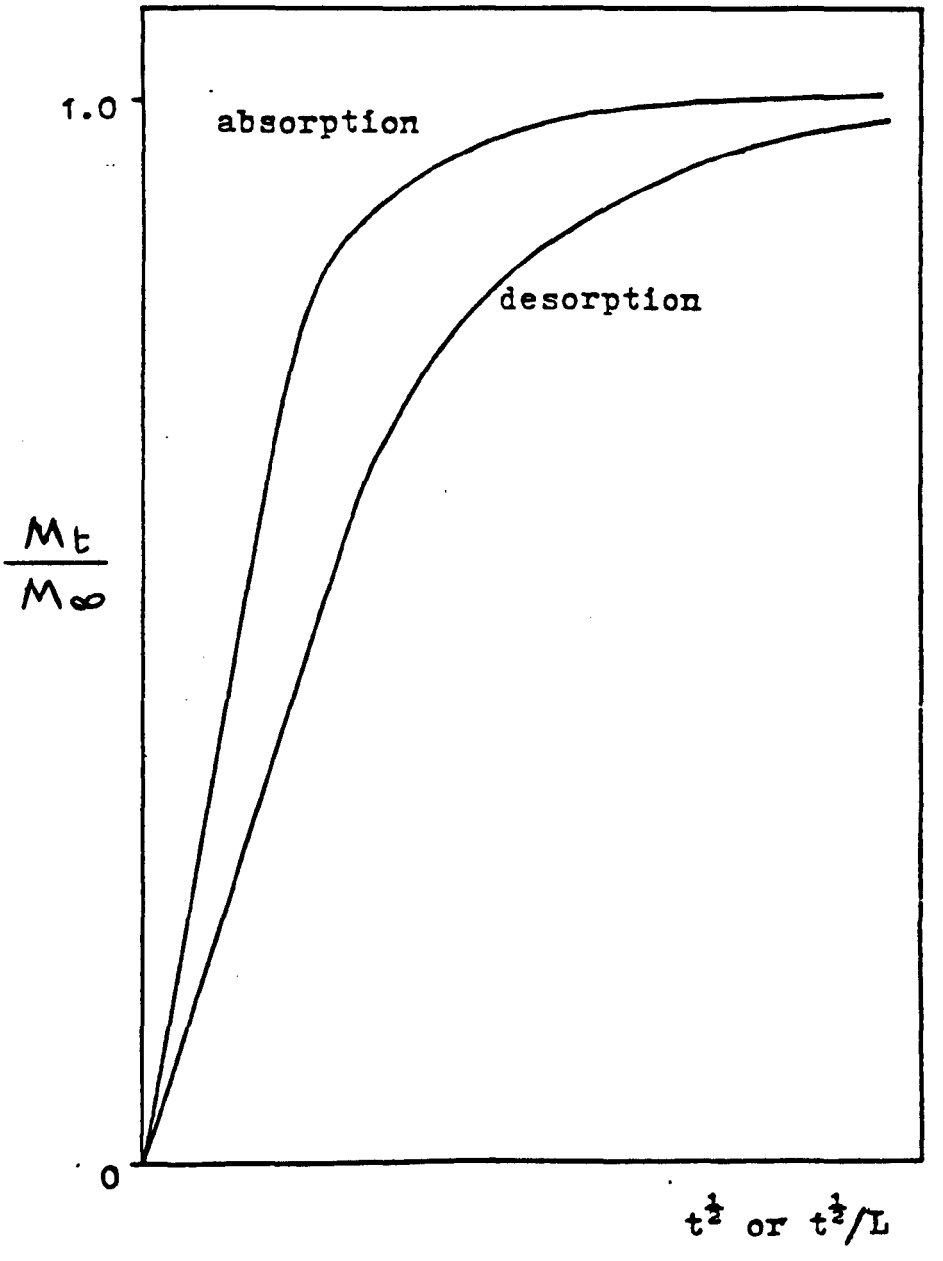


Figure 13. Typical sorption curves showing Fickian diffusion.

Diffusion is said to be non-Fickian in this case and D shows a discontinuity about the time when the polymer has absorbed enough penetrant to pass through its glass transition temperature. Fujita also concludes that diffusion is a rather complex process and that it is not always easy to decide when it is Fickian and when it is not.

Equations (2.7) and (2.8) may be applied to both absorption and desorption kinetics. For desorption data, $\frac{M_t}{M_\infty}$ represents fractional desorption. From a practical point of view these equations show that drying is also a slow process indicating that composites can only be dried in an acceptable time if both heat and vacuum are applied.

2.3.2.1.4 Sorption features

The sorption of solvents by polymers may be classified into three main types, namely, Fickian, non-Fickian (anomalous) and case II sorption. These modes of sorption may be distinguished by their characteristic sorption curves, which are considered below.

2.3.2.1.4.1 Fickian sorption

The important features of Fickian sorption, usually shown by leathery polymers, are summarised as follows -

(a) Both absorption and desorption curves (M_t/M_∞ versus $t^{\frac{1}{2}}$) are linear in the initial stage. The extent of the linear region varies according to the dependence of D upon penetrant concentration, but it usually extends up to at least $M_t/M_\infty = 0.6$.

(b) Above the linear regions, both absorption and desorption curves are concave to the abscissa.

(c) For a given penetrant concentration, a series of absorption curves for films of different thicknesses are superimposable to a single curve if data are plotted in the form of M_t/M_∞ versus $t^{\frac{1}{2}}/L$; these curves are known as reduced curves. The same applies to the corresponding series of desorption curves.

A given system is often regarded as Fickian if criteria (a) and (b) are satisfied. However, some systems do satisfy conditions (a) and (b), but not condition (c). Such behaviour is referred to as pseudo-Fickian.

2.3.2.1.4.2 Non-Fickian sorption

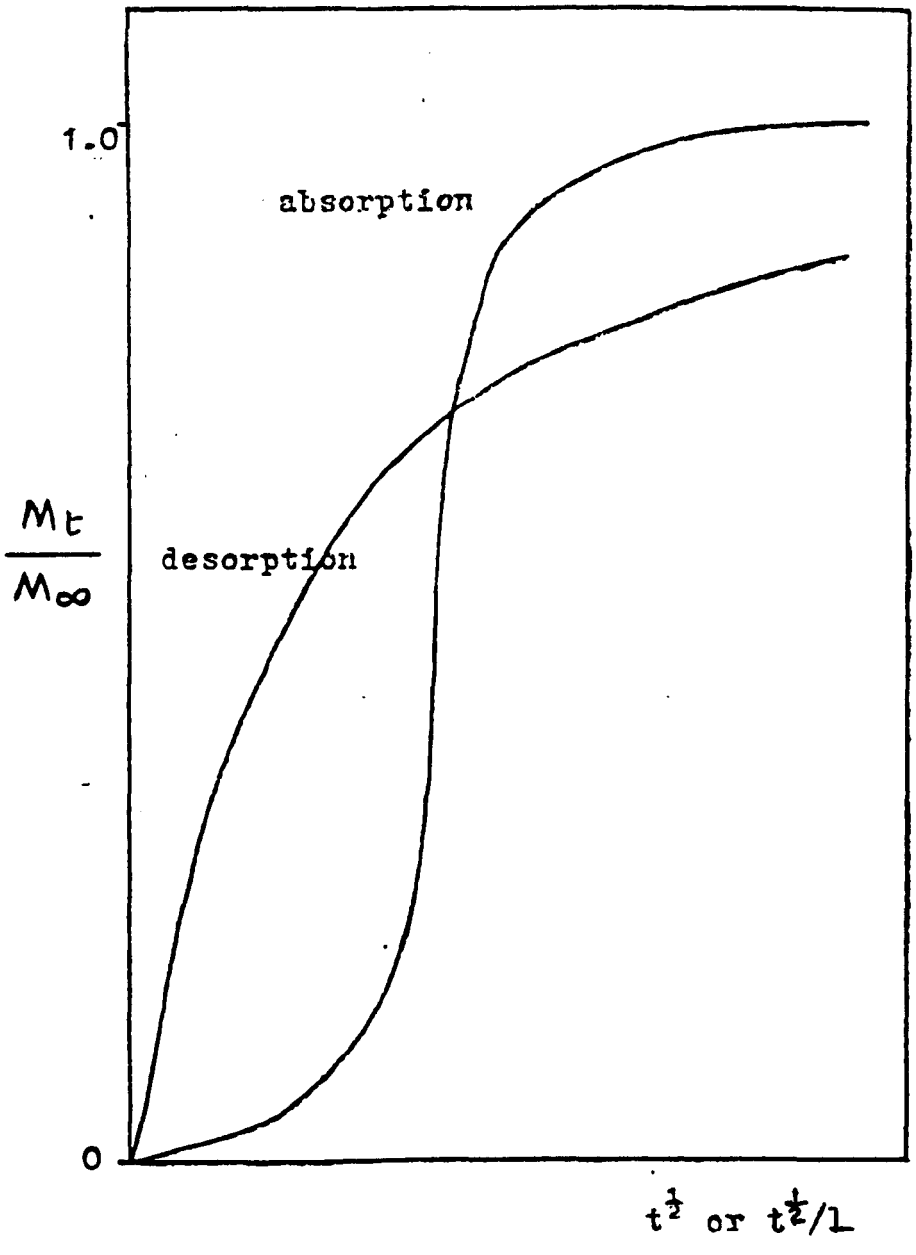
Non-Fickian or anomalous behaviour is usually exhibited by polymers in the glassy state. Some of the many reported deviations from Fickian sorption are summarised below.

(a) Both absorption and desorption curves are non-linear in the initial stage.

(b) The absorption curve is sigmoidal while the desorption curve is initially steep, but crosses the absorption curve before equilibrium is reached (Fig 14) (page 62).

(c) Paired absorption and desorption curves which have coincident initial slopes do not coincide over the entire range of M_t/M_∞.

(d) Series of absorption or desorption curves obtained from films of different thicknesses cannot be reduced to a single curve when plotted against $t^{\frac{1}{2}}/L$.



Sorption curves showing non-Fickian diffusion

FIG: 14

Frequently, a polymer-solvent system which exhibits non-Fickian behaviour in the glassy state, will show Fickian sorption characteristics above the glass transition temperature. This has been demonstrated for the acetone-polyvinylacetate system.

Sorption processes which exhibit any of the above (and other) deviations from Fickian features are referred to as non-Fickian processes, with the exception of case II transport which was defined by Alfrey et al and is considered below.

2.3.2.1.4.3 Case II Sorption

Case II sorption occurs at relatively high penetrant activities and at temperatures in the vicinity of and below the glass transition temperature of the solvent-polymer system. It is characterised by the following features -

(a) A linear relationship exists between the initial weight gain of a polymer film undergoing sorption and time. This is in contrast to Fickian sorption (which Alfrey et al termed case I transport) which leads to a linear relationship between the initial weight gain and the square root of time.

(b) A sharp boundary separates an inner glassy core of essentially zero penetrant concentration from an outer swollen, leathery shell of uniform concentration.

(c) The boundary advances at a constant velocity.

There is evidence that the rate determining step of case II sorption is osmotically induced polymeric relaxations at the boundary between the unpenetrated central core and the swollen, leathery outer shell.

The situation described in sub-paragraph (b) of 2.3.2.1.4.3 above can be demonstrated if a cube of cast-acrylic plastic is placed in a container of acetone. A clear boundary can be seen showing a progressively smaller cube inside the original cube. Weight gain ceases when the central cube is no longer visible. It can also be shown that, if the cube of acrylic is exposed to the atmosphere for several months before immersion, the rate of absorption of acetone is 7 times faster than if the cube is immersed in acetone immediately after drying and cooling to room temperature. This effect is attributed to absorbed moisture providing an easier pathway for the acetone.

2.3.3 Water diffusion computer programme

The computer programme used by Brewis et al (1979) was adapted by the British Airways Information Management Group to fit an IBM PC and given the programme name WATERDIS. The modified programme is given as Appendix 1, page 310 .

It was decided to calculate the water distribution in two typical cases -

(a) The standard lap shear test 1" wide and ½" overlap (25mm x 12.5mm) to ASTM D-1002

(b) A 38mm x 250mm joint to simulate a 1½" overlap commonly used when bonding thin skins during repairs to aircraft parts.

CHAPTER THREE MATERIALS AND APPARATUS

3.1 Materials

The test programme was carried out in four separate sections. The first two sections were carried out for the work reported by Armstrong (1987) and the second two for the work reported by Armstrong (1989).

Initially, four cold-setting adhesives and one potting compound were tested. The materials selected were:-

Hysol EA 9330 Two-part epoxy adhesive

Shell Epikote 815+ Epikure RTU Two-part epoxy matrix resin

Shell Epikote 828+ Versamid 125 Two part epoxy adhesive or matrix resin

3M EC 2216 Two-part epoxy adhesive

3M EC 3524 Two-part epoxy potting compound

Specimens were of the shape and dimensions shown in Fig. 12A (page 48). Data reported by Armstrong (1987) was related to the 100mm gauge length. Elongation to failure was taken from crosshead motion measured by the chart recorder. In most cases bubbles were present and failure often occurred through these so it might be more accurate to take the highest value of the three specimens in each case as the most nearly correct for a thin sheet without bubbles.

In the second section of tests the following adhesives were used:-

Hysol EA 9321 Two-part epoxy adhesive

3M - AF 163 - 2M Film adhesive 120°C cure

3M - EC 3559 Two-part epoxy adhesive

Hysol EA 9330 + 20% microballoons Epoxy potting compound

3M - EC 3568 Two-part epoxy adhesive

3M - EC 3578 Two-part epoxy adhesive

Permabond E34 Two-part epoxy adhesive

In the third section of tests the following adhesives were used -

Redux 408 Two-part epoxy adhesive
Redux 410NA Two-part epoxy adhesive
Redux 501 Two-part epoxy matrix resin
Hysol EA 9309.3NA Two-part epoxy adhesive
Redux 308A Film adhesive 180°C cure
3M - EC 9323 Two-part epoxy adhesive
Bostik 5435/TM2 Two-part acrylic adhesive (pre-mix type)

In the fourth section of tests the following:-

Permabond E37 Two-part epoxy matrix resin RT cured samples only
Permabond E38 Two-part epoxy adhesive 60°C cured samples only
Shell Epikote 815+ Two-part epoxy matrix resin
Shell Epikure RTU 90°C post cure tested dry and wet
120°C post cure tested dry
A large number of RT cured samples made and tested at different strain rates

Shell Epikote 828	100°C post cure for comparison
+Shell Epikure RTU	with manufacturers' data
	60°C post cure
	RT cure tested dry
	RT cure tested wet
Fiber Resin Corp	RT cure tested dry
FR 7020	RT cure tested wet
	55°C post cure
	80°C post cure

Redux 408 and 501 were offered by CIBA-GEIGY as their materials which came closest to meeting the requirements of a British Airways Specification EE-R76-1(A) for cold-setting repair adhesives.

It was decided to use the terms "Adhesive" and "Matrix resin" because the mechanical and physical properties indicated a clear distinction between the two in most cases and because the work of Palmer (1981) showed that the properties of a composite fall off rapidly when the modulus of the matrix falls below 450,000 psi.

A "matrix resin" is defined for the purposes of this thesis as, "A resin fluid enough to wet fabrics easily and having a tensile modulus in excess of 450,000 psi, giving a rigid laminate but having a relatively low shear strength in the lap shear test".

An "adhesive" is defined as "A paste of moderate viscosity, having a tensile modulus of 450,000 psi or less and giving a high shear strength in the lap shear test".

The differences between matrix resins and adhesives will be discussed in more detail later. Inevitably some materials are borderline between the two and Redux 308A, in particular, can fulfil either role.

3.2 Details of Adhesives tested

The following details indicate some of the characteristics of each of the materials used and especially those relevant to this programme.

3.2.1. Adhesive — Hysol EA.9330

Type — R.T. cure two-part paste epoxy

Mix Ratio — 100 parts of base resin to 33 parts of curing agent by weight

Base resin — Type epoxy, contains silica and aluminium oxide
Colour: cream
Viscosity: 960 poise
Smell: Pungent odour - may cause skin and eye irritation

Curing Agent — Colour: Clear light yellow
Viscosity: 16 poise
Type: Aliphatic amine (classified corrosive liquid)
Smell: Ammonia
Toxic if absorbed through skin. Causes severe skin and eye burns

Mixed Viscosity — 168 poise

Ease of Mixing — Easy to mix.
Both components of moderate viscosity. Non-splash.

Pot Life — 1 hour for a one pound mix

Density — 1.15 gm/cc

Cure Time — 7 days at 25° C
or 2 hours at 82° C

Max Service temperature — 80° C

Health & Safety Curing Agent
ANSI classification 4/5
Base resin ANSI classification 2.
Protective goggles, gloves and mask recommended.

Remarks

Curing agent known to be corrosive. Excellent adhesive. Good peel strength, makes tough joints but Al. Alloy adherends can suffer corrosion in the long term especially if not anodised.

Insensitive to bond line thickness.
Do not mix in total quantities greater than one pound or excessive heat build up may occur.

High water uptake.

3.2.2.

Adhesive Type	Shell Epikote 815+ Shell Epikure RTU R.T. cure two-part epoxy laminating resin
Mix Ratio	100 parts 815 to 25 parts RTU, by weight
Base Resin	Epoxy. Epikote 828, an unmodified Bisphenol 'A' with n-butyl glycidyl ether as a diluent. Colour clear.
Viscosity	Viscous fluid
Curing Agent	RTU is an amine adduct Viscosity: 70 poise Colour: Clear pale amber
Mixed viscosity	Fluid 15 poise
Ease of mixing	Very easy to mix
Pot life	Varies with quantity mixed. Use as soon as possible after mixing.
Density	Not given
Cure time	2 - 4 days at 23° C
Max Service Temperature	80° C
Health & Safety	Avoid skin contact

Remarks

Wets fabrics well. Good mechanical properties except for very low fracture energy. Tg 48°C from R.T. cure.
Tg can be increased by post-curing. Some health hazard now associated with n-butyl glycidyl ether.
Safer diluents are being sought for this type of resin system.

Epikote 815 will soon be replaced by Stag Polymers Resin 318. Resin 318 will be Epikote 828 diluted with iso-octyl glycidyl ether which is sometimes called 2-ethyl hexyl ether. Mechanical properties are expected to be very similar to 815.

3.2.3. Adhesive Shell Epikote 828+ Versamid 125

Type RT cure two-part epoxy

Mix Ratio 1 part of 828 to 1 part Versamid 125 by weight

Base resin Colour: Clear
Viscosity: Viscous liquid
Type: Unmodified Bis-phenol 'A'

Curing Agent:
Colour: Clear medium brown
Viscosity: 80-120 poise, viscous liquid
Type: Reactive Polyamide

Mixed viscosity Viscous liquid

Ease of mixing Easy

Pot life Varies with quantity mixed. Use as soon as possible after mixing.

Density Not given

Cure time 2 - 4 days at 23°C

Max service temperature 80°C

Health & Safety Avoid skin contact

Remarks

Fairly low water uptake. Quite a good early type epoxy adhesive.

3.2.4. Adhesive 3M EC 2216 B/A

Type	R.T cure two-part past epoxy
Mix Ratio	100 parts of base resin B to 140 parts of accelerator A
Base resin	Colour: Off white Consistency: Smooth paste Type: Modified epoxy
Accelerator	Colour: Medium grey Consistency: Viscous liquid. Type: Modified amine
Mixed viscosity	Fairly viscous when mixed Some trapped bubbles
Ease of Mixing	Fairly easy to mix
Pot life	2 hours approx for a one pound batch Cure rate increases with temperature and humidity
Density	1.27 gm/cc
Cure time	24 - 48 hrs at 24°C
Max service temperature	80°C
Health & Safety	Product may be irritating to skin. Avoid prolonged or repeated contact. Does not contain asbestos.

Remarks

Low modulus compared to most epoxies.
Low water uptake.

3.2.5. Adhesive 3M EC 3524 B/A Two-part epoxy potting compound

Mix ratio	100 parts of base resin B to 94 parts of accelerator A by weight
Base resin	Colour: Blue
	Consistency: Heavy paste
	Type: Epoxy
Accelerator	Colour: White
	Consistency: Heavy paste
	Type: Modified amine
Mixed viscosity	Stiff thixotropic paste
Ease of Mixing	Easy to mix
Pot life	2 hrs for 200 gm mix Larger quantities will give a shorter working life
Density	0.47 to 0.5 gm/cc
Cure time	16 hrs at 21°C
Max service temperature	80°C
Health & Safety	May cause eye and skin irritations. Use mask when sanding or grinding cured product.

Remarks

Flame retardant. Contrasting coloured compounds for ease of complete mixing. Does not contain asbestos.

3.2.6. Adhesive Hysol EA 9321

Type RT cure two-part epoxy for high temperature service

Mix ratio 100 parts of base to 50 parts of curing agent, by weight

Base resin Colour: Grey
Viscosity: 3,000-6,000 poise (paste)
Type: Epoxy
Smell: Slight odour
Fillers: Silica, Aluminium

Curing Agent Colour: Amber/cream paste
Viscosity: 350 - 100 poise
Type: Polyamide/Diethylene triamine
Aliphatic amine
Smell: Ammoniacal odour
Fillers: Silica, Aluminium oxide

Mixed viscosity Paste

Ease of Mixing A little stiff to mix. Needs warming to reduce viscosity if used with fabrics

Pot life 40 minutes for one pound mix

Density Not given

Cure time 5 days at 24°C or 1 hour at 82°C

Max service temperature 120°C retains modest strength up to 180°C

Health & Safety ANSI classification 4 for both parts. Goggles, gloves and masks recommended.

Remarks

Thixotropic, will not sag on vertical surfaces.
Some bubbles in mix.
Used successfully for wing leading edge composite patches to metal structure on Concorde. Both components are pastes and therefore no splashing problems during mixing. Some bubbles occur in the mix.

Fairly high water uptake from RT cure. Lower uptake when post-cured.

3.2.7. Adhesive 3M AF163 - 2M

Type Film adhesive 120°C cure

Base resin Modified epoxy (Polyether toughened epoxy)

Curing agent Di-cyandiamide

Working life The film is required to be stored at -18°C where it has a shelf life of approx. 12 months.

A maximum of 30 days out time at room temperature is permitted. A log of each removal from the freezer should be kept to ensure that the hours at room temperature are correctly recorded. A useful technique is to warm the roll once, cut it up into 5 metre lengths and seal each in its own bag. This greatly reduces the out time before usage.

On removal from the refrigerator the roll should be allowed to warm to room temperature, before the plastic bag is opened, to avoid condensation on the film. The required amount of film should be cut off, laid up and cured as soon as possible, and the remainder re-sealed in the bag and returned to the refrigerator quickly.

Density Not given

Cure time 60 mins at 250°F to 300°F
90 mins at 225°F to 250°F

Cure pressure Vacuum pressure in the range 8 - 12 inches of mercury is recommended

Max service temperature 120°C +
Tg dry 108°C from 120°C cure
Tg wet 82°C from 120°C cure (after 14 day immersion in water at 70°C)

Health & Safety

May cause skin irritation. Contains epoxy resin. Avoid prolonged or repeated contact with the skin. Avoid inhalation or eye contact with dust from grinding operations.

Remarks

Excessive bond pressure above that recommended leads to resin starved joints.
High fracture toughness
Excellent moisture resistance before and after curing.
Use of a corrosion inhibiting primer is recommended.
EC-3924, EC3960, EC3980 or EC3917 are suggested. Although weight-loss during cure is less than 1% it was not possible to produce void free blocks of adhesive for compression testing. Even under vacuum they were full of holes like 'Aero' chocolate.

3.2.8. Adhesive 3M - EC 3559 B/A

Type RT cure two-part epoxy

Mix ratio 100 parts of base B to 25 parts of accelerator A, by weight

Note Separation of a small amount of white resin in the base of this adhesive is normal. Stir in the white resin before weighing and mixing.

Base resin Colour: light yellow
Viscosity: Thixotropic paste
Type: Epoxy resin, acrylic polymer epoxy acrylic polymer and synthetic fiber
ANSI Class 1 and 2

Accelerator/Curing Agent Colour: Brown
Viscosity: Moderately thin liquid
Type: Amine
Epoxy resin, mixture of aliphatic amines and p-phenylene diamine
ANSI Class 2

Mixed viscosity Paste

Ease of Mixing Care required to mix liquid accelerator in base resin without splashing

Pot life 30 minutes for 50 gm mix
Do not mix larger amounts to avoid exotherm

Density 1.12 gm/cc

Cure time 7 days at 75°F

Max service temperature Up to 120°C

Health & Safety

Accelerator-severely irritating to eyes and skin. Prevent eye and skin contact. Do not breathe vapour.

Base resin - Prevent contact with eyes or skin. Avoid inhalation or eye contact with dust from grinding of cured resin.

May produce gastro-intestinal irritation.

Remarks

Does not contain asbestos. Excellent lap shear strength at temperatures in excess of 120°C. Excellent lap shear and good peel strength at room temperature.

3.2.9. Adhesive 3M - EC 3568 B/A

Type RT cure two-part epoxy

Mix ratio 100 parts of base resin B to 25 parts of accelerator A by weight

Base resin Colour: Metallic
Viscosity: Thixotropic paste
Type: Epoxy resin

Accelerator/Curing Agent Colour: Amber
Viscosity: Moderately viscous liquid
Type: Amine and epoxy resin

Mixed viscosity Paste, thixotropic

Ease of mixing Fairly easy

Pot life 15 mins for 100 gm mix

Density 1.127 gm/cc

Cure time 12 hrs at RT

Max service temperature 350°F (180°C)

Health & Safety

Accelerator A - corrosive to eyes and skin and irritating to respiratory system. Avoid inhalation or eye contact with dust from grinding operations.

Base resin B - may cause eye and skin irritation.

Use both parts only in well ventilated areas.

Curing ovens must be vented to outdoors.

Remarks

This material has a very definite exotherm problem as our workshop staff discovered while making test pieces. Inadvertently more than 100 gm was mixed in the work-shop and left in a plastic cup. The exotherm melted the cup and charred the wooden bench and clouds of unpleasant smoke were produced causing the area to be evacuated.

High water uptake.

Designed as a rapid cure material for very small repairs. Has useful shear strength up to 400°F.

3.2.10. Adhesive 3M - EC 3578 B/A

Type RT cure two-part epoxy

Mix Ratio 100 parts of base resin B to 50 parts of accelerator A

Base resin Colour: Metallic
Viscosity: Thixotropic paste
Type: Epoxy resin, aluminium filler, epoxy resin adduct.

Accelerator/Curing Agent Colour: Amber
Viscosity: Liquid
Type: Amine

Mixed viscosity Paste

Ease of mixing Fairly easy

Pot life 60 mins for 100 gm mix

Density 1.08 gm/cc

Cure time 12 hrs at RT

Max service temperature Up to 350°F (180°C)

Health & Safety

Accelerator - corrosive to eyes and skin. Avoid breathing vapour, use only in well ventilated areas. Avoid inhalation or eye contact with dust from grinding operations on cured adhesive.

Base resin - may cause eye and skin irritation. Curing ovens must be vented to outdoors.

Remarks

Non-asbestos, aluminium filled. Rapid cure.
High service temperature.
Fairly high water uptake.

3.2.11 Adhesive Permabond E 34

Type RT cure two-part epoxy

Mix Ratio 100 parts of base to 16 parts of curing agent, by weight

Base Resin Colour: Whitish
Viscosity: Moderate to high
Type: Epoxy
Di-glycidyl ether of Bisphenol'A'

Curing Agent Colour: Black
Viscosity: Low, soft paste
Type: Primary Amine

Mixed Viscosity Moderate, sticky

Ease of mixing Fair

Pot life 15 minutes per 100 gm mix

Density 1.29 gm/cc

Cure time 2 days at RT

Max service temperature $160^{o}C$

Health & Safety Use in well ventilated areas
Gloves are recommended

Remarks

Low water uptake
Only material to fail at $45^{o}C$ in compression test before 10% plastic strain
A few bubbles developed after mixing

3.2.12 Adhesive CIBA-GEIGY Redux 408

Type RT cure two-part epoxy

Mix ratio 100 parts of base resin to 7.5 parts of curing agent by weight

Base resin
Colour: Green
Viscosity: Very stiff
Type: Modified Epoxy-novolac
Aluminium filled and with a chromatec inhibitor

Note! Data sheet says colour is yellow

Curing Agent
Colour: Violet
Viscosity: Thin liquid
Type: Aliphatic amine di-ethylaminopropylamine
Smell: Ammonia (quite strong)

Mixed viscosity Medium paste. Just about useable with fabrics in the mixed condition

Ease of Mixing Very difficult in the early stages. Stiff base sticks to container, liquid curing agent can splash if great care is not taken. Needs to be worked slowly in small quantities.

Pot Life 1½ hours at RT

Density Not given

Cure time 7 days to 90% strength
7 weeks for full cure

Max service temperature: 120°C

Health & Safety Avoid contact with skin or clothing. Hardener is inflammable Strong ammonia smell from curing agent was found unpleasant. Mixing was done in a fume cupboard with the extractor fan running.

Remarks

Designed for RT or warm cure and for use in conjunction with rivetting or weld bonding.
Contains active corrosion inhibitor. Suitable for bonding metal-metal, metal-honeycomb or carbon-fibre composites to themselves or metals.
Cured material was brittle and some of the cast tensile test pieces were lost on removal from the mould.
High water uptake.

3.2.13 Adhesive CIBA-GEIGY Redux 410 NA

Type RT cure two-part epoxy

Mix Ratio 100 parts of base resin to 40 parts of curing agent, by weight

Base resin Colour: Yellow
Viscosity: Paste
Type: Modified (toughened) bis-phenol 'A' epoxy containing glass beads for glue line control

Curing Agent Colour: Violet liquid
Viscosity: liquid of moderate viscosity
Type: Aliphatic amine

Mixed viscosity Thick liquid

Ease of Mixing Very easy. Outgassing occurs and bubbles are produced.

Pot life 2 hrs for 50 gm mix
1 hr for 100 gm mix

Density Not given

Cure Time 1 - 2 days at 25°C

Max service temperature 60°C from RT cure but can be raised to 80°C by 120°C post-cure

Health & Safety Curing agent may be a dermatitic hazard. Gloves recommended and also good ventilation of working area.

Remarks

Best fracture energy yet found in wedge test. Good impact resistance, good peel resistance. Contains chromate corrosion inhitor. NA version does not contain asbestos. Originally developed for bonding bolt inserts into honeycomb sandwich panels.

3.2.14 Adhesive CIBA-GEIGY Redux 501

Mix ratio 100 parts of base resin to 15 parts of curing agent, by weight

Base resin Colour: Colourless, translucent
Viscosity: medium liquid
Type: Epoxy-novolac (unfilled, no chromate version of Redux 408)

Curing agent Colour: Violet
Viscosity: thin liquid
Type: Aliphatic amine (di-ethylaminopropylamine)

Mixed viscosity thin liquid, good for penetration of fabrics

Ease of mixing Easy

Pot life 1½ hrs at 25°C if mixed in a shallow tray to a depth of not more than 6 mm

Density Not given

Cure time 7 days to 80 - 90% strength
7 weeks to full cure at RT

Max service temperature Claimed to be 120°C

Health & Safety Curing agent may be a dermatitic hazard. Avoid skin contact. Curing agent is inflammable. Strong ammonia smell from curing agent was found unpleasant. Mixing was done in a fume cupboard with the extractor fan running.

Remarks

Approved by Aerospatiale for use in the repair of carbon-fibre flaps on ATR-42 and ATR-72.
Cured material was brittle and some of the cast tensile test pieces were lost on removal from the mould.
High water uptake.

3.2.15 Adhesive Hysol EA 9309.3NA

Type RT cure two-part epoxy

Mix Ratio 100 parts of base resin to 22 parts of curing agent by weight

Base resin Colour: Pink
Viscosity: 3000 poise (paste)
Type: Epoxy - contains .005" dia. glass beads for bondline thickness control

Curing agent Colour: Blue
Viscosity: 0.2 poise (liquid)
Type: Aliphatic Amine
Smell: Ammoniacal odour

Mixed viscosity Soft paste

Ease of Mixing Difficult initially to mix the liquid curing agent with the stiff paste

Pot life 35 minutes for one pound mix
Do not mix more than one pound 454 gm) at a time to avoid dangerous heat build-up

Density Not given

Cure time 3 - 5 days at RT

Max service temperature 80°C

Health & Safety Base resin may cause skin irritation. ANSI Class 2.
Curing agent may cause serious skin burns.
ANSI Class 5. Avoid skin and eye contact. Use good ventilation.

Remarks

A good tough adhesive
High shear strength
High peel strength.

3.2.16 Adhesive 3M-EC 9323 B/A

Type RT cure two-part epoxy

Mix Ratio 100 parts of base resin B to 27 parts of accelerator A

Base resin Colour: Whitish
Viscosity: Stiff paste
Type: Epoxy, toughened contains synthetic resins, fillers and wetting agents

Accelerator/Curing Agent Colour: Reddish brown
Viscosity: Soft gel
Type: Modified, amine 2,4, 6 - Tris (Dimethylaminomethyl) phenol polymeric diamine

Mixed viscosity Soft paste of salmon pink colour

Ease of mixing Very difficult to mix initially. High viscosity prevents bubbles from escaping

Pot life 50 gm - 2½ hrs
125 gm - 2 hrs
160 gm - 1 hr

Density 1.14 gm/cc

Cure time 1 - 2 days at RT
2 hrs at 66°C
5 minutes at 120°C

Max service temperature 80°C (Tg = 77°C)

Health & Safety Avoid contact with skin and eyes. Wear gloves and goggles and avoid breathing vapours.

Remarks

Good lap shear strength
Tough adhesive
Bubbles developed in cast-specimens.
High water uptake.

3.2.17 Adhesive BOSTIK 5435/TM2

Type RT cure two-part mix acrylic

Mix Ratio 2 parts of resin to 1 part of curing agent, by weight

Base resin Colour: Light amber
Viscosity: Viscous liquid
Type: High alkyl methacrylate acrylic resin

Curing agent Colour: Light amber
Viscosity: Liquid
Type: Aniline condensate (Free radical initiator)
Smell: Low odour

Mixed viscosity Viscous liquid

Ease of mixing Easy
Numerous bubbles in casting

Pot life 8 minutes

Density 1.05 gm/cc

Cure time 10 minutes to handling strength

Max service temperature Dry 120°C, Wet 70°C

Health & Safety Avoid prolonged contact with the skin. Wear protective gloves
Use only in areas of adequate ventilation.
Irritant to respiratory tract.
These adhesives are highly inflammable.

Remarks

Very low modulus, tough system, good impact resistance.
High water uptake.
Recommended service temperatures rather high in view of a Tg of only 50°C.

3.2.18

Adhesive	Permabond E 37
Type	RT cure two-part epoxy
Mix Ratio	5 parts of base resin to 1 part of curing agent, by weight
Base resin	Colour: Amber Viscosity: 150 poise Type: Epoxy Di-glycidyl ether of Bisphenol 'A'
Curing Agent	Colour: Dark amber Viscosity: 7 poise liquid Type: Primary Amine
Mixed viscosity	Liquid - 60 poise
Ease of Mixing	Easy
Pot Life	15 minutes for 100 gm mix
Density	1.14 gm/cc
Cure time	2 days at 25^{o}C Working strength in 16 hrs at 25^{o}C
Max service temperature	160^{o}C
Health & Safety	Use in well ventilated areas and wear gloves and goggles

Remarks

Liquid (low viscosity) version of E34. Very brittle. Some of the cast tensile test pieces were lost on removal from the mould. Would be expected to wet fabrics well. Low water uptake.

3.2.19 Adhesive Permabond E 38

Type	RT cure two-part epoxy
Mix Ratio	100 parts of base resin to 80 parts of curing agent
Base resin	Colour: Grey Viscosity: Soft paste Type: Epoxy, filled, Di-glycidyl ether of Bisphenol'A'
Curing Agent	Colour: Grey Viscosity: Soft paste Type: Amino-polyamide
Mixed viscosity	Soft paste
Ease of mixing	Easy
Pot life	2 hours
Density	1.3 gm/cc
Cure time	1 hr at 60°C 3 days at 25°C
Max service temperature	80°C
Health & Safety	Use in well ventilated areas. Gloves should be worn

Remarks

Gap filling - Good impact and peel resistance.
High water uptake.

3.2.20 Adhesive Shell Epikote 828 + Shell Epikure RTU

Type RT cure two-part epoxy laminating resin

Mix Ratio 100 parts of 828 to 25 parts of RTU by weight

Base resin Epikote 828
Colour: Clear
Viscosity: Viscous liquid
Type: Unmodified Bis-phenol 'A'

Curing agent Epikure RTU
Colour: Clear pale amber
Viscosity: 70 poise

Mixed viscosity 100 - 150 poise

Ease of Mixing Easy to mix

Pot life Varies with quantity mixed. Use as soon as possible after mixing.

Density Not given

Cure time 2 - 4 days at 23°C

Max service temperature 80°C

Health & Safety Avoid skin contact

Remarks

Wets fabrics but not as well as 815.
Good mechanical properties except for very low fracture energy.
Tg of 93°C from RT cure (dry), 58°C at saturation with water.
Tg can be increased by post-curing.

3.2.21 Adhesive Fiber Resin Corporation FR 7020 A/B

Type RT cure two-part epoxy

Mix Ratio 100 parts resin to 58 parts of curing agent by weight

Part 'A' Base Resin Colour: Amber

Viscosity: Viscous liquid 250 poise

Type: Epoxy 4-Glycidyloxy-N,N-Diglicidylanilene

Smell: Essentially odourless

Part 'B' Curing Agent Colour: Black

Viscosity: Viscous liquid 32 poise

Type: Amine blend. Polyamide resin+ Triethylenetetramine+ Diethylenetriamine

Smell: Ammonia

Mixed viscosity	200 poise
Ease of mixing	Fairly easy
Pot life	45 minutes for 150 gm mix
Density	1.1 gm/cc
Cure time	3 days to 95% strength 5 days to full strength at room temperature
Max service temperature	150°C
Health & Safety	Avoid eye or skin contact. Do not breathe vapours. Goggles and gloves recommended. Good general mechanical ventilation recommended. Violent exotherm may occur if mixed in large quantities.

Remarks

Room temperature cured, tensile test pieces suffered a considerable reduction in strength after immersion in water. Excellent wet strength claimed if cured at 150°F (66°C). Designed for graphite composite repairs. Fairly high water uptake.

3.2.22

Adhesive	CIBA-GEIGY Redux 308A
Type	180°C cure film adhesive
Base resin	Polymerically modified bis-phenol 'A' epoxy + 1.5% asbestos fibre + glass beads for glue line control
Curing agent	Modified di-cyandiamide
Working life	The film adhesive is stored at -18°C where it has a shelf life of approx. 12 months + 1 month open time at RT See other notes for AF.163-2M Para 3.1.7
Density	Not given
Cure time	1 hour at 150°C or 1 hour at 170°C
Cure pressure	25-50 psi, 170-350 kN/m2
Max service temperature	120°C
Health & Safety	Redux 308A is believed to be harmless to handle but the wearing of clean polythene gloves is recommended during handling to avoid contaminating the adhesive.

Remarks

High strength adhesive
Low water uptake
Contains glass beads for glue line thickness control.
Volatile content well below 1% but attempts to produce a solid block for compression testing failed both at zero pressure and under vacuum.
Results were better under vacuum but the castings were full of holes and resembled "Aero" chocolate. It was not possible to obtain valid compression test data because of this.

3.3. Apparatus

The apparatus used for this programme was as follows -

3.3.1 Electronic balance accurate to 0.1 gramme. This had a zero button which was very useful in that it allowed protective paper and a mixing cup to be added to the scale and zeroed out before mixing began. The base resin was always added first and corrected to the nearest 0.1 gramme. Next the curing agent was added. This was almost always of lower viscosity than the resin. Liquid curing agents could be removed with absorbent paper if necessary to correct their weight to the nearest 0.1 gramme.

3.3.2 Mould for tensile test pieces

This is shown in Fig. 12D (page 51). It consists of a ground base plate to which two thinner profiled plates are screwed. These are also ground plates. Specimens were removed by unscrewing and removing one profiled plate and sliding a piece of shim steel under the specimen. Silicone grease was used as a mould release agent.

3.3.3 Mould for compression test pieces

When making compression test pieces a mixing cup was filled to a suitable depth with adhesive and the mix allowed to cure. The block was then cut and machined into Compression Test pieces. See Fig. 12B (page 49).

3.3.4 Tensile testing machine

The testing machine used as an RDP-Howden EU.500BS. This machine is similar in concept to the better known "Instron" machine, in that the crosshead is driven through two recirculating ball screw drives protected by extensible covers. The ball screw drives give a smooth action and improve the rigidity of the machine compared to a screw thread drive. Load is measured by a strain-gauged load cell and the signal fed to a chart recorder via an

electronic amplifier. The load scale can be varied by push buttons which bring into use a number of pre-determined ranges. The highest load range is 20kN or approx 2 tons. The lowest load range is 2kN when using the 20kN load cell. Smaller load cells with greater accuracy at lower loads are available. The RDP Howden has a wide range of crosshead speeds and can be used anywhere in the range of 0.1mm per minute to 500mm per minute. The recorder chart speed can also be varied over a wide range and easily covers the more limited range required to meet the various ASTM test method speeds for this work.

This machine was used for the tensile tests, compression tests, lap shear tests and to drive wedges into the wedge test pieces at a constant speed. Tensile testing is illustrated in Fig 15A (page 96), compression testing in Fig 15B (page 97) and wedge testing in Fig 15C (page 98).

3.3.5 Chemical laboratory balance

A laboratory balance, accurate to four decimal places of a gramme, was used to weigh the plates of adhesive used for the water uptake tests.

Samples were removed from their sealed jars, blotted dry on all faces and then weighed as soon as possible. This was necessary because the accuracy of the scales was such that some samples could be seen to lose weight during the weighing process.

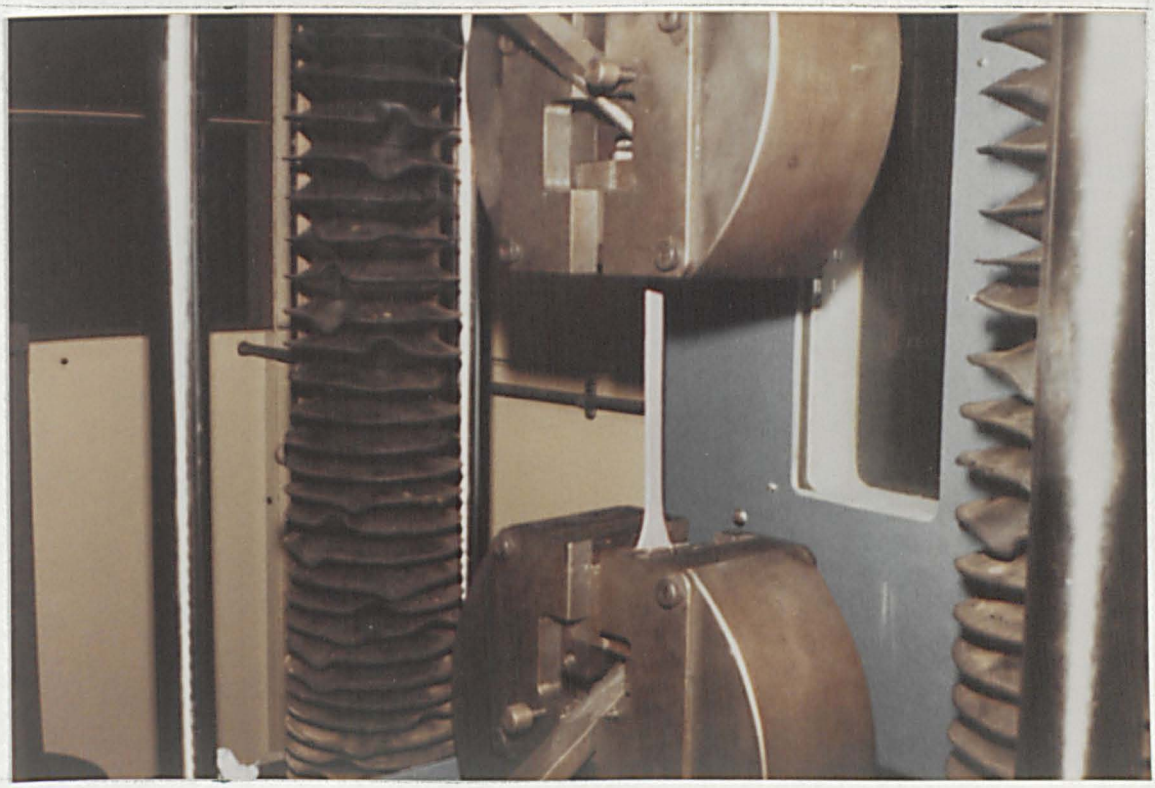


FIG: 15A TENSILE TESTING

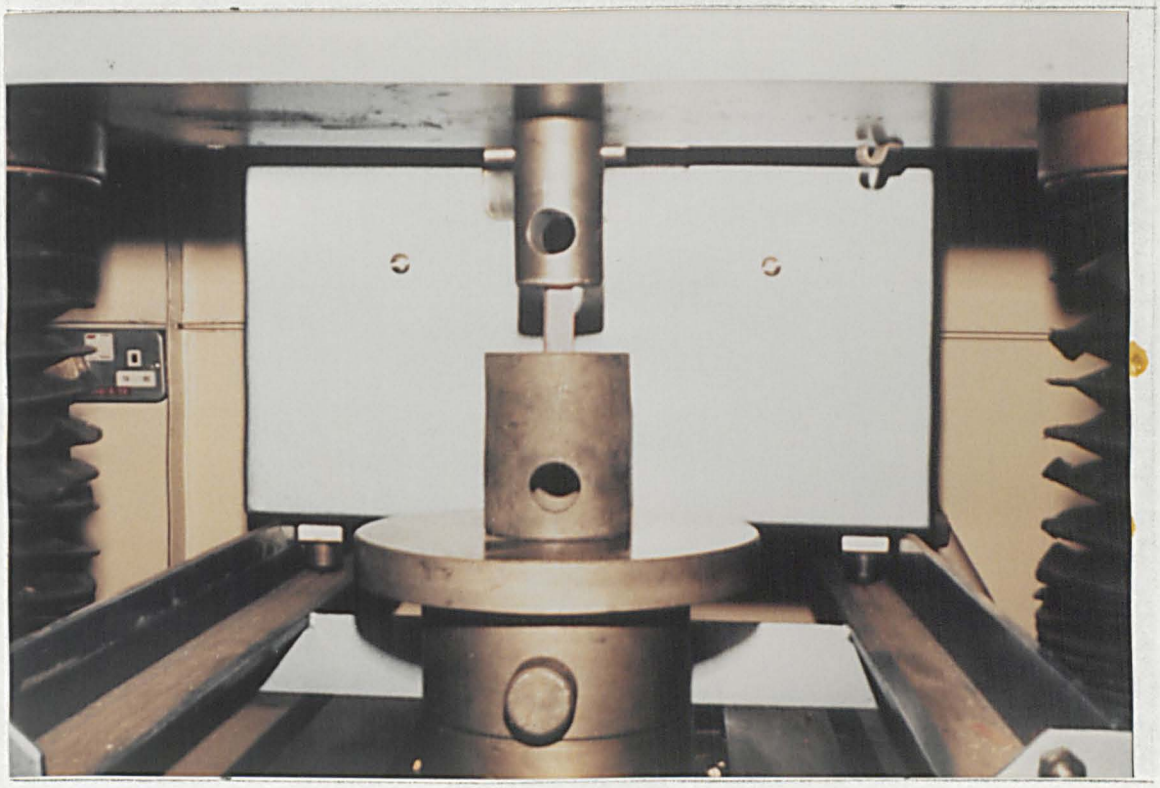


FIG: 15B COMPRESSION TESTING

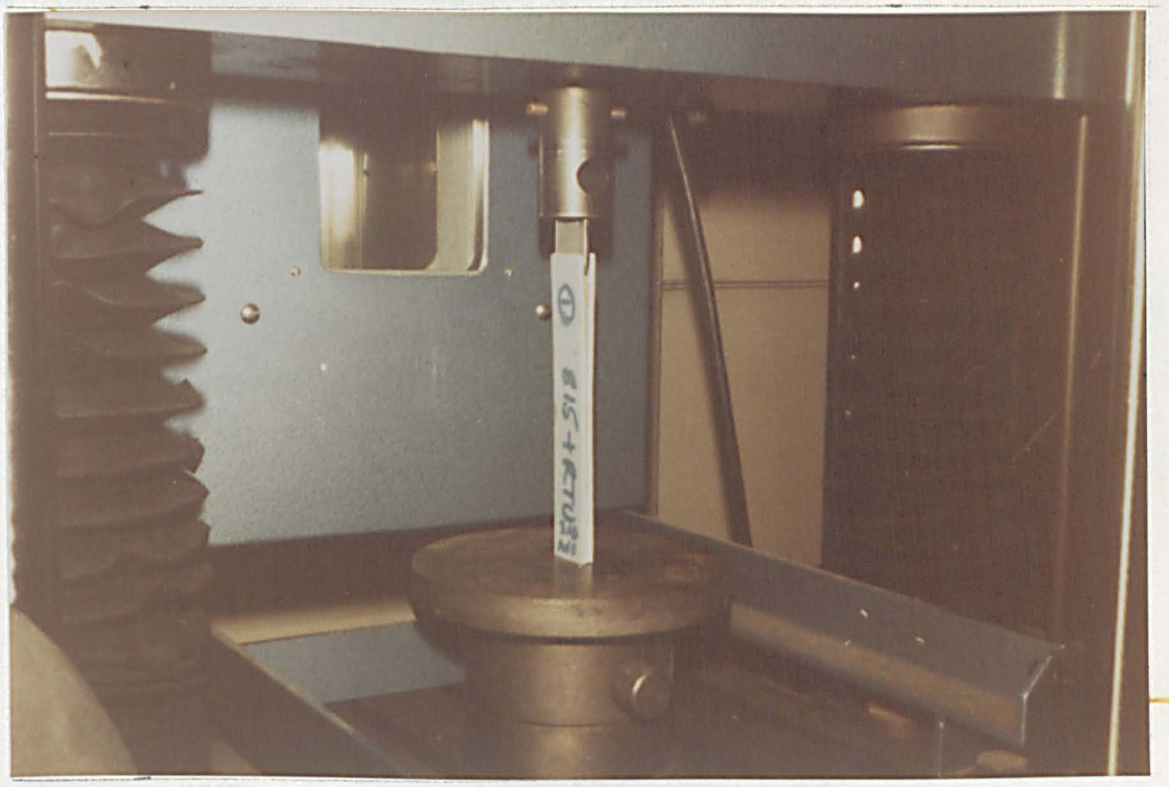


FIG: 15C WEDGE TESTING

3.3.6 General laboratory facilities

The water uptake test pieces were stored in distilled water in sealed glass jars at a controlled room temperature of 20°C in the British Airways Chemical Laboratory in Technical Block "A".

Fume cupboards were used during the mixing of those adhesives that emitted particularly pungent odours.

Moulding of cast specimens, and assembly of lap shear and wedge test pieces were carried out in the chemical laboratory.

Laboratory ovens were used to cure those specimens requiring heat cure or post-cure and to dry Al.Alloy samples after anodising and prior to bonding.

The Al.Alloy samples requiring anodising were all chromic acid anodised (unsealed) in the British Airways Plating Shop on the ground floor of Technical Block "A". This work was done by Plating Shop staff. Their support is greatly appreciated.

CHAPTER FOUR EXPERIMENTAL WORK

4.0 Experimental work

Experimental work was carried out in a number of areas -

(a) Mixing of resins and moulding of tensile test pieces or compression test blocks. This was useful as it provided "hands on" experience of working with a number of resins. It was quickly discovered that some were easier to mix than others and that some had a stronger smell than others. On removal from the mould it soon became obvious that some were very brittle and some were quite tough.

(b) Tensile and compression testing of cast samples using the standard methods of ASTM-D638 and ASTM-D695 respectively. Lap shear testing of Al.Alloy joints to ASTM-D-1002. Wedge testing of Al. Alloy test pieces to ASTM-D-3762 except for tensile test pieces, tested after water immersion, 3 test pieces were used to obtain each data point.

c) Weighing of water immersion samples and later measurement of pH and electrical conductivity of the water solutions when a piece of 7075-T6 Aluminium Alloy had been added to each jar.

4.1 Tensile tests and water immersion tests

Tensile test pieces were moulded from each of the resins listed above in Chapter 3. Only one mould was made and therefore each specimen was an individual resin mix. A few brittle ones were lost on removal from the mould. The brittleness of Permabond E37, Redux 408 and Redux 501 forced the use of Molykote 33, a silicone grease, as a mould release agent. Aerosol spray, non-silicone types were not good enough. A piece of shim steel was used to assist in removing specimens from the mould after curing. The use of a very thin shim was essential because anything thicker caused the more brittle specimens to fracture. Manufacture was spread over about 18 months. Materials were weighed out on electronic scales to 0.1 gramme and great care was taken to work to that accuracy because for some materials even an error of 0.1 gramme was a significant percentage error. The usual quantity mixed was 25 - 30 grammes.

Each mix was stirred for a minimum of two minutes, and longer if necessary, to ensure an even colour of coloured materials and a thorough mixing whether the materials were coloured or not. Low viscosity mixes were allowed to outgas for 5 minutes before pouring. After pouring clear materials; where bubbles could be seen at the lower surface, these were pricked with a paper clip or pin.

Upper surface bubbles were pricked for all materials. Viscous resins were poured immediately in case they became too viscous. Most of the viscous materials were not completely self-levelling in the mould and, because they were too thick to run out of the channel provided at one end, the specimens were often thicker than the less viscous ones.

It is worth noting that resin systems of moderate, non-splashing, viscosity are inherently safer to work with than those where the base resin is very stiff and the curing agent water thin. These require care and patience until they begin to mix and there are two problems with accuracy of mixing. Firstly, the viscous component tends to stick to the container and secondly, there is the danger of losing the liquid curing agent by splashing, which could result in skin or eye contact.
Wherever possible it is desirable to formulate a two-part mix where both parts have a moderate and roughly equal non-splash viscosity. Hysol EA9330 and Redux 410NA typify desirable examples. Gloves and goggles were worn for safety reasons when mixing all types.
Tensile tests were carried out to ASTM-D-638 on each specimen and from these the tensile strength and elongation at failure were obtained from the chart record. Young's Modulus (E) was obtained from the slope of the chart record and the shear modulus (G) was calculated from this using the standard formula

$$G = \frac{E}{2(1 + \nu)}$$

where ν = Poissons ratio

was assumed to be 0.4 for the majority of resins and .45 for EC2216 and Bostik 5435/TM2 because of their low moduli.

These results had been expected to be sufficiently accurate because of the high stiffness of the testing machine and relatively low stiffness of the adhesive test pieces. However, after obtaining some Manufacturers' data, it was found that the modulus values obtained without an extensometer were low. In fact they were only about a third of the manufacturers' values. A formula was found in a German DIN Specification, (DIN 53455) which allowed for the complete length and shape of the test specimen. Even this failed to bring the modulus values anywhere near the required values. See Table 3 (Pages 103 - 104). For calculations see Appendix 2, (Page 311 - 313)

As a result the only way to estimate the true values was considered to be to plot BA test results against the few Manufacturers' data points available. This was done as Fig 16 (page 105), from BA test values. The DIN calculation was used to divide all previous strain values (based on 100 mm gauge length) by 1.4593. This should give more accurate values of strain at failure.

In the first two sections of work published by Armstrong (1987) the tensile test pieces were cured at room temperature only, except for 3M-AF 163-2M cured at 120°C (250°F). After tensile testing the ends of the specimens were cut off to make 40mm x 30mm x approx 2mm plates. As three tensile test pieces were made for each material, six plates were available in each case. One pair was used as it was, one pair was post cured at 50°C for three hours and the other pair at 80°C for one hour. One of each cure temperature was sent to RAE for Tg measurement dry and the other immersed in water until saturation. Periodic weighings were made and the Diffusion Coefficients obtained from plots of

$\frac{Mt}{M\infty}$ v $\sqrt{\text{time}}$.

TABLE 3

TENSILE MODULUS IN BRITISH AIRWAYS TESTS AND MANUFACTURERS DATA OR DATA ESTIMATED FROM FIG.1

ADHESIVE OR COMPOSITE MATRIX RESIN	TENSILE MODULUS BA TESTS PSI	TENSILE MODULUS BA TEST CORRECTED PSI	TENSILE MODULUS (PSI) ASTM D-638 FROM MFR OR ESTIMATED FROM FIG.16(EST)
Redux 308A 170°C Cure	145,691	250,588	480,000 (EST)
Redux 408 RT Cure	213,730	367,616	650,000 (EST)
Redux 408 + 20% 410 RT Cure	213,231	366,757	650,000 (EST)
Redux 408 + 40% 410 RT Cure	168,206	289,314	540,000 (EST)
Redux 410NA RT Cure	106,193	182,652	380,000 (EST)
Hysol EA 9309.3NA RT Cure	115,147	198,053	360,000 (MFR)
Hysol EA 9321 RT Cure	125,000	215,000	380,000 (MFR)
Hysol EA 9330 RT Cure	84,000	144,480	351,000 (MFR)
Permabond E38 RT Cure	83,772	144,087	320,000 (EST)
3M-AF163 120°C Cure	95,650	164,518	350,000 (EST)
3M-EC 2216 RT Cure	3,100	5,332	51,000 (MFR)
3M-EC 3524 RT Cure	33,000	56,760	155,000 (EST)
3M-EC 9323 RT Cure	138,688	238,543	416,280 (MFR)
Bostik 5435/TM2 RT Cure	1,764	3,034	8,820 (EST)

TABLE 3

TENSILE MODULUS IN BRITISH AIRWAYS TESTS AND MANUFACTURERS DATA

OR DATA ESTIMATED FROM FIG.1

ADHESIVE OR COMPOSITE MATRIX RESIN	TENSILE MODULUS BA TESTS PSI	TENSILE MODULUS BA TEST CORRECTED PSI	TENSILE MODULUS (PSI) ASTM D-638 FROM MFR OR ESTIMATED FROM FIG.16(EST)
Epikote 828 + Versamid 125 RT Cure	112,000	192,640	395,000 (EST)
Redux 501 RT Cure	204,435	351,628	630,000 (EST)
Redux 501 + 20% 410	153,352	263,765	500,000 (EST)
Redux 501 + 40% 410	142,471	245,050	475,000 (EST)
Permabond E34 RT Cure	182,000	313,040	570,000 (EST)
Permabond E37 RT Cure	150,530	258,912	510,000 (EST)
Epikote 815 + Epikure RTU RT Cure	178,000	306,160	560,000 (EST)
Epikote 828 + Epikure RTU RT Cure	189,188	325,403	580,000 (EST)
Epikote 828 + Epikure RTU 100°C Cure	139,717	240,313	510,000 (MFR)
Fiber Resin Corp FR 7020 RT Cure	132,221	227,420	450,000 (EST)

BA corrected figure is Column 1 x 1.72, which corrects for specimen effective length and testing speed. Machine effects and grip slippage cannot be included because no extensometer was used.

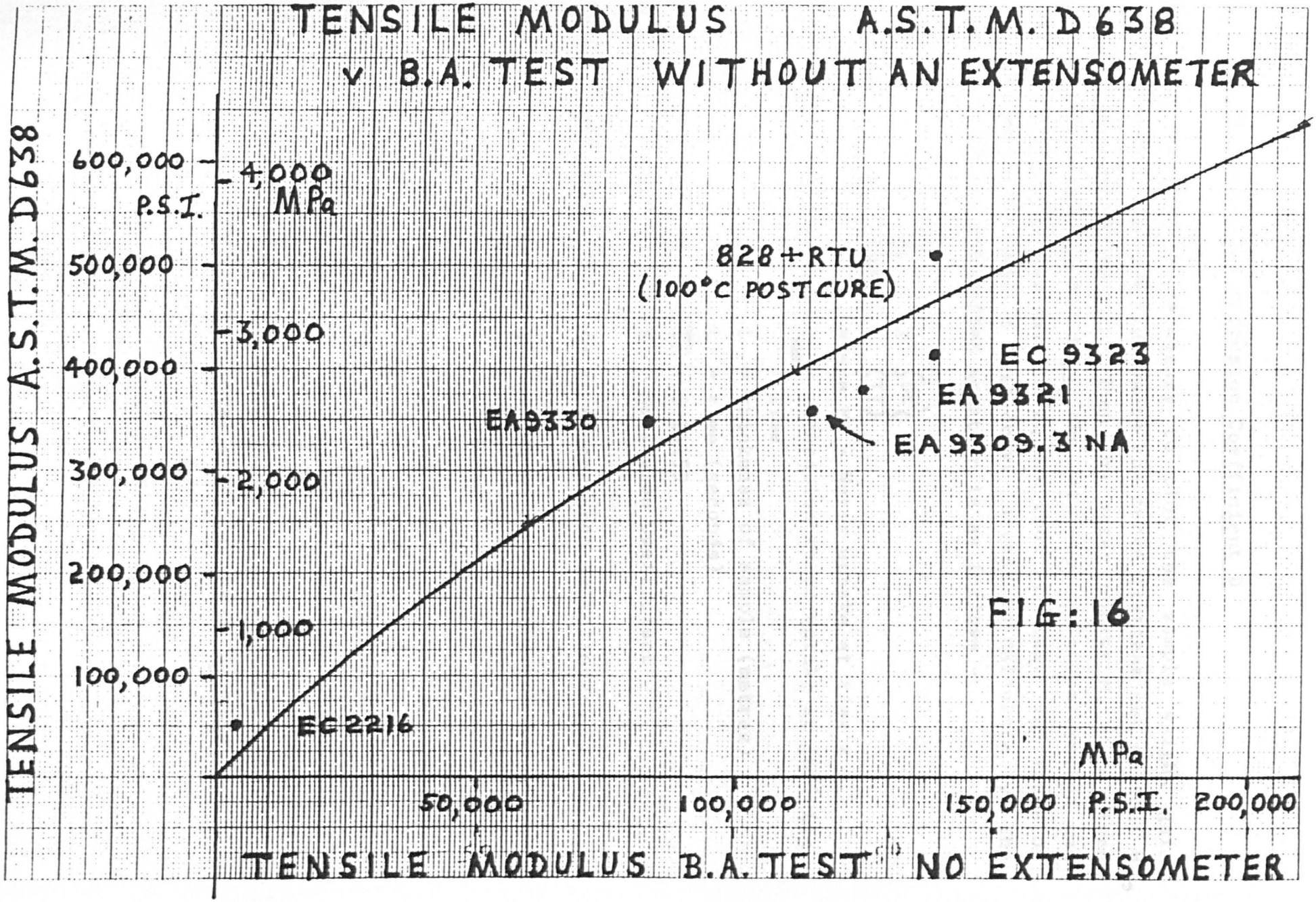

TENSILE MODULUS A.S.T.M. D638
v B.A. TEST WITHOUT AN EXTENSOMETER
TENSILE MODULUS A.S.T.M. D638
600,000 P.S.I.
500,000
400,000
300,000
200,000
100,000
4,000 MPa
3,000
2,000
1,000
828+RTU
(100°C POST CURE)
EC 9323
EA 9321
EA 9330
EA 9309.3 NA
EC 2216
MPa
50,000
100,000
150,000 P.S.I. 200,000
TENSILE MODULUS B.A. TEST NO EXTENSOMETER

FIG: 16

To obtain the Diffusion Coefficient D

First it is necessary to plot the sample weight gain versus time to find where the curve flattens out so that M_∞ can be estimated. Then the water uptake M_t at a given time divided by M_∞ the water uptake at saturation can be plotted against the square root of time. The slope of the early part of this curve is used to calculate D. The standard simplified equation is as follows -

$$\frac{M_t}{M_\infty} = \frac{4}{L}\left\{\frac{Dt}{\pi}\right\}^{\frac{1}{2}}$$

Where M_t = Water uptake at time t

M_∞ = saturation water uptake at infinite time

L = thickness of sample (metres)

t = time (seconds)

π = 3.14159

D = Diffusion Coefficient

The mathematics can be re-arranged as follows:-

$$\frac{M_t}{M_\infty} = \frac{4}{L}\left(\frac{D^{\frac{1}{2}}\ t^{\frac{1}{2}}}{\pi^{\frac{1}{2}}}\right)$$

$$\frac{M_t}{\frac{M}{t^{\frac{1}{2}}}} = \frac{4}{L\,\pi^{\frac{1}{2}}} \times D^{\frac{1}{2}}$$

$\frac{M^t}{M_\infty}$ = the slope of the graph plotted from $t^{\frac{1}{2}}$ fractional water uptake v $\sqrt{\text{time}}$

$$\frac{\frac{M_t}{M\infty}}{t^{\frac{1}{2}}} \cdot \frac{4}{\pi} = \frac{D^{\frac{1}{2}}}{L\pi^{\frac{1}{2}}}$$

from which the Diffusion Coefficient D is obtained

For curves see Figs 17 - 28 (pages 109 - 120) and for data see Table 4 (page 108).

Solubility Coefficients were calculated from

$$\frac{W_1 - W_o}{W_o}$$

where W_o = dry weight

W_1 = saturated weight

During the second two sections of the work the same tests as detailed above were carried out with some extras.

For Redux 408, Redux 410 NA, Redux 501, Hysol EA 9309.3NA 3M- EC 9323 and FR 7020, three complete tensile specimens were post cured at 50°C for three hours and 80°C for one hour to check the effect of post curing and in addition a further three specimens were cured at RT and tested after 2, 4 and 6 months immersion in water to check the effect of water uptake on mechanical properties. All three additional specimens of Redux 408 and Redux 501 were tested after 6 months in water in case the effect of brittleness and bubbles masked the effect of water immersion.

To obtain more detail on materials for use as matrix resins for repair Permabond E37, Shell Epikote 815 + RTU and Shell Epikote 828 + RTU were also tested. Testing of E37 was limited to room temperature cured samples because it was very brittle. Epikote 815 + RTU and Epikote 828 + RTU were studied in some detail as good and easily available systems and FR 7020 because it is recommended by Boeing.

(Text continues on page 121)

TABLE 4
Diffusion Coefficients & Solubility Coefficients
After Various Cure Temperatures

ADHESIVE	DIFFUSION COEFFICIENT "D" m²/s SOLUBILITY COEFFICIENT "S"					
	After RT Cure "D"	After RT Cure "S"	After 50°C Cure "D"	After 50°C Cure "S"	After 80°C Cure "D"	After 80°C Cure "S"
EA 9330	1.63^{-13}	13%	1.63^{-13}	18% **	1.63^{-13}	10.4%
EPIKOTE 815 + RTU	4.74^{-14}	7.35%	3.51^{-14}	5.2%	4.31^{-14}	3.68%
EPIKOTE 828 + VERSAMID 125	4.43^{-14}	6.25%	4.43^{-14}	6.6%	4.43^{-14}	7%
EC 2216	1.575^{-14}	5.7%	9.07^{-14}	6.0%	9.07^{-14}	5.4%
EC 3524	1.194^{-13}	35%	1.194^{-13}	32.9%	1.194^{-13}	34.4%
EA 9321	9.34^{-14}	7.88%	3.46^{-14}	4.89%	4.33^{-14}	4.28%
AF 163 *	--	--	--	--	8.04^{-14}	1.89%
EC 3559	8.81^{-14}	5.15%	4.33^{-14}	5.4%	6.38^{-14}	4.76%
EA 9330 + 20% MICROBALLOONS	7.22^{-14}	79.7%	2.83^{-14}	67%	8.72^{-14}	102%
EC 3568	NR	18.7%	--	--	--	--
EC 3578	NR	9.7%	NR	18.1%	NR	9.5%
PERMABOND E34	NR	1.9%	NR	1.9%	NR	2.15%

* AF 163-2M film adhesive cured at 120°C for 1 hour
** Suspect mix
NR No result. These materials gave a sigmoidal uptake curve from which no normal diffusion coefficent could be obtained

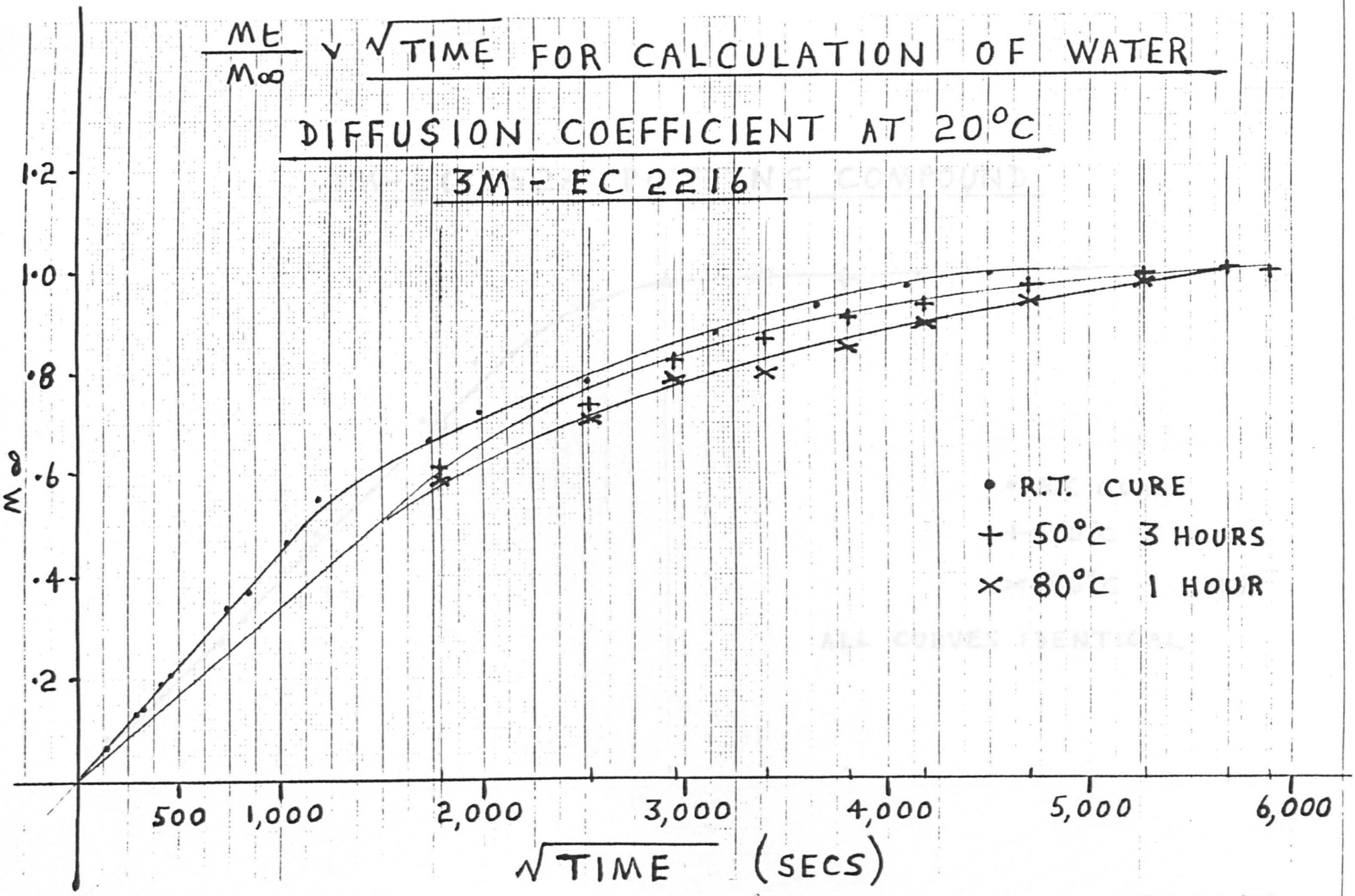

Mt/M∞ V √TIME FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
3M - EC 2216
Mt/M∞
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
√TIME (SECS)
• R.T. CURE
+ 50°C 3 HOURS
× 80°C 1 HOUR

FIG: 17

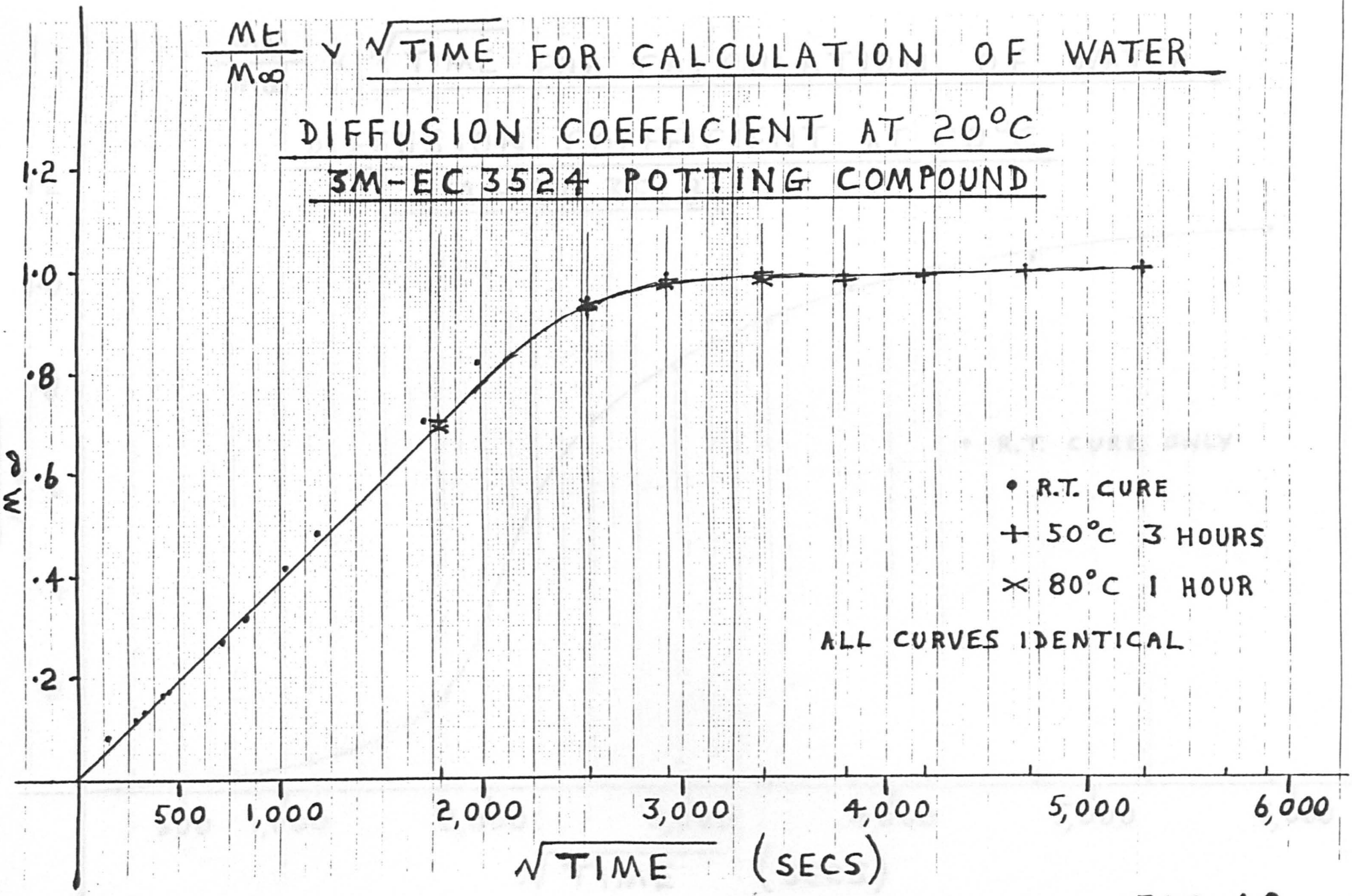

Mt/M∞ √TIME FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
3M-EC 3524 POTTING COMPOUND
Mt/M∞
1·2
1·0
·8
·6
·4
·2
• R.T. CURE
+ 50°C 3 HOURS
× 80°C 1 HOUR
ALL CURVES IDENTICAL
500
1,000
2,000
3,000
4,000
5,000
6,000
√TIME (SECS)

FIG: 18

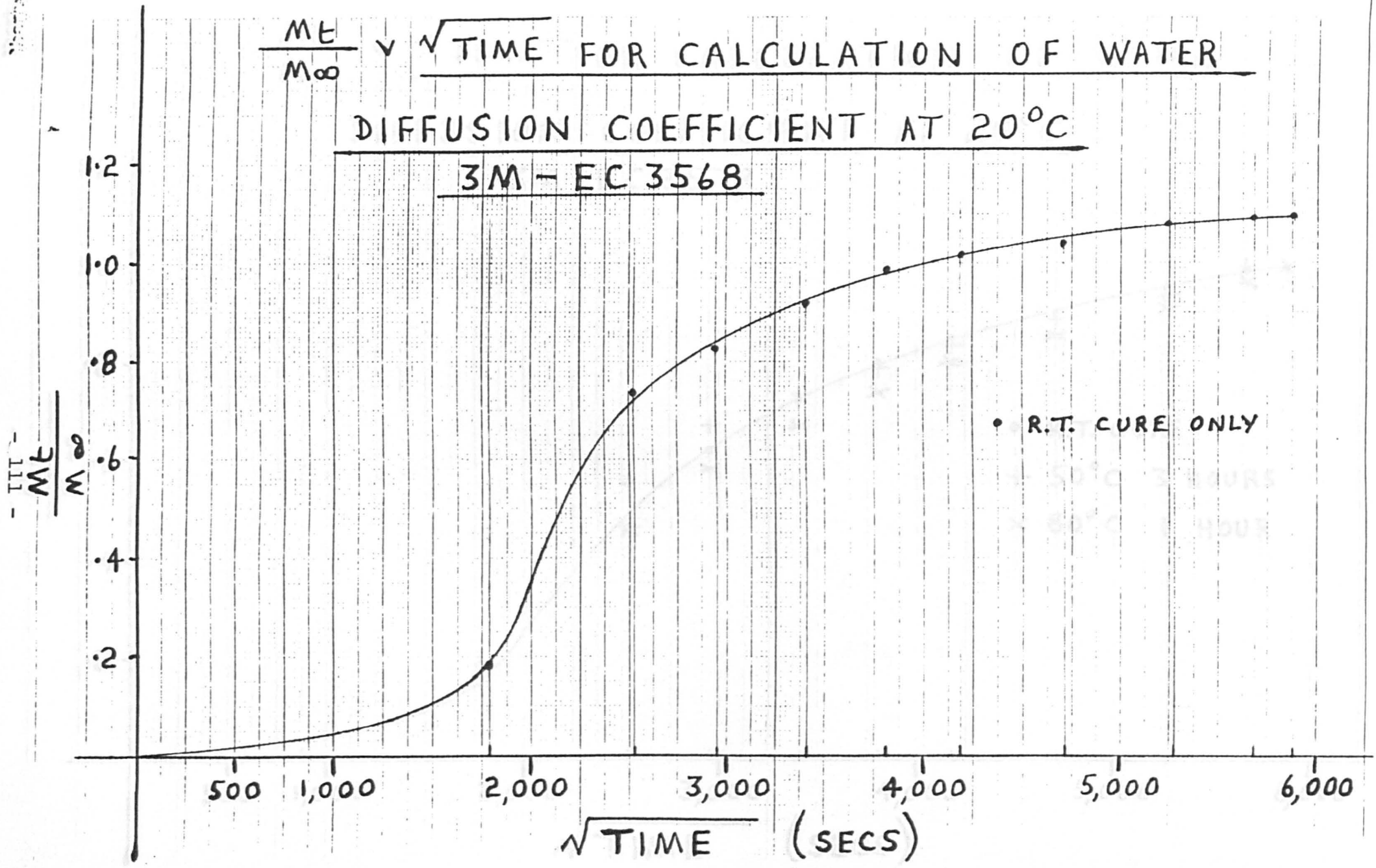

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
3M - EC 3568
1·2
1·0
·8
·6
·4
·2
$\frac{M_t}{M_\infty}$
• R.T. CURE ONLY
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)

FIG: 19

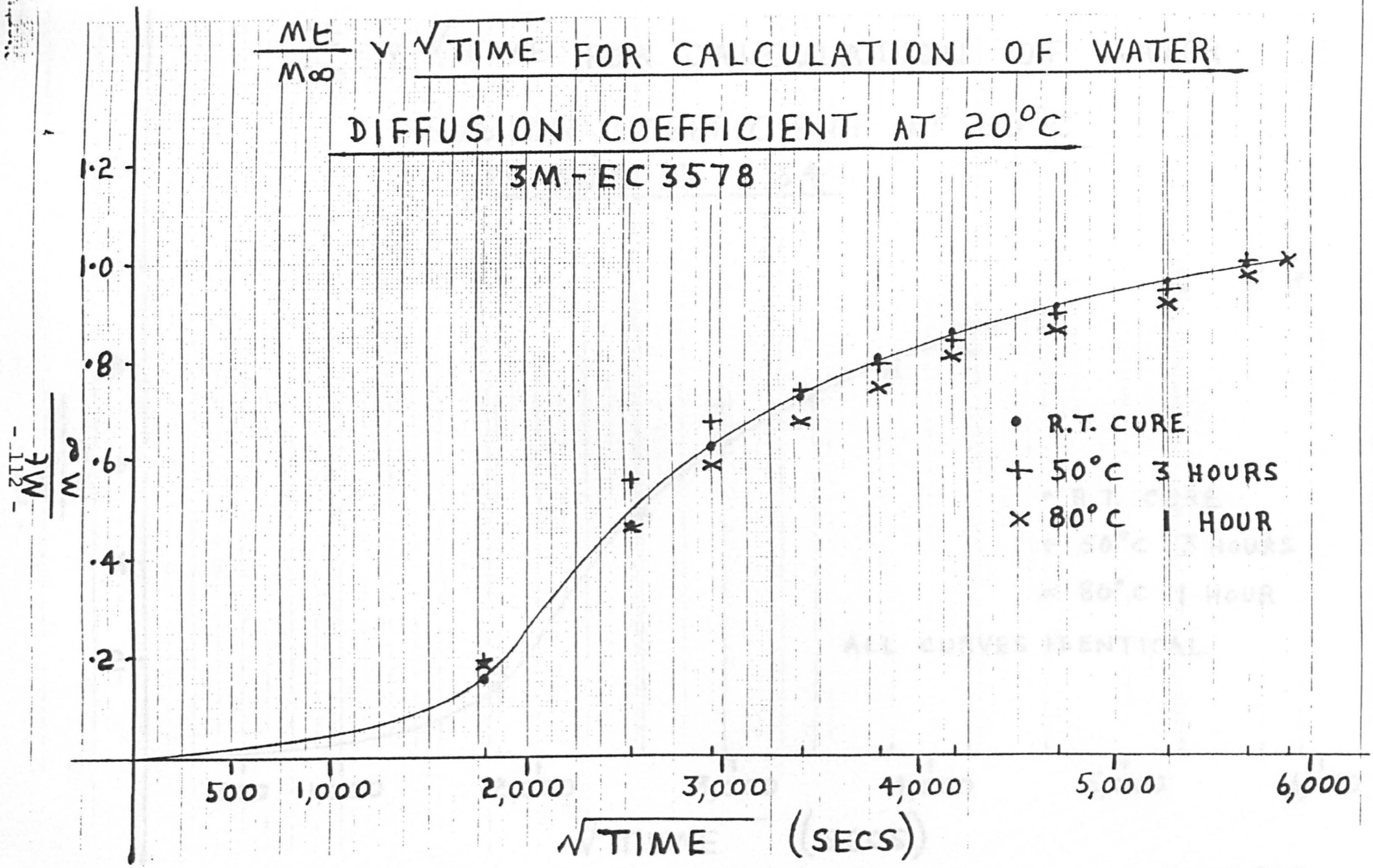

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER DIFFUSION COEFFICIENT AT 20°C
3M-EC 3578
$\frac{M_t}{M_\infty}$
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)
• R.T. CURE
+ 50°C 3 HOURS
× 80°C 1 HOUR

FIG: 20

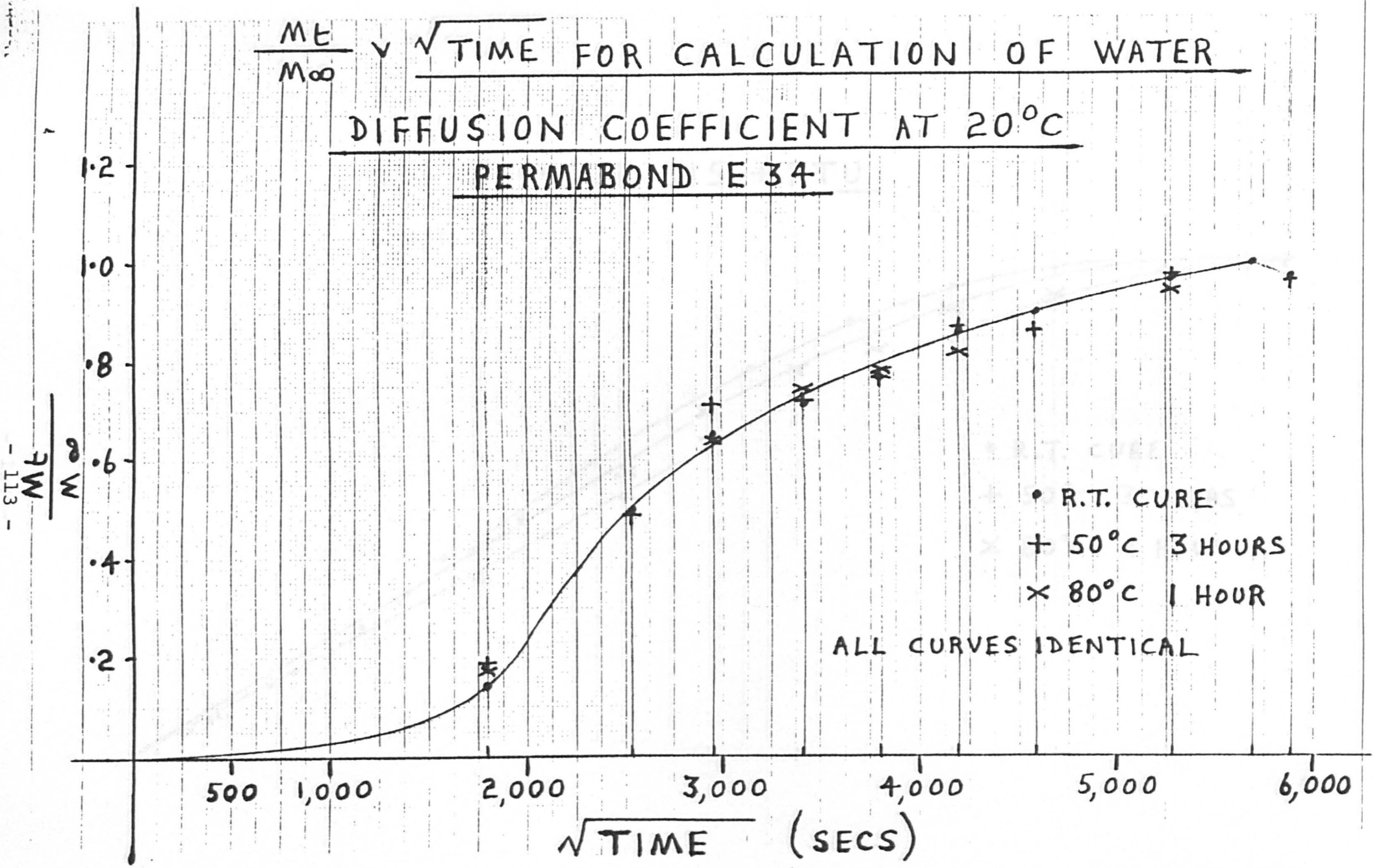

Mt/M∞ √TIME FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
PERMABOND E 34
Mt/M∞
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
√TIME (SECS)
• R.T. CURE
+ 50°C 3 HOURS
× 80°C 1 HOUR
ALL CURVES IDENTICAL

FIG:21

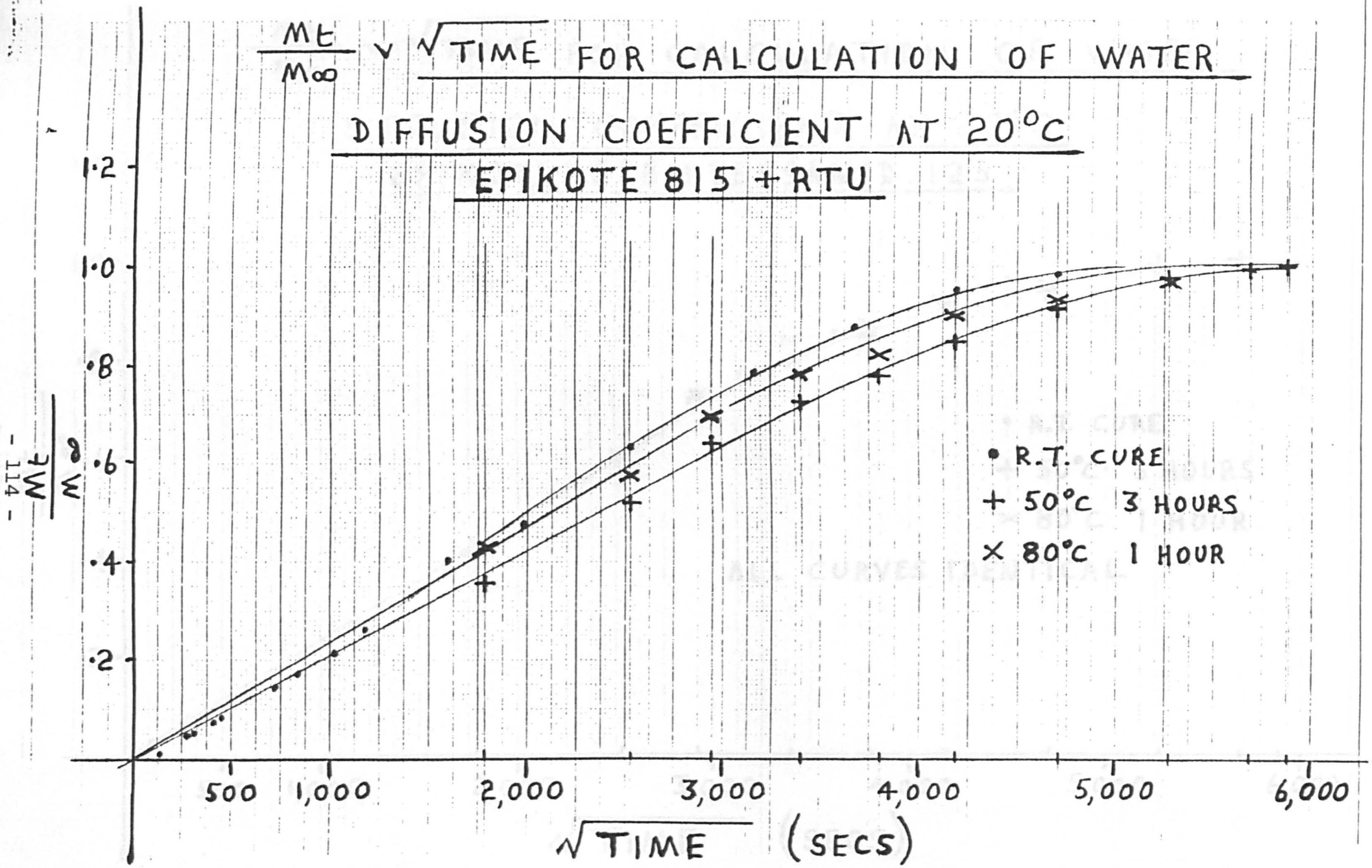

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
EPIKOTE 815 + RTU
$\frac{M_t}{M_\infty}$
1·2
1·0
·8
·6
·4
·2
• R.T. CURE
+ 50°C 3 HOURS
× 80°C 1 HOUR
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)

FIG: 22

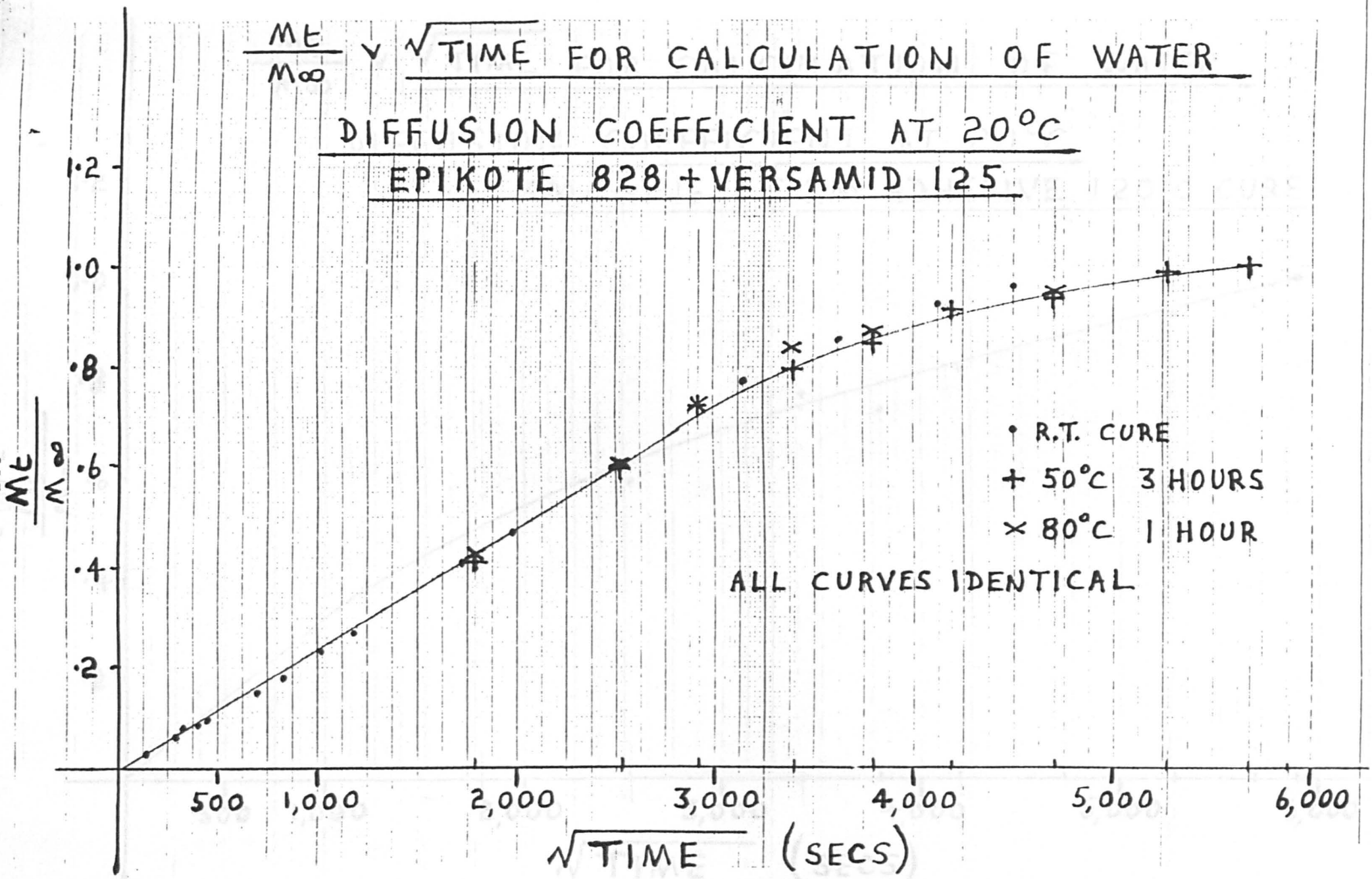

Mt/M∞ v √TIME FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
EPIKOTE 828 + VERSAMID 125
Mt/M∞
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
√TIME (SECS)
• R.T. CURE
+ 50°C 3 HOURS
× 80°C 1 HOUR
ALL CURVES IDENTICAL

FIG: 23

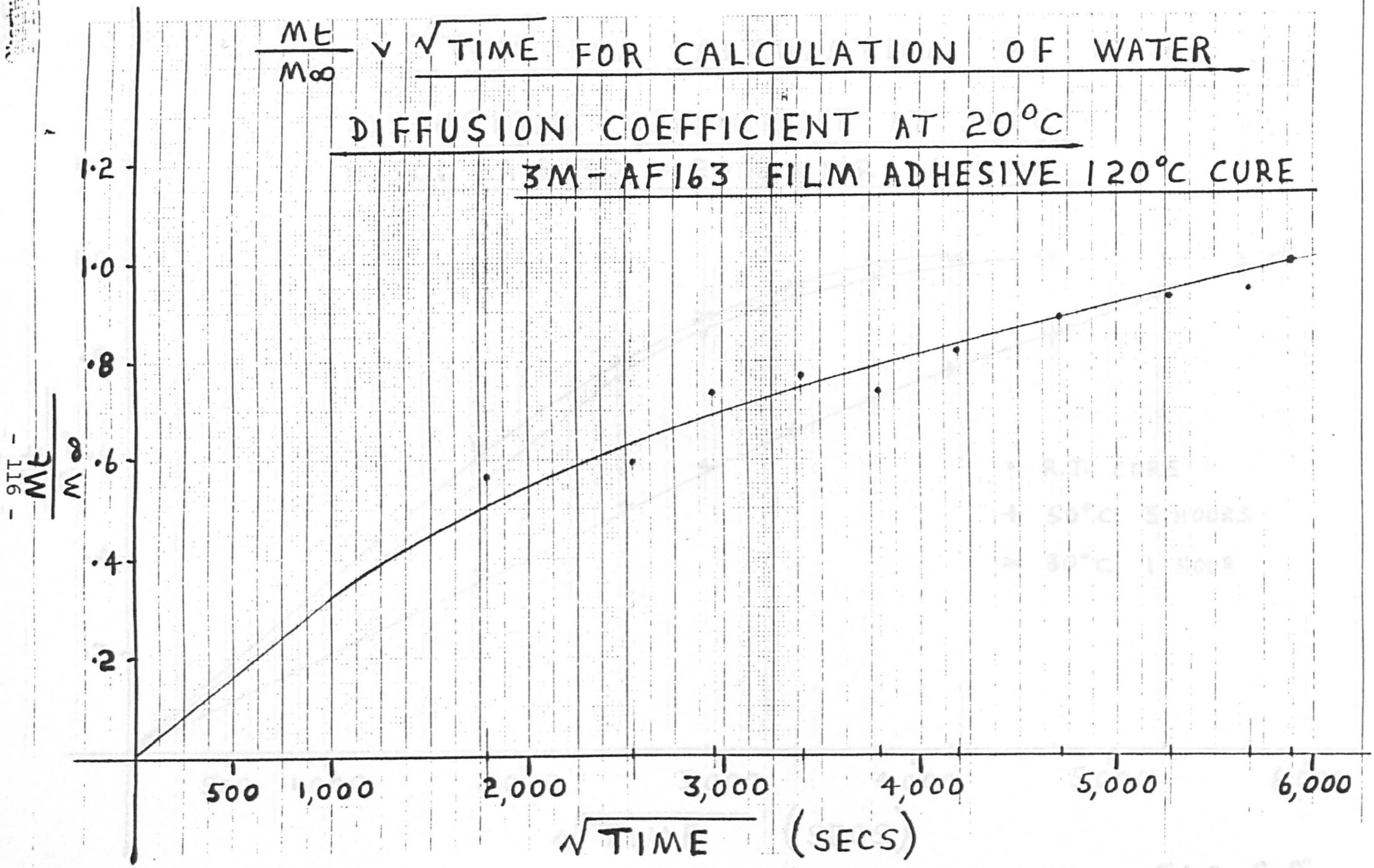

Mt/M∞ v √TIME FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
3M-AF163 FILM ADHESIVE 120°C CURE
Mt/M∞
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
√TIME (SECS)

FIG: 24

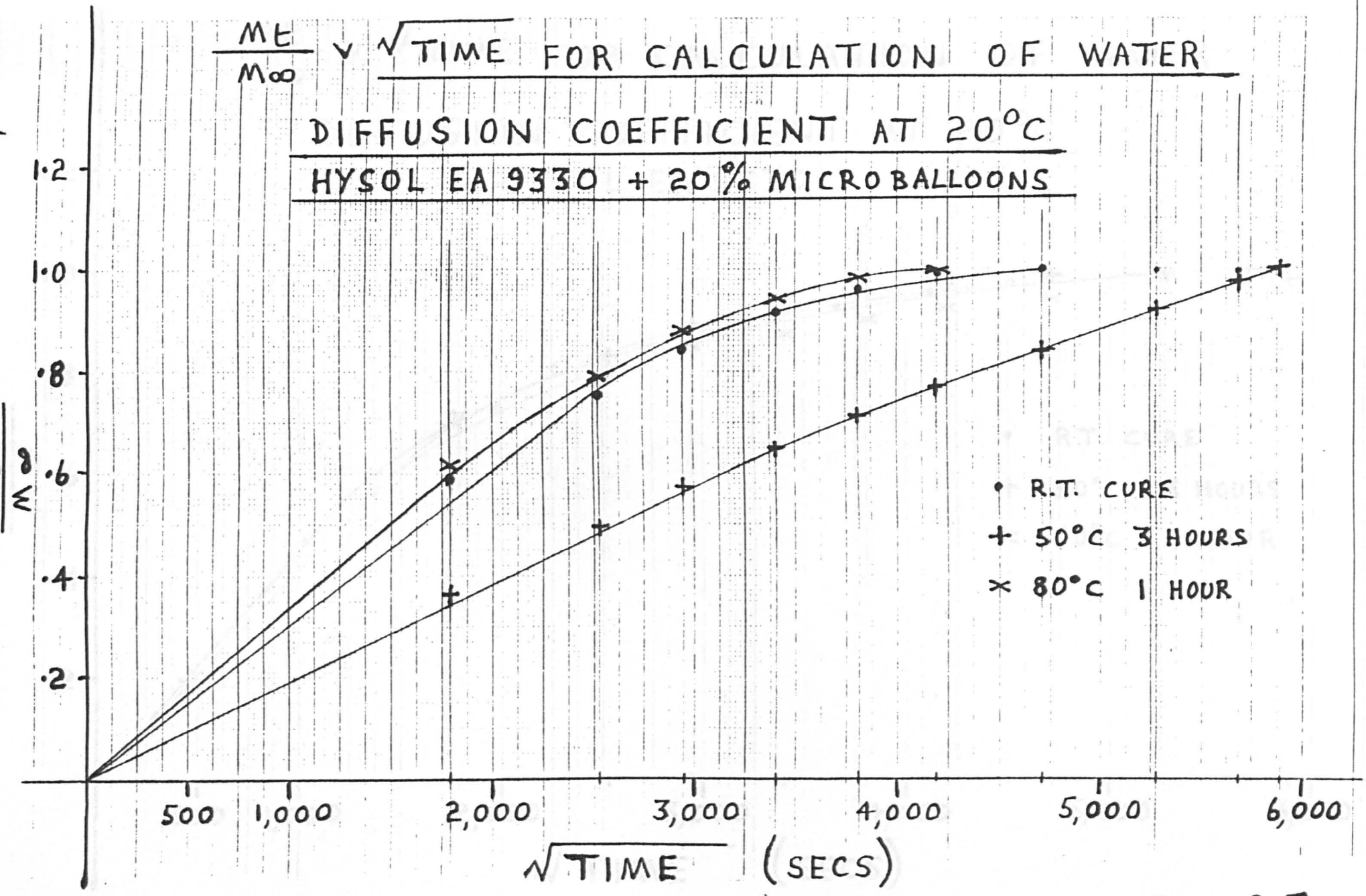

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
HYSOL EA 9330 + 20% MICROBALLOONS
$\frac{M_t}{M_\infty}$
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)
• R.T. CURE
+ 50°C 3 HOURS
× 80°C 1 HOUR

FIG: 25

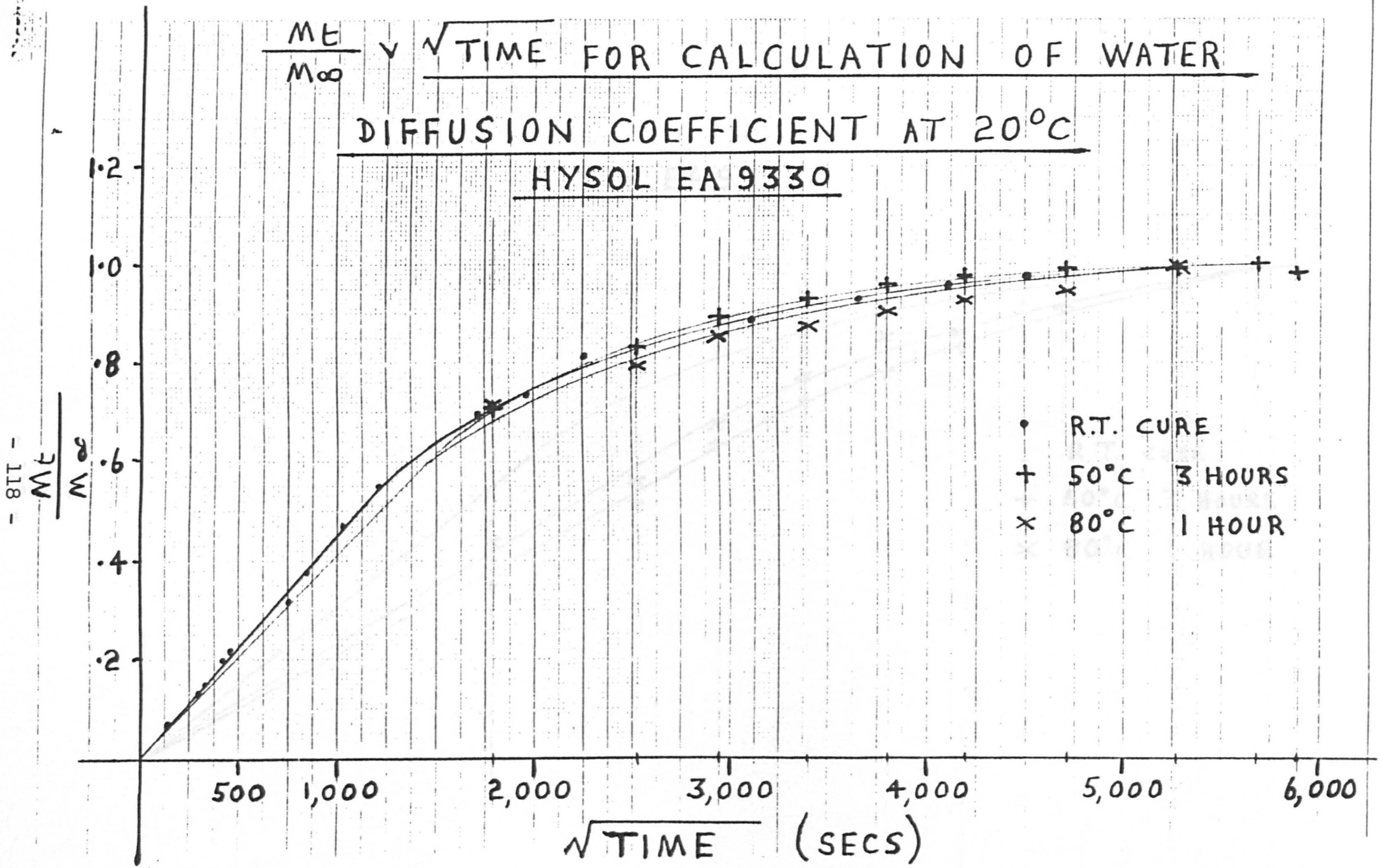

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER DIFFUSION COEFFICIENT AT 20°C
HYSOL EA 9330
$\frac{M_t}{M_\infty}$
1·2
1·0
·8
·6
·4
·2
R.T. CURE
50°C 3 HOURS
80°C 1 HOUR
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)

FIG: 26

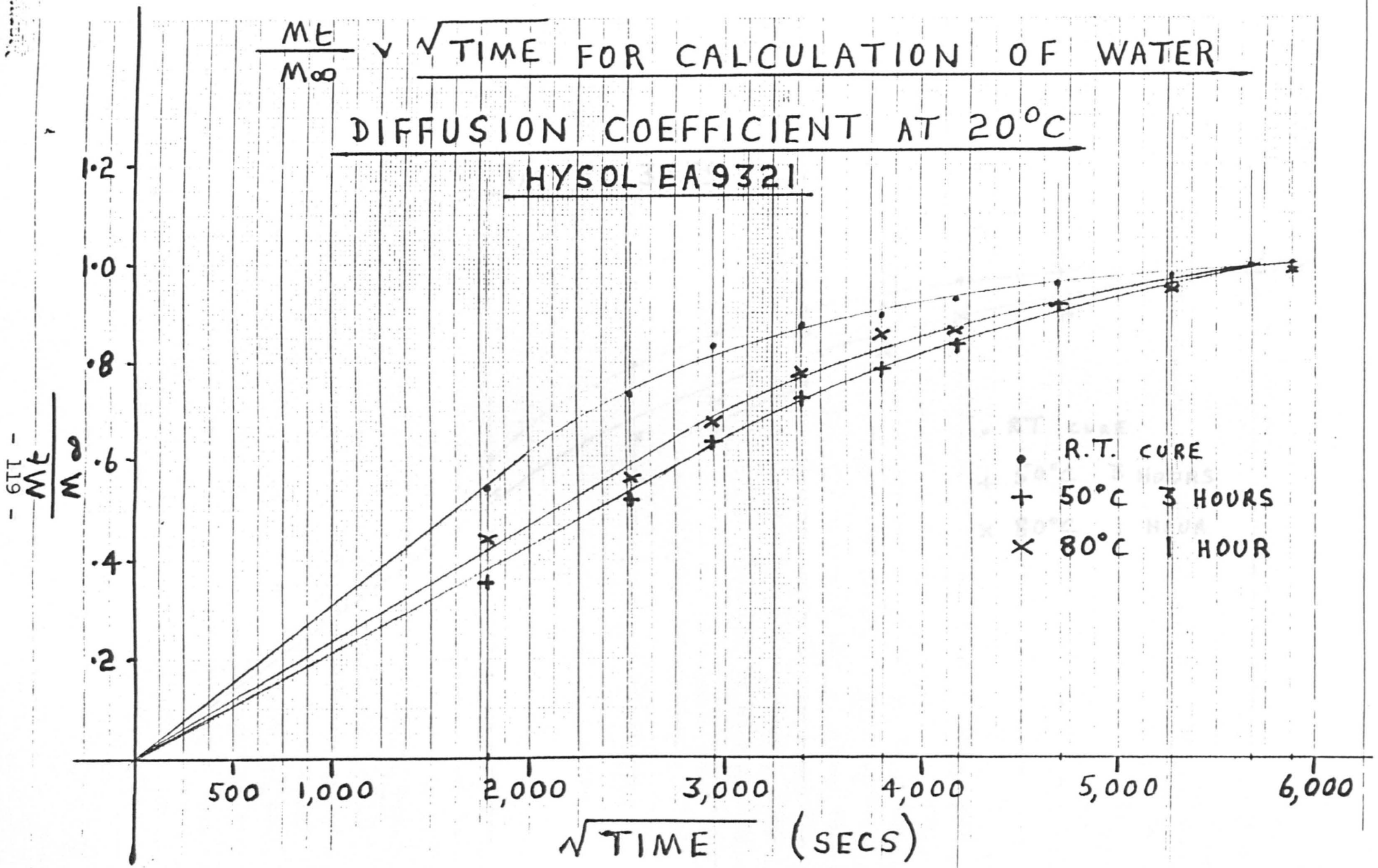

Mt/M∞ v √TIME FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
HYSOL EA 9321
Mt/M∞
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
√TIME (SECS)
R.T. CURE
50°C 3 HOURS
80°C 1 HOUR

FIG: 27

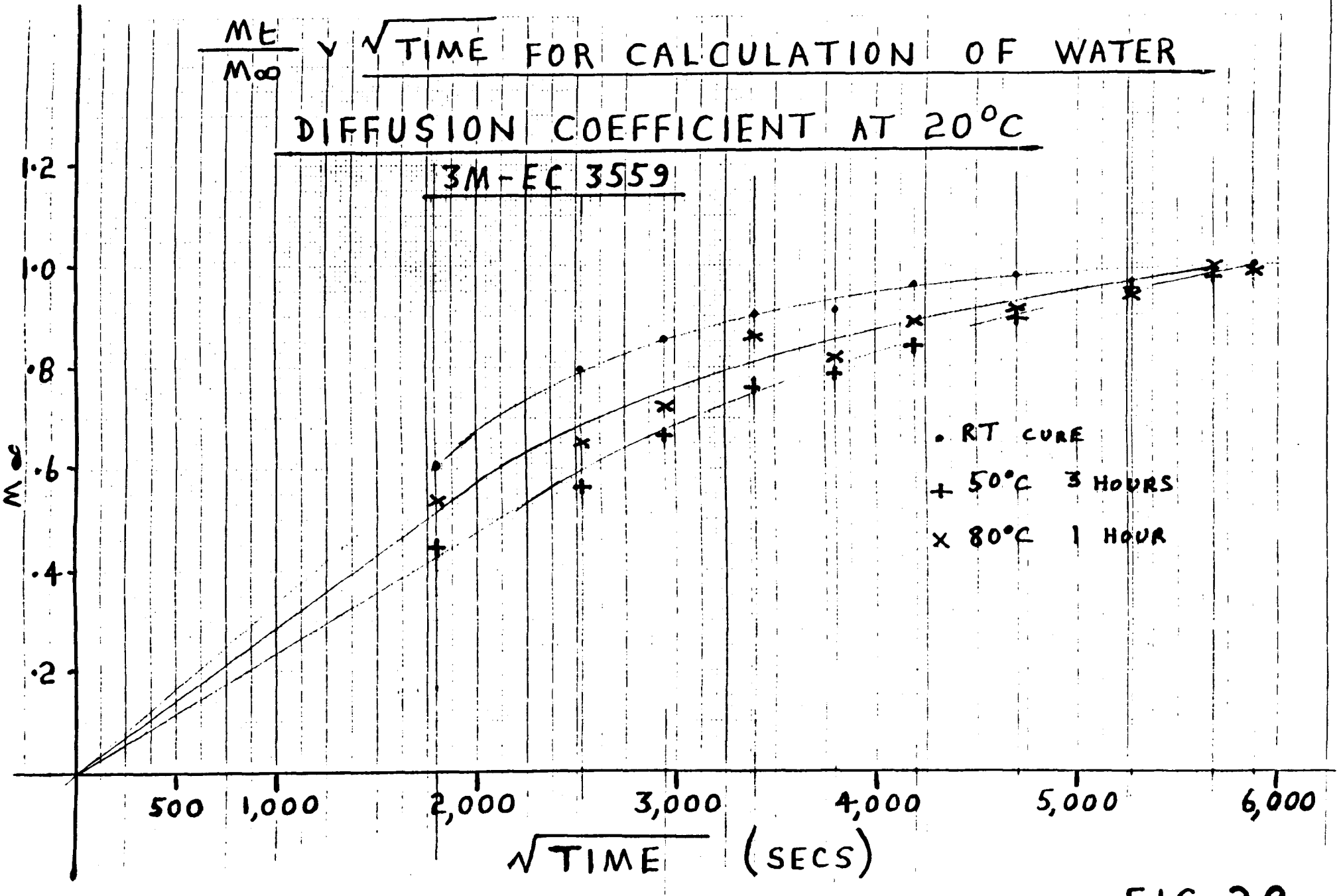

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
3M-EC 3559
1·2
1·0
·8
·6
·4
·2
$\frac{M_t}{M_\infty}$
• RT CURE
+ 50°C 3 HOURS
× 80°C 1 HOUR
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)

FIG: 28

For comparison two film adhesives were also moulded. They were 3M - AF 163 - 2M and CIBA GEIGY Redux 308A. Both gave good results.

Again Diffusion and Solubility Coefficients were obtained, see Figs 29 - 43 (pages 127 - 141) and Table 4A (pages 125 and 126).

Glass transition temperature Tg was obtained, both dry and wet, for each tensile test material and cure temperature by Dr W.W. Wright of RAE, Farnborough. Table 1A (page 13 - 14)

In the last two sections of the work it was again found that in almost every case failure occurred through bubbles. Where bubbles could be seen by holding the specimens up to a bright light the positions were marked, holes drilled and filled with the next mix of adhesive. However, this technique, although generally successful, only served to reduce the size of bubble through which failure occurred. Small bubbles could not be seen and so could not be repaired.

It was considered that Bostik 5435/TM2, Redux 410NA, Hysol 9309.3NA, FR7020 and 3M EC9323 were too viscous to permit full outgassing without a vacuum chamber. However, additional specimens of Redux 501 were made, allowed to outgas for 10 minutes and then poured. Previously a release sheet had been placed on top of the poured adhesive and a plate of metal pushed across the specimen to "squeeze" the specimen down to mould thickness. Unfortunately, this technique resulted in bubbles being trapped and creating voids in the specimen. Because Redux 501 was quite fluid it was found that a specimen could be poured and moulded only a little thicker than the mould. Outgassing continued from the free face. However, specimens made from resins of higher viscosity were thicker and somewhat uneven in thickness compared to the low viscosity resins, which easily found their own level and were fairly even in thickness.

A comparison of tensile strength was made of free surface and "squeezed" specimens where both types were made. Differences were observed for 408 (a little better), 410NA (a little worse) but no significant difference for 501. Numerous bubbles were found in the lower surface of FR7020 in spite of a free upper surface.

Tensile testing proved difficult in two ways:-

1. It was found that the cast adhesive materials were not adequately gripped by the serrated wedge grips fitted to the RDP/Howden EU500 BS testing machine. 320 grade aluminium oxide paper folded over the ends of the specimens was found to be sufficient to provide an adequate grip after release agent had been removed with glasspaper.

2. Having loaded the tensile specimen into the lower grip and taken care to achieve the best possible alignment it was found that on lowering the upper grip the specimen buckled. This occurred because the tapered wedges came down a little further after some load was applied as the abrasive paper gripped the specimen.

The buckling that resulted, fractured one of the brittle specimens and caused the design of "sideplates". The following technique proved successful. Sideplates were made from pieces of aluminium alloy, approx. 50 mm wide, 3 mm thick and shorter than the specimens by the length of one of the ends required to be held in the grips. Abrasive paper was bonded to one face of each sideplate with Redux 410 NA. The specimen was fitted in the lower grip and carefully aligned. Next the upper grip was locked open and lowered to a position found by experiment to be suitable. The sideplates were then positioned carefully to stand on the lower grip and inside the open

upper grip. The upper grip was then released to clamp the sideplates and through them to grip the specimen. This technique was completely successful but prevented observation of the specimen while under load.

This did not matter in the case of brittle specimens because they failed suddenly and without warning. Tougher specimens were tested, as follows, without sideplates. Each specimen was located in the lower grip complete with abrasive paper as before. The upper grip was then released but held open by hand and allowed to progressively clamp onto the upper end of the specimen with the abrasive paper in place. As this caused progressive buckling of the specimen the grip was kept open by hand to prevent the buckle becoming excessive and the machine started. As the slack was taken up by the machine the grip was allowed to fully close on the specimen. This always occurred with some buckling remaining and the specimen finally came under pure tensile load as it straightened out.

The advantage of this technique was that some toughened adhesives, in particular Hysol EA 9309.3NA and 3M-EC.9323 could be seen to craze in several places other than at the point of failure. In some cases bubbles could be seen to elongate before failure.

The toughest adhesive of all those tested, Bostik 5435/TM2 was also sensitive to bubble size. The bubbles were so big that they could easily be measured with a small magnifier. A plot of failing load v bubble size showed a clear relationship and a calculation of stress x $\sqrt{\text{bubble}}$ size showed that even such a tough material followed Griffith's equation. No wonder the brittle materials were sensitive to bubbles and flaws too small to see.

A number of materials were tested in tension after various periods of water immersion. The only difference in technique was that these specimens were removed from storage in distilled water, wiped dry and weighed immediately. They were then taken to the testing machine and tested within 30 minutes of removal from the water.

(Text continues on page 152)

TABLE 4A
Phase Two Additional Work

ADHESIVE OR MATRIX RESIN	DIFFUSION COEFFICIENT "D" m .s SOLUBILITY COEFFICIENT "S"					
	RT Cure "D"	RT Cure "S"	50°C Post Cure "D"	50°C Post Cure "S"	80°C Post Cure "D"	80°C Post Cure "S"
REDUX 408	NR	13%	NR	12.4%	NR	7.9%
REDUX 408 +20% REDUX 410NA	3.36^{-14}	11.3%	--	--	--	--
REDUX 408 +40% REDUX 410NA	4.96^{-14}	8.35%	--	--	--	--
REDUX 410NA	1.38^{-13}	4.8%	1.38^{-13}	4.8%	1.38^{-13}	4.95%
REDUX 501	6.02^{-14}	14.2%	1.36^{-13}	19.9%	9.92^{-14}	13.4%
REDUX 501 + 20% REDUX 410NA	3.58^{-14}	15.1%	--	--	--	--
REDUX 501 + 40% REDUX 410NA	3.8^{-14}	15.36%	--	--	--	--
EC9323	1.67^{-13}	9.1%	1.46^{-13}	8.2%	1.64^{-13}	6.8%
BOSTIK 5435/ TM2	NR	10.6%	--	--	--	--
REDUX 308A *	--	--	--	--	2.7^{-13}	3.6%
EA9309.3NA	1.14^{-13}	5%	1.14^{-13}	4.6%	1.07^{-13}	4.4%
PERMABOND E37	2.28^{-13}	2.8%	--	--	--	--
PERMABOND E38 **	--	--	1.07^{-13}	15.9%	--	--

TABLE 4A
Phase Two Additional Work

ADHESIVE OR MATRIX RESIN	DIFFUSION COEFFICIENT "D" m .s SOLUBILITY COEFFICIENT "S"					
	RT Cure "D"	RT Cure "S"	50°C Post Cure "D"	50°C Post Cure "S"	80°C Post Cure "D"	80°C Post Cure "S"
REDUX 408 #	NR	11.4%	--	--	--	--
REDUX 410 #	1.38^{-13}	4.88%	--	--	--	--
REDUX 501 #	6.02^{-14}	17.6%	--	--	--	--
828 + RTU	7.14^{-14}	4.6%	7.14^{-14}	3.6% +	6.45^{-14}	2.3% ++
FR 7020	6.18^{-14}	9.3%	6.18^{-14}	8.8%	6.18^{-14}	7.8%
REDUX 775 * 100 PSI CURE	--	--	--	--	7.36^{-14}	46.4%
REDUX 775 * ZERO PSI CURE	--	--	--	--	7.59^{-13}	111%
815 + RTU ***	--	--	--	--	9.26^{-14}	3.4%

* 170°C Cure
** 60°C Cure
*** 120°C Cure
\+ 60°C Post Cure
++ 100°C Post Cure
\# Free Surface
NR No result - A sigmoidal Curve

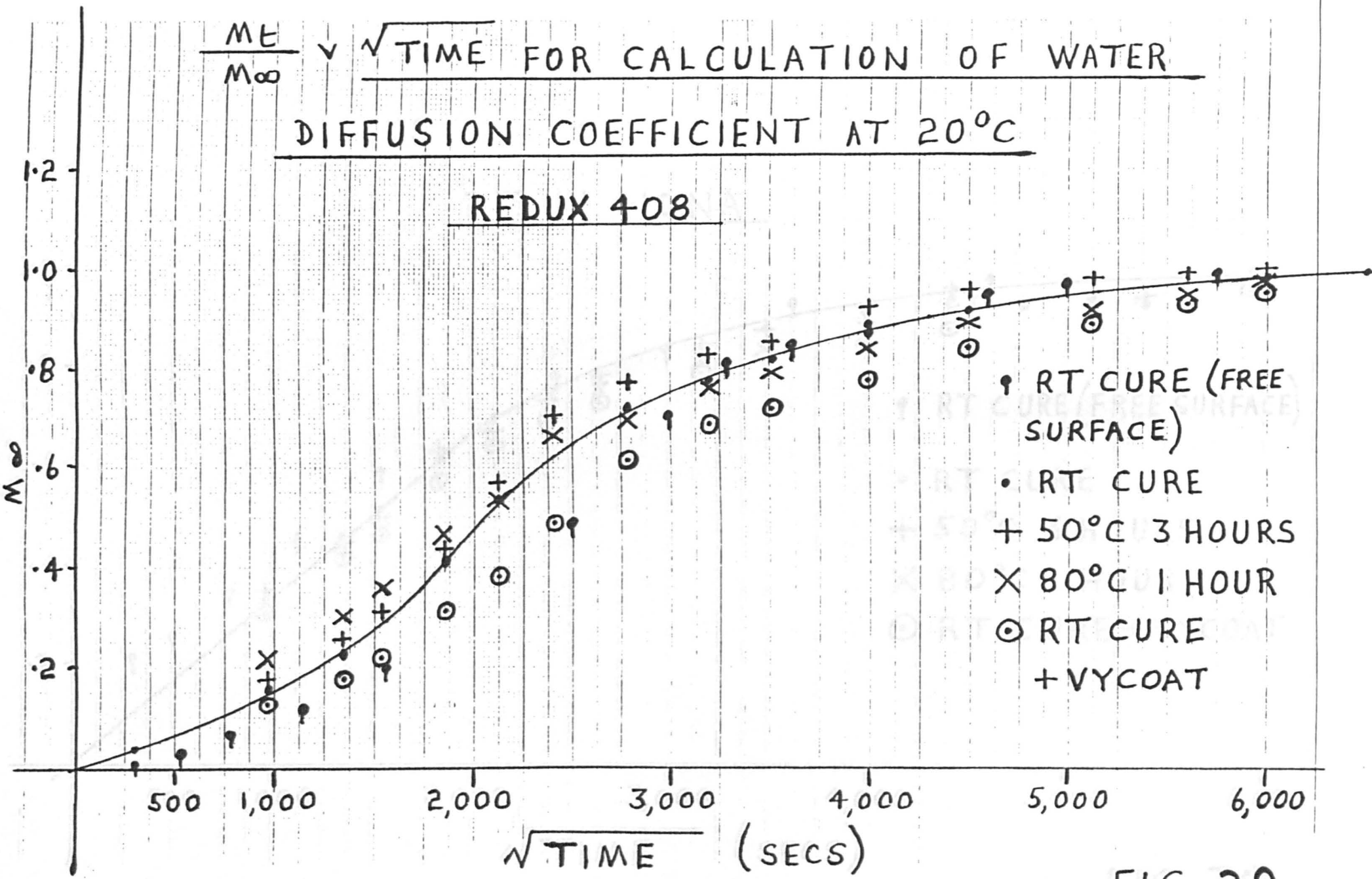

Mt/M∞ √TIME FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
REDUX 408
Mt/M∞
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
√TIME (SECS)
RT CURE (FREE SURFACE)
RT CURE
+ 50°C 3 HOURS
× 80°C 1 HOUR
⊙ RT CURE + VYCOAT

FIG: 29

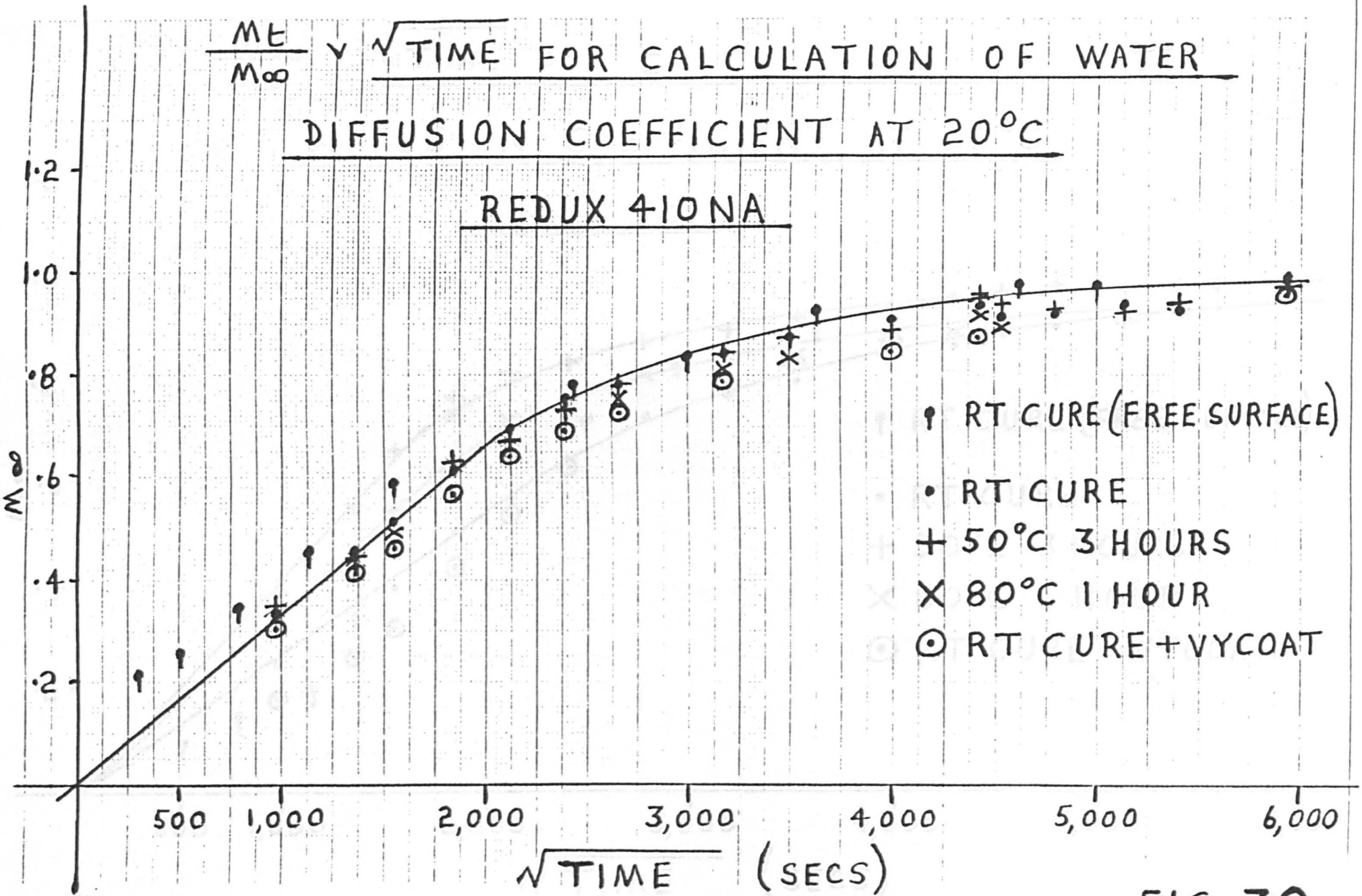

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
REDUX 410NA
$\frac{M_t}{M_\infty}$
1·2
1·0
·8
·6
·4
·2
RT CURE (FREE SURFACE)
RT CURE
+ 50°C 3 HOURS
× 80°C 1 HOUR
⊙ RT CURE + VYCOAT
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)

FIG: 30

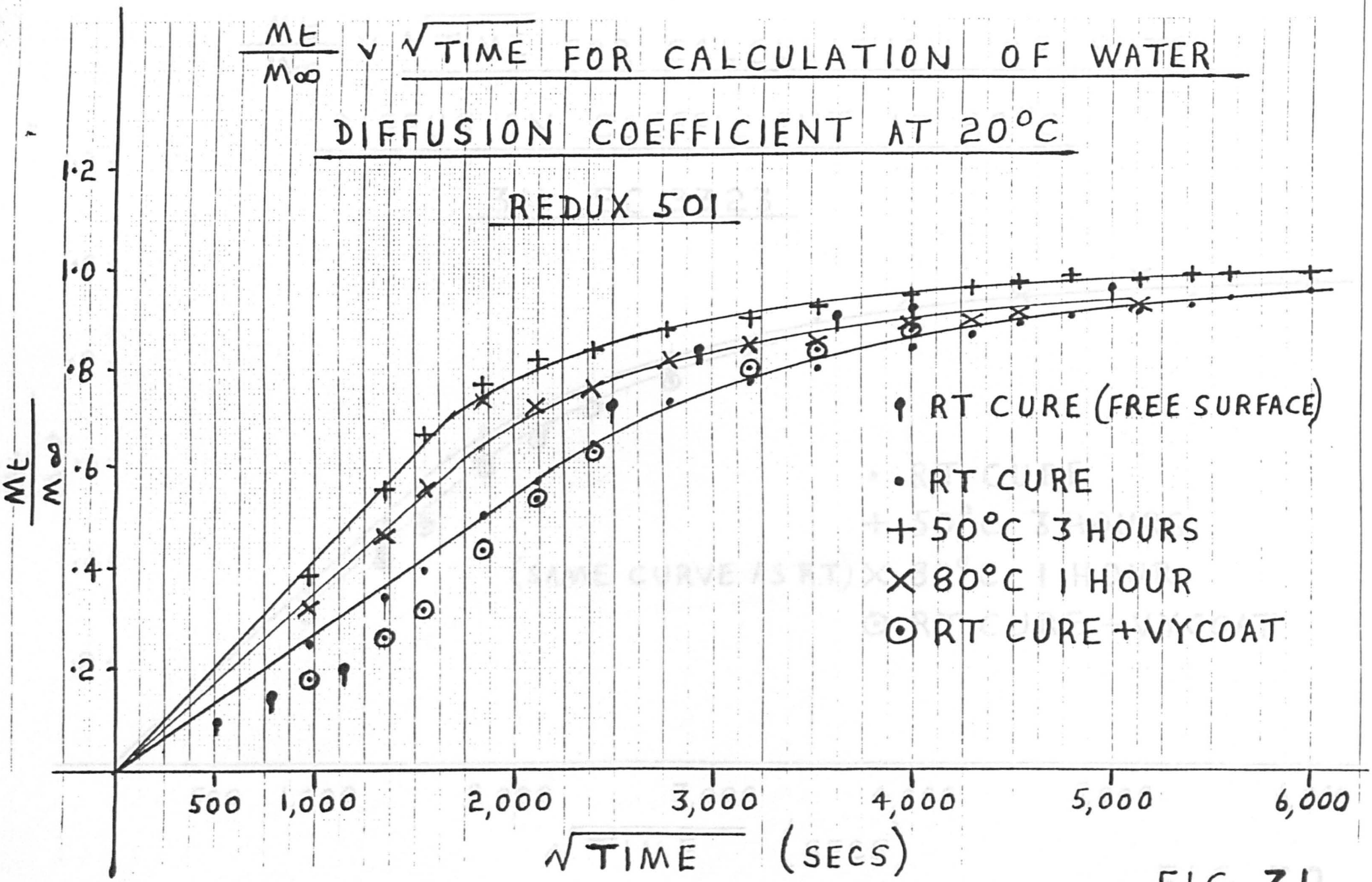

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER DIFFUSION COEFFICIENT AT 20°C
REDUX 501
$\frac{M_t}{M_\infty}$
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)
RT CURE (FREE SURFACE)
RT CURE
+ 50°C 3 HOURS
× 80°C 1 HOUR
⊙ RT CURE + VYCOAT

FIG: 31

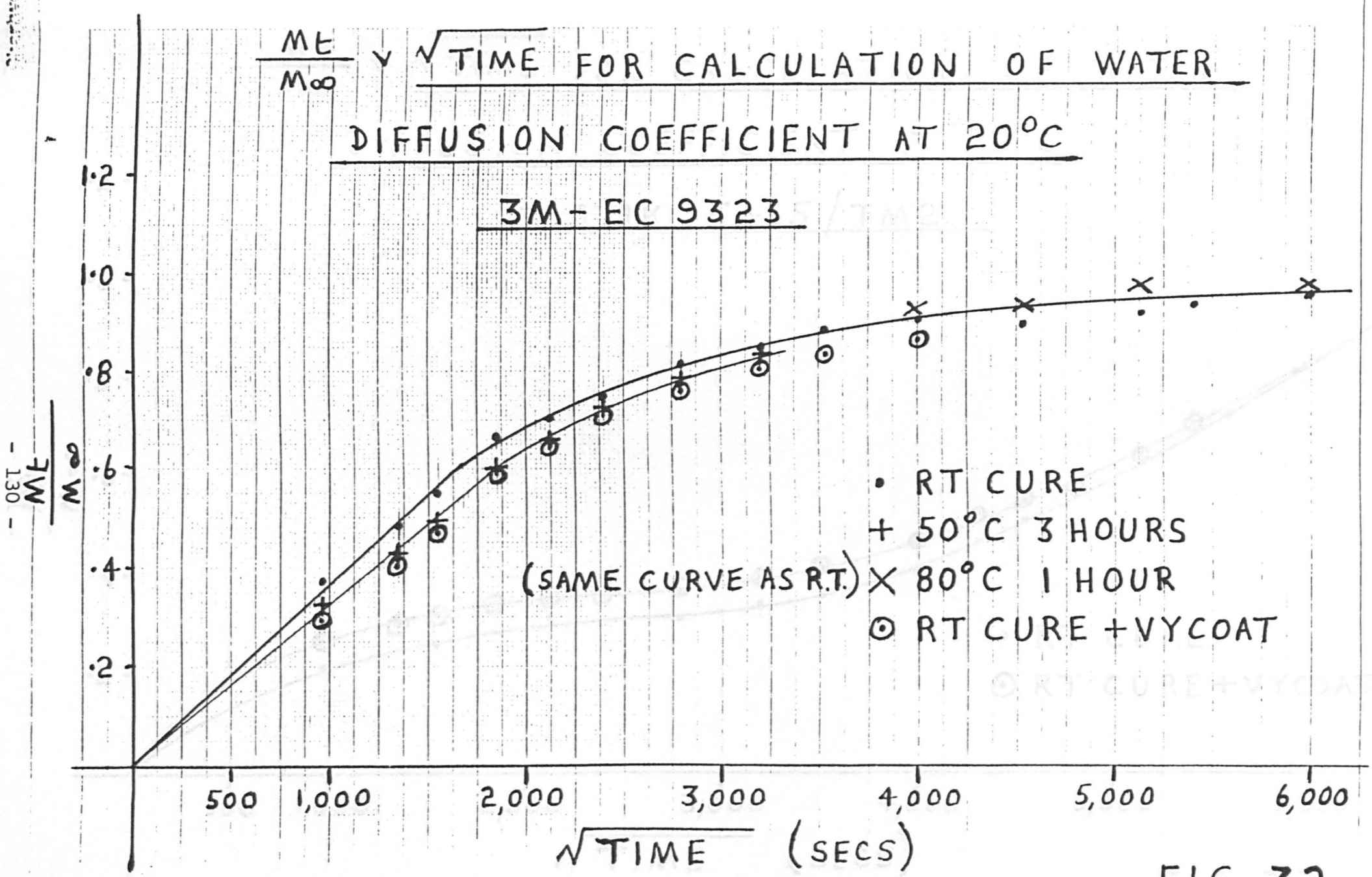

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
3M-EC 9323
$\frac{M_t}{M_\infty}$
1·2
1·0
·8
·6
·4
·2
• RT CURE
+ 50°C 3 HOURS
(SAME CURVE AS R.T.) × 80°C 1 HOUR
⊙ RT CURE + VYCOAT
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)

FIG: 32

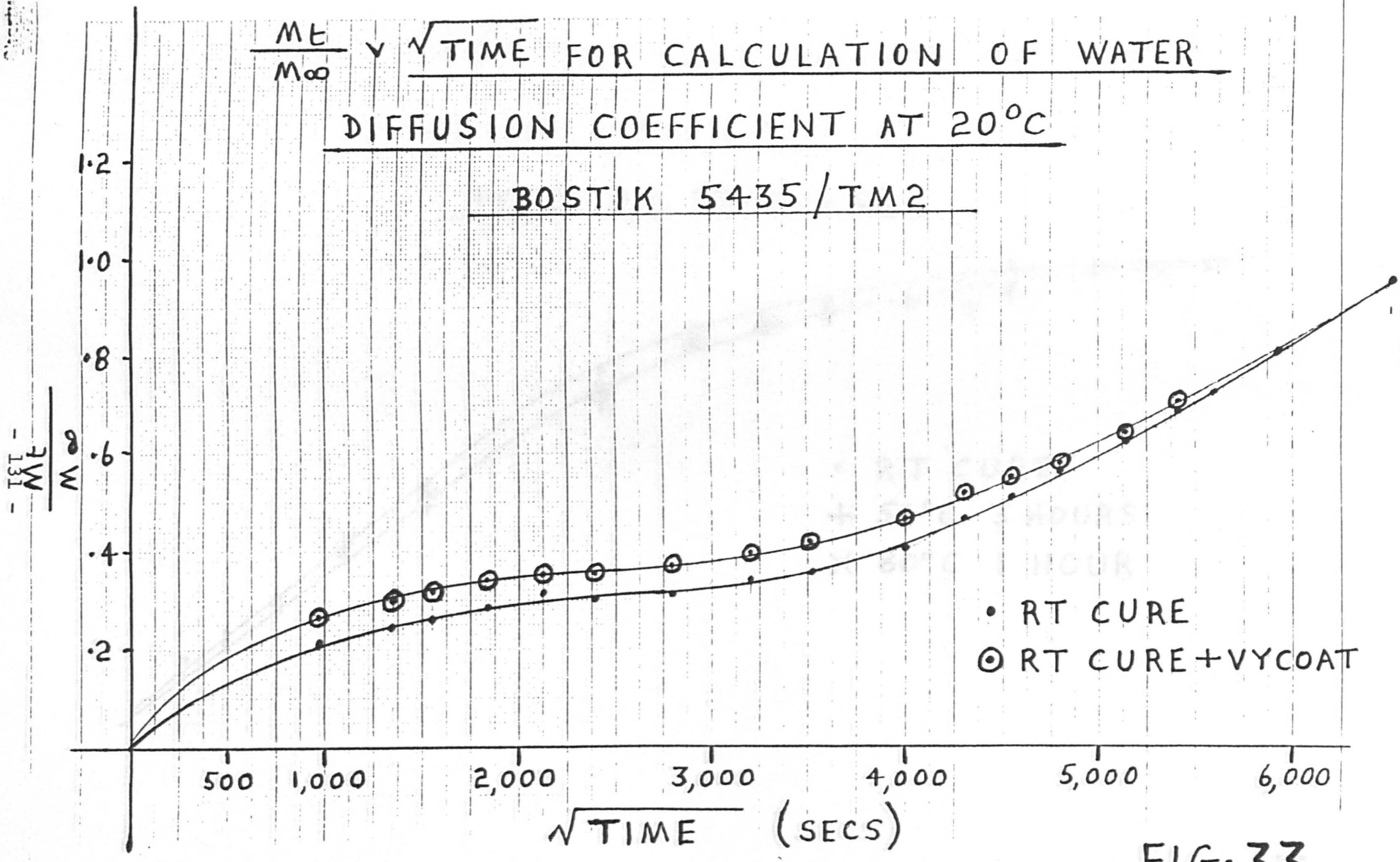

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
BOSTIK 5435/TM2
$\frac{M_t}{M_\infty}$
·2
·4
·6
·8
1·0
1·2
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)
• RT CURE
⊙ RT CURE + VYCOAT

FIG: 33

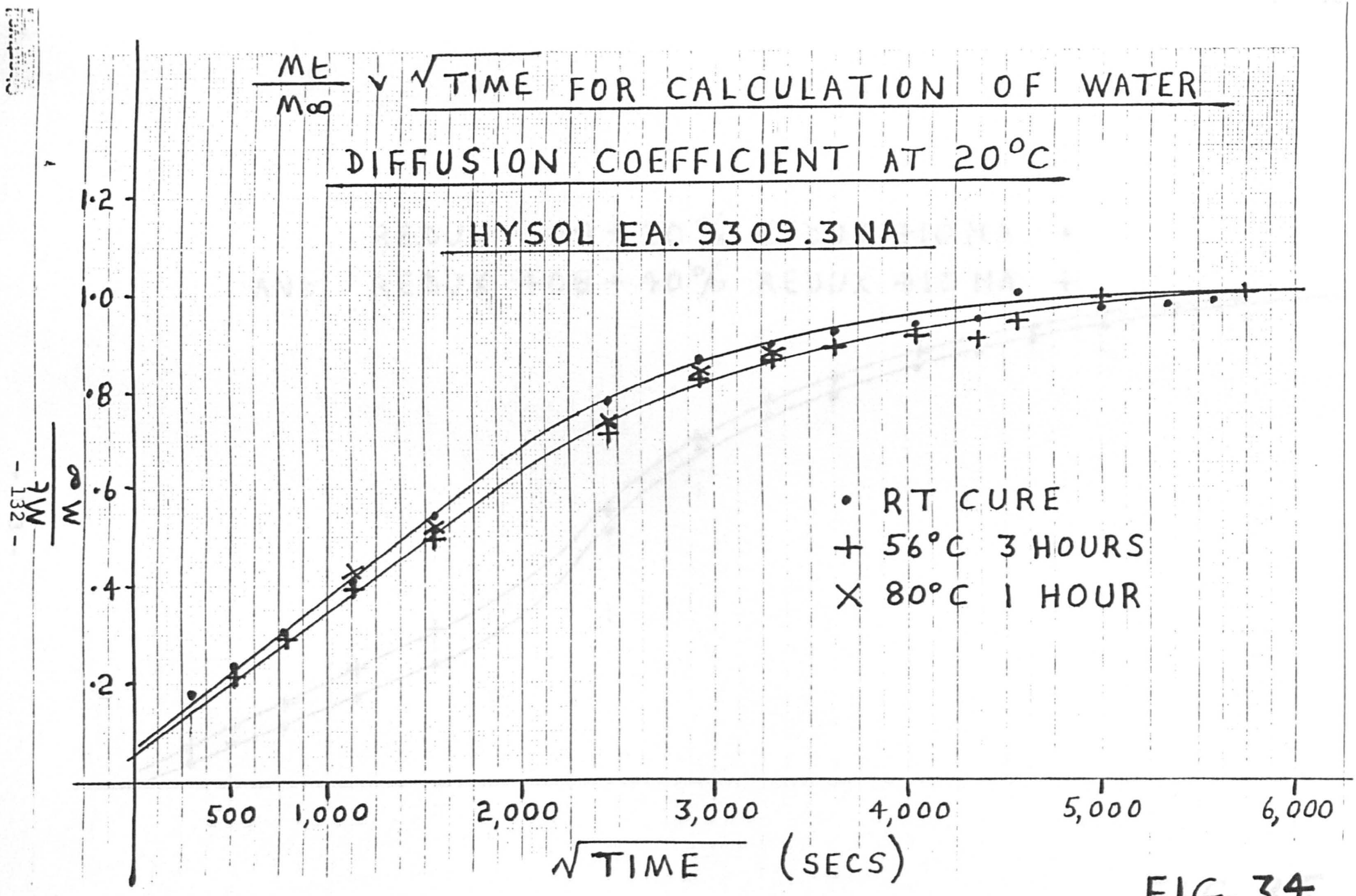

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
HYSOL EA. 9309.3 NA
$\frac{M_t}{M_\infty}$
1·2
1·0
·8
·6
·4
·2
• RT CURE
+ 56°C 3 HOURS
× 80°C 1 HOUR
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)

FIG: 34

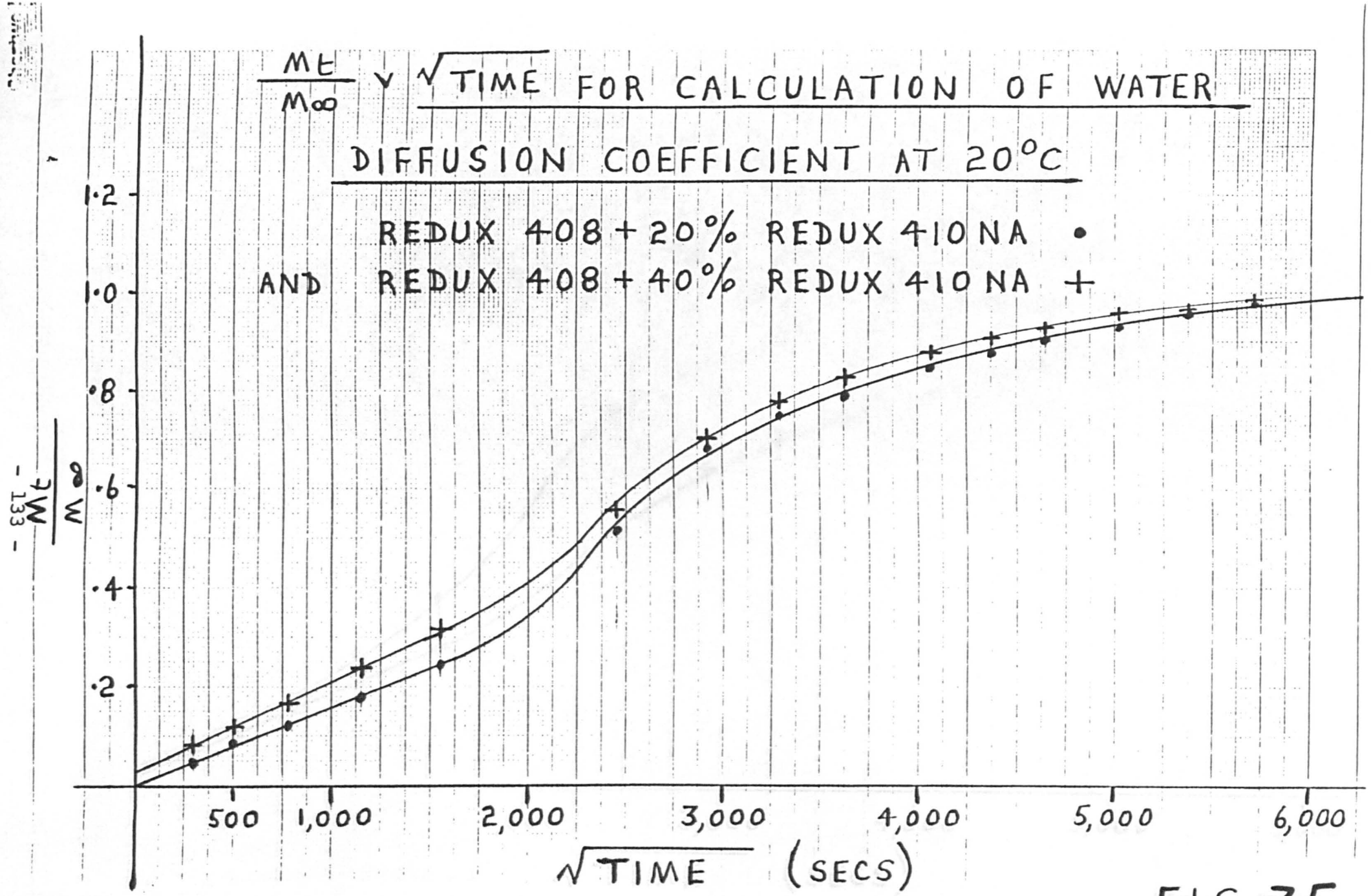

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER DIFFUSION COEFFICIENT AT 20°C
REDUX 408 + 20% REDUX 410 NA •
AND REDUX 408 + 40% REDUX 410 NA +
$\frac{M_t}{M_\infty}$
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)

FIG:35

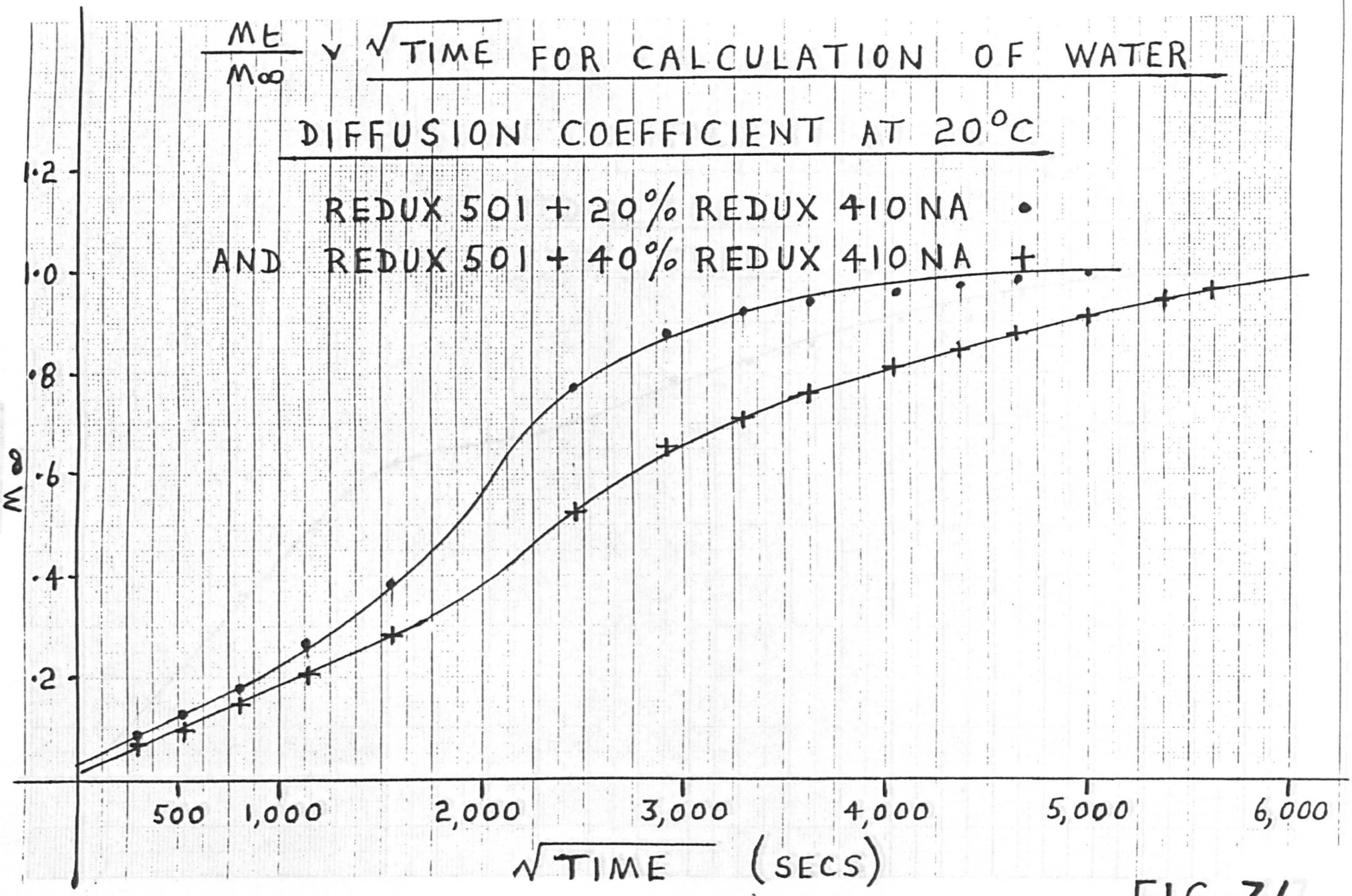

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
REDUX 501 + 20% REDUX 410 NA •
AND REDUX 501 + 40% REDUX 410 NA +
$\frac{M_t}{M_\infty}$
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)

FIG: 36

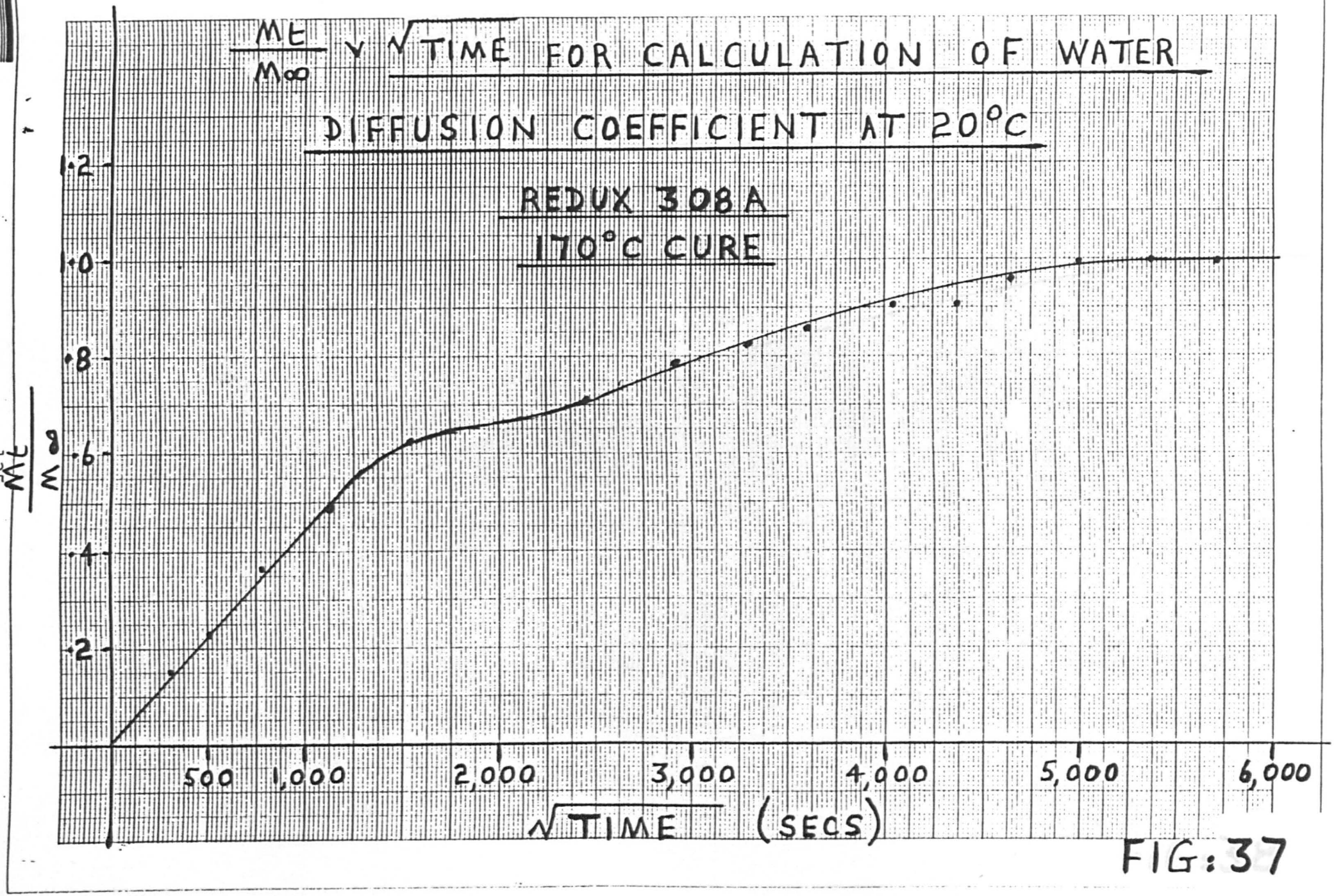

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER DIFFUSION COEFFICIENT AT 20°C
REDUX 308A
170°C CURE
$\frac{M_t}{M_\infty}$
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)

FIG: 37

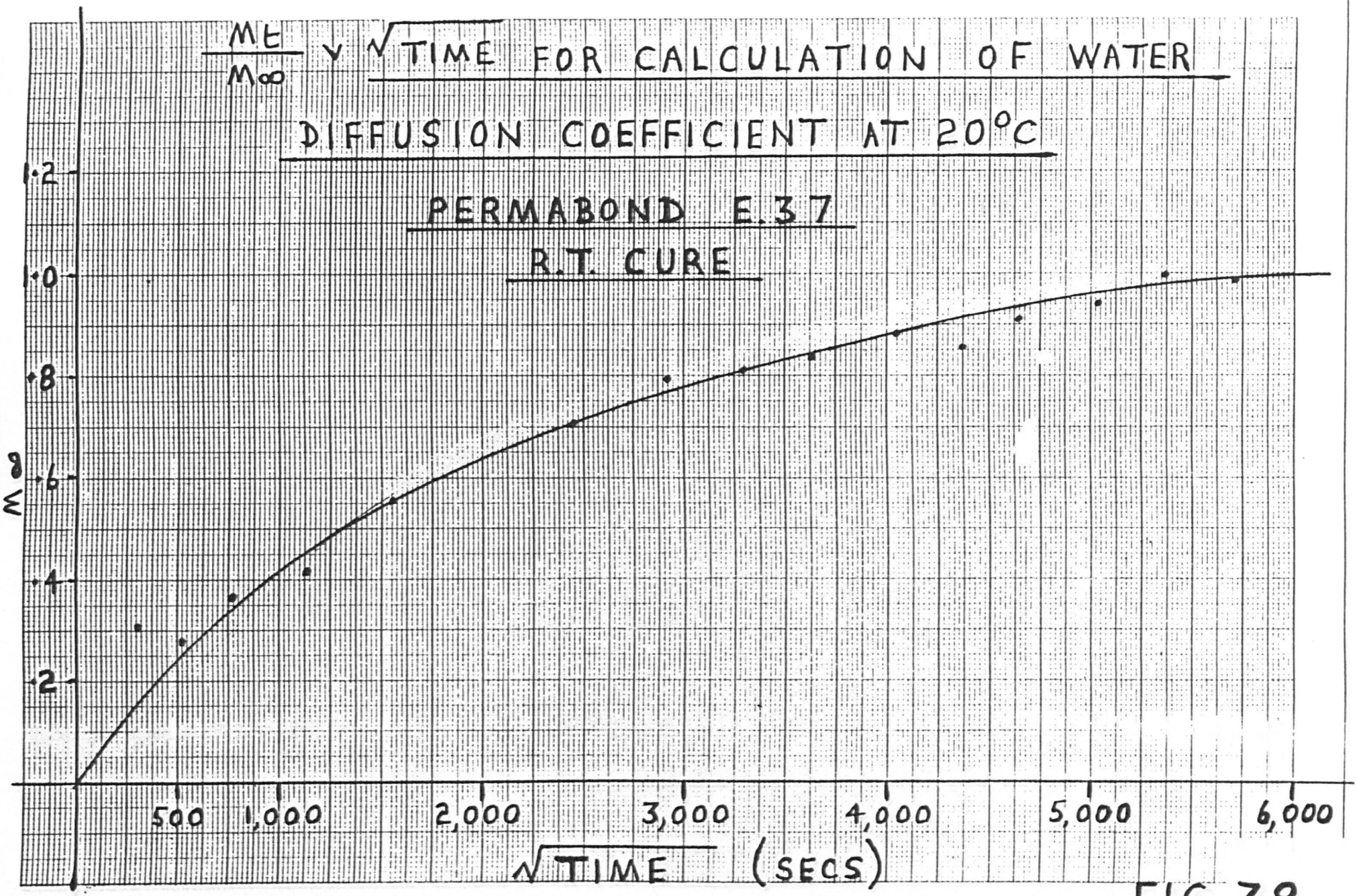

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
PERMABOND E.37
R.T. CURE
$\frac{M_t}{M_\infty}$
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)

FIG:38

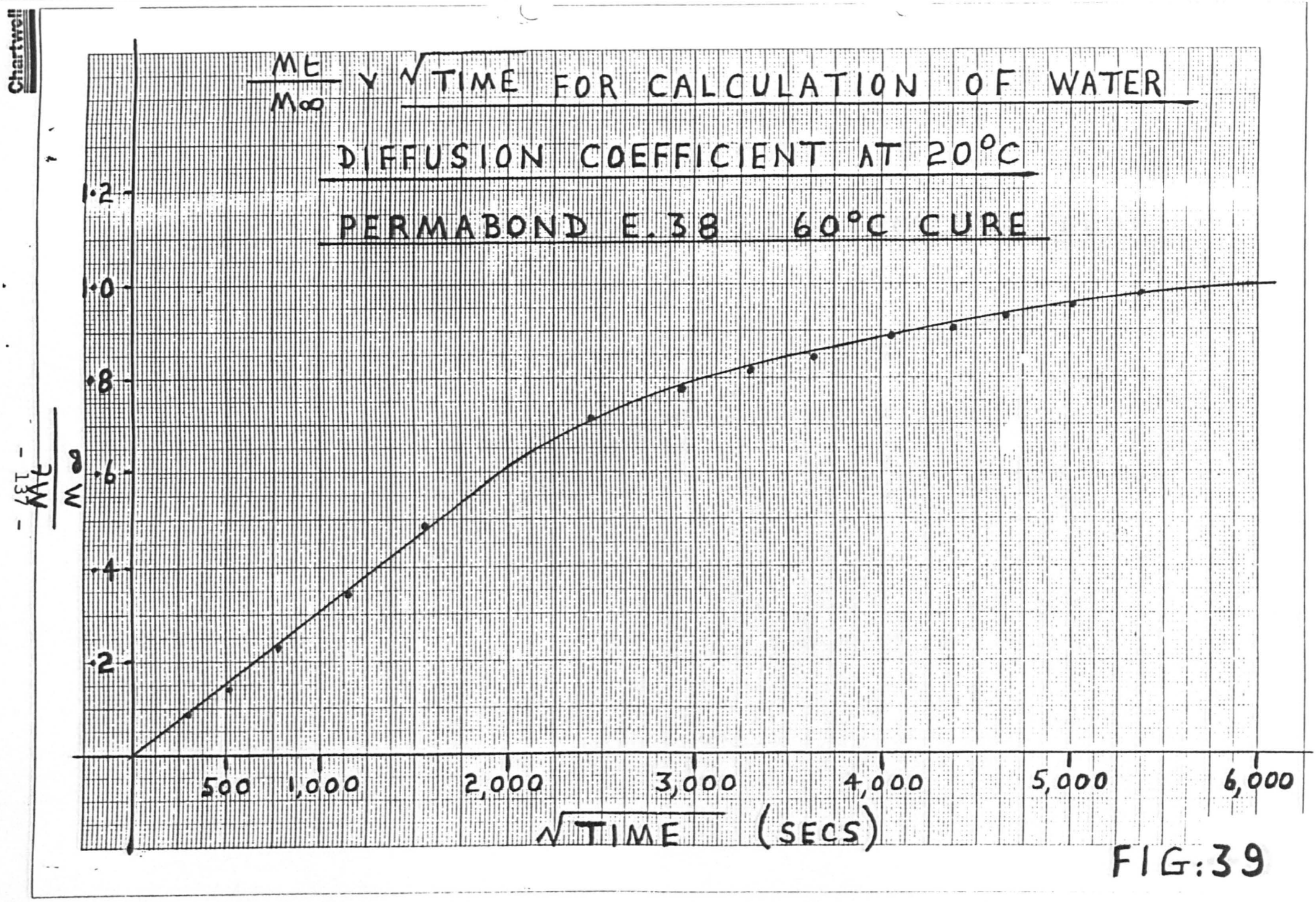

$\frac{M_t}{M_\infty}$ V $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER DIFFUSION COEFFICIENT AT 20°C
PERMABOND E.38 60°C CURE
$\frac{M_t}{M_\infty}$
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)

FIG:39

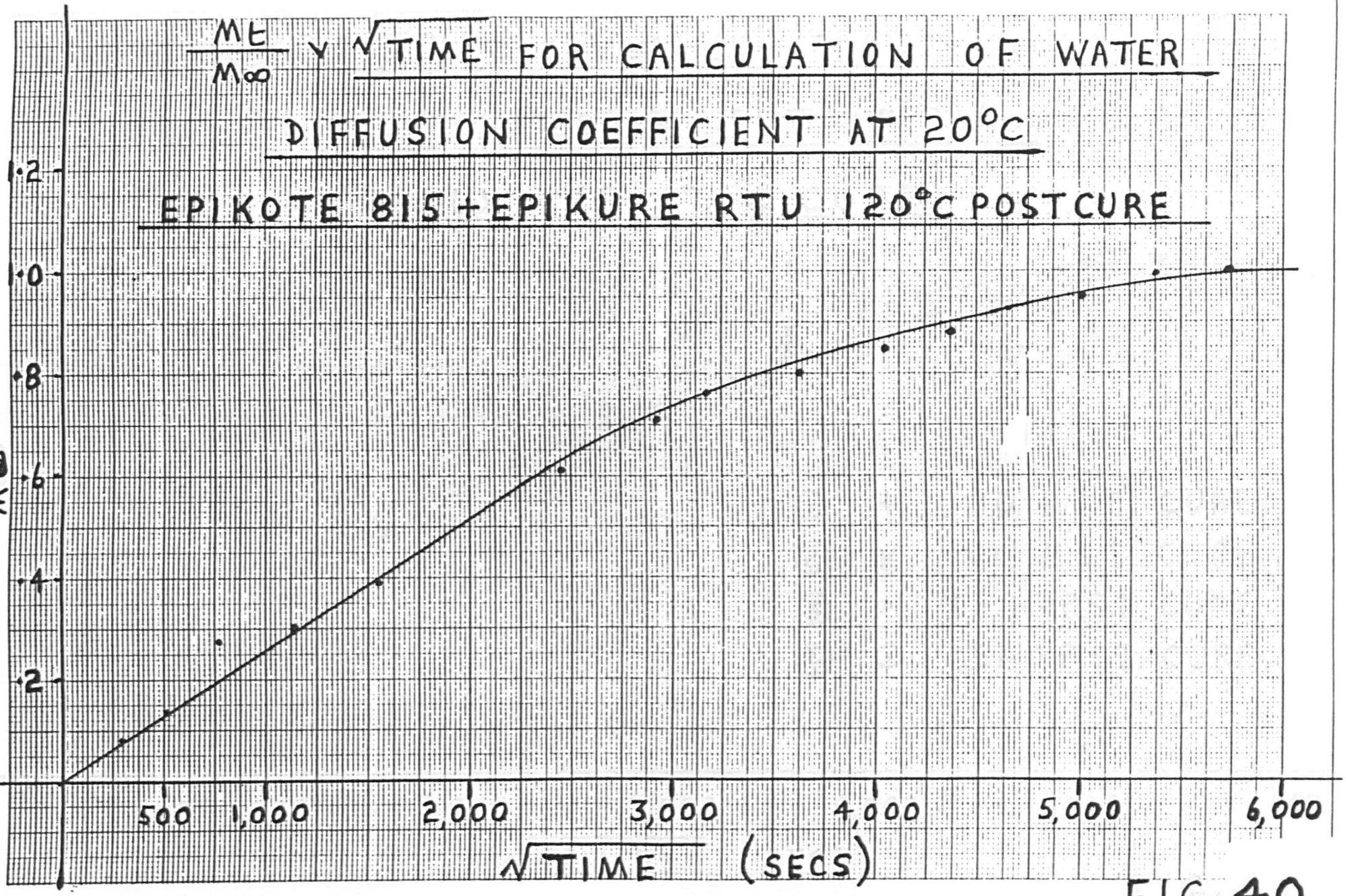

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER DIFFUSION COEFFICIENT AT 20°C
EPIKOTE 815 + EPIKURE RTU 120°C POSTCURE
$\frac{M_t}{M_\infty}$
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)

FIG: 40

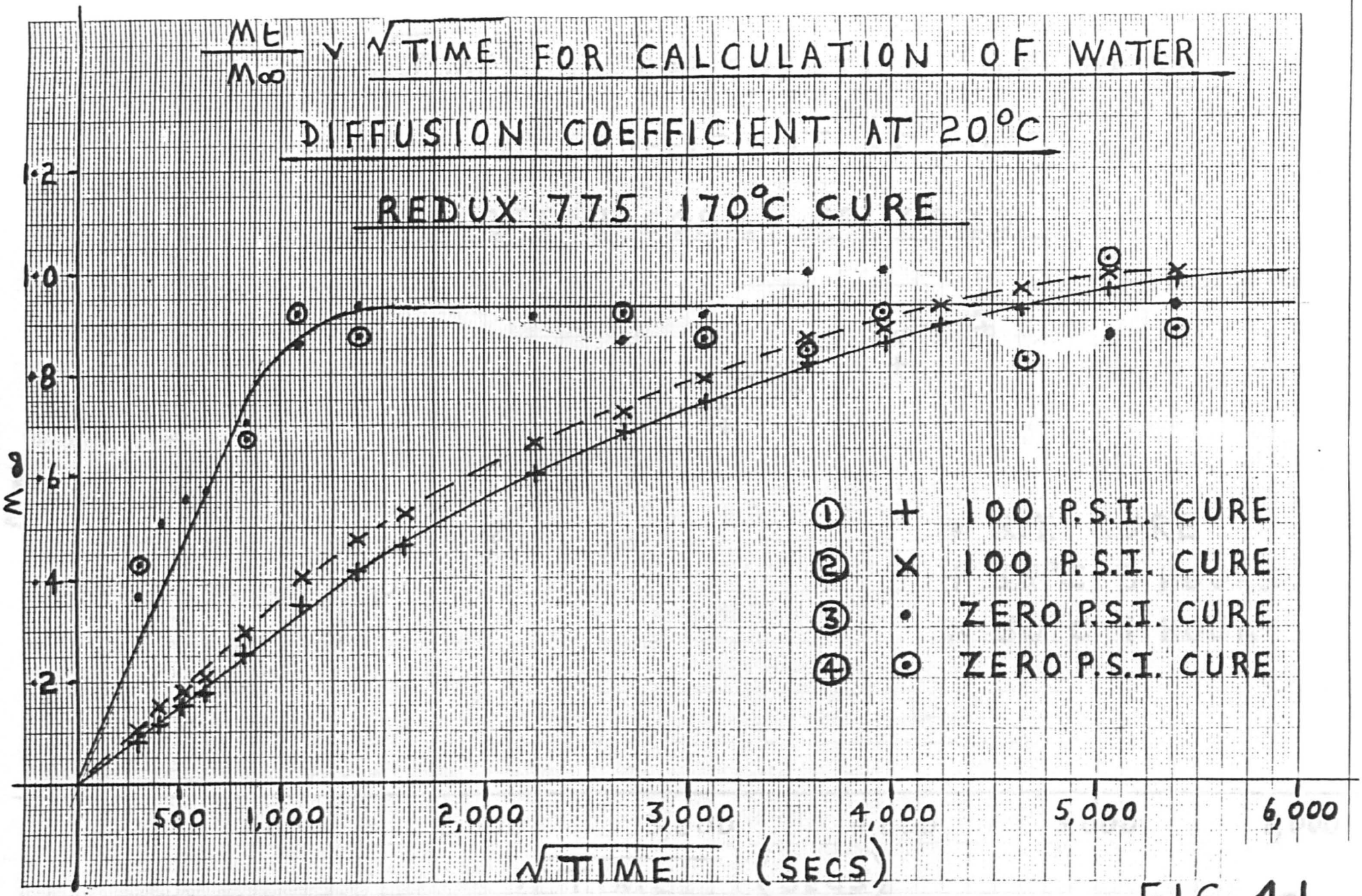

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
REDUX 775 170°C CURE
$\frac{M_t}{M_\infty}$
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)
① + 100 P.S.I. CURE
② × 100 P.S.I. CURE
③ • ZERO P.S.I. CURE
④ ⊙ ZERO P.S.I. CURE

FIG: 41

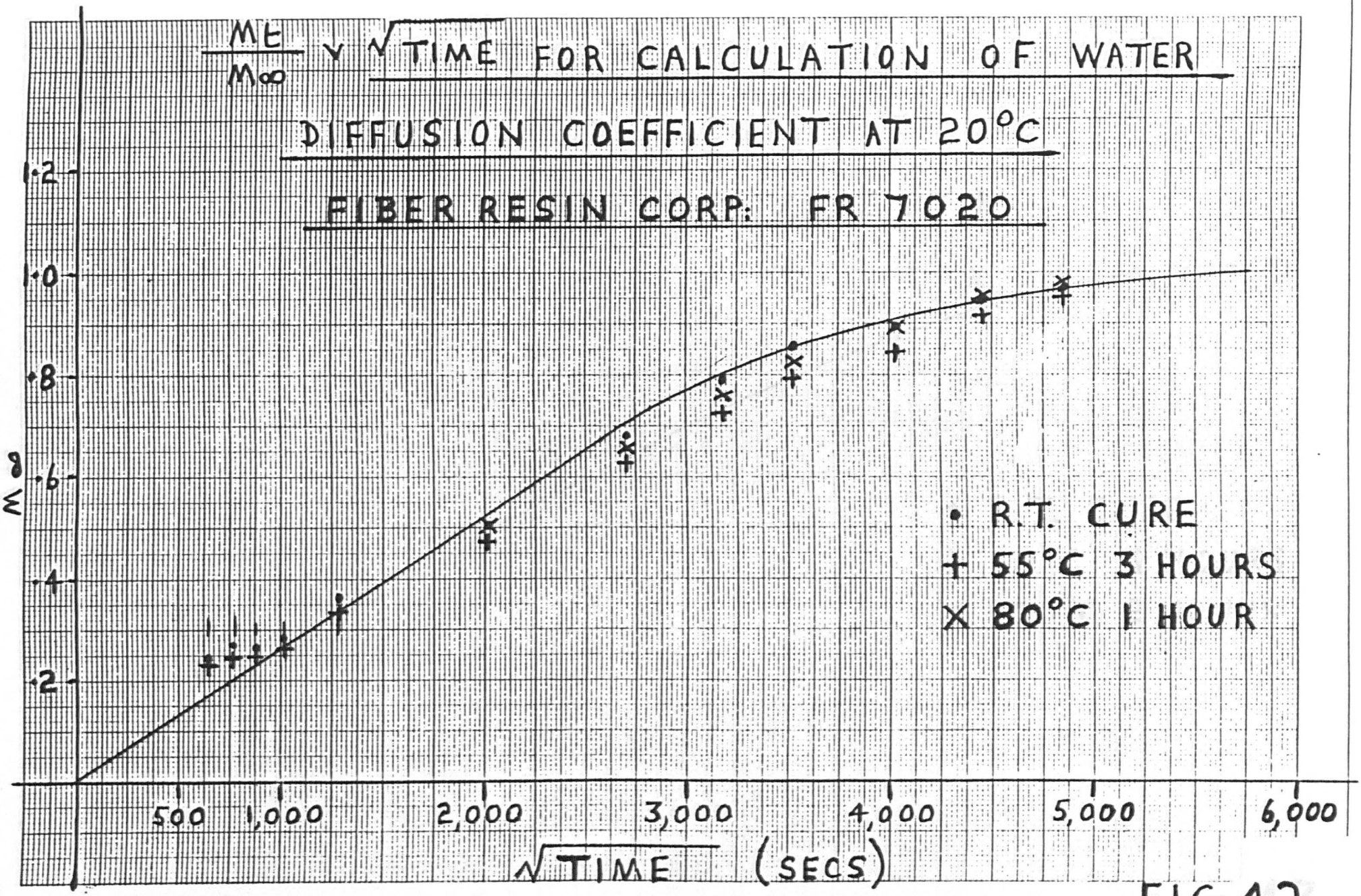

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER
DIFFUSION COEFFICIENT AT 20°C
FIBER RESIN CORP: FR 7020
$\frac{M_t}{M_\infty}$
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)
• R.T. CURE
+ 55°C 3 HOURS
× 80°C 1 HOUR

FIG: 42

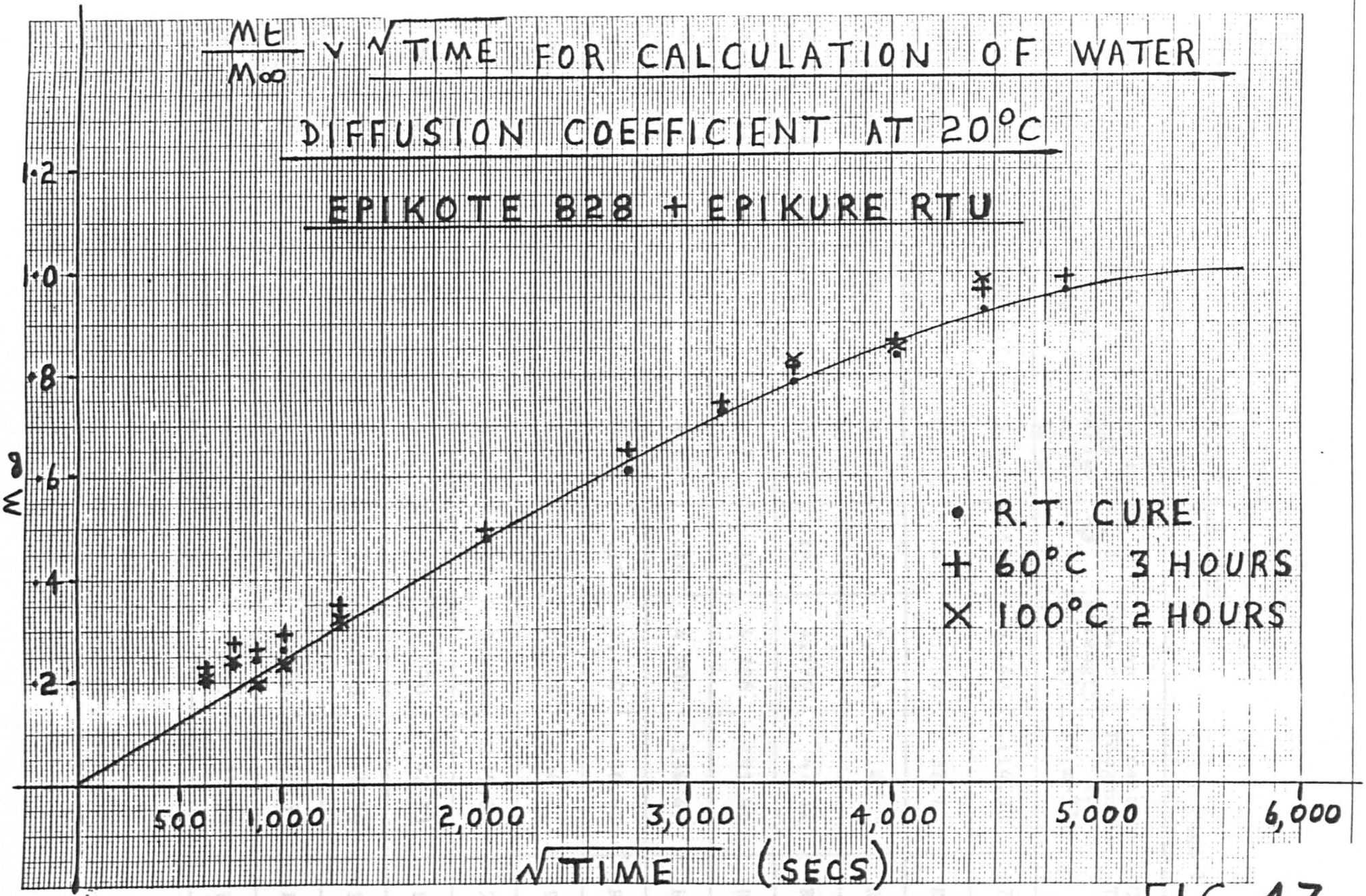

$\frac{M_t}{M_\infty}$ v $\sqrt{\text{TIME}}$ FOR CALCULATION OF WATER DIFFUSION COEFFICIENT AT 20°C
EPIKOTE 828 + EPIKURE RTU
$\frac{M_t}{M_\infty}$
1·2
1·0
·8
·6
·4
·2
500
1,000
2,000
3,000
4,000
5,000
6,000
$\sqrt{\text{TIME}}$ (SECS)
• R.T. CURE
+ 60°C 3 HOURS
× 100°C 2 HOURS

FIG:43

TABLE 5

DATA FOR FIG. 44D

Adhesive or Matrix Resin	Young's Mod E ASTM D.638 psi/ Mpa	Initial Fracture Energy Gl average of 3 kJ/m^2	ν^2	Lap shear strength (psi)	Fracture Toughness K_{1c} MN.m-3/2	Cure Temp
Redux 308A	480,000 (3,330)	3.3	.16	6,740	114.38	170°C
Redux 408	650,000 (4,490)	0.2	.16	2,756	32.7	RT
Redux 408 + 20% 410NA	650,000 (4,490)	0.33	.16	2,266	42	RT
Redux 408 + 40% 410NA	540,000 (3,720)	0.51	.16	2,590	47.52	RT
Redux 410NA	380,000 (2,620)	11.7	.16	4,786	191.03	RT
Hysol EA.9309.3NA	360,000 (2,490)	6.1	.16	4,200	134.47	RT
Hysol EA.9321	380,000 (2,620)	0.43	.16	4,190	36.62	RT
Hysol EA.9330	351,000 (2,420)	6.3	.16	3,500	134.72	RT
3M - AF163	350,000 (2,415)	6.4	.16	5,800	135.6	120°C
3M EC.2216	51,000 (353)	4.1	.2	1,920	42.53	RT
Redux 501	630,000 (4,350)	0.04	.16	1,150	14.39	RT
Redux 501 + 20% 410NA	500,000 (3,460)	0.1 from graph	.16	1,400	20.3	RT
Redux 501 + 40% 410NA	475,000 (3,280)	0.2	.16	1,650	27.95	RT

TABLE 5

DATA FOR FIG. 44D

Adhesive or Matrix Resin	Young's Mod E ASTM D.638 psi/ Mpa	Initial Fracture Energy G1 average of 3 kJ/m^2	ν^2	Lap shear strength (psi)	Fracture Toughness K_{1c} $MN.m-3/2$	Cure Temp
Epikote 815 +RTU	560,000 (3,870)	0.11	.16	783	22.51	RT
Epikote 828 +RTU	580,000 (4,000)	0.03	.16	1,567	11.95	RT
FR 7020	450,000 (3,110)	0.056	.16	2,400	14.4	RT

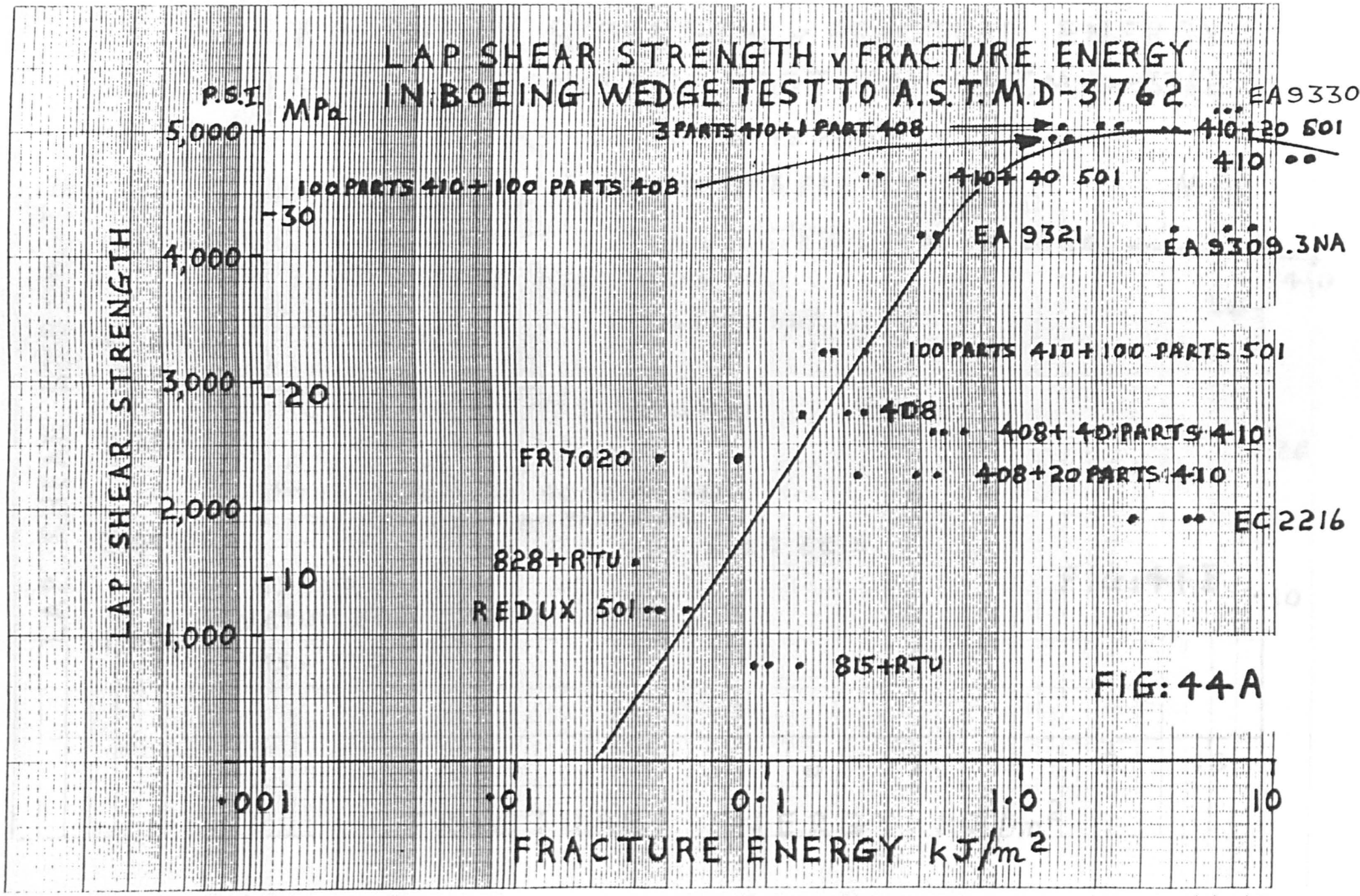
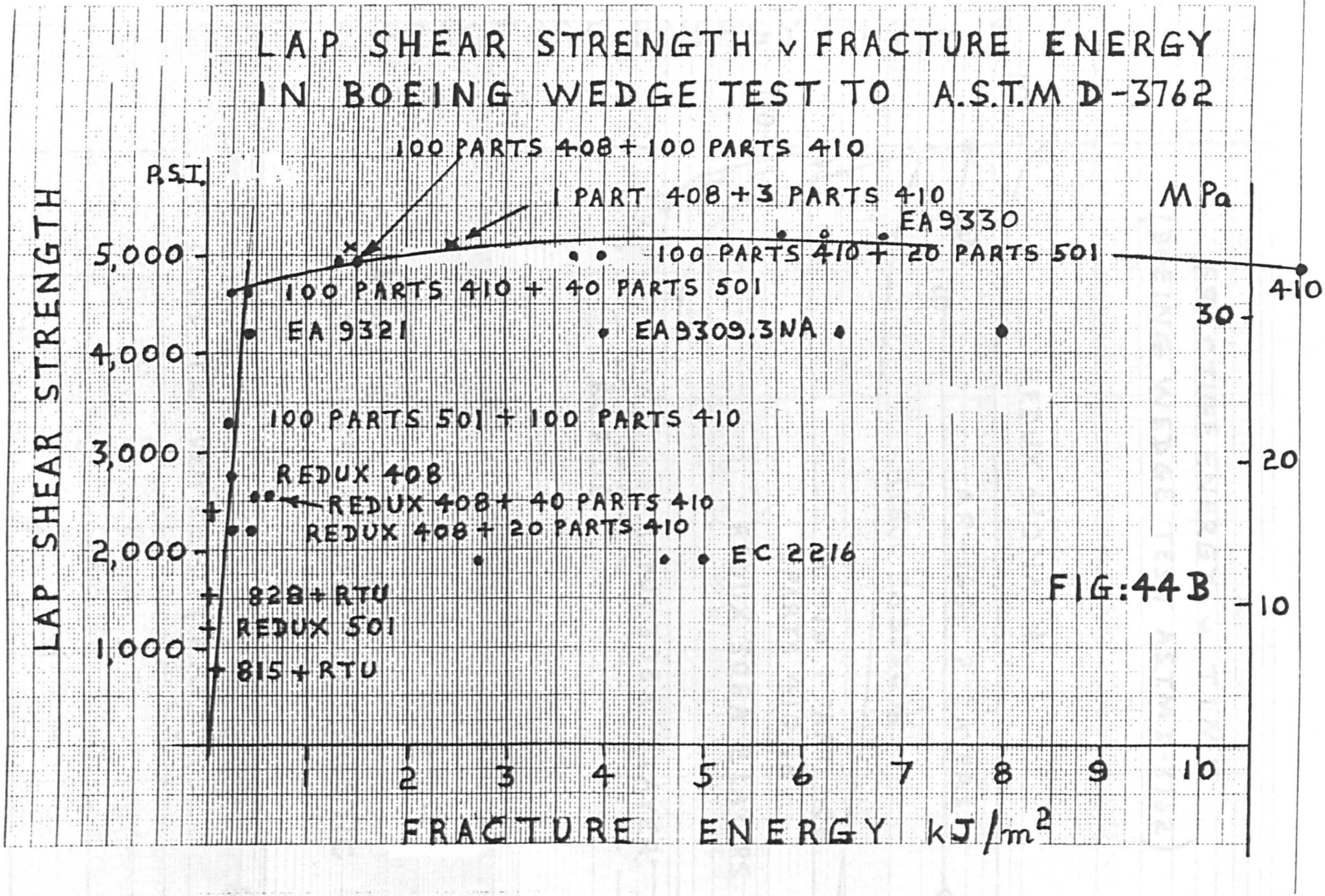

LAP SHEAR STRENGTH v FRACTURE ENERGY
IN BOEING WEDGE TEST TO A.S.T.M.D-3762
P.S.I.
MPa
LAP SHEAR STRENGTH
5,000
4,000
3,000
2,000
1,000
30
20
10
3 PARTS 410 + 1 PART 408
100 PARTS 410 + 100 PARTS 408
410 + 40 501
410 + 20 501
410
EA 9330
EA 9321
EA 9309.3NA
100 PARTS 410 + 100 PARTS 501
408
408 + 40 PARTS 410
408 + 20 PARTS 410
EC 2216
FR 7020
828 + RTU
REDUX 501
815 + RTU
.001
.01
0.1
1.0
10
FRACTURE ENERGY kJ/m²

FIG: 44A


LAP SHEAR STRENGTH v FRACTURE ENERGY
IN BOEING WEDGE TEST TO A.S.T.M D-3762
LAP SHEAR STRENGTH
R.S.I.
MPa
5,000
4,000
3,000
2,000
1,000
40
30
20
10
100 PARTS 408 + 100 PARTS 410
1 PART 408 + 3 PARTS 410
EA9330
100 PARTS 410 + 20 PARTS 501
100 PARTS 410 + 40 PARTS 501
EA 9321
EA9309.3NA
100 PARTS 501 + 100 PARTS 410
REDUX 408
REDUX 408 + 40 PARTS 410
REDUX 408 + 20 PARTS 410
EC 2216
828 + RTU
REDUX 501
815 + RTU
1
2
3
4
5
6
7
8
9
10
FRACTURE ENERGY kJ/m²
FIG:44B

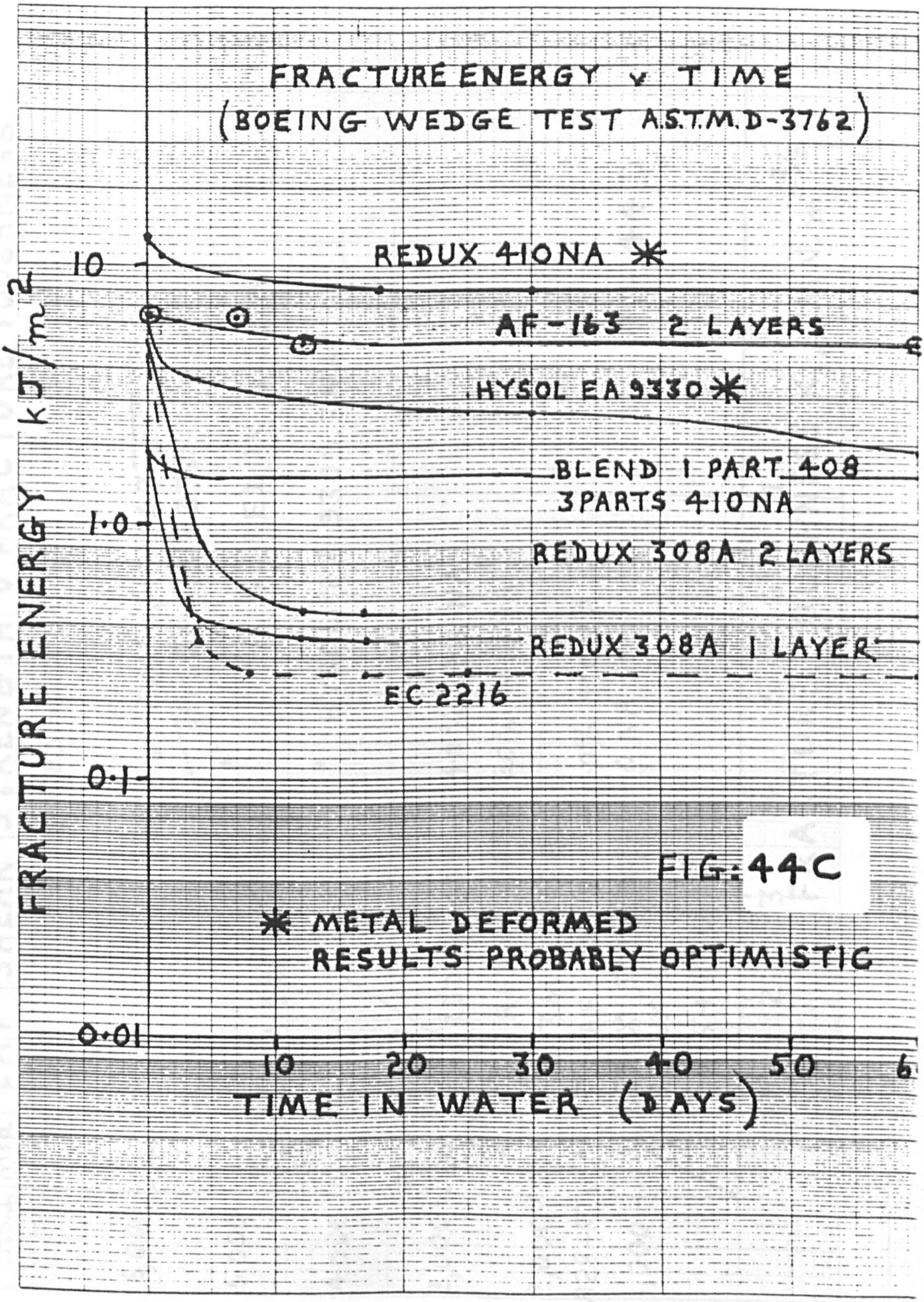

FRACTURE ENERGY v TIME
(BOEING WEDGE TEST A.S.T.M.D-3762)
FRACTURE ENERGY KJ/m²
10
1·0
0·1
0·01
REDUX 410NA *
AF-163 2 LAYERS
HYSOL EA 9330 *
BLEND 1 PART 408
3 PARTS 410NA
REDUX 308A 2 LAYERS
REDUX 308A 1 LAYER
EC 2216
10
20
30
40
50
TIME IN WATER (DAYS)
* METAL DEFORMED
RESULTS PROBABLY OPTIMISTIC

FIG. 44C

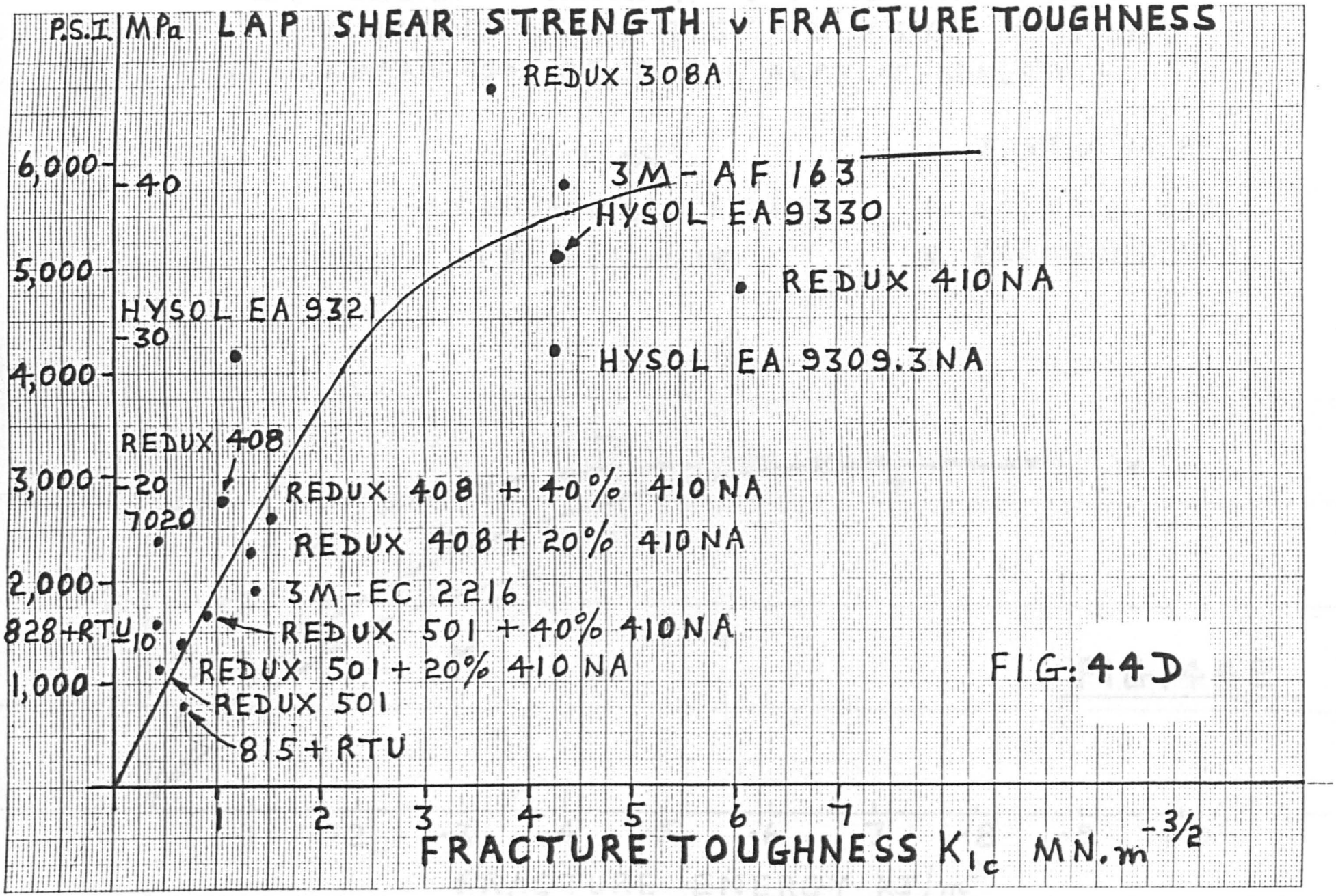

LAP SHEAR STRENGTH v FRACTURE TOUGHNESS
P.S.I
MPa
LAP SHEAR STRENGTH
6,000
-40
5,000
4,000
-30
3,000
-20
2,000
1,000
-10
REDUX 308A
3M-AF 163
HYSOL EA 9330
REDUX 410 NA
HYSOL EA 9321
HYSOL EA 9309.3NA
REDUX 408
7020
REDUX 408 + 40% 410 NA
REDUX 408 + 20% 410 NA
3M-EC 2216
828+RTU
REDUX 501 + 40% 410 NA
REDUX 501 + 20% 410 NA
REDUX 501
815+RTU
1
2
3
4
5
6
7
FRACTURE TOUGHNESS K_{1c} MN.m$^{-3/2}$

FIG: 44D

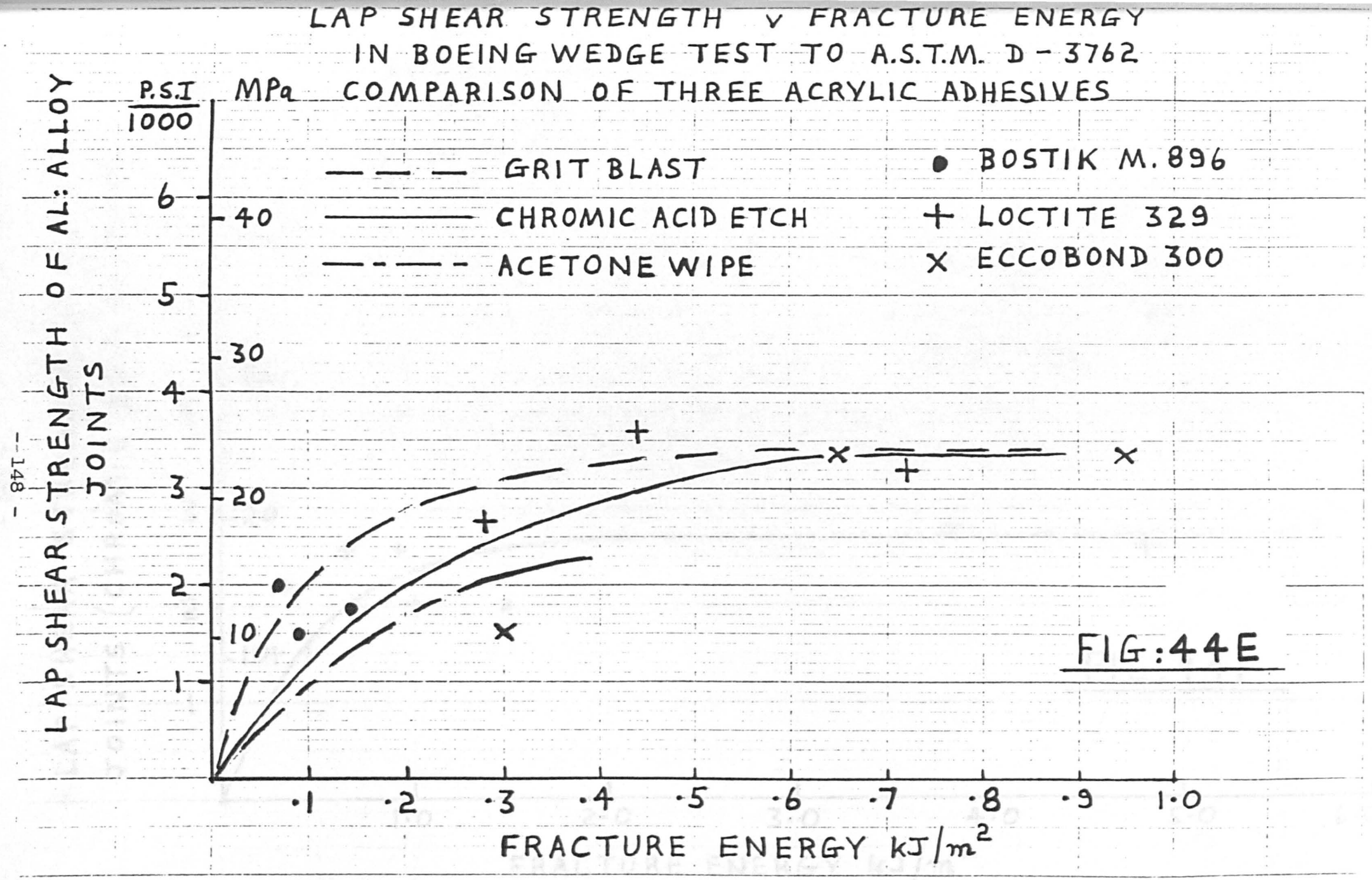

LAP SHEAR STRENGTH v FRACTURE ENERGY
IN BOEING WEDGE TEST TO A.S.T.M. D - 3762
COMPARISON OF THREE ACRYLIC ADHESIVES
P.S.I / 1000
MPa
LAP SHEAR STRENGTH OF AL: ALLOY JOINTS
GRIT BLAST
CHROMIC ACID ETCH
ACETONE WIPE
BOSTIK M.896
LOCTITE 329
ECCOBOND 300
6
5
4
3
2
1
40
30
20
10
·1
·2
·3
·4
·5
·6
·7
·8
·9
1·0
FRACTURE ENERGY kJ/m²

FIG:44E

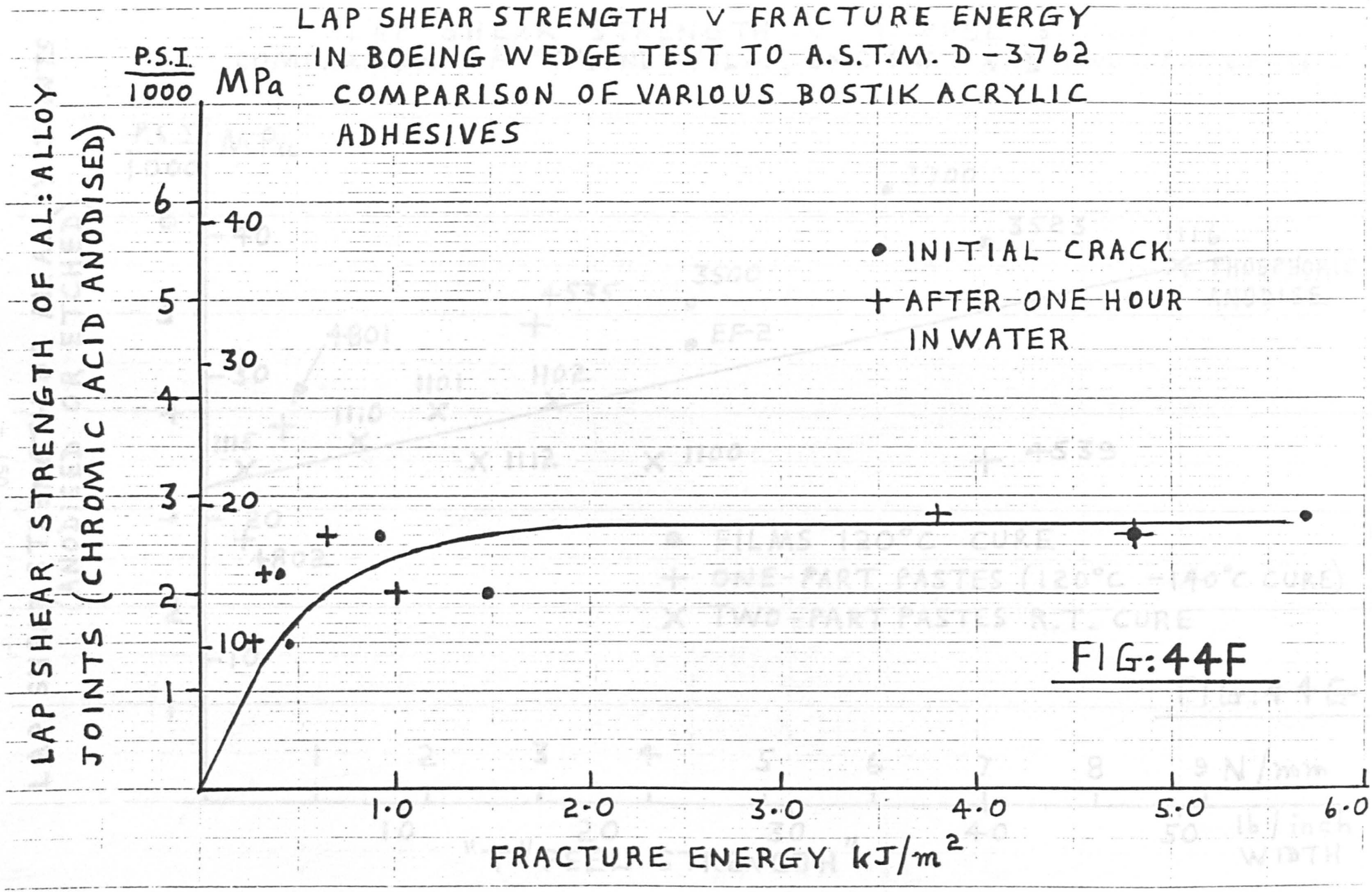
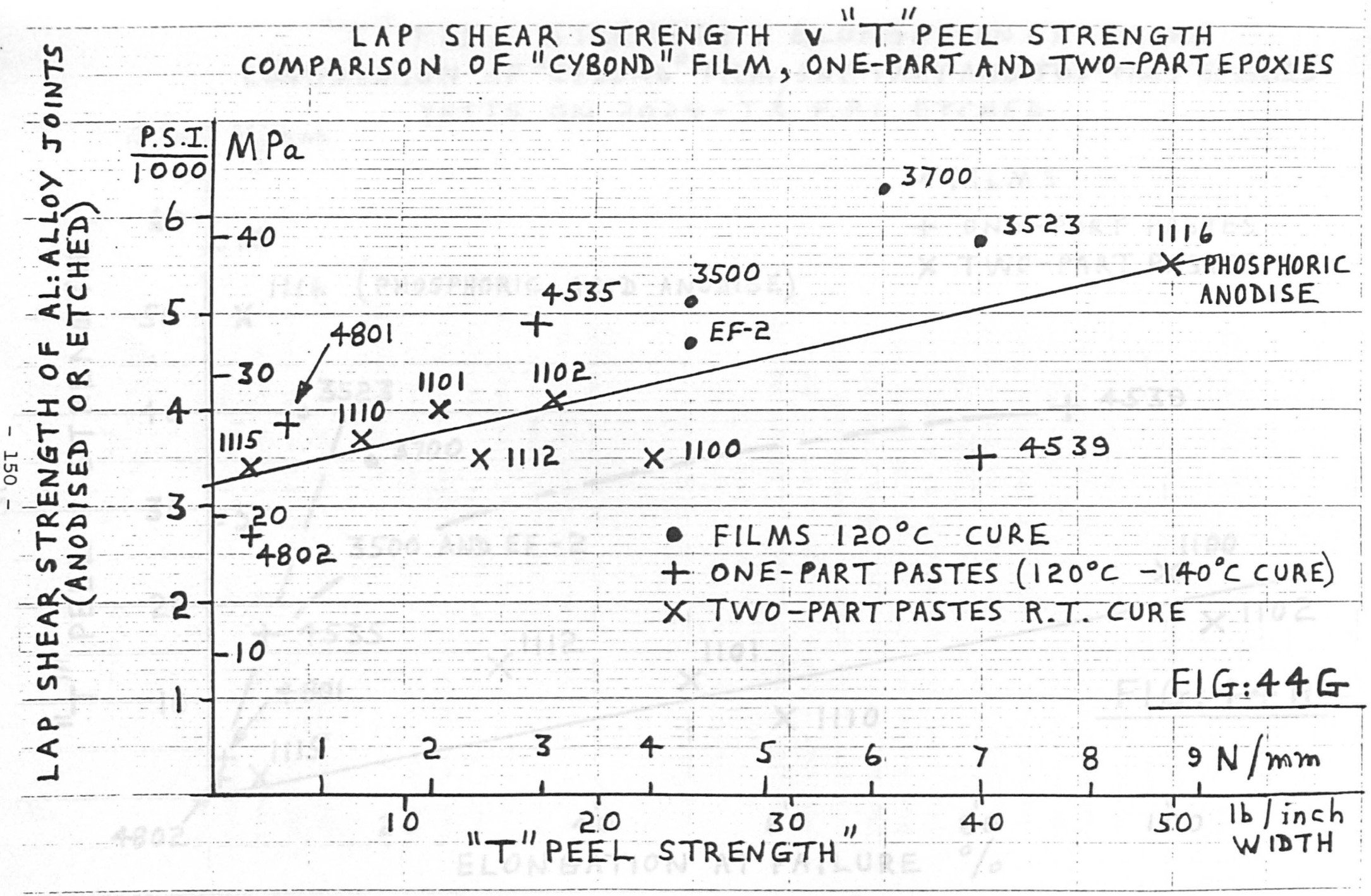

LAP SHEAR STRENGTH V FRACTURE ENERGY
IN BOEING WEDGE TEST TO A.S.T.M. D-3762
COMPARISON OF VARIOUS BOSTIK ACRYLIC
ADHESIVES
P.S.I. / 1000
MPa
LAP SHEAR STRENGTH OF AL: ALLOY JOINTS (CHROMIC ACID ANODISED)
6
5
4
3
2
1
40
30
20
10
INITIAL CRACK
AFTER ONE HOUR IN WATER
1·0
2·0
3·0
4·0
5·0
6·0
FRACTURE ENERGY kJ/m²

FIG: 44F


LAP SHEAR STRENGTH v "T" PEEL STRENGTH
COMPARISON OF "CYBOND" FILM, ONE-PART AND TWO-PART EPOXIES
LAP SHEAR STRENGTH OF AL:ALLOY JOINTS (ANODISED OR ETCHED)
P.S.I. / 1000
MPa
6
5
4
3
2
1
40
30
20
10
3700
3523
1116
PHOSPHORIC ANODISE
3500
4535
EF-2
4801
1101
1102
1110
1115
1112
1100
4539
4802
FILMS 120°C CURE
+ ONE-PART PASTES (120°C - 140°C CURE)
X TWO-PART PASTES R.T. CURE
FIG:44G
1 2 3 4 5 6 7 8 9 N/mm
10 20 30 40 50 lb/inch WIDTH
"T" PEEL STRENGTH"

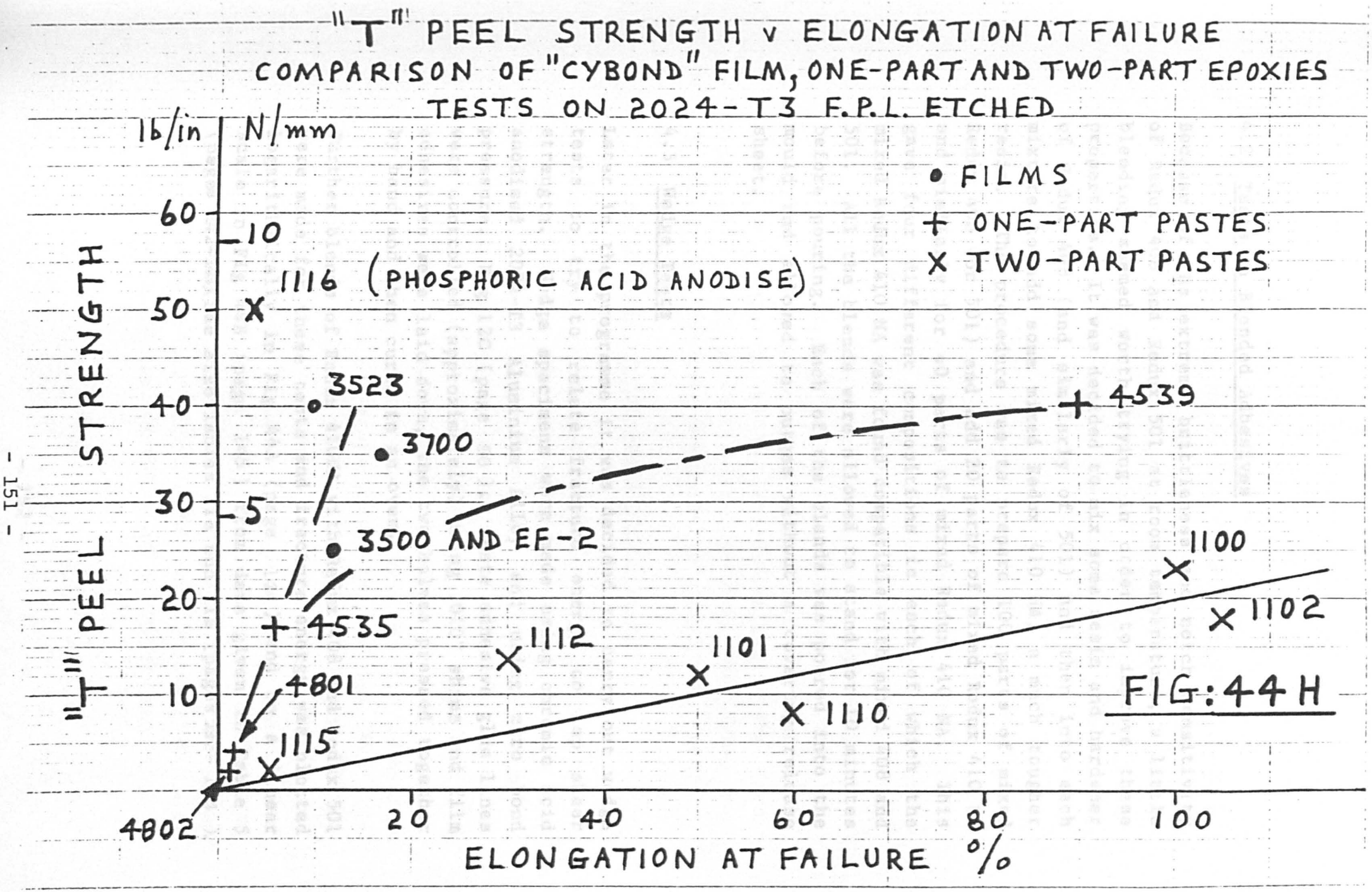

"T" PEEL STRENGTH v ELONGATION AT FAILURE
COMPARISON OF "CYBOND" FILM, ONE-PART AND TWO-PART EPOXIES
TESTS ON 2024-T3 F.P.L. ETCHED
lb/in
N/mm
"T" PEEL STRENGTH
60
10
50
40
5
30
20
10
• FILMS
+ ONE-PART PASTES
X TWO-PART PASTES
1116 (PHOSPHORIC ACID ANODISE)
3523
3700
3500 AND EF-2
4539
4535
4801
1115
4802
1112
1101
1110
1100
1102
20
40
60
80
100
ELONGATION AT FAILURE %

FIG: 44 H

4.2. Tests on Blended Adhesives

Because of the extreme brittleness and notch sensitivity of Redux 408 and Redux 501 at room temperature, a little blending seemed worth trying in order to improve these properties. It was decided to mix some resin and hardener of Redux 408 (and similarly of 501) and then into each mixture to add some mixed Redux 410 NA, a much tougher resin. The procedure was to prepare 100 parts of mixed Redux 408 (or 501) and add 20 parts of mixed Redux 410 NA and similarly for 40 parts of mixed Redux 410 NA. This gave four different compositions in each of which the mixed Redux 410 NA was found compatible with mixed 408 and 501. All the blends were allowed to stand for 10 minutes before pouring. Each of the blends was poured into the mould and allowed to outgas without a covering release sheet.

4.3 Wedge Tests

Later in the programme it was decided to carry out wedge tests to try to relate fracture energy to lap shear strength. Wedge specimens were made using chromic acid anodised 2024-T3 Aluminium Alloy and using zero bond pressure. Fig 12C (page 50). Paste adhesive glue lines were controlled (approximately) using .010" shims and film adhesives were laid down, the two halves pressed together by hand and then cured in an oven.

Further blends of Redux 410NA with Redux 408 and Redux 501 were made for these tests and fracture energy was plotted logarithmically in Fig 44A (page 144) and on a linear scale in Fig 44B (page 145) from data given in Table 5 (pages 142-143)(See also Tables 11A and 11B (pages 192- 194).

Some fracture energy data after water immersion is given in Fig. 44C (page 146). Fracture toughness data is shown in Fig. 44D (page 147). Figs 44E to 44H (pages 148 - 151) show fracture energy data from the results of other workers. Fracture energy v blending ratio is shown in Fig 111 (page 268).

Wedge tests were also carried out on EC 2216, AF-163-2K, Hysol EA 9330, Hysol EA 9309.3NA, Hysol EA 9321, Redux 308A, Epikote 815 + Epikure RTU, Epikote 828 + Epikure RTU AND FR 7020. Wedges were driven in at 10 mm/minute using the RDP/Howden machine and taking advice given in Joneja et al (1985). This was successful and critical to producing the fairly low scatter in results that was achieved. The wedges were stabilised by hand until sufficiently far in to be self-supporting. The force required to drive the wedge, although variable, was related to the fracture energy of the adhesives tested.

4.4 Some Effects of Adhesives on Corrosion

At a later stage in the water uptake tests, carried out to obtain Diffusion and Solubility Coefficients, it was decided to add a strip of 7075-T6 unclad Aluminium Alloy to each jar and note if any corrosion occurred. This was done because one of the adhesives tested in the first section mentioned above was suspected of causing corrosion in service under fibreglass repairs to thin Aluminium Alloy parts. Control tests showed that unclad 7075 - T6 corroded rapidly in the presence of distilled water alone. It was found that corrosion occurred during the time period of the test (130 days) with all adhesives tested except Redux 410 NA, Redux 408 and Redux 308A. No corrosion visible to the naked eye was found on the strips immersed with Bostik 5435/TM2 but some pitting was later found at a longer time by RAE using a microscope.

CORROSION TESTS WITH 7075-T6
UNCLAD ALUMINIUM ALLOY
AL: ALLOY STRIPS IMMERSED IN JARS OF
DISTILLED WATER EACH CONTAINING A PLATE
OF CURED ADHESIVE 40 mm x 30 mm x 2 mm APPROX:
DISTILLED WATER ONLY
828+RTU
815+RTU
E38
E37
EA9330
EA9321
EA 9309.3NA
EC 9323
EC 2216
REDUX 775
REDUX 501
FR7020
S435/ TM2
REDUX 308A
REDUX 410 NA
REDUX 408
INHIBITED
INHIBITED
BOSTIK
ALL CORRODED
NO CORROSION
9
8
7
6
5
4
pH
BAR CHART OF PEAK pH DURING IMMERSION
FIG: 45

pH and conductivity were measured in each jar and plotted v time. No corrosion, visible to the naked eye, was found on any specimen until pH 7 was reached. The starting pH of the distilled water was 5.4. The highest pH reached in each of these tests is shown in Fig. 45 (page 154).

Bostik 5435/TM2 kept the water pH down to 5.3. It would seem from these preliminary findings that the pH of an adhesive needs to be related to the metal being bonded.

A recent paper Hamill et al (1987) tends to confirm the possibility of an effect of pH or resin chemistry when it says "It was shown that the ability of surface treatment to provide joint durability is dependent on the adhesive selected, supporting the belief that joint durability is determined by the interface comprising the aluminium surface and the adhesive". It is hoped to report this work at a later date.

4.5 Compression Tests

Blocks of resin were also cast for each of the resin systems and three specimens of each material 10mm square x 25mm were machined and tested in compression to ASTM-D695. See Fig 12B (page 49).

Compression modulus values (obtained without an extensometer and using the chart record only) were generally lower than the Manufacturers but much closer to them than tensile modulus values.

Insufficient Manufacturers' data was available to allow British Airways compression tests to be compared with the Manufacturers' results. For data obtained see Table 10 (pages 188 - 191).

Some difficulty with the compression tests was found when attempting to make specimens of Redux 308A and AF.163 film adhesives. Blocks were made by pressing together about 50 layers of film. Curing in an oven, without pressure, produced a dense foam bearing no relation to the normal cured film. A further attempt was made using vacuum pressure. A more dense foam was produced but the results are marked "suspect" because the values seem too low compared with the two-part pastes.

The foaming suggests that film adhesives contain more volatiles than is generally admitted or that some outgassing occurs during the curing reaction. See Allen (1984) and Brockmann et al (1986). Brockman carried out ageing tests at 70°C and 95% RH on "open joints". These are a system metal/oxide/primer/adhesive where the second adherend is omitted to achieve faster water uptake. The systems AF.126 and AF.163, which both contain dicyandiamide as hardener, developed bubbles on Chrome Sulphuric Acid Anodised Al. Alloy. In other tests with FM 73, another epoxy in which no dicyandiamide could be detected, (although it does contain DICY in more stoichiometric quantities) and the phenolic system Redux 775 caused no such drastic macroscopically visible effects. Bolger et al (1985) state that epoxies cured with DICY give off ammonia for long periods after cure. It is therefore no surprise that attempts to cure AF.163 in thick blocks at 120°C or Redux 308A at 150°C should have produced bubbles, as they are both known to contain dicyandiamide. Honeycomb panels made with these adhesives give off a strong smell during climbing drum peel tests.

The two-part pastes also contained a few bubbles but test results were generally very consistent. Results would be expected to be more consistent for compression tests than for tensile tests because:-

(a) The three samples in each case were made from the same block and therefore only one mix was involved.

(b) Compression properties are less sensitive to flaws and bubbles.

CHAPTER FIVE RESULTS AND DISCUSSION

5.0 Results and Discussion

Initially the programme was started to obtain data for the comparison of one adhesive with another. However, it was soon considered worthwhile to plot the data obtained for various mechanical properties of the cured resins against lap shear strength to try to find the factor or factors governing the strength of a standard lap joint. This will be dealt with later. The various mechanical properties used to plot a number of figures are listed in Tables 5 - 11B (pages 158 - 194).

5.1 Tensile Tests

Tensile tests on neat resin test pieces of the shape shown in Fig 12A (page 48) were carried out on all the resin systems used in all four sections of this programme. In each case values for tensile strength, tensile modulus, elongation at failure and strain energy at failure were obtained. For many of the materials used in sections three and four these tests were also carried out after the complete test piece had been immersed in distilled water for periods from two to six months. See Tables 6A, 6B and 6C (pages 176 - 179) and 9A and 9B (pages 184 - 187).
In the first two sections of the programme most of the systems used showed very little plastic strain at failure. Epikote 828 + Versamid 125 failed at 1.6% plastic strain and EA 9330 at 1% but Epikote 815 + RTU, Permabond E 34, EC 3524, EC 3559, EC 3568 and EC 3578 were completely brittle and showed virtually zero plastic strain at failure. 3M - AF 163 - 2M (a 120°C (250°F) cure film adhesive) failed at 1.8% plastic strain.

(Text continues on page 195)

TABLE 5A

ADHESIVE	LAP SHEAR PSI	E PSI	$\sqrt{G}$	G CALCULATED PSI	ADHESIVE TENSILE STRENGTH $\div\sqrt{G}$
EA9330	5,000	84,000	173	30,000	23
EA9321	4,190	125,000	217	47,000	20.7
EPIKOTE 828 VERSAMID 125	2,180	112,000	5	42,000	33.7
EPIKOTE 815 + RTU	783	178,000	259	67,000	38.6
EC2216	1,920	3,100	32	1,030	50
EC3559	5,450	94,000	181	33,000	19.9
AF163	5,000	95,650	184	34,000	34.5
EC3524	1,350	33,000	105	11,000	12.4
EC3568	3,150	98,550	187	35,000	12.79
EC3578	2,878	87,000 av	175	30,500	14.5
PERMABOND E34	2,174	182,500	262	68,500	14.9

TABLE 5B - PHASE TWO ADDITIONAL WORK

ADHESIVE	LAP SHEAR PSI	E (PSI) BA SQUEEZED DOWN * BA FREE SURFACE ASTM D-638	$\sqrt{G}$	G CALCULATED PSI	ADHESIVE TENSILE STRENGTH $\div\sqrt{G}$
REDUX 308A	6,740 MFR	* 145,691 495,000	224 413	50,238 170,690	32.37 17.55
REDUX 408	2,756 MFR	213,730 * 219,374 600,000	276 280 463	76,332 78,348 214,286	13.11 17.93 8.08
REDUX 408+20% REDUX 410NA	2,266	* 213,231 600,000	276 463	76,154 214,286	17.57 10.47
REDUX 408+40% REDUX 410NA	2,590	* 168,206 540,000	245 439	60,074 192,857	18.22 10.17
REDUX 410NA	4,786 MFR	105,600 * 82,286 415,000	191 168 378	36,414 28,374 143,103	21.29 20.85 10.76
REDUX 501	1,151	199,572 * 146,356 580,000	262 229 455	68,818 52,270 207,142	14.18 17.54 8.16
REDUX 501+20% REDUX 410NA	1,443	* 153,352 530,000	234 435	54,769 189,286	38.7 20.82
REDUX 501+40% REDUX 410NA	1,619	* 142,471 490,000	222 411	49,128 168,965	29.58 15.98
EC 9323	5,250 MFR	131,330 416,280 MFR	213 379	45,286 143,545	21.78 12.24
BOSTIK 5435/TM2	5,250 MFR	2,158 10,000	26.82 57.73	719 3,333	17.56 8.16
EA 9309.3NA	4,200 MFR	* 115,147 430,000	199 385	39,706 148,276	22.12 11.43
PERMABOND E37	1,200 MFR	* 150,530 495,000	232 429	53,761 183,928	7.65 4.14
PERMABOND E38	4.061 MFR	* 83,771 350,000	170 347	28,886 120,690	16.24 7.96
EPIKOTE 828 + RTU	1,567	* 189,933 570,000	260 451	67,833 203,571	23.58 13.6
FR 7020	2,400	* 132,222 450,000	221 408	48,971 166,667	24.73 13.39

* Free Surface (No Release Sheet) to minimise bubbles

Values not marked * were obtained when a Melinex Release sheet was used to allow the specimen thickness to be "squeezed" down to mould thickness. This technique was later abandoned. Any adhesive with a low enough viscosity to find its own level was allowed to do so. High viscosity adhesives were scraped approximately level with the mould and the surface left free. This slightly reduced the size of bubbles but it was found that above some critical viscosity bubbles tend to remain trapped. ASTM D-638 values were estimated from Fig.1 except where marked MFR. All data listed obtained from samples cured at room temperature except for Redux 308A (cured at 170°C) and Permabond E38 (cured at 60°C).

TABLE 6

SPECIMEN NO	ADHESIVE	ADHESIVE TENSILE STRENGTH		REMARKS
		PSI	MPa	
22	Redux 308A (170°C Cure)	7,422	51.17	Failed at two surface bubbles, one 1.3mm, one 1.0mm dia Cured at ZERO pressure
23	Redux 308A (170°C Cure)	8,113	55.94	Failed at edge bubble 1.3mm dia. Cured at ZERO pressure
24	Redux 308A (170°C Cure)	6,214	42.84	Failed at large edge bubble 2.0mm dia. Smaller bubbles at centre. Cured at ZERO pressure
41	Redux 408 RT Cure	3,385	23.34	2.2mm X 1.7mm bubble at surface at centre
41A	Redux 408 RT Cure	3,498	24.11	Made by Training School 1.6mm X 1.3mm bubble at failure
42A	Redux 408 RT Cure	3,272	22.56	Failure at 1.2mm edge bubble
43	Redux 408 RT Cure	4,318	29.77	Failure at 1.2mm bubble at surface
44	Redux 408 RT Cure	2,880	19.85	Tested after 183 days in water. Water content 11.6%
45	Redux 408 RT Cure	2,999	20.674	Tested after 183 days in water. Water content 12.2%
46	Redux 408 RT Cure	2,624	18.09	Tested after 183 days in water. Water content 12.2%

TABLE 6

SPECIMEN NO	ADHESIVE	ADHESIVE TENSILE STRENGTH		REMARKS
		PSI	MPa	
47	Redux 408 Cured 50°C for 3 hours	2,932	20.22	Broke across repaired hole 1.4mm X 1.0mm bubble plus 0.7mm bubble
48	Redux 408 Cured 50°C for 3 hours	3,799	26.19	Broke at 0.8mm dia bubble at edge in end radius
49	Redux 408 Cured 50°C for 3 hours	3,929	27.1	Bubble 1.4mm across width X 1.0mm at surface
50	Redux 408 Cured 80°C for 1 hour	3,670	25.3	Edge bubble 2mm dia. Other bubble 2.2mm X 1.6mm
51	Redux 408 Cured 80°C for 1 hour	2,494	17.19	Some uncured adhesive at centre not completely mixed
52	Redux 408 Cured 80°C for 1 hour	3,433	23.67	Edge bubble 1.8mm X 1.4mm
52A	Redux 408 Cured 80°C for 1 hour	4,491	30.96	2 bubbles 0.2mm dia
53	Redux 410 NA Cured at RT	4,017	27.70	1.5mm dia bubble at centre of thickness and near one edge, other small ones

TABLE 6

SPECIMEN NO	ADHESIVE	ADHESIVE TENSILE STRENGTH		REMARKS
		PSI	MPa	
54	Redux 410 NA Cured at RT	4,082	28.14	1.0mm dia bubble at edge, 0.9mm bubble at surface
55	Redux 410 NA Cured at RT	4,099	28.26	1.0mm dia bubble at edge, 2 X 0.5mm bubbles at centre
56	Redux 410 NA Cured at RT	3,278	22.6	Tested after 69 days in water, water content 3.65%
57	Redux 410 NA Cured at RT	3,718	25.63	Tested after 107 days in water, water content 4.8%
58	Redux 410 NA Cured at RT	3,440	23.72	Tested after 183 days in water, water content 3.36%
59	Redux 410 NA Cured 50°C for 3 hours	4,245	29.27	3 X 0.7mm bubbles at centre, several smaller bubbles
60	Redux 410 NA Cured 50°C for 3 hours	3,866	26.65	1.7mm dia bubble at edge, another 0.4mm dia plus some smaller ones
61	Redux 410 NA Cured 50°C for 3 hours	4,047	27.9	3 bubbles 0.6mm dia, several others smaller
62	Redux 410 NA Cured 80°C for 1 hour	4,160	28.68	Largest bubble 0.6mm dia, many smaller bubbles

TABLE 6

SPECIMEN NO	ADHESIVE	ADHESIVE TENSILE STRENGTH		REMARKS
		PSI	MPa	
63	Redux 410 NA Cured 80°C for 1 hour	3,553	24.495	1.8mm dia bubble at edge
64	Redux 410 NA Cured 80°C for 1 hour	4,078	28.11	Largest bubble 1.4mm across width X 1.0mm across thickness
65	Redux 501 RT cure	1,928	13.29	Tiny bubbles on mould upper face
66A	Redux 501 RT cure	4,319	29.78	0.5mm bubble on upper face
66B	Redux 501 RT cure	4,790	33.02	Failure at 1.5mm dia bubble at surface and centre of end radius
67A	Redux 501 RT cure	3,383	23.32	0.5mm dia bubble at upper face in radius
67B	Redux 501 RT cure	4,154	28.64	Failed at corner bubble in radius, 1.0mm dia bubble nearby
68	Redux 501 Cured RT Tested wet	2,885	19.9	Tested after 183 days in distilled water, water content 14.2%
69	Redux 501 Cured RT Tested wet	2,728	18.81	Tested after 183 days in water, water content 15.8%

TABLE 6

SPECIMEN NO	ADHESIVE	ADHESIVE TENSILE STRENGTH		REMARKS
		PSI	MPa	
70	Redux 501 Cured RT Tested wet	2,371	16.34	Tested after 183 days in water, water content 15.4%
71	Redux 501 Cured 50°C for 3 hours	3,201	22.07	0.65mm bubble at surface plus several tiny ones
72	Redux 501 Cured 50°C for 3 hours	6,356	43.82	0.5mm bubble at surface and at origin of fracture
73	Redux 501 Cured 50°C for 3 hours	5,016	34.58	No obvious bubbles
74	Redux 501 Cured 80°C for 1 hour	1,460	10.065	2.0mm X 1.6mm bubble at edge of top radius of specimen
75	Redux 501 Cured 80°C for 1 hour	9,970	68.735	No obvious bubbles
76	Redux 501 Cured 80°C for 1 hour	8,222	56.685	One very small surface bubble
76A	Redux 501 Cured 80°C for 1 hour	9,687	66.78	No obvious bubbles

TABLE 6

SPECIMEN NO	ADHESIVE	ADHESIVE TENSILE STRENGTH		REMARKS
		PSI	MPa	
77	EC9323 RT Cure	4,635	31.96	1.1mm dia bubble at centre and a few smaller ones
78	EC9323 RT Cure	4,966	34.24	1.5mm dia bubble at edge, some smaller ones
79	EC9323 RT Cure	4,316	29.76	0.8mm dia bubble at centre + a cluster of smaller ones
80	EC9323 RT Cure Tested wet	3,436	23.64	Tested after 69 days in water, water content 6.04%
81	EC9323 RT Cure Tested wet	3,654	25.19	Tested after 107 days in water, water content 7.5%
82	EC9323 RT Cure Tested wet	3,337	23.0	Tested after 183 days in water, water content 6.6%
83	EC9323 Cured 50°C for 3 hours	5,030	34.68	Elliptical bubble 1.5mm across width at edge and 1.3mm across thickness plus smaller bubbles
84	EC9323 Cured 50°C for 3 hours	5,489	37.84	One 1.0mm dia bubble at edge and corner, another at centre
85	EC9323 Cured 50°C for 3 hours	5,403	37.25	1.2mm dia bubble near edge plus several smaller ones

TABLE 6

SPECIMEN NO	ADHESIVE	ADHESIVE TENSILE STRENGTH		REMARKS
		PSI	MPa	
86	EC9323 Cured 80°C for 1 hour	5,043	34.77	1.3mm dia bubble at edge, 1.1mm dia bubble nearer centre
87	EC9323 Cured 80°C for 1 hour	4,991	34.41	One elliptical bubble 1.9mm across width X 1.6mm across thickness
88	EC9323 Cured 80°C for 1 hour	5,426	37.41	1.3mm dia bubble near edge, a few smaller ones around it
89	Bostik 5435/TM2 RT Cure	662	4.57	0.5mm bubble at surface, 2 X 0.5mm bubbles at centre
90	Bostik 5435/TM2 RT Cure	422	2.91	0.9mm bubble at surface, 0.5mm bubble at centre
91	Bostik 5435/TM2 RT Cure	279	1.92	2.3mm bubble at edge & surface, 0.8mm bubble at centre
92	Redux 408 RT Cure Free Surface	5,246	36.17	Not covered with release sheet to permit outgassing. Small bubbles at fracture
93	Redux 408 RT Cure Free Surface	5,355	36.78	1.5mm dia bubble at edge of fracture
94	Redux 408 RT Cure Free Surface	4,459	30.74	Several small bubbles at fracture

TABLE 6

SPECIMEN NO	ADHESIVE	ADHESIVE TENSILE STRENGTH		REMARKS
		PSI	MPa	
95	Redux 408 plus 20% Redux 410NA RT Cure	4,400	30.34	Free surface. Failure at 1.5mm dia surface bubble
95A	Redux 408 plus 20% Redux 410NA RT Cure	5,299	36.53	0.5mm bubble at edge, 2 X 0.3mm bubbles at surface
96	Redux 408 plus 40% Redux 410NA RT Cure	4,464	30.78	Free surface, 0.5mm dia bubble plus smaller ones at fracture
97	Redux 410NA RT Free Surface	3,220	22.2	1.9mm dia bubble at failure
98	Redux 410NA RT Free Surface	3,550	24.47	1.5mm X 1.0mm bubble plus others
99	Redux 410NA RT Free Surface	3,584	24.7	0.8mm bubble, 0.4mm bubble plus others
100	Redux 501 RT Free Surface	3,690	25.44	No visible failure origin at 10X magnification
101	Redux 501 RT Free Surface	2,879	19.84	No visible failure origin at 10X magnification. Failed in radius just outside parallel gauge length where a bubble had been repaired with the next mix

Free Surface means not covered with a release sheet to allow bubbles more freedom to outgas.

TABLE 6

SPECIMEN NO	ADHESIVE	ADHESIVE TENSILE STRENGTH		REMARKS
		PSI	MPa	
102	Redux 501 RT Free Surface	5,479	37.77	Very small bubbles at fracture
103	Redux 501 + 20% Redux 410NA RT Cure	9,056	62.44	Free surface. Fractured at 0.4mm dia bubble
104	Redux 501 + 40% Redux 410NA RT Cure	6,566	45.27	Free surface. Fractured at both ends. Very small bubbles in both places
105	See 22 - 24			
106	EA 9309.3NA RT Cure	4,594	31.67	Free Surface, one 1.0mm dia bubble, many small ones
107	EA 9309.3NA RT Cure	4,692	32.35	Free Surface, one 1.0mm dia bubble, 2 X 0.5mm bubbles, many small ones
108	EA 9309.3NA RT Cure	3,920	27.03	Free Surface, one 1.0mm dia bubble, 2 X 0.8mm, 3 X 0.5 and smaller bubbles
109	EA 9309.3NA Cured 50°C for 3 hours	5,000	34.47	Free Surface, failed in radius, 2 small bubbles
110	EA 9309.3NA Cured 50°C for 3 hours	5,068	34.94	Free Surface, failed at start of radius, 4 X 0.5mm bubbles

TABLE 6

SPECIMEN NO	ADHESIVE	ADHESIVE TENSILE STRENGTH		REMARKS
		PSI	MPa	
111	EA 9309.3NA Cured 50°C for 3 hours	4,444	30.64	Free Surface, failed in radius, 1.0mm bubble, one 0.5mm one 0.4mm
112	EA 9309.3NA Cured 80°C for 1 hour	5,261	36.27	Free Surface, failed at 1.0mm dia bubble plus smaller ones at centre
113	EA 9309.3NA Cured 80°C for 1 hour	4,689	32.33	Failed from 0.9mm bubble at edge, Free Surface Moulded
114	EA 9309.3NA Cured 80°C for 1 hour	5,030	34.68	Free Surface Moulded, failure from 1.2mm dia bubble at edge plus smaller ones at centre
115	EA 9309.3NA RT Cure Tested wet	4,003	27.6	Free Surface, 38 days in water, water content 4.3%
116	EA 9309.3NA RT Cure Tested wet	3,946	27.2	Free Surface Moulded, 109 days in water, water content 4.6%
117	EA 9309.3NA RT Cure Tested wet	3,940	27.17	Free Surface Moulded, 195 days in water, water content 5.1%

TABLE 6

SPECIMEN NO	ADHESIVE	ADHESIVE TENSILE STRENGTH		REMARKS
		PSI	MPa	
118	Permabond E37 RT Cure	1,760	12.14	0.7mm dia bubble plus some smaller ones at failure point
119	Permabond E37 RT Cure	1,607	11.08	Small bubbles at surface
120A	Permabond E37 RT Cure	1,499	10.34	0.7mm dia bubble at surface
120B	Permabond E37 RT Cure	2,232	15.39	Very brittle
121	Permabond E38	2,980	20.54	Failed through 1.5mm dia bubble and smaller ones. Cured at 60°C for 1 hour
122	Permabond E38	2,541	17.52	3.0 x 2.0mm bubble at edge, cured 24 hours at 60°C
123	Permabond E38			Poor result, cured 1 hour at RT before heating to 60°C
124	815 + RTU 90°C Post cure	9,011	62.13	No obvious bubbles at failure
125	815 + RTU 90°C Post cure	8,528	58.8	Failure through 1.5mm dia bubble at centre and surface
125A	815 + RTU 90°C Post cure	8,430	58.12	Failure at 0.8mm dia edge bubble

TABLE 6

SPECIMEN NO	ADHESIVE	ADHESIVE TENSILE STRENGTH		REMARKS
		PSI	MPa	
126	815 + RTU 90°C Post cure	9,047	62.375	Failed at 0.4mm dia edge bubble
127	815 + RTU 90°C Post cure Tested wet after 2 months	6,746	46.51	No obvious bubbles at fracture point, 67 days in water, water content 2.36%
128	815 + RTU 90°C Post cure Tested wet after 4 months	6,714	46.29	Tiny bubbles near origin of failure, 122 days in water, water content 2.6%
129	815 + RTU 90°C Post cure Tested wet after 6 months	6,266	43.2	Tiny bubbles at failure, 187 days in water, water content 3.15%
130	815 + RTU 120°C Post cure	5,000	34.48	No obvious bubbles at fracture point
131	815 + RTU 120°C Post cure	6,835	47.12	Only very tiny bubbles near fracture point
132	815 + RTU 120°C Post cure	7,222	49.79	Fractured at large surface bubble
133	815 + RTU RT Cure	6,124	42.22	Strain rate .005 X head speed .5mm/min, no obvious bubbles at point of fracture
134	815 + RTU RT Cure	4,224	29.12	Strain rate .005 X head speed .5mm/min, numerous very tiny bubbles at fracture

TABLE 6

SPECIMEN NO	ADHESIVE	ADHESIVE TENSILE STRENGTH		REMARKS
		PSI	MPa	
135	815 + RTU RT cure	7,067	48.73	Strain rate .005 X head speed .5mm/min, failed at 0.4mm dia edge bubble
136	815 + RTU RT cure	7,291	50.26	Strain rate .05 X head speed 5mm/min, numerous tiny bubbles at fracture face
137	815 + RTU RT cure	8,539	58.87	Strain rate .05 X head speed 5mm/min, 0.3mm dia bubble at fracture plus numerous tiny ones, fracture at start of radius
138	815 + RTU RT cure	8,576	59.13	Strain rate .05 X head speed 5mm/min, several 0.2mm dia bubbles at fracture face at surface, fracture at start of radius
139	815 + RTU RT cure	7,812	53.86	Strain rate 0.1 X head speed 10mm/min, fracture from a cluster of 0.2mm dia bubbles
140	815 + RTU RT cure	4,676	32.24	Strain rate 0.1 X head speed 10mm/min, fracture at start of radius from surface bubbles & a dirt inclusion
141	815 + RTU RT cure	6,372	43.93	Strain rate 0.1 X head speed 10mm/min, failure at small surface bubbles in parallel section
142	815 + RTU RT cure	3,924	27.05	Strain rate 0.5 X head speed 50mm/min, failure from one edge in parallel length, many tiny bubbles at centre of fracture
143	815 + RTU RT cure	7,207	49.69	Strain rate 0.5 X head speed 50mm/min, failure from one corner where tiny bubbles were present

TABLE 6

SPECIMEN NO	ADHESIVE	ADHESIVE TENSILE STRENGTH		REMARKS
		PSI	MPa	
144	815 + RTU RT cure	6,140	42.33	Strain rate 0.5 X head speed 50mm/min, failure from one edge where tiny bubbles were present of about 0.05mm dia
145	828 + RTU 100°C cure	9,012	62.134	Failure from surface bubble about 0.6mm dia
146	828 + RTU 100°C cure	9,791	67.5	Failure from a flow at the centre away from all surfaces
147	828 + RTU 100°C cure	6,606	45.54	Failure at a flow at centre near one edge at centre of cluster of small bubbles
148	815 + RTU RT cure	6,843	47.178	Failure from a corner bubble
149	FR 7020 RT Cure	4,665	32.16	Failed at large bubble 2.0 X 1.8mm
150	FR 7020 RT Cure	5,920	40.82	A few small bubbles at fracture surface
151	FR 7020 RT Cure	5,811	40.06	Failed from 0.8mm dia bubble at one corner and at start of radius
152	FR 7020 RT cure 2 months wet	2,098	14.46	Tested after 77 days in water, water content 6.35%, failed at large bubble at corner 1.50mm dia, numerous tiny bubbles at fracture surface

TABLE 6

SPECIMEN NO	ADHESIVE	ADHESIVE TENSILE STRENGTH		REMARKS
		PSI	MPa	
153	FR 7020 RT cure 4 months wet	2,660	18.34	Tested after 142 days in water, water content 7.14%, failed at 1.2mm dia bubble
154	FR 7020 RT cure 6 months wet	2,594	17.88	Tested after 200 days in water, water content 8.73%,
155	FR 7020 55°C Post cure For 3 hours	5,722	39.45	Failed from two surface bubbles, one 1.2mm & one 0.5mm dia about 6mm into radius at one end
156	FR 7020 55°C Post cure For 3 hours	5,798	39.97	Failed at corner bubble 1.0mm dia
157	FR 7020 55°C Post cure For 3 hours	6,141	42.34	Failure at 0.9mm dia bubble
158	FR 7020 80°C Post cure For 1 hour	6,282	43.31	Surface bubble 0.6mm and cluster of small bubbles at point of failure
159	FR 7020 80°C Post cure For 1 hour	7,065	48.71	Failed at start of radius
160	FR 7020 80°C Post cure For 1 hour	6,141	42.34	Failed at start of radius
161	Scrapped			

TABLE 6

SPECIMEN NO	ADHESIVE	ADHESIVE TENSILE STRENGTH		REMARKS
		PSI	MPa	
162	828 + RTU RT cure	5,589	38.53	No obvious bubbles at failure
162A	828 + RTU RT cure	7,281	50.2	No obvious bubbles at failure
163	828 + RTU RT cure	5,238	36.74	No obvious bubbles at failure
164	828 + RTU RT cure	7,570	52.19	No obvious bubbles at failure
165	828 + RTU RT cure	7,077	48.79	Tested after 55 days in water, water content 2.1%
166	828 + RTU RT cure	6,626	45.68	Tested after 90 days in water, water content 3.9%
167	828 + RTU RT cure	5,365	36.99	Tested after 178 days in water, water content 3.42%
168	828 + RTU 60°C post cure For 3 hours	9,420	64.95	Only very tiny bubbles visible
169	828 + RTU 60°C post cure For 3 hours	6,489	44.74	Only very tiny bubbles visible
170	828 + RTU RT cure For 3 hours	9,851	67.92	Only very tiny bubbles visible

TABLE 6A (PHASE ONE UPDATED)

COMPARISON OF ADHESIVES BY VARIOUS MECHANICAL & PHYSICAL PROPERTIES - ROOM TEMPERATURE DATA

ADHESIVE	LAP SHEAR STRENGTH ON ANODISED AL.ALLOY	TENSILE STRENGTH OF RESIN	TENSILE MODULUS OF RESIN BA TEST (ASTM D-638)	STRAIN TO FAILURE TOTAL	PLASTIC STRAIN AT FAILURE	WATER SOLUBILITY COEFFICIENT AFTER R.T. CURE	STRAIN ENERGY AT FAILURE N.mm
EA9330	3,500	4,000	84,000 (351,000)	4.45%	0.69% (2) 2.05% (3)	13%	2043.5
EA9321	4,190	4,500	125,000 (380,000)	2.74%	NIL	7.88%	2016
EPIKOTE 828 + VERSAMID 125	2,180	6,900	112,000 (395,000 EST)	5.28%	1.1%	6.25%	4700
EC2216	1,920	1,600	3,100 (51,000)	34%	NIL	5.7%	7150
EC3559	5,450*	3,600	94,000 (345,000 EST)	2.6%	NIL	5.15%	1064
AF163 (120°C Cure)	5,000	6,341	95,650 (350,000 EST)	5.9%	1.23%	1.89%	4550
EC 3524	1,350	1,300	33,000 (155,000)	2.74%	0.2%	35%	446.5
EPIKOTE 815 + RTU	783	8,135	178,000 (560,000 EST)	4.1%	NIL	7.35%	4200
EC 3568	3,150	2,391	98,550 (355,000 EST)	1.71%	NIL	18.7%	412.5
EC 3578	2,872	2,536	87,000 (325,000 EST)	1.71%	NIL	9.7%	455
PERMABOND E34	2,174	3,913	182,000 (570,000 EST)	1.37%	NIL	1.9%	540

* F.P.L. etch (2) Test Specimen Number (3) Test Specimen Number

TABLE 6 B (PHASE TWO)

COMPARISON OF ADHESIVES BY VARIOUS MECHANICAL & PHYSICAL PROPERTIES - DATA AFTER R.T. CURE

ADHESIVE	LAP SHEAR STRENGTH ON ANODISED AL.ALLOY PSI	TENSILE STRENGTH OF RESIN PSI	TENSILE MODULUS OF RESIN (PSI) BA TEST (ASTM D-638)	STRAIN TO FAILURE TOTAL %	PLASTIC STRAIN AT FAILURE %	WATER SOLUBILITY COEFFICIENT %	STRAIN ENERGY AT FAILURE N.mm
REDUX 308A ***	6,740	* 7,250	145,691 (480,000 EST)	3.58	1.14	3.6	2,757
REDUX 408	2,756	3,740	213,730 (650,000 EST)	1.42	NIL	13.0	532
REDUX 408 + 20% 410NA	# 2,266	* 4,845	213,231 (650,000 EST)	1.65	NIL	11.3	836
REDUX 408 + 40% 410NA	# 2,590	* 4,464	168,206 (540,000 EST)	1.85	NIL	8.35	831
REDUX 410NA	4,786	4,080	106,193 (380,000 EST)	3.34	1.44	4.8	1,769
HYSOL EA9309.3NA	4,200	* 4,402	115,147 (360,000 MFR)	3.9	2.01	5.0	2,010
HYSOL EA 9330	3,500	4,000	84,000 (351,000 MFR)	4.45	0.69 (2) 2.05 (3)	13.0	2,044
HYSOL EA 9321	4,190	4,500	125,000 (380,000 MFR)	2.74	NIL	7.88	2,016
3M EC 2216	1,920	1,600	3,100 (51,000 MFR)	34%	NIL	5.7	7,150

TABLE 6.B (PHASE TWO)

COMPARISON OF ADHESIVES BY VARIOUS MECHANICAL & PHYSICAL PROPERTIES - DATA AFTER R.T. CURE

ADHESIVE	LAP SHEAR STRENGTH ON ANODISED AL.ALLOY PSI	TENSILE STRENGTH OF RESIN PSI	TENSILE MODULUS OF RESIN (PSI) BA TEST (ASTM D-638)	STRAIN TO FAILURE TOTAL %	PLASTIC STRAIN AT FAILURE %	WATER SOLUBILITY COEFFICIENT %	STRAIN ENERGY AT FAILURE N.mm
3M EC 9323	5,250	4,715	138,688 (416,280 MFR)	2.51	0.55	9.1	1,205
BOSTIK 5435/TM2	2,700	466	1,764 (8,820 EST)	23.0	12.8	10.6	1,498
EPIKOTE 828 + VERSAMID 125	2,180	6,900	112,000 (395,000 EST)	5.28	1.1	6.25	4,700
EC 3524	1,350	1,300	33,000 (155,000 EST)	2.74	0.2	35.0	446
AF 163 (120°C Cure)	5,000	6,341	95,650 (350,000 EST)	5.90	1.23	1.89	4,550
PERMABOND E38 **	4,061	* 2,761	83,772 (320,000 EST)	2.23	0.48	15.9	568

\# - Adhesive failures in B.A. Lap Shear Test. All other results are from Manufacturer's Data Sheets.
* - Free Surface (No release sheet).
** - Cured at 60°C.
*** - Cured at 170°C.
Note: Values are an average of three results except for water solubility which is a single result. Permabond E38 are an average of two

TABLE 6C (PHASE TWO)

COMPARISON OF COMPOSITE MATRIX RESINS BY VARIOUS MECHANICAL & PHYSICAL PROPERTIES - DATA AFTER R.T. CURE

COMPOSITE MATRIX RESIN	LAP SHEAR STRENGTH ON ANODISED AL.ALLOY PSI	TENSILE STRENGTH OF RESIN PSI	TENSILE MODULUS OF RESIN (PSI) BA TEST (ASTM D-638)	STRAIN TO FAILURE TOTAL %	PLASTIC STRAIN AT FAILURE %	WATER SOLUBILITY COEFFICIENT %	STRAIN ENERGY AT FAILURE N.mm
REDUX 501	# 1,151	4,161	204,435 (630,000 EST)	1.57	NIL	14.2	853
REDUX 501 + 20% 41ONA	# 1,443	* 9,056	153,352 (500,000 EST)	4.39	1.51	15.1	4,176
REDUX 501 + 40% 41ONA	# 1,619	* 6,566	142,471 (475,000 EST)	3.29	NIL	15.36	2,217
EPIKOTE 815 + EPIKURE RTU	# 783	* 9,154	178,000 (560,000 EST)	4.11	NIL	7.35	4,700
EPIKOTE 828 + EPIKURE RTU	# 1,567	* 6,420	189,188 (580,000 EST)	2.33	NIL	4.6	1,512
EPIKOTE 828 + VERSAMID 125	2,180	6,900	112,000 (395,000 EST)	5.28	1.1	6.25	4,700
PERMABOND E34	2,174	3,442	182,000 (570,000 EST)	1.37	NIL	1.9	540
PERMABOND E37	1,200	* 1,775	150,530 (510,000 EST)	0.81	NIL	2.8	145
FR 7020	2,400	* 5,465	132,221 (450,000 EST)	2.81	NIL	9.3	1,483

- Adhesive failures in B.A. Tests. All other lap shear results results are from Manufacturer's Data.
* - Free Surface moulded (No release sheet)
Note: All values are an average of three results except for water solubility which is a single result.

TABLE 7A (PHASE TWO)

COMPARISON OF ADHESIVES BY VARIOUS MECHANICAL PROPERTIES - DATA AFTER POST CURE AT 50°C FOR 3 HOURS

ADHESIVE	LAP SHEAR STRENGTH ON ANODISED AL.ALLOY	TENSILE STRENGTH OF RESIN PSI	TENSILE MODULUS OF RESIN (PSI) BA TEST (ASTM D-638)	STRAIN TO FAILURE TOTAL %	PLASTIC STRAIN AT FAILURE %	WATER SOLUBILITY COEFFICIENT %	STRAIN ENERGY AT FAILURE N.mm
REDUX 408	-	3,553	259,764 (650,000)	1.0	NIL	12.4	393
REDUX 410 NA	-	4,053	92,449 (345,000)	4.93	3.05	4.8	2,514
HYSOL EA 9309.3NA	-	4,837	97,100 (360,000)	3.97	1.6	4.6	2,140
3M-EC9323	-	5,307	127,458 (435,000)	3.13	1.07	8.2	1,862

NOTE: All values are an average of three results except for water solubility which is a single result. Hysol EA9309.3NA was inadvertently cured at 56°C for 3 hours.

TABLE 7B (PHASE TWO)

COMPARISON OF COMPOSITE MATRIX RESINS BY VARIOUS MECHANICAL PROPERTIES - DATA AFTER POST CURE AT 50°C FOR 3 HOURS

COMPOSITE MATRIX RESIN	LAP SHEAR STRENGTH ON ANODISED AL.ALLOY	TENSILE STRENGTH OF RESIN PSI	TENSILE MODULUS OF RESIN (PSI) BA TEST (ASTM D-638)	STRAIN TO FAILURE TOTAL %	PLASTIC STRAIN AT FAILURE %	WATER SOLUBILITY COEFFICIENT %	STRAIN ENERGY AT FAILURE N.mm
REDUX 501	-	4,858	183,028 (575,000)	1.8	NIL	19.9	943
FR 7020	-	5,887	124,035 (427,000)	3.01	NIL	8.8	1,577

NOTE: All values are an average of three results except for water solubility which is a single result. FR 7020 was inadvertently cured at 55°C.

TABLE 8A (PHASE TWO)

COMPARISON OF ADHESIVES BY VARIOUS MECHANICAL PROPERTIES - DATA AFTER POST CURE AT 80°C FOR 1 HOUR

ADHESIVE	LAP SHEAR STRENGTH ON ANODISED AL.ALLOY	TENSILE STRENGTH OF RESIN PSI	TENSILE MODULUS OF RESIN (PSI) BA TEST (ASTM D-638)	STRAIN TO FAILURE TOTAL %	PLASTIC STRAIN AT FAILURE %	WATER SOLUBILITY COEFFICIENT %	STRAIN ENERGY AT FAILURE N.mm
REDUX 408	-	3,522	239,678 (640,000)	1.37	NIL	7.9	389
REDUX 410 NA	-	3,930	90,550 (336,000)	4.09	2.12	4.95	1,987
HYSOL EA 9309.3NA	-	4,993	111,151 (395,000)	3.81	1.28	4.4	2,170
3M-EC9323	5,915	5,153	115,907 (407,000)	3.96	2.04	6.8	2,424

NOTE: All values are an average of three results except for water solubility which is a single result.

TABLE 8B (PHASE TWO)

COMPARISON OF COMPOSITE MATRIX RESINS BY VARIOUS MECHANICAL PROPERTIES - DATA AFTER POST CURE AT VARIOUS TEMPERATURES

COMPOSITE MATRIX RESIN	LAP SHEAR STRENGTH ON ANODISED AL.ALLOY	TENSILE STRENGTH OF RESIN PSI	TENSILE MODULUS OF RESIN (PSI) BA TEST (ASTM D-638)	STRAIN TO FAILURE TOTAL %	PLASTIC STRAIN AT FAILURE %	WATER SOLUBILITY COEFFICIENT %	STRAIN ENERGY AT FAILURE N.mm
REDUX 501	80°C for 1 hour	9,292	157,081 (510,000)	4.54	3.01	13.4	4,621
EPIKOTE 815 + EPIKURE RTU	90°C for 1 hour	8,754	168,339 (537,000)	5.11	2.42	-	5,754
EPIKOTE 815 + EPIKURE RTU	120°C for 1.5 hours	6,352	163,217 (525,000)	2.92	0.87	3.4	2,033
EPIKOTE 828 + EPIKURE RTU	60°C for 3 hours	8,587	183,711 (575,000)	3.84	1.37	-	3,958
EPIKOTE 828 + EPIKURE RTU	100°C for 2 hours during cure	8,470	139,717 (470,000)	4.61	1.44	-	4,368
FR 7020	80°C for 1 hour	6,496	127,950 (440,000)	3.04	NIL	7.8	1,660

NOTE: All values are an average of three results except for water solubility which is a single result.

TABLE 9A - PHASE TWO

COMPARISON OF ADHESIVES BY VARIOUS MECHANICAL PROPERTIES - DATA AFTER RT CURE AND VARIOUS PERIODS OF WATER IMMERSION AT RT

ADHESIVE	WATER IMMERSION TIME (DAYS)	WATER CONTENT %	TENSILE STRENGTH OF RESIN (PSI)	TENSILE MODULUS OF RESIN BA TEST (PSI) (ASTM D-638)	STRAIN TO TOTAL FAILURE	PLASTIC STRAIN AT FAILURE	STRAIN ENERGY AT FAILURE N.mm
REDUX 408	183	12.2	2,999	119,976 (417,000)	1.85	-	540.7
REDUX 408	183	12.2	2,624	122,810 (425,000)	1.5	-	392
REDUX 408	183	11.6	2,880	121,603 (421,000)	1.85	-	578.5
REDUX 410NA	69	3.65	3,278	90,276 (337,000)	4.45	3.0	2,047
REDUX 410NA	107	4.8	3,718	98,749 (360,000)	3.97	2.33	1,877
REDUX 410NA	183	3.36	3,440	118,278 (412,000)	3.22	0.96	1,238

TABLE 9A - PHASE TWO

COMPARISON OF ADHESIVES BY VARIOUS MECHANICAL PROPERTIES - DATA AFTER RT CURE AND VARIOUS PERIODS OF WATER IMMERSION AT RT

ADHESIVE	WATER IMMERSION TIME (DAYS)	WATER CONTENT %	TENSILE STRENGTH OF RESIN (PSI)	TENSILE MODULUS OF RESIN BA TEST (PSI) (ASTM D-638)	STRAIN TO TOTAL FAILURE	PLASTIC STRAIN AT FAILURE	STRAIN ENERGY AT FAILURE N.mm
HYSOL 9309.3NA	38	4.3	4,003	105,534 (380,000)	3.08	1.3	1,413
HYSOL 9309.3NA	109	4.6	3,946	87,499 (330,000)	3.97	1.64	2,210
HYSOL 9309.3NA	195	5.1	3,940	99,546 (365,000)	3.77	1.71	1,872
3M-EC9323	69	6.04	3,436	94,251 (350,000)	3.56	2.06	1,470
3M-EC9323	107	7.5	3,654	101,749 (370,000)	2.95	1.16	1,212
3M-EC9323	183	6.6	3,337	88,230 (330,000)	3.15	1.1	1,193

TABLE 9B - PHASE TWO

COMPARISON OF COMPOSITE MATRIX RESINS BY VARIOUS MECHANICAL PROPERTIES - DATA AFTER RT CURE AND VARIOUS PERIODS OF WATER IMMERSION AT RT

COMPOSITE MATRIX RESIN	WATER IMMERSION TIME (DAYS)	WATER CONTENT %	TENSILE STRENGTH OF RESIN (PSI)	TENSILE MODULUS OF RESIN BA TEST (PSI) (ASTM D-638)	STRAIN TO TOTAL FAILURE	PLASTIC STRAIN AT FAILURE	STRAIN ENERGY AT FAILURE N.mm
REDUX 501	183	14.2	2,885	103,951 (375,000)	1.92	NIL	551
REDUX 501	183	15.8	2,728	96,056 (355,000)	1.85	NIL	489
REDUX 501	183	15.4	2,371	99,127 (362,000)	1.64	NIL	402
EPIKOTE 815 + EPIKURE RTU	67	2.36	6,746	168,158 (537,000)	3.15	0.685	2,224
EPIKOTE 815 + EPIKURE RTU	122	2.6	6,714	172,296 (550,000)	2.74	NIL	1,900
EPIKOTE 815 + EPIKURE RTU	187	3.15	6,266	166,780 (535,000)	2.74	0.68	1,761

NOTE: 815 + RTU was post-cured at 90°C for 1 hour, all others RT cure

TABLE 9B - PHASE TWO

COMPARISON OF COMPOSITE MATRIX RESINS BY VARIOUS MECHANICAL PROPERTIES - DATA AFTER RT CURE AND VARIOUS PERIODS OF WATER IMMERSION AT RT

COMPOSITE MATRIX RESIN	WATER IMMERSION TIME (DAYS)	WATER CONTENT %	TENSILE STRENGTH OF RESIN (PSI)	TENSILE MODULUS OF RESIN BA TEST (PSI) (ASTM D-638)	STRAIN TO TOTAL FAILURE	PLASTIC STRAIN AT FAILURE	STRAIN ENERGY AT FAILURE N.mm
EPIKOTE 828 + EPIKURE RTU	55	2.1	7,077	161,967 (520,000)	3.43	0.89	1,383
EPIKOTE 828 + EPIKURE RTU	90	3.9	6,626	156,475 (510,000)	3.29	1.23	2,373
EPIKOTE 828 + EPIKURE RTU	178	3.4	5,365	152,848 (500,000)	2.47	NIL	1,351
FR 7020	77	6.35	2,098	110,858 (395,000)	1.2	NIL	233
FR 7020	142	7.14	2,660	89,723 (327,500)	1.78	NIL	417
FR 7020	200	8.73	2,594	104,834 (380,000)	1.71	NIL	458

TABLE 10

COMPRESSION TEST DATA (ADDITIONAL WORK FOR PHASE TWO)

ADHESIVE	COMPRESSION STRENGTH AT ELASTIC LIMIT	COMPRESSION ULTIMATE STRENGTH	COMPRESSION MODULUS	ELASTIC LIMIT STRAIN	TOTAL STRAIN AT ULTIMATE LOAD	MODE OF FAILURE & REMARKS
REDUX 408	65 N/mm2 9,428 psi	95 N/mm2 13,780 psi	2612.5 N/mm2 378,930 psi	2.5%	4.9%	No failure at 10% plastic strain, no bubbles
REDUX 408 + 20% 410 NA	53.7 N/mm2 7,790 psi	80.49 N/mm2 11,675 psi	2525.7 N/mm2 366,343 psi	2.125%	4.7%	No failure at 10% plastic strain, no bubbles, sample 9 mm sq
REDUX 408 + 40% 410 NA	55 N/mm2 7,977 psi	77.47 N/mm2 11,237 psi	2389 N/mm2 346,496 psi	2.33%	4.4%	No failure at 10% plastic strain, no bubbles
REDUX 410 NA	29.5 N/mm2 4,279 psi	38.87 N/mm2 5,638 psi	1409.37 N/mm2 204,423 psi	2.2%	3.8%	No failure at 10% plastic strain, some bubbles
BOSTIK 5435/TM2	10.65 N/mm2 1,548 psi	No Value Found	100 N/mm2 14,505 psi	10.63%	Not Found	No failure at 10% plastic strain, some bubbles
3M-EC 2216	5.0 N/mm2 725 psi	No Value Found	69.17 N/mm2 10,032 psi	8%	Not Found	No failure at 10% plastic strain, some bubbles,

Compression strength at elastic limit taken at the point of departure from the straight line portion of the stress/strain curve. All testing was carried out at Room Temperature at a strain rate of 0.01 in an ROP-Howden screw driven electronic testing machine. Specimens were 10mm x 10mm x 25mm to BA drawing 4-43497 except where stated otherwise.
EC 2216 gave an increase in the slope of the curve above 5 N/mm2 with a progressive increase in lateral dimensions of the specimen. No true yield strength was found and no ultimate strength occurred up to 10% plastic strain.
Bostik 5435/TM2 was similar except that a progressive decrease in the slope of the curve occurred beyond 10.65 N/mm2.
Note: All materials except Permabond E34 were tested to 10% plastic strain without failure. Redux 408 results are an average of 2 tests. Redux 410NA results are an average of 4 tests. All others are an average of 3 tests.

TABLE 10

COMPRESSION TEST DATA (ADDITIONAL WORK FOR PHASE TWO) PAGE 2 OF 4

ADHESIVE	COMPRESSION STRENGTH AT ELASTIC LIMIT	COMPRESSION ULTIMATE STRENGTH	COMPRESSION MODULUS	ELASTIC LIMIT STRAIN	TOTAL STRAIN AT ULTIMATE LOAD	MODE OF FAILURE & REMARKS
3M-EC 9323	34 N/mm2 4,932 psi	47.5 N/mm2 6,890 psi	1704.2 N/mm2 247,181 psi	2.03%	3.5%	No failure at 10% plastic strain, some bubbles
HYSOL EA9309.3NA	34.75 N/mm2 5,040 psi	42.65 N/mm2 6,186 psi	1429 N/mm2 207,270 psi	2.45%	3.6%	No failure at 10% plastic strain, some bubbles
HYSOL EA 9330	30 N/mm2 4,351 psi	42.3 N/mm2 6,135 psi	1500 N/mm2 217,568 psi	1.97%	3.3%	No failure at 10% plastic strain, some bubbles
HYSOL EA 9321	40 N/mm2 5,802 psi	56 N/mm2 8,123 psi	1683 N/mm2 244,160 psi	2.4%	4.83%	No failure. Load continued to rise, some bubbles. Test stopped at 10% plastic strain.
3M-AF163 *	8.875 N/mm2 1,287 psi	18.37 N/mm2 2,665 psi	424.18 N/mm2 61,525 psi	2%	15%	Cured as a block under vacuum but full of small voids at 10X magnification
REDUX 308A *	12.55 N/mm2 1,820 psi	24.28 N/mm2 3,521 psi	715.81 N/mm2 103,824 psi	1.8%	7%	Cured under vacuum pressure, some large voids full of small voids No failure at 10% plastic strain
EA 9330 + 20% Microballoons	6.83 N/mm2 991 psi	11.55 N/mm2 1,675 psi	407.5 N/mm2 59,105 psi	1.7%	12%	Many small voids. Wide variation in modulus values

* It was found difficult to produce blocks of film adhesive for this type of test. Their high exotherm produces many small voids even under vacuum pressure. These results are certainly far too low.

TABLE 10

COMPRESSION TEST DATA (ADDITIONAL WORK FOR PHASE TWO)

ADHESIVE	COMPRESSION STRENGTH AT ELASTIC LIMIT	COMPRESSION ULTIMATE STRENGTH	COMPRESSION MODULUS	ELASTIC LIMIT STRAIN	TOTAL STRAIN AT ULTIMATE LOAD	MODE OF FAILURE & REMARKS
PERMABOND E34	60 N/mm2 8,703 psi	82.17 N/mm2 11,918 psi	2616.7 N/mm2 379,535 psi	2.23%	3.77%	Shear fractures occurred between 6% & 12% total strain, some bubbles
PERMABOND E38	21 N/mm2 3,046 psi	35.53 N/mm2 5,153 psi	1267 N/mm2 183,738 psi	1.7%	4.23%	5.0-4.0 mix 60°C 1 hour Samples 9 mm sq.
PERMABOND E38	22.22 N/mm2 3,223 psi	33.66 N/mm2 4,882 psi	1214 N/mm2 176,085 psi	1.9%	4.7%	5.0-4.0 mix 60°C 24 hours
PERMABOND E38	24.3 N/mm2 3,525 psi	36.2 N/mm2 5,251 psi	1261 N/mm2 182,950 psi	2.0%	4.13%	5.2 - 4.0 mix 60°C 1 hour

TABLE 10

COMPRESSION TEST DATA (ADDITIONAL WORK FOR PHASE TWO)

COMPOSITE MATRIX RESIN	COMPRESSION STRENGTH AT ELASTIC LIMIT	COMPRESSION ULTIMATE STRENGTH	COMPRESSION MODULUS	ELASTIC LIMIT STRAIN	TOTAL STRAIN AT ULTIMATE LOAD	MODE OF FAILURE & REMARKS
REDUX 501	80 N/mm2 11,603 psi	105 N/mm2 15,230 psi	2508.3 N/mm2 363,822 psi	3.2%	5.37%	No failure at 10% plastic strain, no bubbles
REDUX 501 + 20% 410 NA	68.52 N/mm2 9,938 psi	94.05N/mm2 13,642 psi	2304.53 N/mm2 334,261 psi	3.0%	5.53%	No failure at 10% plastic strain, no bubbles sample 9 mm sq
REDUX 501 + 40% 410 NA	59.26 N/mm2 8,595 psi	83.46 N/mm2 12,105 psi	2139.92 N/mm2 310,385 psi	2.77%	5%	No failure at 10% plastic strain, no bubbles sample 9 mm sq
SHELL EPIKOTE 815 + RTU	60 N/mm2 8,703 psi	93.17 N/mm2 13,514 psi	2150 N/mm2 315,473 psi	2.7%	7.34%	No failure at 10% plastic strain, no bubbles
815 + RTU 80°C Cure	56.67 N/mm2 8,220 psi	93.33 N/mm2 13,537 psi	2044.67 N/mm2 296,569 psi	2.8%	7.5%	No failure at 10% plastic strain, no bubbles
815 + RTU 120°C Cure	54.32 N/mm2 7,879 psi	92.47 N/mm2 13,412 psi	2167 N/mm2 314,350 psi	2.57%	7.1%	No failure at 10% plastic strain, no bubbles, sample 9 mm sq
828 + RTU RT Cure	41 MPa 5,947 psi	101.6 N/mm2 14,737 psi	1790 MPa 259,631 psi	2.3%	13.9%	Average of two results. Ultimate load and strain at ultimate not clearly defined
PERMABOND E37	91 N/mm2 13,199 psi	107.87 N/mm2 15,646 psi	2766.5 N/mm2 401,268 psi	3.4%	4.4%	Third sample crumbled at 5% strain. Other two went to 10% without failure
FR 7020 # RT Cure	53.5 MPa 7,760 psi	72.67 N/mm2 10,541 psi	1736.1 MPa 251,809 psi	5.5%	5.5%	Black spots on machined faces indicated possible areas of incomplete mixing

No failure at 10% plastic strain

TABLE 11A

ASTM D-3762 FRACTURE ENERGY TEST RESULTS - ADHESIVES

Adhesive	Lap Shear Strength PSI	Glue Line Thickness Inch	Initial Crack Length mm ao	Crack Growth After 24 hrs mm	Initial Fracture Energy kJ/m2	Fracture Energy After 24 hrs kJ/m2	% Cohesive Failure And Remarks
3M-EC2216	1,920	.020 .014 .015	26.5 27.0 31.0	7.5 8.0 7.0	5 4.6 2.7	1.8 1.7 1.25	100% Cohesive 100% Cohesive 100% Cohesive
HYSOL 9330	3,500	.012 .014 .014	24.5 25.0 25.5	1.0 1.0 NIL	6.8 6.2 5.8	5.8 5.4 5.8	100% Cohesive 100% Cohesive 100% Cohesive
HYSOL EA9321	4,190	.014 .013 .023	51 49.75 ---	2.0 2.0 ---	0.4 0.46 ---	0.35 0.39 ---	60% Cohesive 60% Cohesive 40% Cohesive, Split at end of test
REDUX 408	2,756	.011 .003 .004	58.5 61.0 68.0	2.0 2.5 NIL	0.24 0.21 0.135	0.21 0.175 0.135	100% Cohesive 100% Cohesive 100% Cohesive
100 PARTS REDUX 408 + 20 PARTS 410 NA	2,266	.015 .011 .014	59.5 51.5 49.0	1.25 NIL 0.5	0.22 0.39 0.46	0.2 0.39 0.45	50% Cohesive 95% Cohesive 100% Cohesive
100 PARTS REDUX 408 + 40 PARTS 410 NA	2,590	.014 .013 .009	49.25 48.25 46.0	NIL 1.5 1.5	0.45 0.48 0.60	0.45 0.45 0.54	90% Cohesive 65% Cohesive 100% Cohesive

Note: Crack growth after 24 hours is for dry specimens

TABLE 11A

ASTM D-3762 FRACTURE ENERGY TEST RESULTS - ADHESIVES

Adhesive	Lap Shear Strength PSI	Glue Line Thickness Inch	Initial Crack Length mm ao	Crack Growth After 24 hrs mm	Initial Fracture Energy kJ/m2	Fracture Energy After 24 hrs kJ/m2	% Cohesive Failure And Remarks
100 PARTS REDUX 408 + 100 PARTS 410 NA	4,940	.012 .011 .014	37.5 37.5 36.0	1.0 0.5 0.75	1.3 1.3 1.5	1.2 1.25 1.4	100% Cohesive 100% Cohesive 100% Cohesive
1 PART REDUX 408 + 3 PARTS 410 NA	5,002	.009 .013 .016	36.5 33.5 32.0	3.5 NIL 2.75	1.4 2.0 2.4	1.05 2.0 1.75	100% Cohesive 100% Cohesive 100% Cohesive
REDUX 410NA	4,786	.016 .015 .017	21.0 22.0 22.0	0.5 3.5 2.5	13.0 11.0 11.0	11.8 6.0 6.8	100% Cohesive 100% Cohesive 100% Cohesive
REDUX 308A 150° CURE	6,924	.010 .010 .018	29.75 33.5 26.0	2.0 NIL NIL	3.1 2.0 5.4	2.5 2.0 5.4	100% Cohesive 100% Cohesive 100% Cohesive
REDUX 308A 170° CURE	6,740	.007 .007 .018	30.0 30.75 27.75	1.0 2.5 NIL	3.0 2.8 4.1	2.7 2.05 4.1	100% Cohesive 100% Cohesive 100% Cohesive
3M AF163-2K 120°C CURE	5,800	.010 .0105 .020 .0215	24.5 26.5 24.0 25.0	1.25 2.0 NIL NIL	6.8 5.0 7.4 6.4	5.6 3.7 7.4 6.4	100% Cohesive 100% Cohesive 100% Cohesive 100% Cohesive
HYSOL EA9309.3NA	4,200	.012 .013 .014	28.0 23.75 25.0	2.0 1.0 2.0	4.0 8.0 6.4	3.0 6.6 4.6	100% Cohesive 100% Cohesive 100% Cohesive

Note: Crack growth after 24 hours is for dry specimens

TABLE 11B

ASTM D-3762 FRACTURE ENERGY TEST RESULTS - COMPOSITE MATRIX RESINS

Adhesive	Lap Shear Strength PSI	Glue Line Thickness Inch	Initial Crack Length mm ao	Crack Growth After 24 hrs mm	Initial Fracture Energy kJ/m2	Fracture Energy After 24 hrs kJ/m2	% Cohesive Failure And Remarks
EPIKOTE 815 + EPIKURE RTU	783	.018 .011 .014	68.0 73.0 75.0	NIL NIL NIL	0.135 0.1 0.09	0.135 0.1 0.09	100% Cohesive, Tiny bubbles 100% Cohesive, Tiny bubbles 100% Cohesive, Tiny bubbles
EPIKOTE 828 + EPIKURE RTU	1,567	.012 .013 .015	99.5 SPLIT SPLIT	NIL - -	0.03 - -	0.03 - -	100% Cohesive, Tiny bubbles 100% Cohesive, Tiny bubbles 100% Cohesive, Tiny bubbles
FR 7020	2,400	.020 .015 .017	SPLIT 94.5 79.0	- NIL NIL	- 0.037 0.075	- 0.037 0.075	100% Adhesive, Tiny bubbles 100% Adhesive, Tiny bubbles 100% Adhesive, Tiny bubbles
REDUX 501	1,200	.006 .006 .007	95.0 88.5 96.5	7 10 9	0.037 0.048 0.034	0.027 0.031 0.024	100% Adhesive, Very tiny bubbles 100% Adhesive, Very tiny bubbles 100% Adhesive, Very tiny bubbles
100 PARTS REDUX 410NA + 20 PARTS 501	5,000 From Graph	.012 .015 .016	28.5 28.0 28.0	2 1.25 1.0	3.7 4.0 4.0	2.8 3.4 3.5	100% Cohesive, Tiny bubbles 100% Cohesive, Tiny bubbles 100% Cohesive, Tiny bubbles
100 PARTS REDUX 410NA + 40 PARTS 501	4,676	.016 .013 .016	51.0 58.0 56.5	NIL NIL 2.5	0.4 0.245 0.27	0.4 0.245 0.23	100% Cohesive, Tiny bubbles 100% Cohesive, Tiny bubbles 100% Cohesive, Tiny bubbles
100 PARTS REDUX 410NA + 100 PARTS 501	3,238	.006 .004 .006	62.5 58.0 63.5	NIL NIL NIL	0.185 0.25 0.175	0.185 0.25 0.175	92% Cohesive, Tiny bubbles 90% Cohesive, Tiny bubbles 24% Cohesive, Tiny bubbles
3 PARTS REDUX 501 + 1 PART 410NA	1,500 From Graph	.002 .003 .013	72.0 73.0 56.5	4.5 NIL NIL	0.11 0.1 0.27	0.085 0.1 0.27	100% Adhesive 100% Adhesive 100% Cohesive, Thicker glue line than other two

Note: Crack growth after 24 hours is for dry specimens

However, study of this set of data suggests that total strain at failure correlates better with lap shear strength of Aluminium Alloy joints than plastic strain. Total strain is the sum of the elastic and plastic strains. From the second two sections of the work it was found, in general, that the tensile modulus was little affected by post-curing. Figs 46-57 (pages 198 - 209).

Some resins actually reached their highest modulus from a room temperature cure and values after post-cure were slightly lower. Redux 408 showed a slight increase in modulus after a 50°C post-cure. A 90°C post-cure was found to be beneficial to the tensile strength of Epikote 815 + RTU but a 120°C post-cure reduced it almost to the RT cure level. See Tables 7A and 7B (pages 180 - 181) and 8A and 8B (pages 182 - 183).

For Epikote 828 + RTU both 60°C and 100°C post-cures improved the tensile strength. At a constant modulus, improved tensile strength goes hand-in-hand with improved elongation. See Figs 58 - 72 (pages 210 - 224) and 73-84 (pages 225 - 236).

The tensile elongation of Redux 501 is shown in Fig 106 (page 263). These results are also reflected in strain energy at failure for Redux 501 in Fig 109 (page 266) See also Figs 85 - 97 (pages 237 - 249).

The Effect of Water on Resin Mechanical Properties

The effect of water on these tensile tests was generally as expected i.e. Tensile modulus was reduced except for Redux 410 NA, Hysol 9309 3NA, Epikote 815 + RTU (90°C post-cure) in which cases it made very little difference. Only a small loss occurred with Epikote 828 + RTU after RT cure. As would be expected adhesives with a low water uptake suffered the lowest losses. See Figs 46 - 57 (pages 198 - 209). See also Tables 9A and 9B (pages 184 - 187).

Tensile strength effects were surprising in some cases. Redux 408, showed little loss of tensile strength in spite of a high water uptake. Redux 501 with a very high water uptake showed less scatter and only a slight loss compared to the more scattered average RT values. Regrettably, FR 7020 (recommended by Boeing) showed a considerable loss of tensile strength after water immersion, Epikote 815 + RTU showed a smaller but significant loss. See Figs 58 - 72 (pages 210 - 224).

Tensile elongation (See Figs 73 - 84) (pages 225-236) Redux 408 showed no change in spite of a high water uptake. Redux 410NA showed no change in total value but the proportion of plastic strain was slightly increased. Redux 501 showed a very slight increase.

EC9323 showed a slight increase in total strain and plastic strain and a slight reduction of elastic strain.

EA9309.3NA showed no significant effect.

Epikote 815 + RTU (90°C post cure) was unusual in that a significant loss of elongation occurred and nearly all of it from the plastic strain component. In this case water

had an embrittling effect. Sauer and Smith (1985) state that for glassy polymers water acts as both a crazing and a plasticising agent. In cases where crazing is the dominant effect embrittlement would be expected

Epikote 828 + RTU (RT cure) showed the reverse effect, elongation increased and a plastic component was added to the total strain except for the third specimen.

FR 7020 showed a significant loss of elastic strain in parallel with its loss of tensile strength.

Strain Energy at Failure (Figs 85 - 97) (pages 237 - 249)

Redux 408 - A slight loss
Redux 410NA - No effect
Redux 501 - A loss of strain energy, on average, but far less scatter of results.
EC 9323 - No significant effect
EA 9309.3NA - A slight loss
Epikote 815 + RTU (90°C post cure) - a loss of 65% in parallel with the loss of plastic strain
Epikote 828 + RTU (RT cure) - A slight gain with water immersion

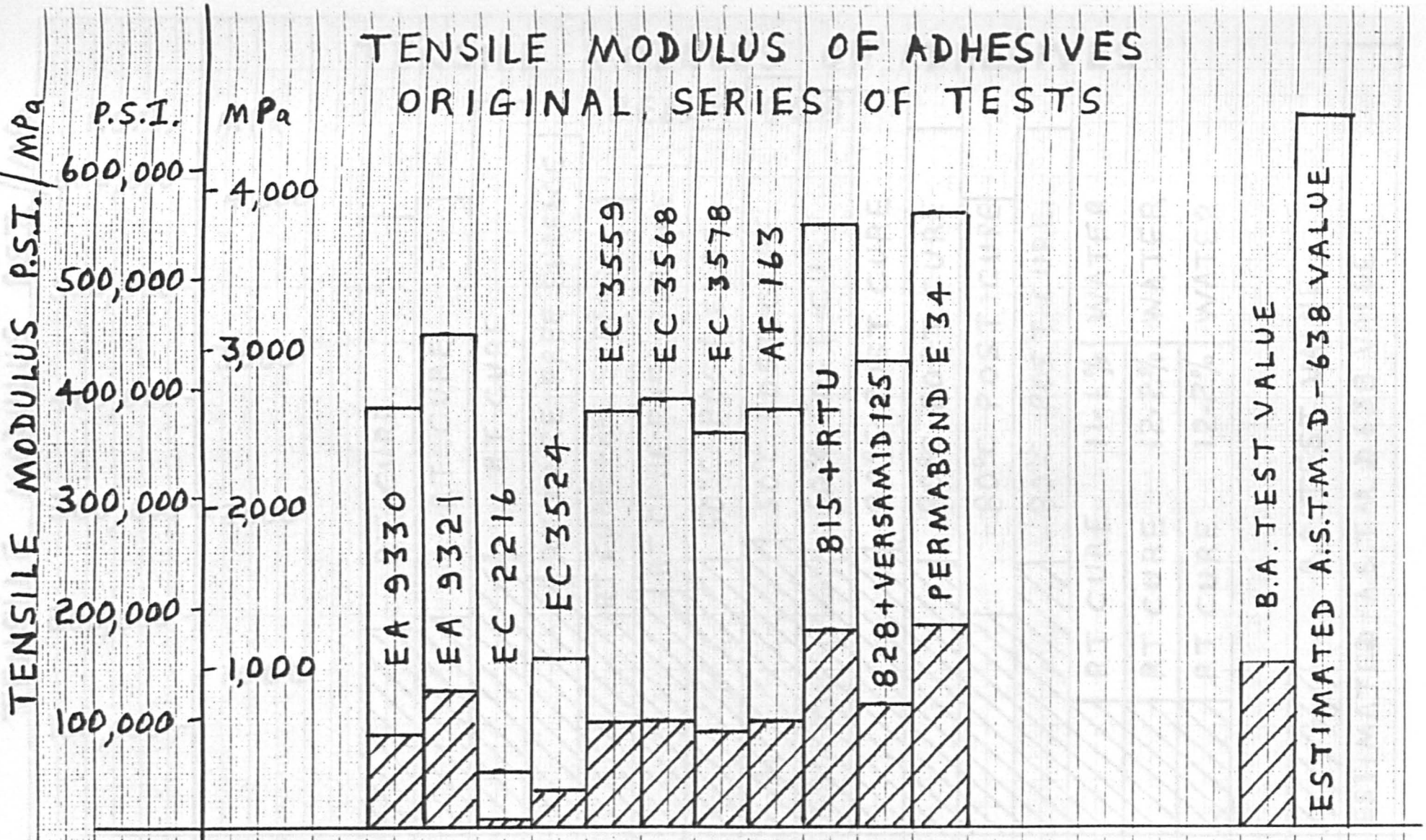
The last two are most interesting because the curing agent is the same and Epikote 815 is Epikote 828 diluted with a n-butyl glycidyl ether. The diluent appears to have a dramatic effect on the consequences of water immersion. FR 7020 showed a loss of 65% in parallel with a loss of tensile strength and elongation. Workshop experience with FR 7020 shows that it does not wet out fabrics easily because of its viscosity. Other resins are easier to use and also have better properties.

(Text continues on page 250)

TENSILE MODULUS OF ADHESIVES
MANUFACTURER'S DATA
HYSOL
TENSILE MODULUS P.S.I./MPa
P.S.I.
MPa
700,000
600,000
500,000
400,000
300,000
200,000
100,000
4,000
3,000
2,000
1,000
EA 934NA
EA 956
EA 9309.3NA
EA 9313
EA 9314
EA 9320
EA 9321
EA 9330
EA 9628
EA 9649
865,000

FIG: 46

TENSILE MODULUS OF ADHESIVES
ORIGINAL SERIES OF TESTS



IN FIGS 47 TO 57 THE CROSS-HATCHED VALUE IS THAT OBTAINED FROM THE B.A. TEST AND THE PLAIN BAR VALUE IS ESTIMATED FROM FIG: 16, PAGE 105.

FIG: 47

TENSILE MODULUS OF ADHESIVES
REDUX 408
TENSILE MODULUS P.S.I./MPa
P.S.I.
MPa
600,000
500,000
400,000
300,000
200,000
100,000
4,000
3,000
2,000
1,000
RT CURE
RT CURE
RT CURE FREE SURFACE
RT CURE FREE SURFACE
RT CURE FREE SURFACE
RT CURE FREE SURFACE
50°C POST CURE
50°C POST CURE
50°C POST CURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
RT CURE 11·6% WATER
RT CURE 12·2% WATER
RT CURE 12·2% WATER
B.A. TEST VALUE
ESTIMATED A.S.T.M D638 VALUE

FIG: 48

TENSILE MODULUS OF ADHESIVES
REDUX 410 NA
TENSILE MODULUS P.S.I./MPa
P.S.I.
MPa
600,000
500,000
400,000
300,000
200,000
100,000
4,000
3,000
2,000
1,000
RT CURE
RT CURE
RT CURE
RT CURE FREE SURFACE
RT CURE FREE SURFACE
RT CURE FREE SURFACE
50°C POST CURE
50°C POST CURE
50°C POST CURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
RT CURE 3.65% WATER
RT CURE 4.8% WATER
RT CURE 3.36% WATER
B.A. TEST VALUE
ESTIMATED A.S.T.M. D 638 VALUE

FIG: 49

TENSILE MODULUS OF ADHESIVES
REDUX 501
TENSILE MODULUS P.S.I. / MPa
P.S.I.
MPa
600,000
500,000
400,000
300,000
200,000
100,000
4,000
3,000
2,000
1,000
RT CURE
RT CURE
RT CURE
RT CURE
RT CURE
RT CURE FREE SURFACE
RT CURE FREE SURFACE
RT CURE FREE SURFACE
50°C POST CURE
50°C POST CURE
50°C POST CURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
RT CURE 14·2% WATER
RT CURE 15·8% WATER
RT CURE 15·4% WATER
B.A. TEST VALUE
ESTIMATED A.S.T.M. D 638 VALUE

FIG: 50

TENSILE MODULUS OF ADHESIVES
3M - EC 9323
TENSILE MODULUS P.S.I. / MPa
P.S.I.
MPa
600,000
500,000
400,000
300,000
200,000
100,000
4,000
3,000
2,000
1,000
RT CURE
RT CURE
RT CURE
50°C POST CURE
50°C POST CURE
50°C POST CURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
RT CURE 6·04% WATER
RT CURE 7·5% WATER
RT CURE 6·6% WATER
B.A. TEST VALUE
ESTIMATED A.S.T.M. D 638 VALUE

FIG: 51

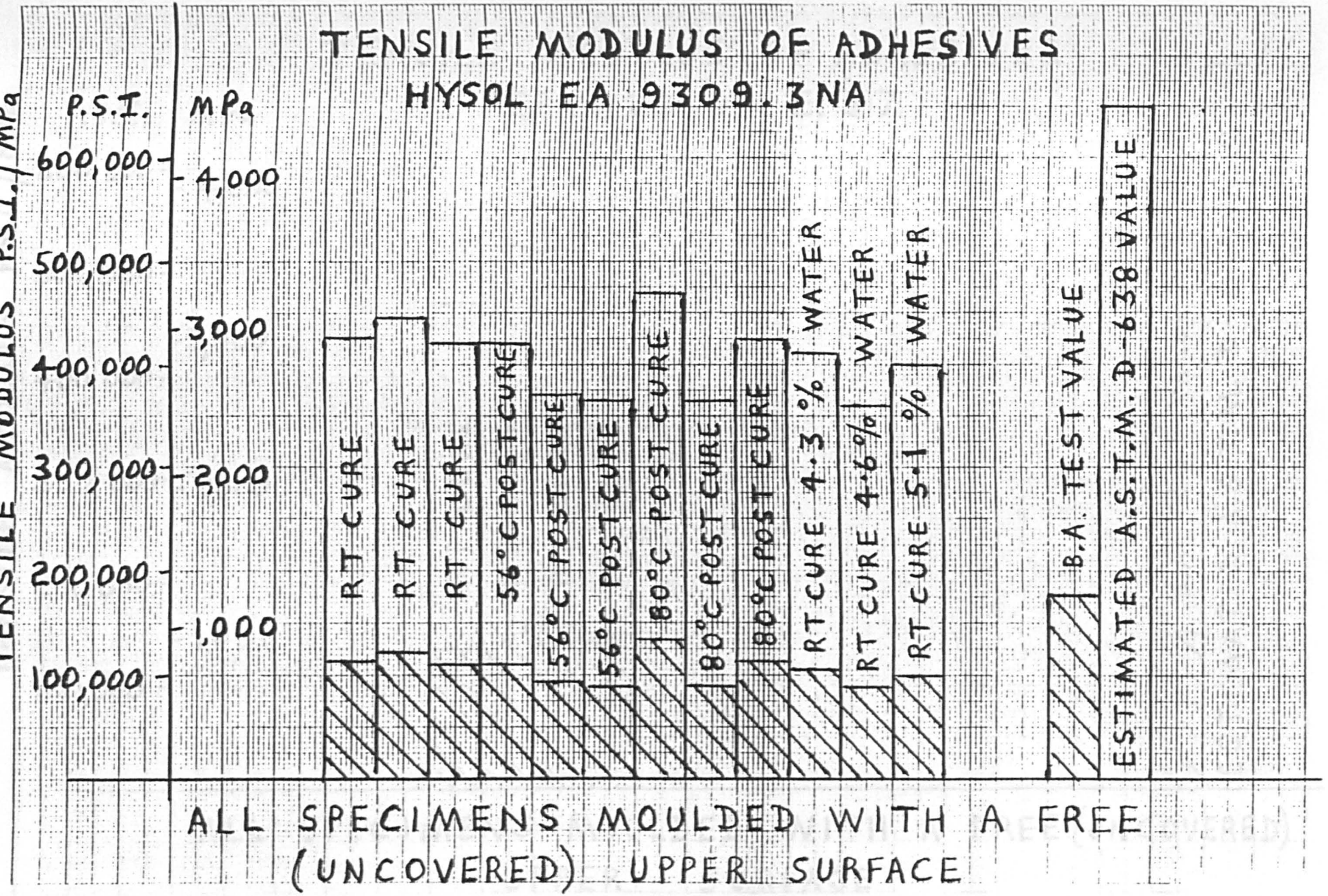

TENSILE MODULUS OF ADHESIVES
HYSOL EA 9309.3NA
TENSILE MODULUS P.S.I. / MPa
P.S.I.
MPa
600,000
500,000
400,000
300,000
200,000
100,000
4,000
3,000
2,000
1,000
RT CURE
RT CURE
RT CURE
56°C POST CURE
56°C POST CURE
56°C POST CURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
RT CURE 4.3 % WATER
RT CURE 4.6 % WATER
RT CURE 5.1 % WATER
B.A. TEST VALUE
ESTIMATED A.S.T.M. D-638 VALUE
ALL SPECIMENS MOULDED WITH A FREE (UNCOVERED) UPPER SURFACE

FIG: 52

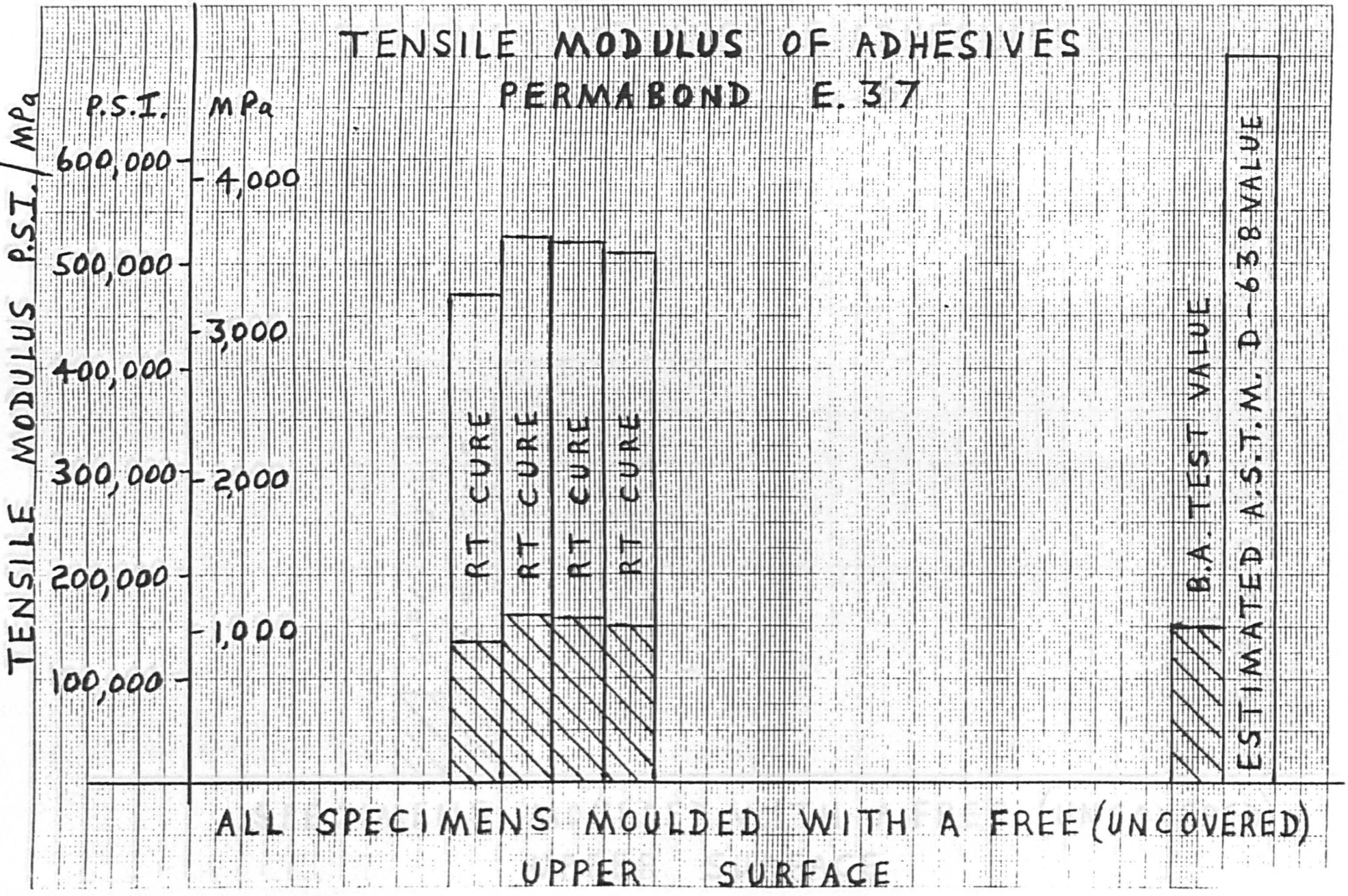

TENSILE MODULUS OF ADHESIVES
PERMABOND E.37
TENSILE MODULUS P.S.I. / MPa
P.S.I.
MPa
600,000
500,000
400,000
300,000
200,000
100,000
4,000
3,000
2,000
1,000
RT CURE
RT CURE
RT CURE
RT CURE
B.A. TEST VALUE
ESTIMATED A.S.T.M. D-638 VALUE
ALL SPECIMENS MOULDED WITH A FREE (UNCOVERED)
UPPER SURFACE

FIG: 53

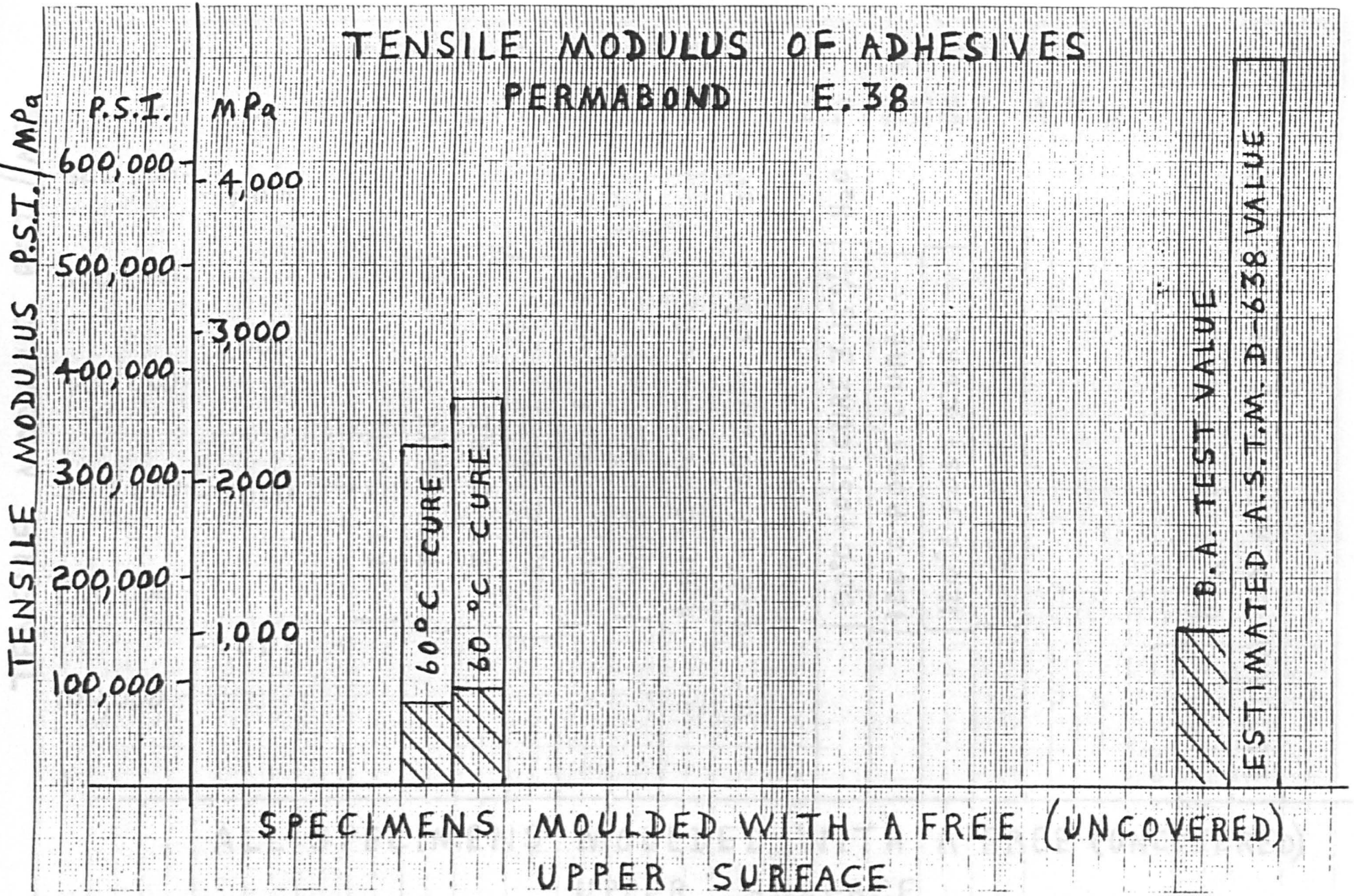

TENSILE MODULUS OF ADHESIVES
PERMABOND E.38
TENSILE MODULUS P.S.I. / MPa
P.S.I.
MPa
600,000
500,000
400,000
300,000
200,000
100,000
4,000
3,000
2,000
1,000
60°C CURE
60 °C CURE
B.A. TEST VALUE
ESTIMATED A.S.T.M. D-638 VALUE
SPECIMENS MOULDED WITH A FREE (UNCOVERED)
UPPER SURFACE

FIG: 54

TENSILE MODULUS OF ADHESIVES
SHELL EPIKOTE 815 + EPIKURE RTU
TENSILE MODULUS P.S.I./MPa
P.S.I.
MPa
600,000
500,000
400,000
300,000
200,000
100,000
4,000
3,000
2,000
1,000
ALL SPECIMENS MOULDED WITH A FREE (UNCOVERED) UPPER SURFACE
RT CURE
RT CURE
RT CURE
90°c POST CURE
90°c POST CURE
90°c POST CURE
90°c POST CURE
90°c POST CURE 2·36% H2O
90°c POST CURE 2·6% H2O
90°c POST CURE 3·15% H2O
120°c POST CURE
120°c POST CURE
120°c POST CURE
B.A. TEST VALUE
ESTIMATED A.S.T.M. D-638 VALUE

FIG: 55

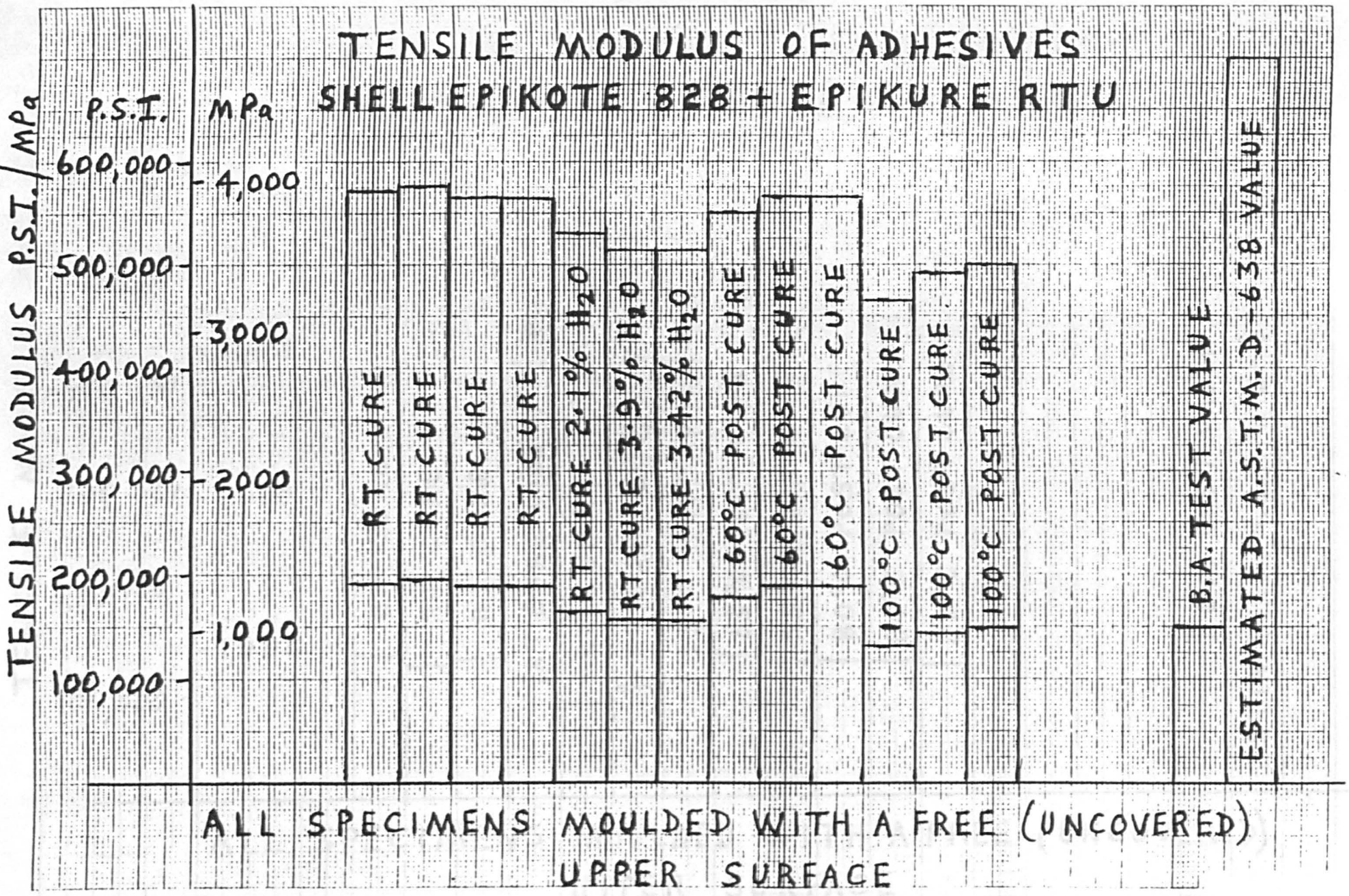

TENSILE MODULUS OF ADHESIVES
SHELL EPIKOTE 828 + EPIKURE RTU
TENSILE MODULUS P.S.I. / MPa
P.S.I.
MPa
600,000
500,000
400,000
300,000
200,000
100,000
4,000
3,000
2,000
1,000
RT CURE
RT CURE
RT CURE
RT CURE
RT CURE 2.1% H2O
RT CURE 3.9% H2O
RT CURE 3.42% H2O
60°C POST CURE
60°C POST CURE
60°C POST CURE
100°C POST CURE
100°C POST CURE
100°C POST CURE
B.A. TEST VALUE
ESTIMATED A.S.T.M. D-638 VALUE
ALL SPECIMENS MOULDED WITH A FREE (UNCOVERED)
UPPER SURFACE

FIG: 56

TENSILE MODULUS OF ADHESIVES
FIBER RESIN CORPORATION FR7020

ALL SPECIMENS MOULDED WITH A FREE (UNCOVERED) UPPER SURFACE

FIG: 57

TENSILE STRENGTH OF ADHESIVES
MANUFACTURER'S DATA
HYSOL
TENSILE STRENGTH P.S.I./MPa
P.S.I
MPa
12,000
10,000
8,000
6,000
4,000
2,000
80
70
60
50
40
30
20
10
EA 934NA
EA 956
EA 9309.3NA
EA 9313
EA 9314
EA 9320
EA 9321
EA 9330
EA 9628
EA 9649

FIG:58

TENSILE STRENGTH OF ADHESIVES
FIRST SERIES OF TESTS RT CURE EXCEPT AF-163
TENSILE STRENGTH P.S.I./MPa
12,000 10,000 8,000 6,000 4,000 2,000
80 70 60 50 40 30 20 10
MPa
P.S.I
HYSOL EA9330
HYSOL EA9330
815+RTU
815+RTU
815+RTU
828+VERSAMID 125
828+VERSAMID 125
828+VERSAMID 125
3M-EC2216
3M-EC2216
3M-EC2216
3M-EC3524
3M-EC3524
3M-EC3524
HYSOL EA-9321
HYSOL EA-9321
HYSOL EA-9321
3M-AF163

FIG:59

TENSILE STRENGTH OF ADHESIVES
FIRST SERIES OF TESTS RT CURE
TENSILE STRENGTH P.S.I./MPa
12,000
10,000
8,000
6,000
4,000
2,000
P.S.I.
80
70
60
50
40
30
20
10
MPa
3M-EC 3559
3M-EC 3559
3M-EC 3559
HYSOL EA 9330 +20% MB
HYSOL EA 9330 +20% MB
HYSOL EA 9330 +20% MB
3M-EC 3568
3M-EC 3578
3M-EC 3578
3M-EC 3578
PERMABOND E34
PERMABOND E34

FIG: 60

TENSILE STRENGTH OF ADHESIVES
REDUX 408
TENSILE STRENGTH P.S.I./MPa
12,000 10,000 8,000 6,000 4,000 2,000
80 70 60 50 40 30 20 10
P.S.I
MPa
RT CURE
RT CURE
RT CURE
RT CURE
RT CURE
FREE SURFACE
RT CURE
FREE SURFACE
RT CURE
FREE SURFACE
50°C POST CURE
50°C POST CURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
408 + 20% 410 NA
408 + 20% 410 NA
408 + 40% 410 NA
RT CURE 11·6% WATER
RT CURE 12·2% WATER
RT CURE 12·2% WATER
* FREE SURFACE MOULDED

FIG: 61

TENSILE STRENGTH OF ADHESIVES
REDUX 410NA
TENSILE STRENGTH P.S.I./MPa
12,000 10,000 8,000 6,000 4,000 2,000
80 70 60 50 40 30 20 10
M Pa
P.S.I
RT CURE
RT CURE
RT CURE
RT CURE FREE SURFACE
RT CURE FREE SURFACE
RT CURE FREE SURFACE
50°C POST CURE
50°C POST CURE
50°C POST CURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
RT CURE 3.65% WATER
RT CURE 4.8% WATER
RT CURE 3.36% WATER

FIG. 62

TENSILE STRENGTH OF ADHESIVES
REDUX 501
TENSILE STRENGTH P.S.I./MPa
P.S.I
MPa
12,000
10,000
8,000
6,000
4,000
2,000
80
70
60
50
40
30
20
10
RT CURE
RT CURE
RT CURE
RT CURE
RT CURE
RT CURE FREE SURFACE
RT CURE FREE SURFACE
50°C POST CURE
50°C POST CURE
50°C POST CURE (LARGE BUBBLE)
80°C POST CURE
80°C POST CURE
80°C POST CURE
RT CURE 501 + 20% 410NA *
RT CURE 501 + 40% 410NA *
RT CURE 14·2 % WATER
RT CURE 15·8 % WATER
RT CURE 15·4% WATER
* FREE SURFACE MOULDED

FIG: 63

TENSILE STRENGTH OF ADHESIVES
BOSTIK 5435/TM2
TENSILE STRENGTH P.S.I./MPa
P.S.I
MPa
12,000
10,000
8,000
6,000
4,000
2,000
80
70
60
50
40
30
20
10
RT CURE
RT CURE
RT CURE

FIG: 64

TENSILE STRENGTH OF ADHESIVES
3M - EC 9323
TENSILE STRENGTH P.S.I./MPa
12,000
10,000
8,000
6,000
4,000
2,000
P.S.I
80
70
60
50
40
30
20
10
MPa
RT CURE
RT CURE
RT CURE
50°C POST CURE
50°C POST CURE
50°C POST CURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
RT CURE 6·04%WATER
RT CURE 7·5 % WATER
RT CURE 6·6 % WATER

FIG: 65

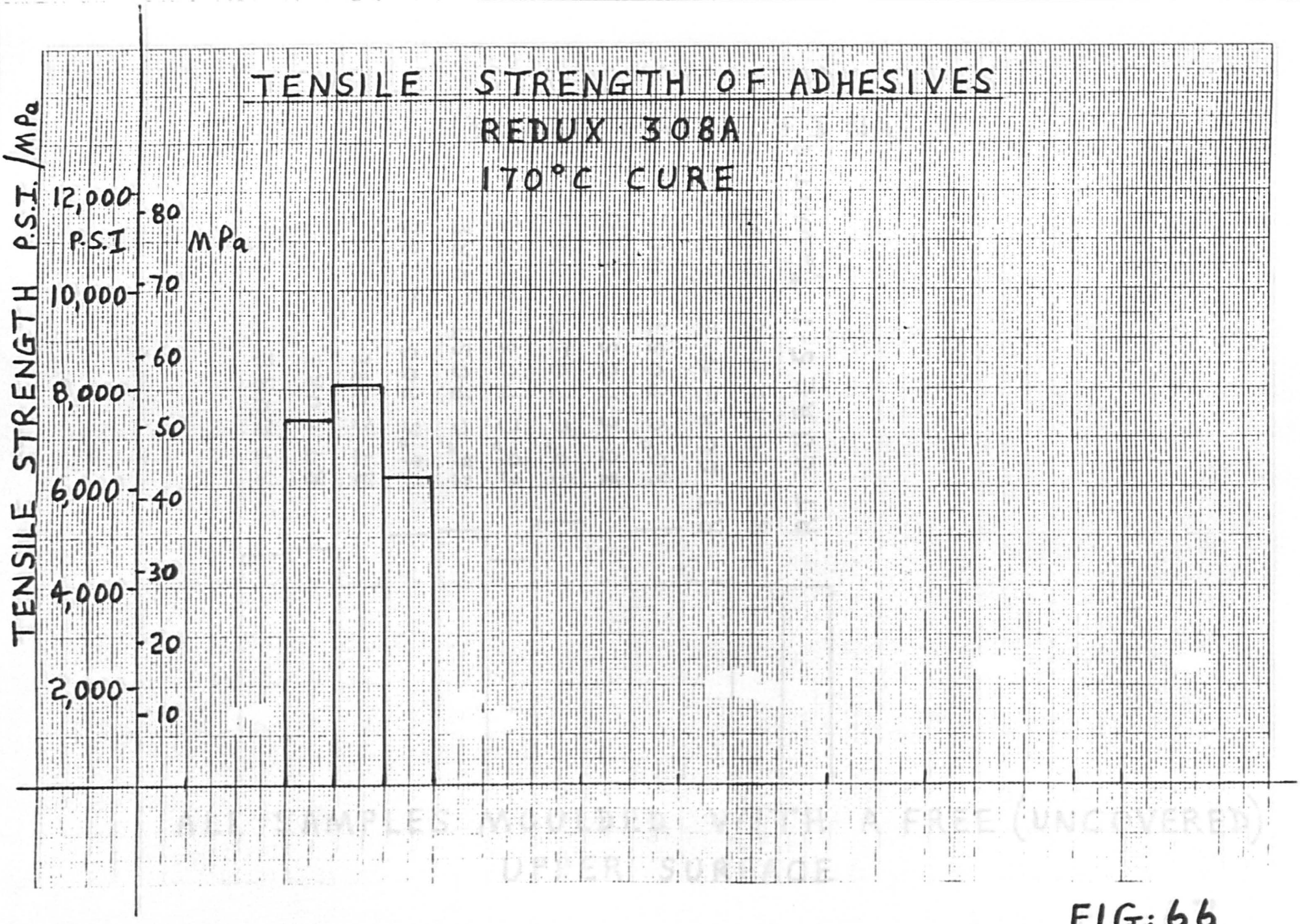

TENSILE STRENGTH OF ADHESIVES
REDUX 308A
170°C CURE
TENSILE STRENGTH P.S.I. /MPa
12,000 P.S.I
10,000
8,000
6,000
4,000
2,000
MPa
80
70
60
50
40
30
20
10

FIG: 66

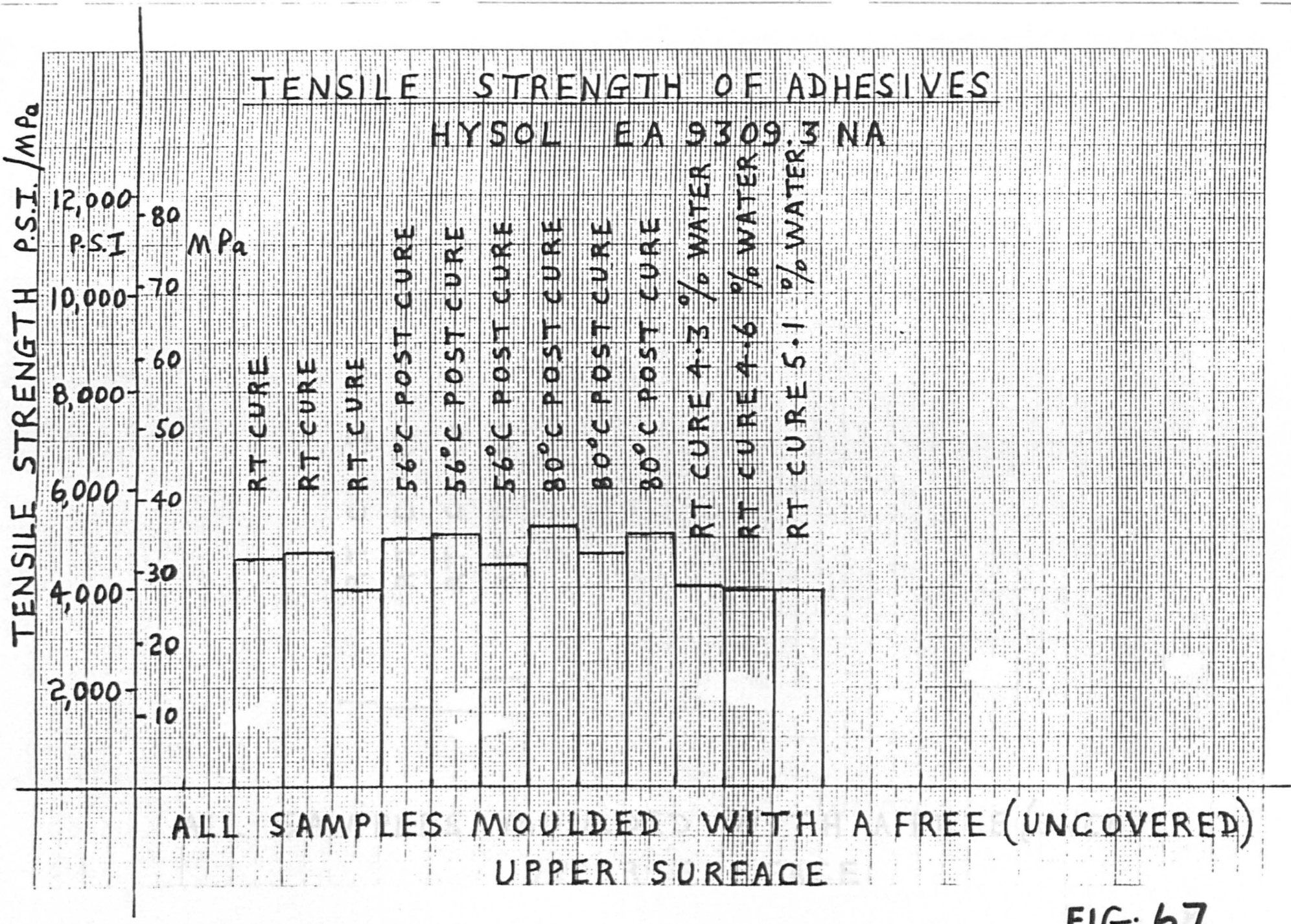

TENSILE STRENGTH OF ADHESIVES
HYSOL EA 9309.3 NA
TENSILE STRENGTH P.S.I. /MPa
P.S.I
MPa
12,000
10,000
8,000
6,000
4,000
2,000
80
70
60
50
40
30
20
10
RT CURE
RT CURE
RT CURE
56°C POST CURE
56°C POST CURE
56°C POST CURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
RT CURE 4.3 % WATER
RT CURE 4.6 % WATER
RT CURE 5.1 % WATER
ALL SAMPLES MOULDED WITH A FREE (UNCOVERED)
UPPER SURFACE

FIG: 67

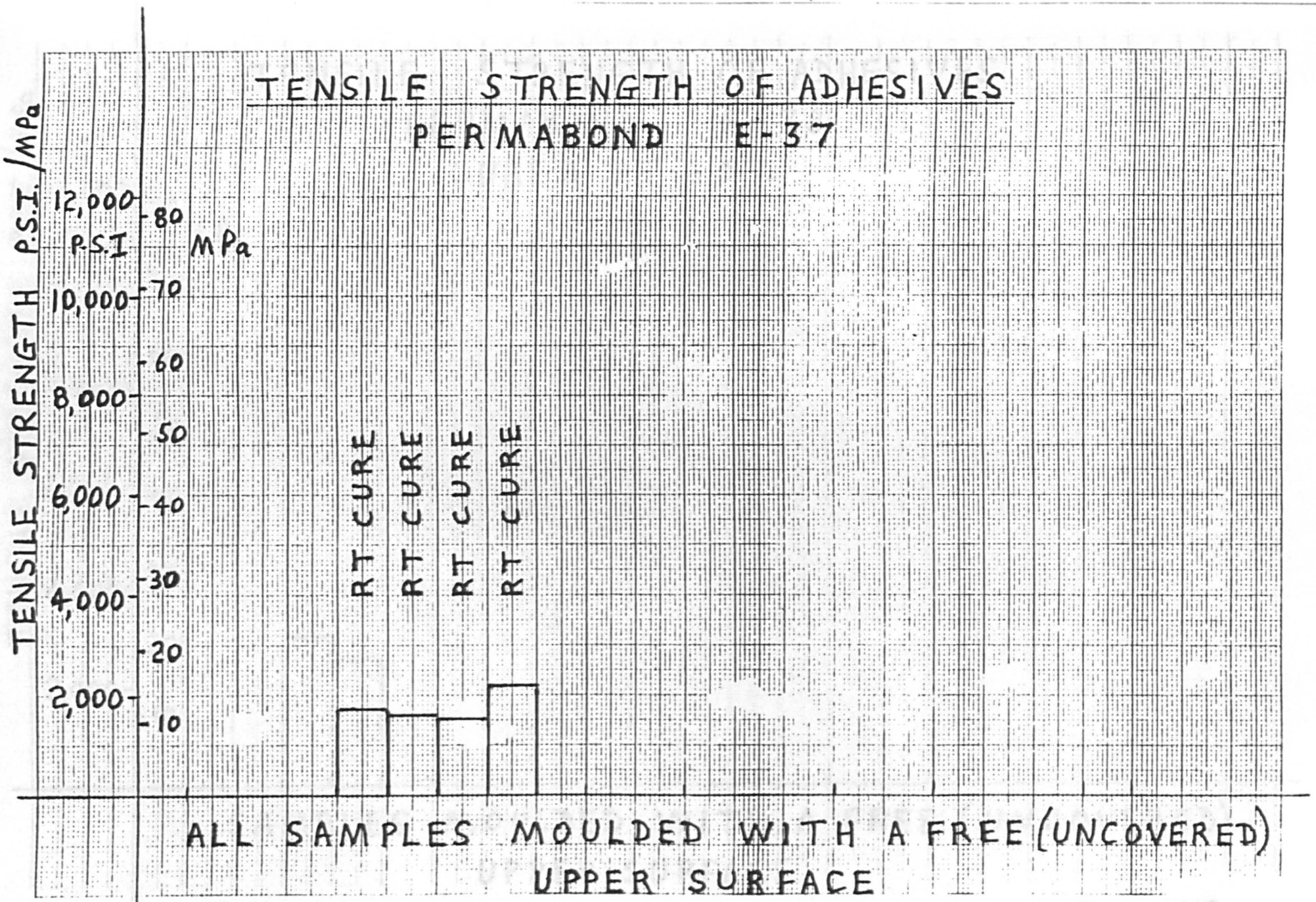

TENSILE STRENGTH OF ADHESIVES
PERMABOND E-37
TENSILE STRENGTH P.S.I. /MPa
P.S.I
MPa
12,000
10,000
8,000
6,000
4,000
2,000
80
70
60
50
40
30
20
10
RT CURE
RT CURE
RT CURE
RT CURE
ALL SAMPLES MOULDED WITH A FREE (UNCOVERED)
UPPER SURFACE

FIG: 68

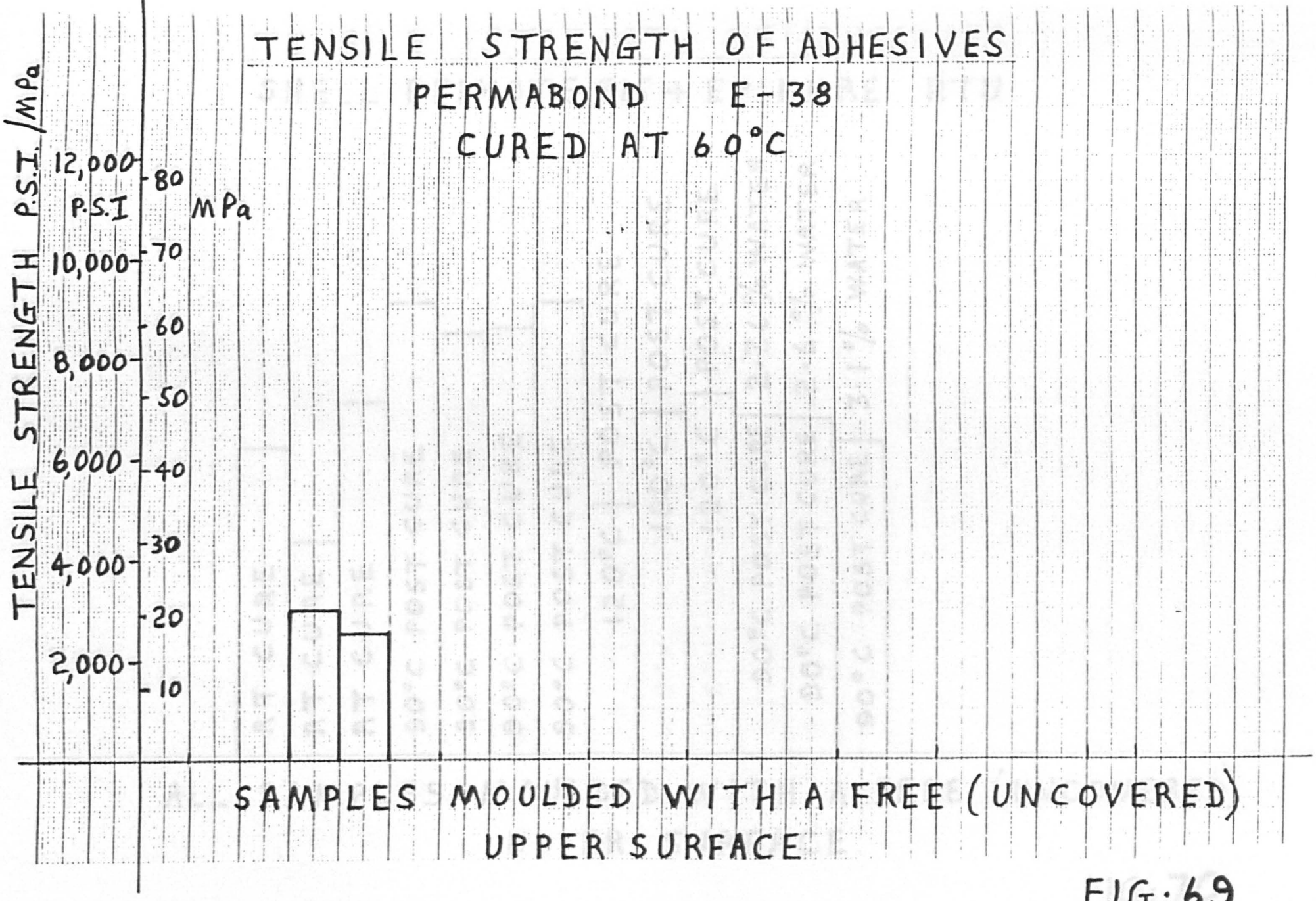

TENSILE STRENGTH OF ADHESIVES
PERMABOND E-38
CURED AT 60°C
TENSILE STRENGTH P.S.I. /MPa
P.S.I
MPa
12,000
10,000
8,000
6,000
4,000
2,000
80
70
60
50
40
30
20
10
SAMPLES MOULDED WITH A FREE (UNCOVERED)
UPPER SURFACE

FIG:69

TENSILE STRENGTH OF ADHESIVES
SHELL EPIKOTE 815 + EPIKURE RTU
ALL SAMPLES MOULDED WITH A FREE (UNCOVERED) UPPER SURFACE
TENSILE STRENGTH P.S.I. /MPa
P.S.I
MPa
12,000
10,000
8,000
6,000
4,000
2,000
80
70
60
50
40
30
20
10
RT CURE
RT CURE
RT CURE
90°C POST CURE
90°C POST CURE
90°C POST CURE
90°C POST CURE
120°C POST CURE
120°C POST CURE
120°C POST CURE
90°C POST CURE 2·36 % WATER
90°C POST CURE 2·6 % WATER
90°C POST CURE 3·1 % WATER

FIG: 70

TENSILE STRENGTH OF ADHESIVES
SHELL EPIKOTE 828 + EPIKURE RTU
ALL SAMPLES MOULDED WITH A FREE (UNCOVERED) UPPER SURFACE
TENSILE STRENGTH P.S.I. /MPa
P.S.I
MPa
12,000
10,000
8,000
6,000
4,000
2,000
80
70
60
50
40
30
20
10
RT CURE
RT CURE
RT CURE
RT CURE
60°C POST CURE
60°C POST CURE
60°C POST CURE
100°C POST CURE
100°C POST CURE
100°C POST CURE
RT CURE 2·1% WATER
RT CURE 3·9% WATER
RT CURE 3·42% WATER

FIG: 71

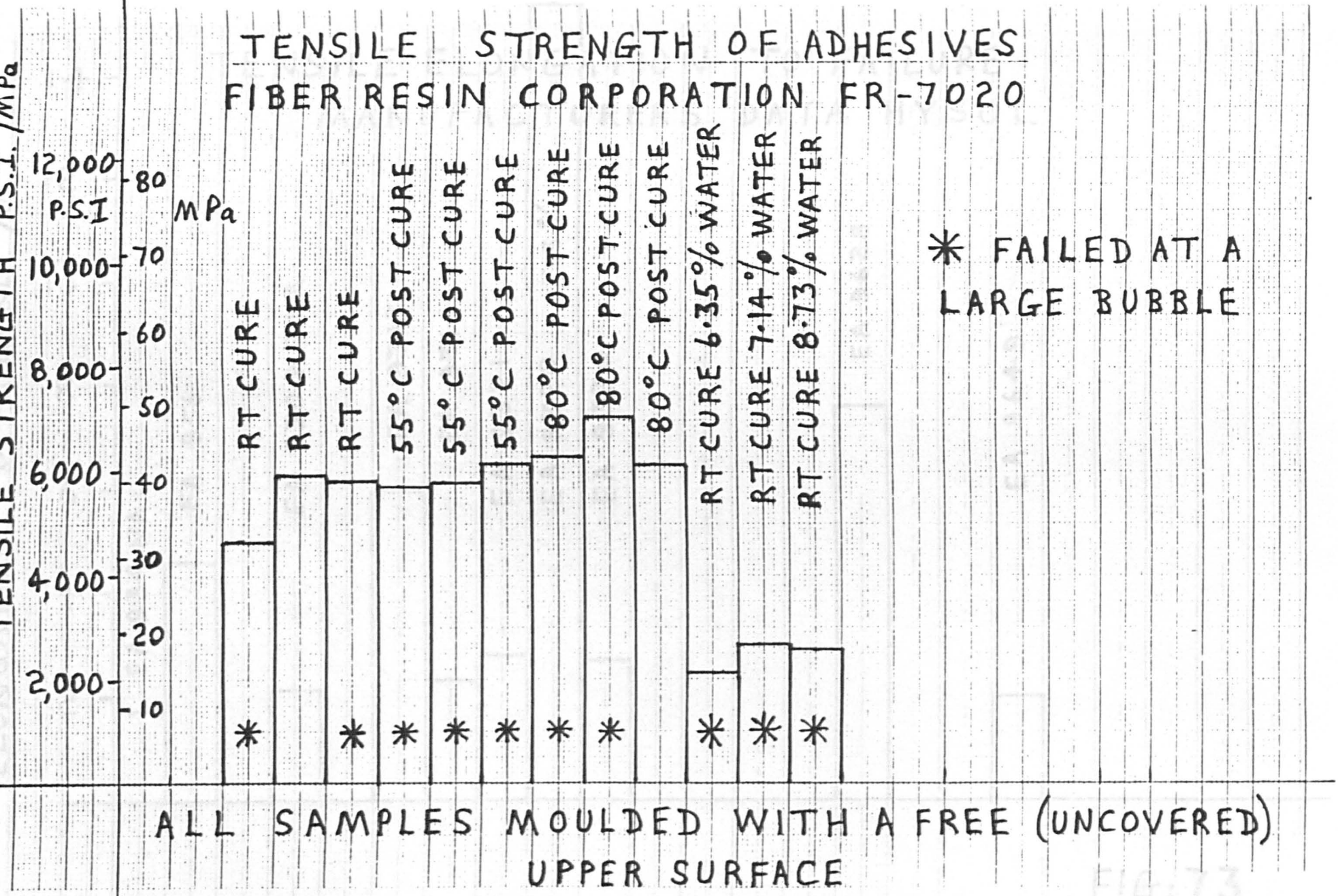

TENSILE STRENGTH OF ADHESIVES
FIBER RESIN CORPORATION FR-7020
TENSILE STRENGTH P.S.I. /MPa
12,000 P.S.I
10,000
8,000
6,000
4,000
2,000
MPa
80
70
60
50
40
30
20
10
RT CURE
RT CURE
RT CURE
55°C POST CURE
55°C POST CURE
55°C POST CURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
RT CURE 6·35% WATER
RT CURE 7·14% WATER
RT CURE 8·73% WATER
* FAILED AT A LARGE BUBBLE
ALL SAMPLES MOULDED WITH A FREE (UNCOVERED) UPPER SURFACE

FIG:72

TENSILE ELONGATION TO FAILURE
MANUFACTURER'S DATA HYSOL
ELONGATION TO FAILURE %
14
12
10
8
6
4
2
EA 934 NA
EA 956
EA 9309.3NA
EA 9313
EA 9314
EA 9321
EA 9320 15.3%
EA 9330
EA 9628
EA 9649

FIG: 73

TENSILE ELONGATION TO FAILURE
ORIGINAL SERIES OF TESTS (VALUES CORRECTED FOR SPECIMEN SHAPE)
//// PLASTIC STRAIN
% ELONGATION TO FAILURE
12
10
8
6
4
2
HYSOL EA 9330
HYSOL EA 9321
3M-EC 2216
34.26
3M-EC 3524
3M-EC 3559
3M-EC 3568
3M-EC 3578
3M-AF 163
SHELL 815 + RTU
SHELL 828 + VERSAMID 125
PERMABOND E34

FIG: 74

TENSILE ELONGATION TO FAILURE
REDUX 408
ELONGATION TO FAILURE %
12
10
8
6
4
2
RT CURE
RT CURE
RT CURE
RT CURE
RT CURE FREE SURFACE
RT CURE FREE SURFACE
RT CURE FREE SURFACE
50°C POST CURE
50°C POST CURE
50°C POST CURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
408 +20% 410 RT CURE
408 +20% 410 RT CURE
408 +40% 410 RT CURE
RT CURE 12·2 % WATER
RT CURE 12·2 % WATER
RT CURE 11·6 % WATER
ALL FAILURES WERE IN THE ELASTIC RANGE
NO PLASTIC STRAIN

FIG:75

TENSILE ELONGATION TO FAILURE
REDUX 410NA
PLASTIC STRAIN
RT CURE
RT CURE
RT CURE
RT CURE FREE SURFACE
RT CURE FREE SURFACE
RT CURE FREE SURFACE
50°C POST CURE
50°C POST CURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
RT CURE 3.65 % WATER
RT CURE 4.8 % WATER
RT CURE 3.36 % WATER
ELONGATION TO FAILURE %
12
10
8
6
4
2

FIG: 76

TENSILE ELONGATION TO FAILURE
REDUX 5.01
//// PLASTIC STRAIN
ELONGATION TO FAILURE %
12
10
8
6
4
2
RT CURE
RT CURE
RT CURE
RT CURE
RT CURE
50°C POST CURE
50°C POST CURE
50°C POST CURE
FAILED AT LARGE BUBBLE 80°C POSTCURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
RT CURE 14.2 % WATER
RT CURE 15.8 % WATER
RT CURE 15.4 % WATER
RT CURE 501 + 20% 4IONA
RT CURE 501 + 40% 4IONA
RT CURE FREE SURFACE
RT CURE FREE SURFACE
RT CURE FREE SURFACE

FIG: 77

TENSILE ELONGATION TO FAILURE
3M - EC 9323
//// PLASTIC STRAIN
RT CURE 6·6 % WATER
RT CURE 7·5 % WATER
RT CURE 6·04% WATER
80°C POST CURE
80°C POST CURE
80°C POST CURE
50°C POST CURE
50°C POST CURE
50°C POST CURE
RT CURE
RT CURE
RT CURE
% ELONGATION TO FAILURE
12
10
8
6
4
2

FIG: 78

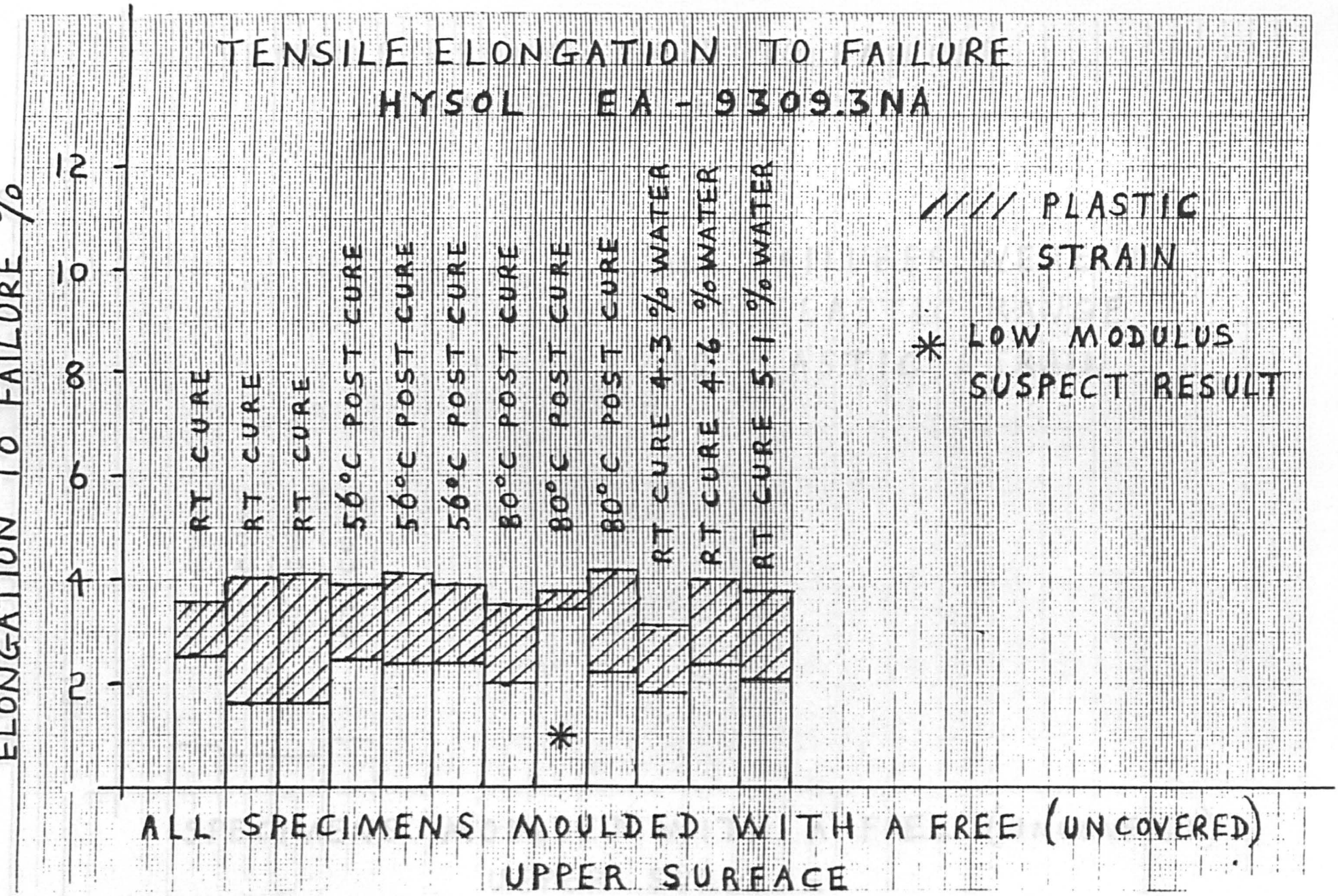

TENSILE ELONGATION TO FAILURE
HYSOL EA-9309.3NA
ELONGATION TO FAILURE %
12
10
8
6
4
2
RT CURE
RT CURE
RT CURE
56°C POST CURE
56°C POST CURE
56°C POST CURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
RT CURE 4.3 % WATER
RT CURE 4.6 % WATER
RT CURE 5.1 % WATER
//// PLASTIC STRAIN
* LOW MODULUS SUSPECT RESULT
ALL SPECIMENS MOULDED WITH A FREE (UNCOVERED) UPPER SURFACE

FIG: 79

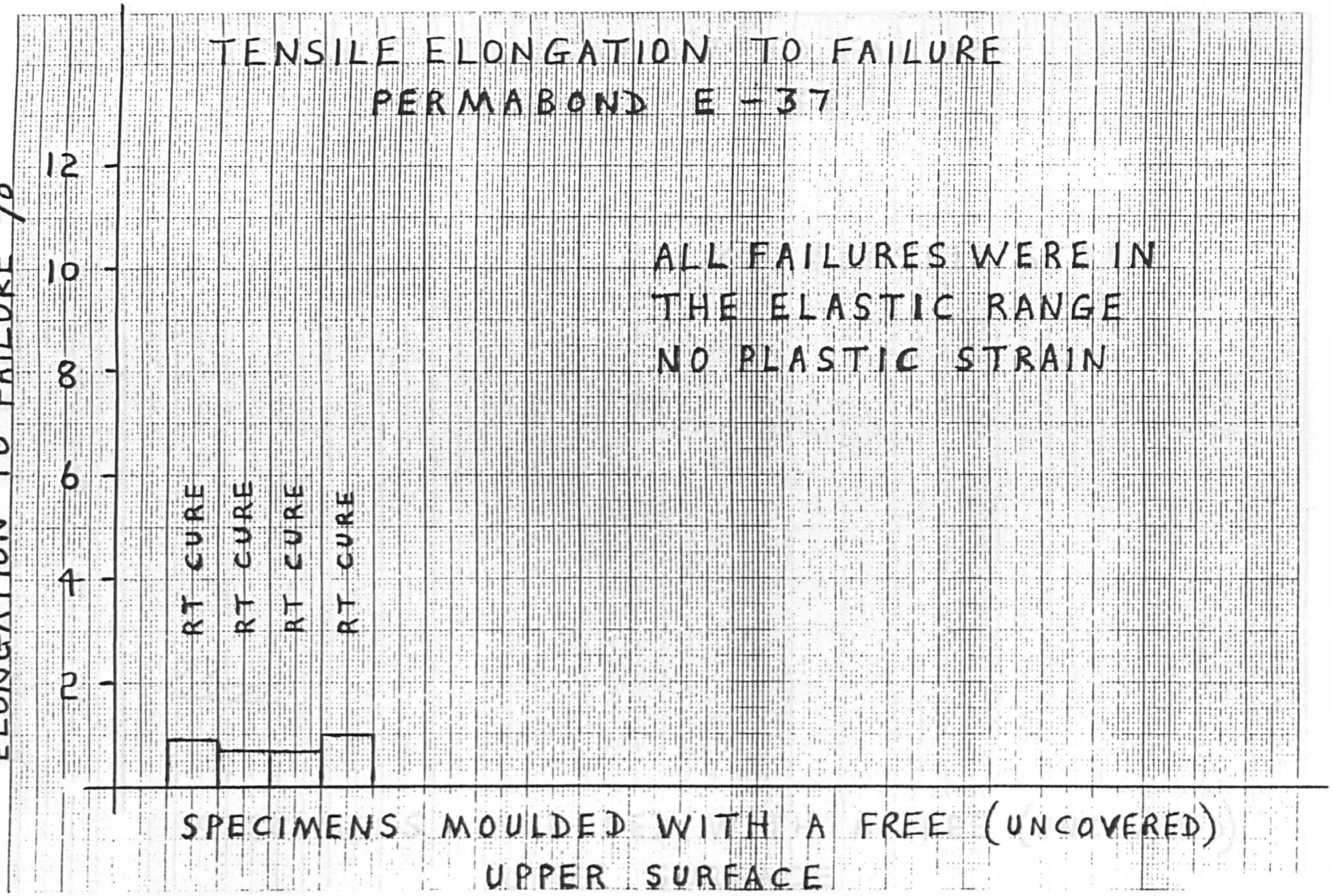

TENSILE ELONGATION TO FAILURE
PERMABOND E-37
ELONGATION TO FAILURE %
12
10
8
6
4
2
RT CURE
RT CURE
RT CURE
RT CURE
ALL FAILURES WERE IN
THE ELASTIC RANGE
NO PLASTIC STRAIN
SPECIMENS MOULDED WITH A FREE (UNCOVERED)
UPPER SURFACE

FIG: 80

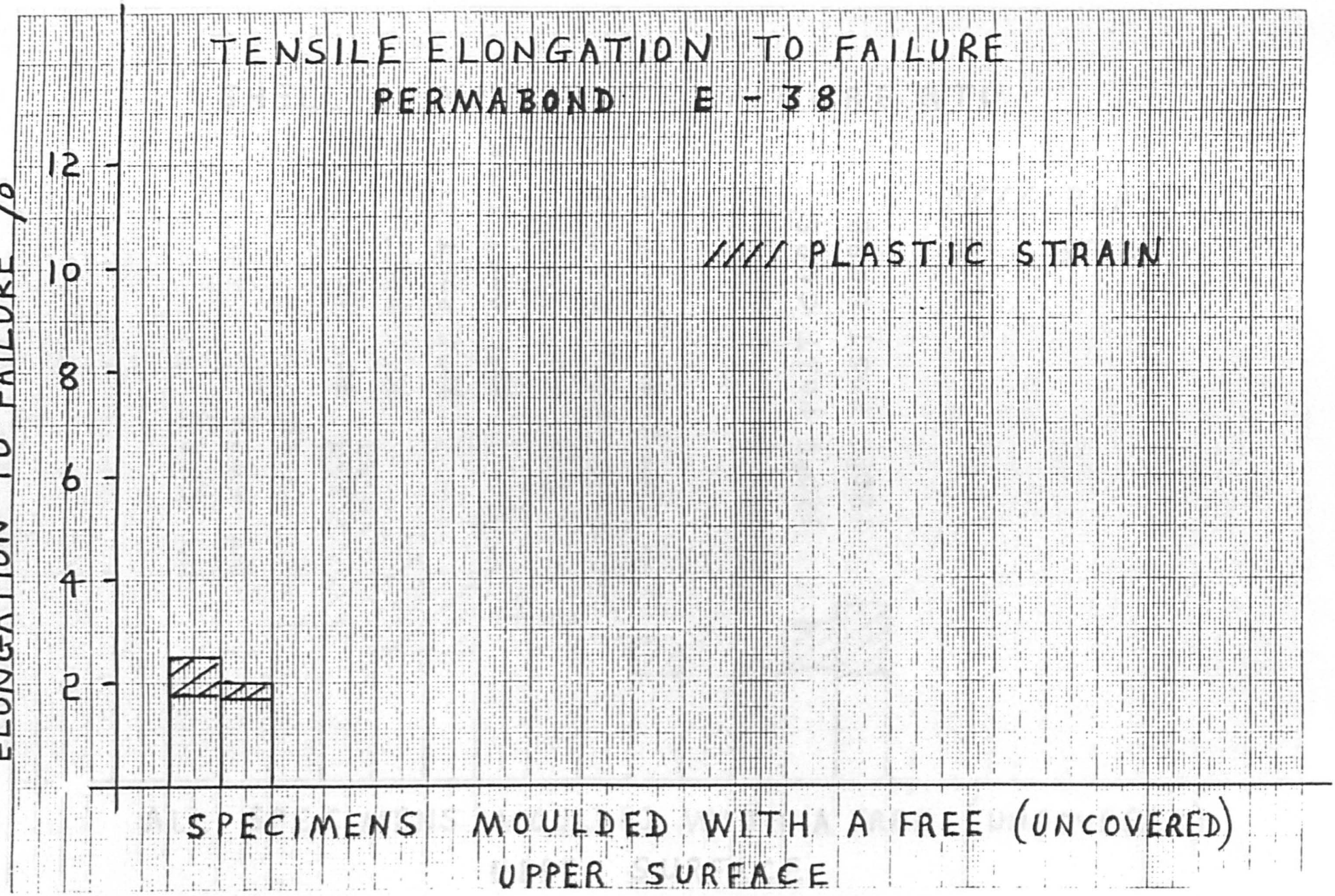

TENSILE ELONGATION TO FAILURE
PERMABOND E-38
//// PLASTIC STRAIN
ELONGATION TO FAILURE %
12
10
8
6
4
2
SPECIMENS MOULDED WITH A FREE (UNCOVERED)
UPPER SURFACE

FIG: 81

TENSILE ELONGATION TO FAILURE
SHELL EPIKOTE BIS+ EPIKURE RTU
//// PLASTIC STRAIN
ELONGATION TO FAILURE %
12
10
8
6
4
2
RT CURE
RT CURE
RT CURE
90°c POST CURE
90°c POST CURE
90°c POST CURE
90°c POST CURE
90°c POST CURE 2·36% H2O
90°c POST CURE 2·6% H2O
90°c POST CURE 3·15% H2O
120°c POST CURE
120°c POST CURE
120°c POST CURE
ALL SPECIMENS MOULDED WITH A FREE (UNCOVERED) UPPER SURFACE

FIG: 82

FIG: 83

TENSILE ELONGATION TO FAILURE
FIBERESIN CORPORATION FR 7020
ALL FAILURES WERE IN
THE ELASTIC RANGE
NO PLASTIC STRAIN
RT CURE 8·73% WATER
RT CURE 7·14% WATER
RT CURE 6·35% WATER
80°C POST CURE
80°C POST CURE
80°C POST CURE
55°C POST CURE
55°C POST CURE
55°C POST CURE
RT CURE
RT CURE
RT CURE
ELONGATION TO FAILURE %
12
10
8
6
4
2
ALL SPECIMENS MOULDED WITH A FREE (UNCOVERED)
UPPER SURFACE

FIG: 84

STRAIN ENERGY AT FAILURE IN TENSILE TEST

FIRST SERIES OF TEST'S - AVERAGE OF THREE RESULTS IN EACH CASE

FIG: 85

STRAIN ENERGY AT FAILURE IN TENSILE TEST
REDUX 408
STRAIN ENERGY AT FAILURE N.mm
2,000
1,000
RT CURE
RT CURE
RT CURE
RT CURE
RT CURE FREE SURFACE
RT CURE FREE SURFACE
RT CURE FREE SURFACE
50°C POST CURE
50°C POST CURE
50°C POST CURE
80°C POST CURE
80°C POST CURE (FLAW AT CENTRE)
80°C POST CURE
80°C POST CURE
RT CURE 11·6% WATER
RT CURE 12·2% WATER
RT CURE 12·2% WATER
RT CURE 408+20% 410NA
RT CURE 408+20% 410NA
RT CURE 408+40% 410NA
FREE SURFACE

FIG: 86

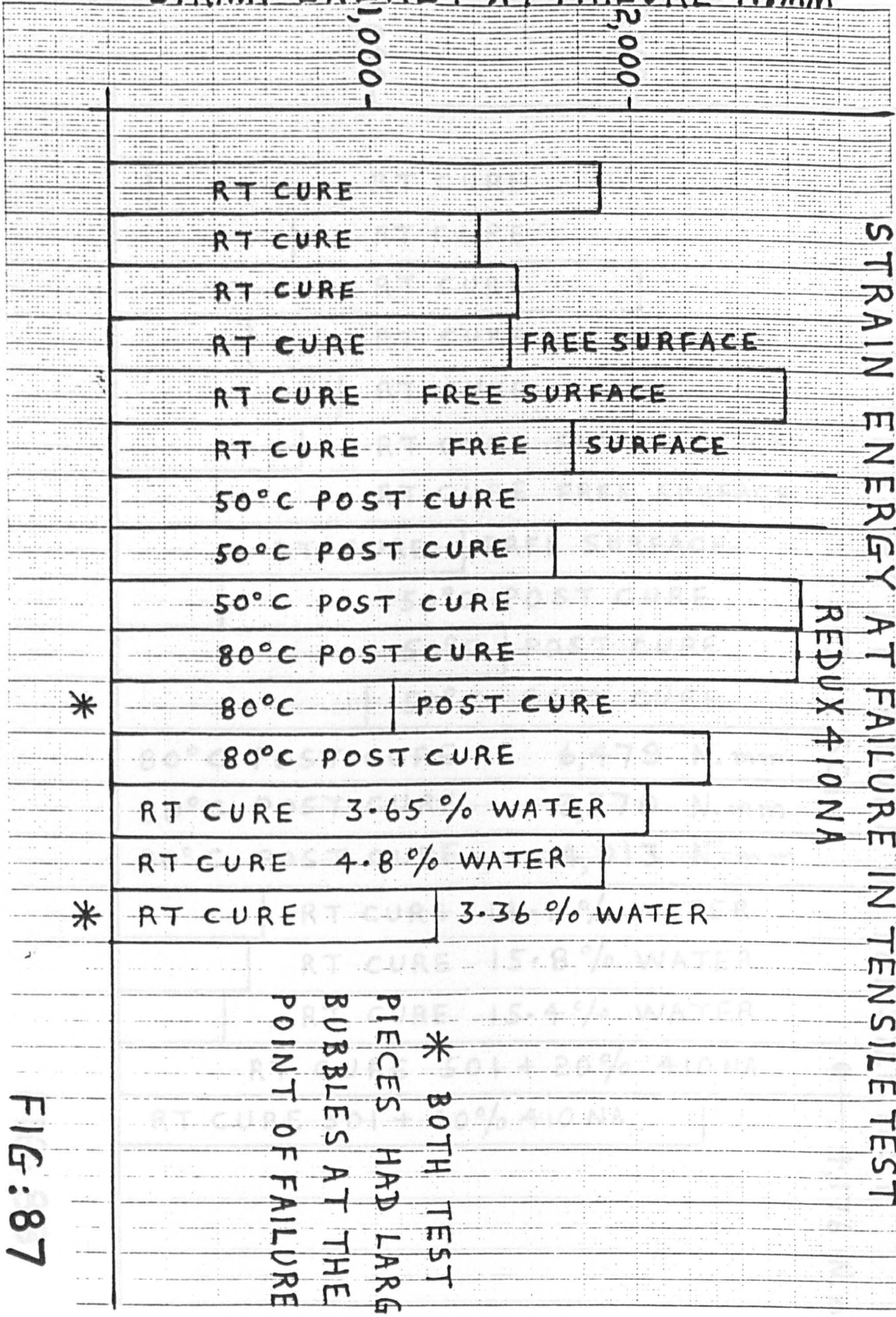


FIG: 87

STRAIN ENERGY AT FAILURE IN TENSILE TEST
REDUX 501
STRAIN ENERGY AT FAILURE N.mm
2,000
4,000
4,176 N.mm
RT CURE 501 + 40% 410 NA
RT CURE 501 + 20% 410NA
RT CURE 15.4% WATER
RT CURE 15.8% WATER
RT CURE 14.2% WATER
80°C POST CURE 4,013 N.mm
80°C POST CURE 3,370 N.mm
80°C POST CURE 6,479 N.mm
50°C POST CURE
50°C POST CURE
50°C POST CURE
RT CURE FREE SURFACE
RT CURE FREE SURFACE
RT CURE
RT CURE
RT CURE
RT CURE
RT CURE

FIG: 88

STRAIN ENERGY AT FAILURE IN TENSILE TEST
3M - EC 9323
STRAIN ENERGY AT FAILURE N.mm
3,000
2,000
1,000
RT CURE
RT CURE
RT CURE
50°C POST CURE
50°C POST CURE
50°C POST CURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
RT CURE 6·04% WATER
RT CURE 7·5% WATER
RT CURE 6·6% WATER

FIG: 89

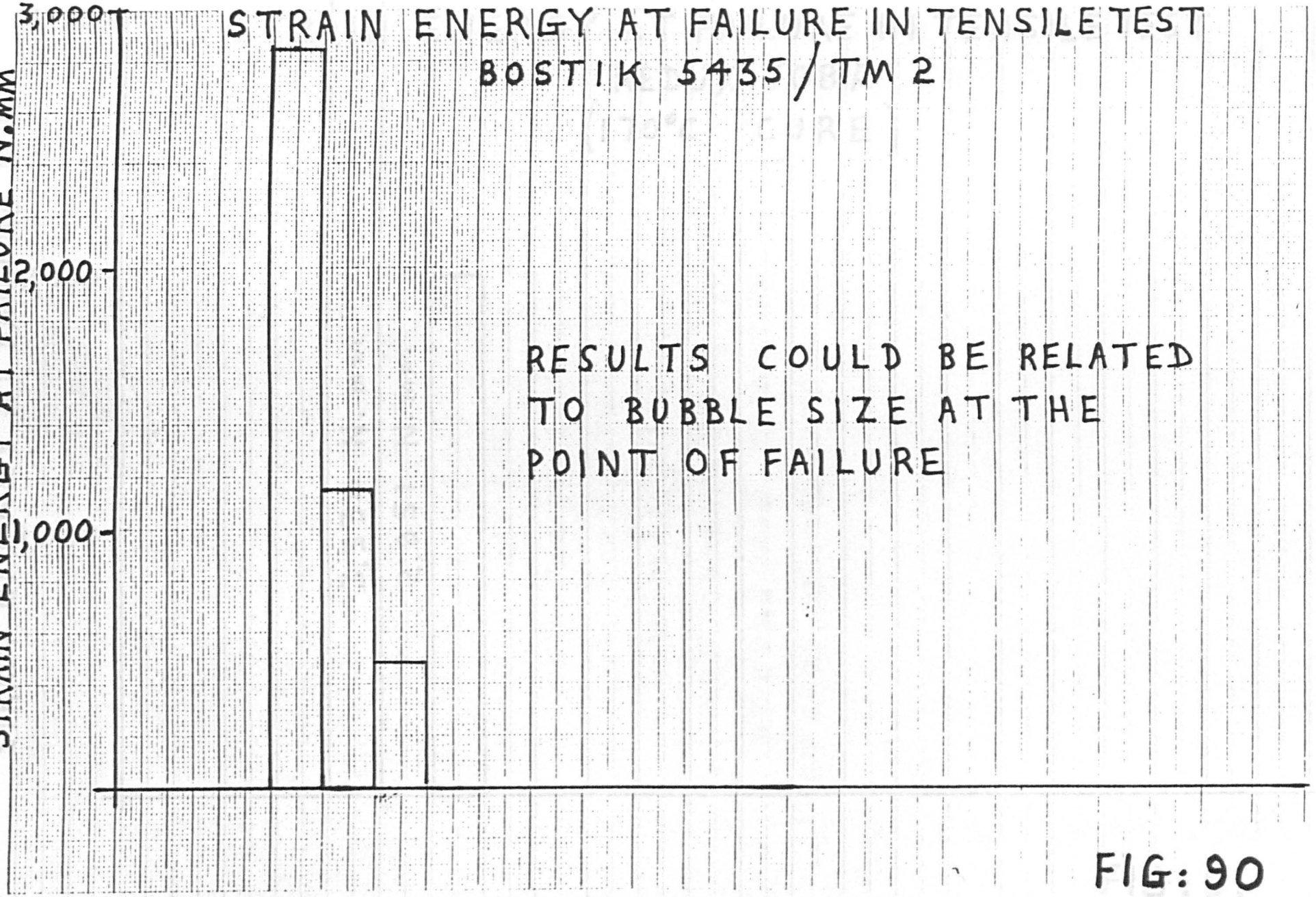

STRAIN ENERGY AT FAILURE IN TENSILE TEST
BOSTIK 5435/TM 2
STRAIN ENERGY AT FAILURE N.MM
3,000
2,000
1,000
RESULTS COULD BE RELATED
TO BUBBLE SIZE AT THE
POINT OF FAILURE

FIG: 90

STRAIN ENERGY AT FAILURE IN TENSILE TEST
(REDUX 308A
170°C CURE)
STRAIN ENERGY AT FAILURE N.mm
3,000
2,000
1,000
3,330 N.mm
2,951 N.mm

FIG: 91

STRAIN ENERGY AT FAILURE IN TENSILE TEST
HYSOL EA - 9309.3NA
STRAIN ENERGY AT FAILURE N.mm
3,000
2,000
1,000
ALL SAMPLES MOULDED WITH A FREE (UNCOVERED) UPPER SURFACE
RT CURE
RT CURE
RT CURE
56°C POST CURE
56°C POST CURE
56°C POST CURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
RT CURE 4·3 % WATER
RT CURE 4·6 % WATER
RT CURE 5·1 % WATER

FIG: 92

STRAIN ENERGY AT FAILURE IN TENSILE TEST
PERMABOND E-37
STRAIN ENERGY AT FAILURE N.mm
2,000
1,000
RT CURE
RT CURE
RT CURE
RT CURE
SAMPLES MOULDED WITH A FREE (UNCOVERED)
UPPER SURFACE

FIG:93

STRAIN ENERGY AT FAILURE IN TENSILE TEST
PERMABOND E-38
STRAIN ENERGY AT FAILURE N.mm
2,000
1,000
60°C CURE
60°C CURE

FIG: 94

STRAIN ENERGY AT FAILURE IN TENSILE TEST
SHELL EPIKOTE 815 + EPIKURE RTU
STRAIN ENERGY AT FAILURE N.mm
3,000
2,000
1,000
90°C POST CURE 8,051 N.mm
90°C POST CURE 4,933 N.mm
90°C POST CURE 3,916 N.mm
90°C POST CURE 6,115 N.mm
90°C P.C. 2·36 % WATER
90°C P.C. 2·6 % WATER
90°C P.C. 3·15 % WATER
120°C POST CURE
120°C POST CURE 2,825 N.mm
120°C POST CURE
RT CURE
RT CURE
RT CURE
ALL SAMPLES MOULDED WITH A FREE (UNCOVERED) UPPER SURFACE

FIG: 95

STRAIN ENERGY AT FAILURE IN TENSILE TEST
SHELL EPIKOTE 828 + EPIKURE RTU
STRAIN ENERGY AT FAILURE N.mm
3,000
2,000
1,000
120°c POST CURE 5,507 N.mm
120°c POST CURE 5,633 N.mm
120°c POST CURE
60°c POST CURE 4,059 N.mm
60°c POST CURE
60°c POST CURE 6,199 N.mm
RT CURE
RT CURE
RT CURE
RT CURE 2·1% WATER
RT CURE 3·9% WATER
RT CURE 3·42% WATER
ALL SAMPLES MOULDED WITH A FREE (UNCOVERED) UPPER SURFACE

FIG: 96

STRAIN ENERGY AT FAILURE IN TENSILE TEST
FIBER RESIN CORPORATION FR-7020
* FAILED AT A LARGE BUBBLE AT ONE EDGE
ALL SAMPLES MOULDED WITH A FREE (UNCOVERED) UPPER SURFACE
STRAIN ENERGY AT FAILURE N.mm
2,000
1,000
RT CURE
RT CURE
RT CURE
55°C POST CURE
55°C POST CURE
55°C POST CURE
80°C POST CURE
80°C POST CURE
80°C POST CURE
RT CURE 6.35% WATER
RT CURE 7.14% WATER
RT CURE 8.73% WATER
*
*
*

FIG:97

Electron microscope studies of the effect of heat treatment on microstructure could be helpful to assist in developing optimum cure cycles. However, in doing this it must be remembered that 80°C in the sun or other temperatures for engine cowlings and during supersonic flight may be met in service and some unintentional heat treatment or cure cycle can occur. Adhesives are likely to be operated nearer to their upper temperature limits than most materials and therefore "worst case" values would need to be used for design.

After consideration of the effects of moisture the results from the many test pieces tested dry in sections three and four of the programme (room temperature cure data only) were added to figures from Armstrong (1987) and in the case of tensile modulus they were corrected using Fig 16 (page 105). (Tensile modulus ASTM-D638 v Tensile Modulus in BA test without an extensometer). This graph was plotted using BA data and Manufacturers' data for a few materials to estimate the modulus that other materials tested at BA might have had if they had been tested using an extensometer.

It had originally been thought that it would be possible to obtain sufficiently accurate values of modulus without an extensometer because of the rigidity of the machine, the length of the tensile test piece and relative softness of the adhesives. This proved not to be the case and even calculations based on a formula from a German DIN Spec, Appendix 2 and taking into account the size and shape of the specimen still did not approach the moduli obtained by the Manufacturers using an extensometer. Fig 16 (page 105)then seemed the best method of retrospectively estimating the true modulus values of BA tests.

Using these corrected values of modulus and the additional test data from Armstrong (1989a) the various figures from Armstrong (1987) were redrawn and a further attempt made to relate lap shear strength to the various mechanical properties of the resin systems tested.

A study of Figs 98, 99, 100, 101 and 102 (pages 252 - 257) shows that Epikote 815 + RTU and Epikote 828 + RTU do not show up as well as one might expect. Fig 98 (page 252) shows some correlation of resin tensile strength with lap shear strength but beyond about 4,000 psi this drops off for some resins although the hot- cured AF 163 and Redux 308A do better. Fig 99 (page 253) shows a correlation with tensile modulus but this falls off beyond 350,000 psi.

Fig 100A (page 254) shows quite a good correlation of elongation to failure with lap shear strength but it is not good for Redux 501 blended with Redux 410NA or for Epikote 815 + RTU or Epikote 828 + RTU.
A function (tensile strength $\div \sqrt{G}$) was used to represent a function of the Volkersen Stress Concentration Factor. In Fig 101 (page 256) this function was plotted against lap shear strength in an attempt to get an order of merit of joint strength related to resin strength and this Stress Concentration Factor. Again, it can be seen that composite matrix resins (usually brittle compared with adhesives) fall out of the pattern of adhesives used for making joints. Finally in Fig 102 (page 257) it can be clearly seen that again, most of the composite matrix resins have a high strain energy at failure but a poor lap shear strength. Those materials not fitting the curve have a high tensile strain energy that goes with a good elongation to failure but a low fracture energy.

(Text continues on page 258)

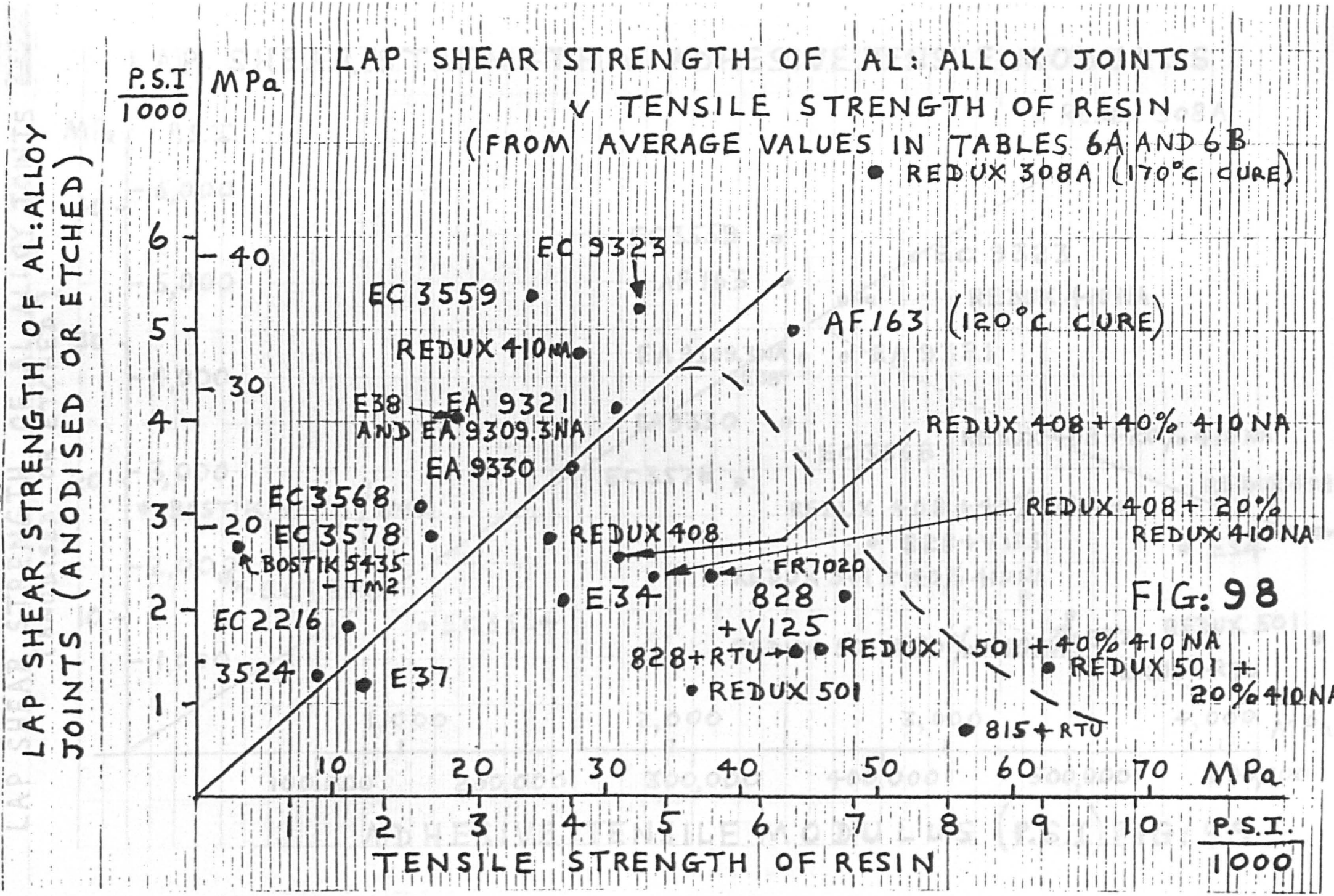

LAP SHEAR STRENGTH OF AL: ALLOY JOINTS
V TENSILE STRENGTH OF RESIN
(FROM AVERAGE VALUES IN TABLES 6A AND 6B
REDUX 308A (170°C CURE)
P.S.I / 1000
MPa
LAP SHEAR STRENGTH OF AL:ALLOY JOINTS (ANODISED OR ETCHED)
EC 9323
EC 3559
AF 163 (120°C CURE)
REDUX 410NA
E38 — EA 9321
AND EA 9309.3NA
EA 9330
REDUX 408 + 40% 410 NA
EC3568
EC 3578
REDUX 408 + 20% REDUX 410 NA
REDUX 408
BOSTIK 5435 + TM2
FR7020
E34
828
+V125
828+RTU
REDUX 501 + 40% 410 NA
REDUX 501 + 20% 410 NA
REDUX 501
EC2216
3524
E37
815+RTU
TENSILE STRENGTH OF RESIN
P.S.I. / 1000

FIG: 98

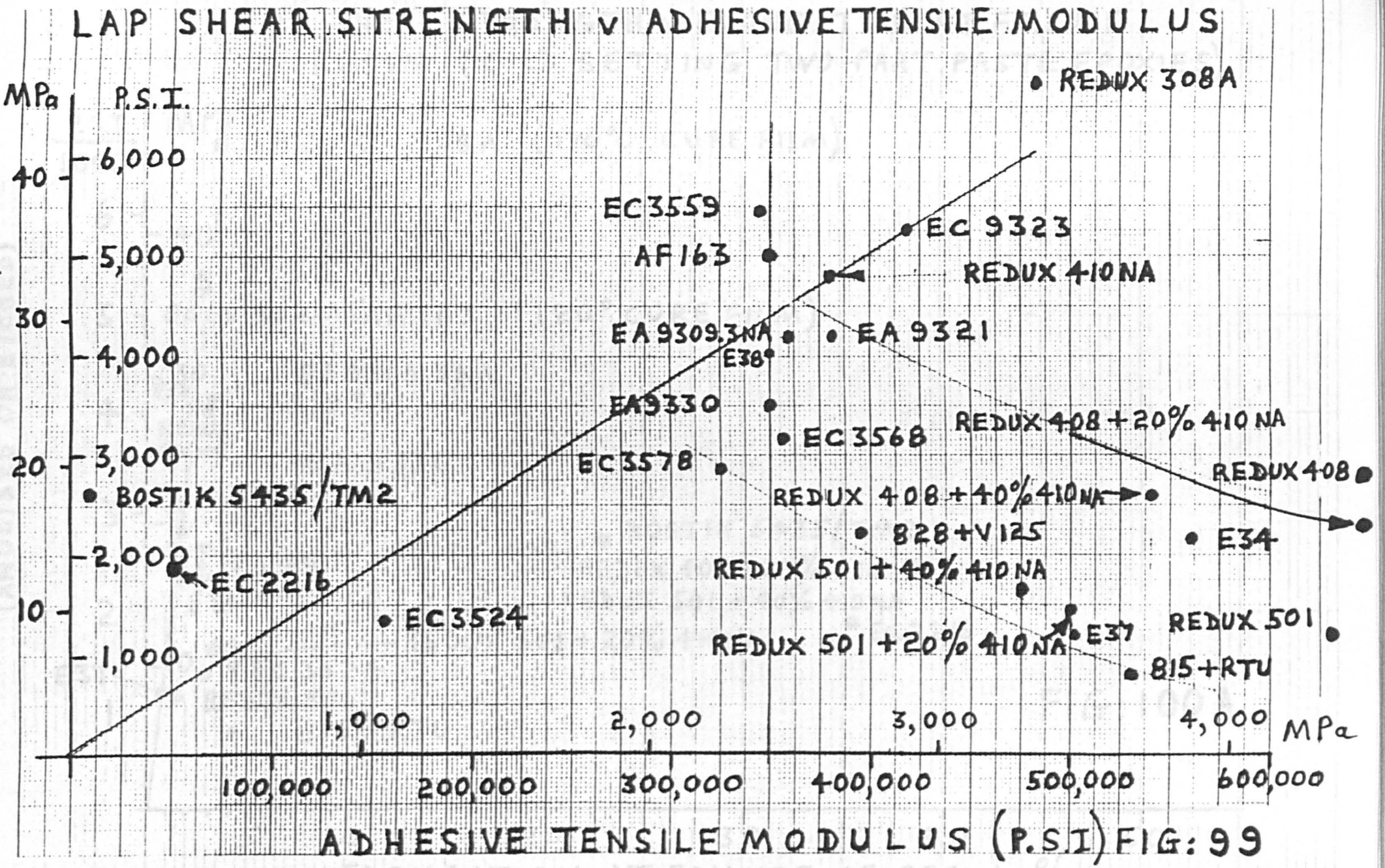

LAP SHEAR STRENGTH v ADHESIVE TENSILE MODULUS
LAP SHEAR STRENGTH OF AL. ALLOY JOINTS (ANODISED OR ETCHED)
MPa
P.S.I.
40
30
20
10
6,000
5,000
4,000
3,000
2,000
1,000
REDUX 308A
EC3559
AF163
EC 9323
REDUX 410 NA
EA 9309.3NA
E38
EA 9321
EA9330
EC3568
REDUX 408 + 20% 410 NA
EC3578
REDUX 408
BOSTIK 5435/TM2
REDUX 408 + 40% 410 NA
828 + V125
E34
EC2216
REDUX 501 + 40% 410 NA
EC3524
E37
REDUX 501
REDUX 501 + 20% 410 NA
815 + RTU
1,000
2,000
3,000
4,000
MPa
100,000
200,000
300,000
400,000
500,000
600,000
ADHESIVE TENSILE MODULUS (P.S.I)

FIG: 99

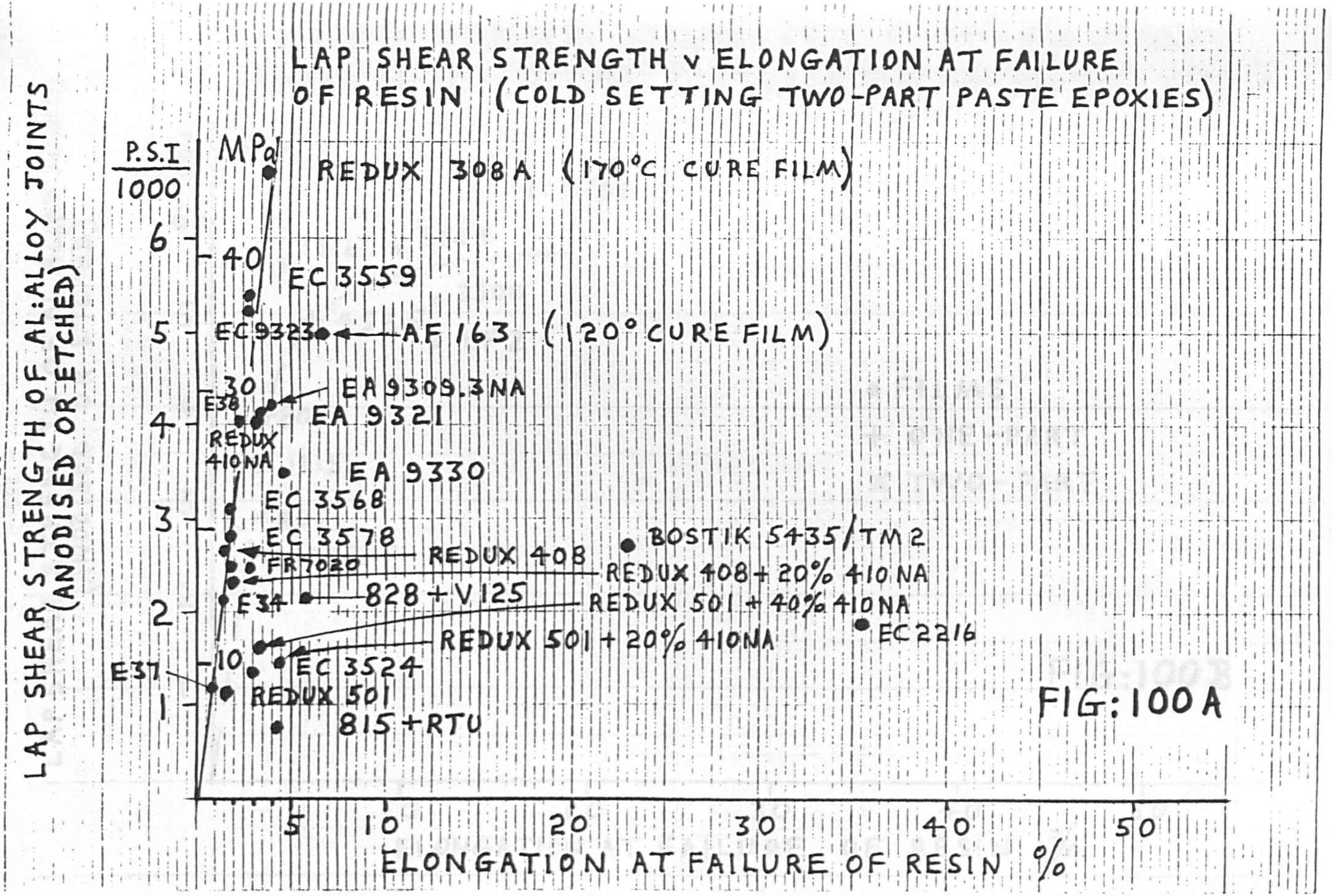
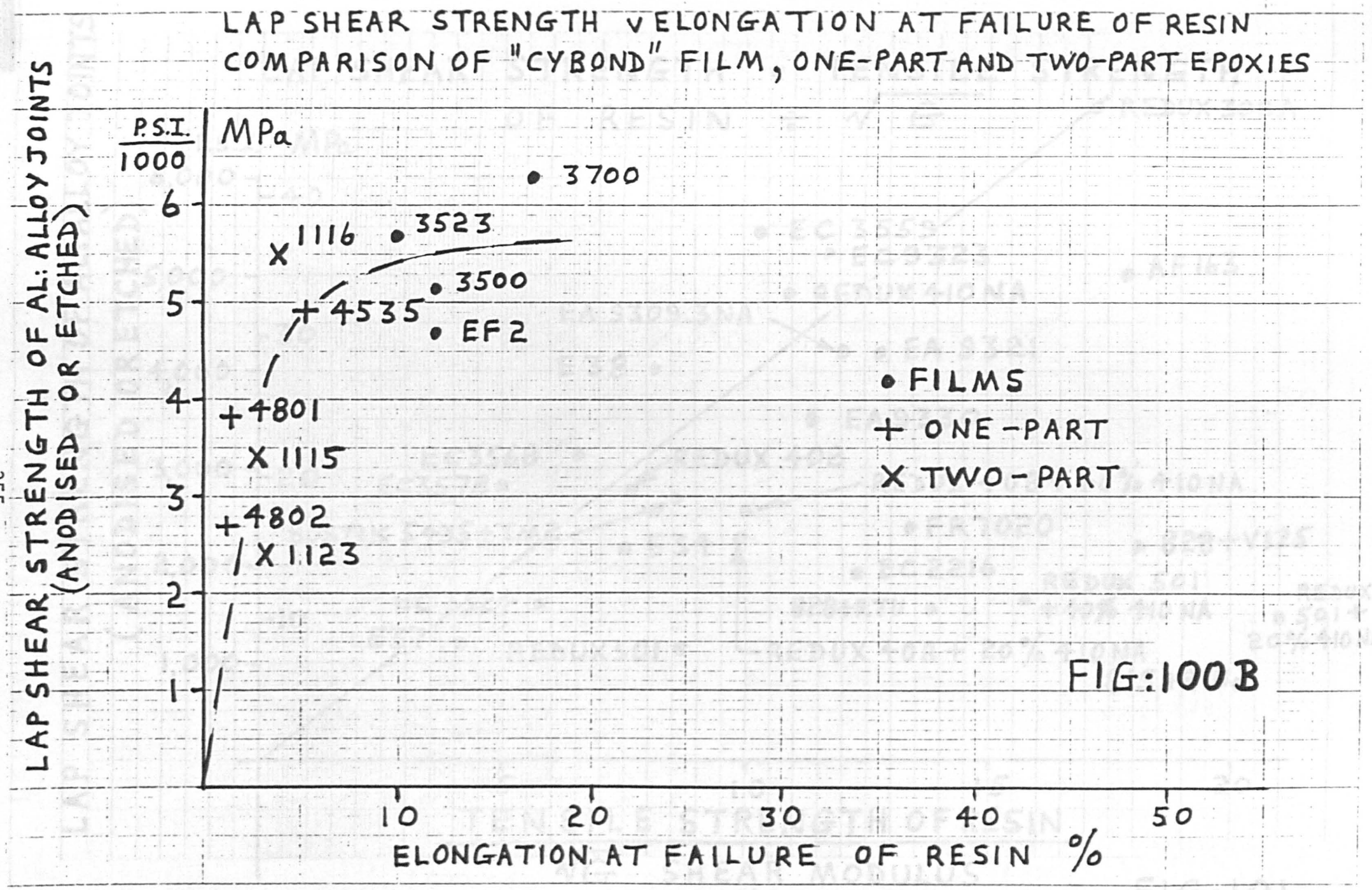

LAP SHEAR STRENGTH v ELONGATION AT FAILURE OF RESIN (COLD SETTING TWO-PART PASTE EPOXIES)
LAP SHEAR STRENGTH OF AL:ALLOY JOINTS (ANODISED OR ETCHED)
P.S.I / 1000
MPa
REDUX 308A (170°C CURE FILM)
EC 3559
EC 9323
AF 163 (120° CURE FILM)
EA 9309.3NA
EA 9321
E38
REDUX 410NA
EA 9330
EC 3568
EC 3578
FR7020
REDUX 408
BOSTIK 5435/TM2
REDUX 408 + 20% 410NA
828 + V125
E34
REDUX 501 + 40% 410NA
EC 2216
REDUX 501 + 20% 410NA
EC 3524
E37
REDUX 501
815 + RTU
6
5
4
3
2
1
40
30
10
5
10
20
30
40
50
ELONGATION AT FAILURE OF RESIN %

FIG: 100A


LAP SHEAR STRENGTH v ELONGATION AT FAILURE OF RESIN
COMPARISON OF "CYBOND" FILM, ONE-PART AND TWO-PART EPOXIES
LAP SHEAR STRENGTH OF AL: ALLOY JOINTS (ANODISED OR ETCHED)
P.S.I. / 1000
MPa
6
5
4
3
2
1
• 3700
X 1116
• 3523
• 3500
+ 4535
• EF 2
+ 4801
X 1115
+ 4802
X 1123
• FILMS
+ ONE-PART
X TWO-PART
10
20
30
40
50
ELONGATION AT FAILURE OF RESIN %
FIG:100B

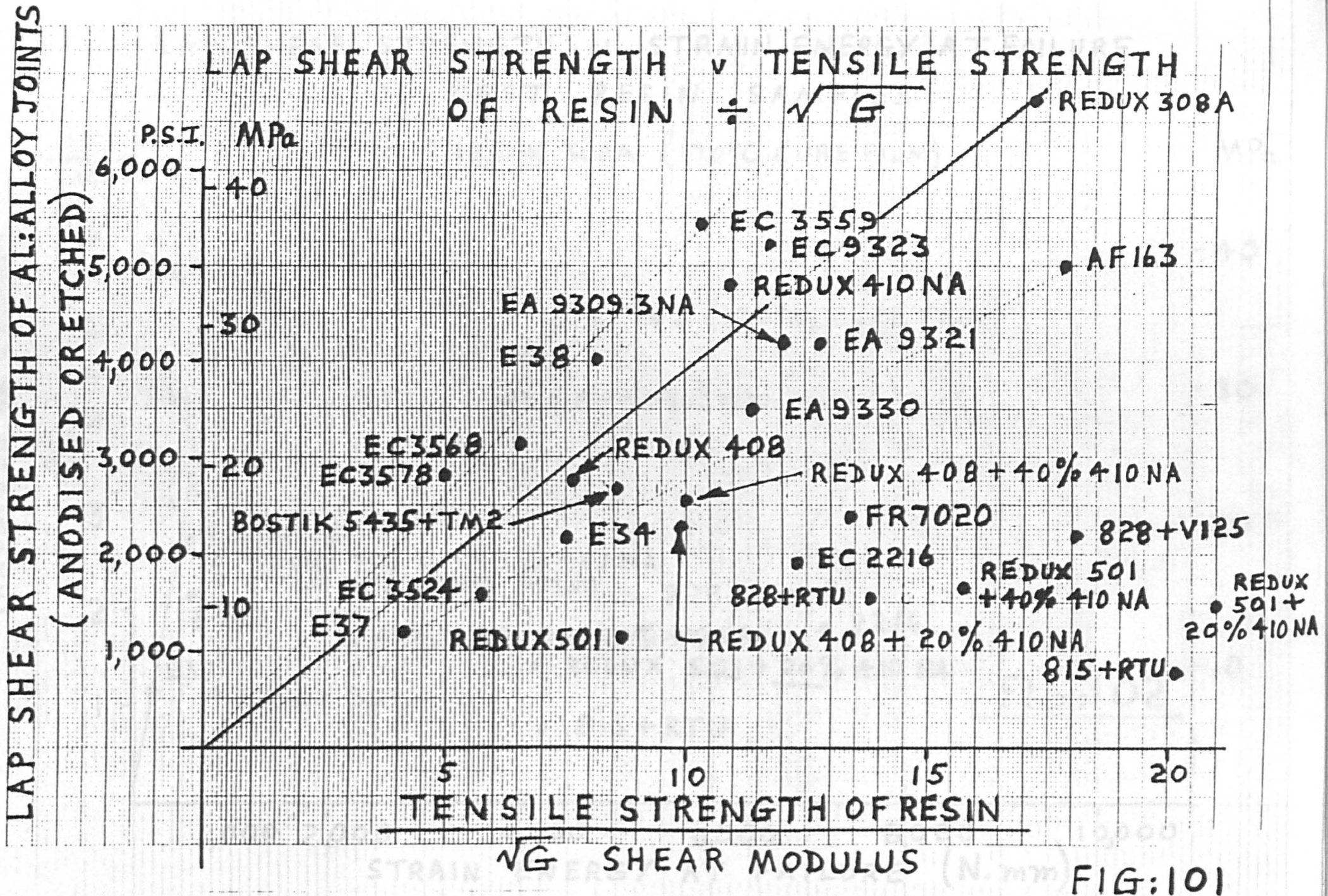

LAP SHEAR STRENGTH v TENSILE STRENGTH OF RESIN ÷ √G
LAP SHEAR STRENGTH OF AL:ALLOY JOINTS (ANODISED OR ETCHED)
P.S.I.
MPa
6,000
5,000
4,000
3,000
2,000
1,000
40
30
20
10
REDUX 308A
EC 3559
EC 9323
AF 163
REDUX 410 NA
EA 9309.3NA
EA 9321
E38
EA 9330
EC3568
REDUX 408
EC3578
REDUX 408 + 40% 410 NA
BOSTIK 5435+TM2
FR7020
828+V125
E34
EC 2216
REDUX 501 +40% 410 NA
EC 3524
828+RTU
REDUX 501 + 20% 410 NA
E37
REDUX501
REDUX 408 + 20% 410 NA
815+RTU
5
10
15
20
TENSILE STRENGTH OF RESIN
√G SHEAR MODULUS

FIG:101

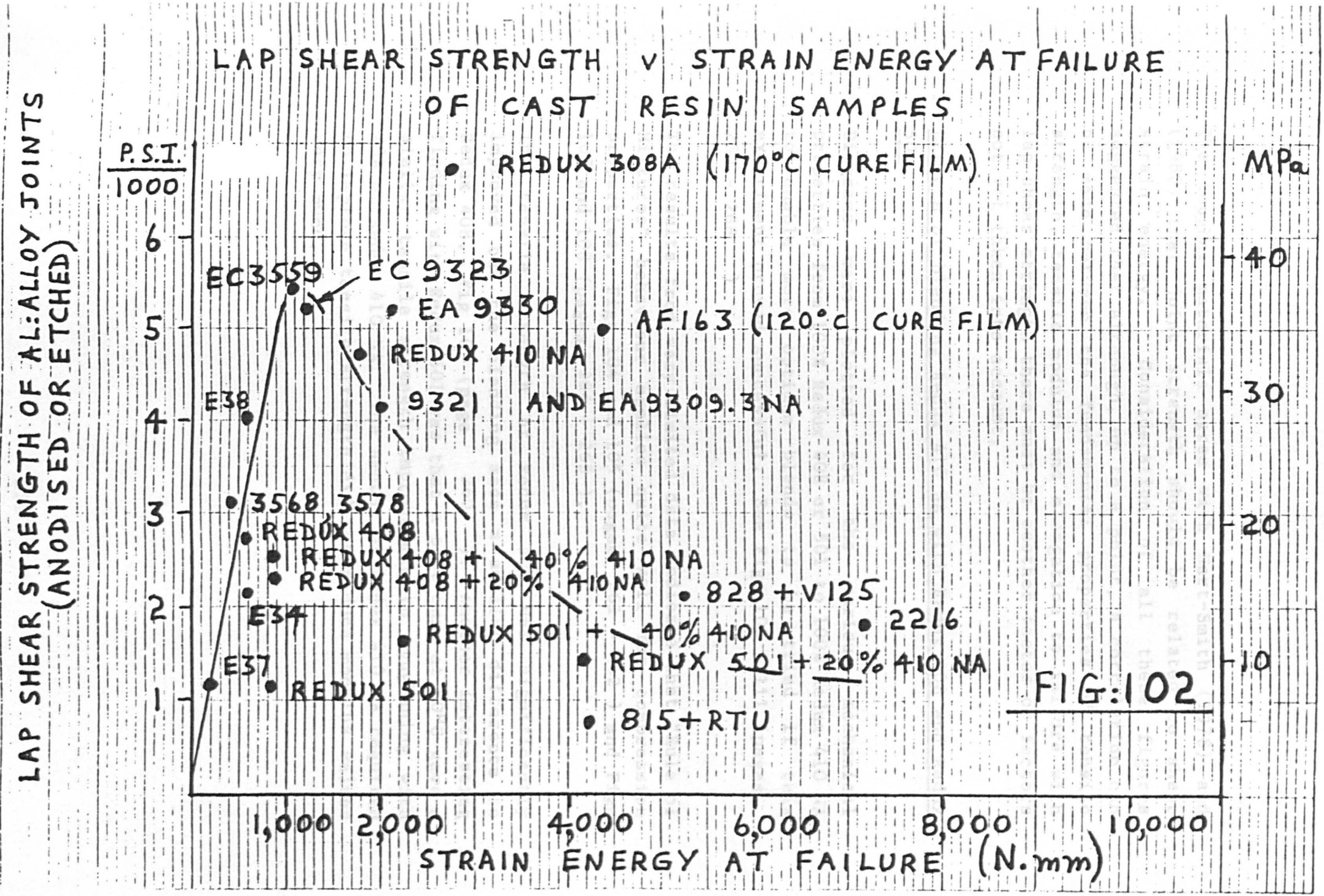

LAP SHEAR STRENGTH v STRAIN ENERGY AT FAILURE
OF CAST RESIN SAMPLES
LAP SHEAR STRENGTH OF AL:ALLOY JOINTS
(ANODISED OR ETCHED)
P.S.I. / 1000
MPa
REDUX 308A (170°C CURE FILM)
EC3559
EC 9323
EA 9330
AF163 (120°C CURE FILM)
REDUX 410 NA
9321 AND EA 9309.3 NA
E38
3568 3578
REDUX 408
REDUX 408 + 40% 410 NA
REDUX 408 + 20% 410 NA
828 + V125
E34
2216
REDUX 501 + 40% 410 NA
E37
REDUX 501 + 20% 410 NA
REDUX 501
815 + RTU
1 2 3 4 5 6
10 20 30 40
1,000 2,000 4,000 6,000 8,000 10,000
STRAIN ENERGY AT FAILURE (N.mm)

FIG:102

The tougher materials agree with Hart-Smith (1978) and (1980) that joint strength should be related to shear strain energy. Consideration of all these figures suggested that although, up to a point, a correlation can be made between the fundamental properties of tensile strength, tensile modulus and elongation to failure with lap shear strength there must be another factor or factors not yet taken into account.

Effects of blending Redux 410 NA with Redux 408 and Redux 501

Diagrams were plotted for the various mechanical properties from 100% Redux 408 or 501 to 100% Redux 410 NA to enable more optimum blends to be tried if this experiment proved successful. See Figs 103 - 111 (pages 260 - 268).

The results from very limited data indicate that "Rule of Mixtures" behaviour applies quite well for compression properties. Figs 104 and 105 (pages 261 - 262) and Figs 107 and 108 (pages 264 - 265).

The tensile strength of Redux 501 was significantly improved but the blending made a smaller difference to Redux 408. Fig 103 (page 260). Another interesting finding with Redux 501 was that a post-cure at 80°C gave a similar tensile strength improvement to toughening with 20% of Redux 410 NA. The amount of Redux 410 NA required to improve tensile strength did not reduce modulus values very much.

A study of Figs 103 (page 260), 106 (page 263) and 109 (page 266) revealed that tensile strength, elongation to failure and strain energy all go together as would be expected. However, Fig 110 (page 267) showed very little improvement in lap shear strength by blending in small amounts of Redux 410 NA with Redux 408 and 501. This was particularly interesting because Epikote 815 + RTU and Epikote 828 + RTU also have quite good tensile strengths, elongation to failure and strain energy at failure but in spite of these desirable characteristics they develop poor lap shear strength.

It was therefore considered that the missing factor, required to define the properties of a good adhesive, might well be fracture energy and to check this possibility a considerable amount of wedge testing was undertaken. Previous work in this area was studied. Marceau et al (1977), Allen et al (1984) and (1985), Stone and Peet (1980) Cognard (1986) (1988).

Detailed data of wedge testing is given in Tables 11A and 11B (pages 192 - 194).

(Text continues on page 269)

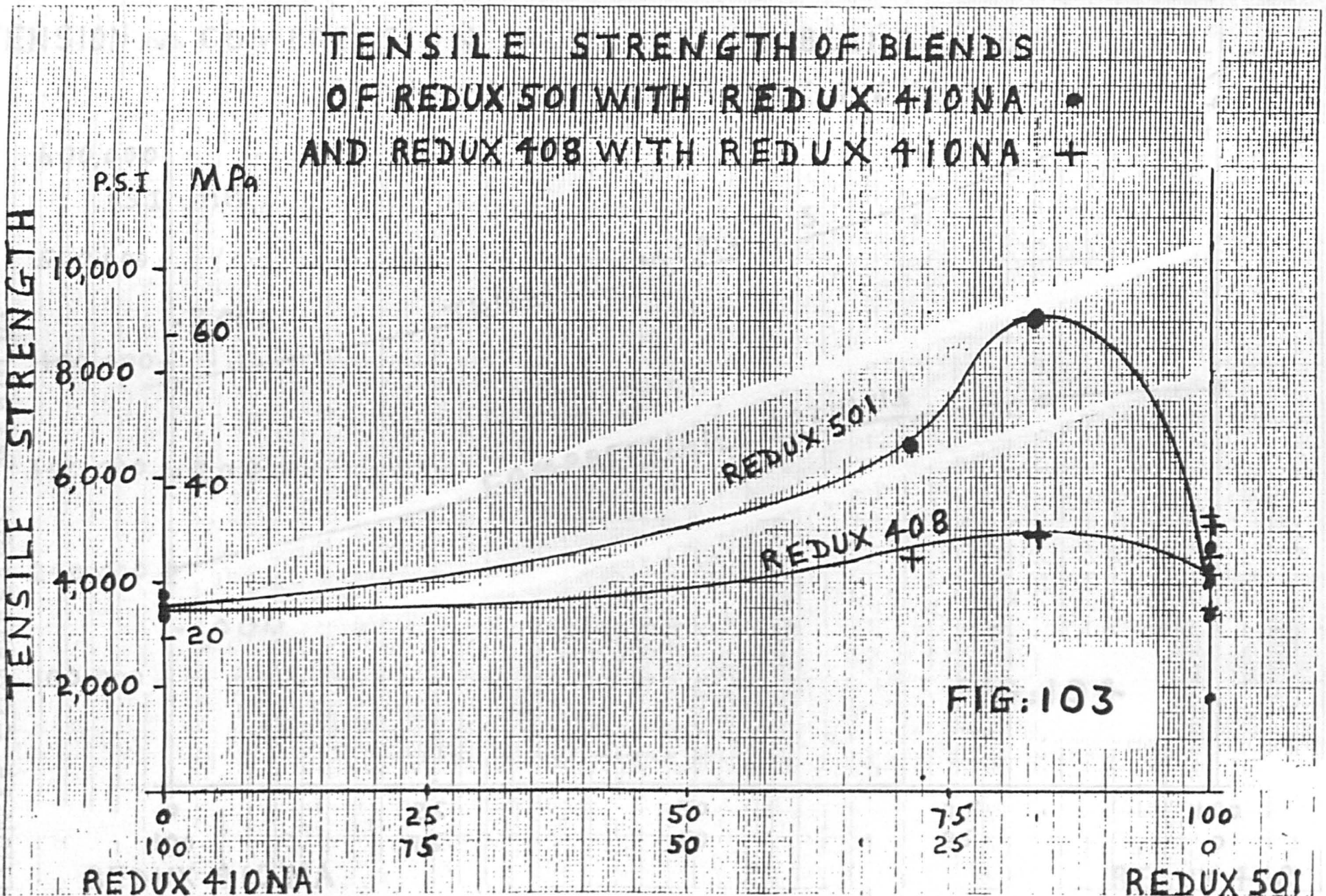

TENSILE STRENGTH OF BLENDS
OF REDUX 501 WITH REDUX 410NA •
AND REDUX 408 WITH REDUX 410NA +
TENSILE STRENGTH
P.S.I
MPa
10,000
8,000
6,000
4,000
2,000
60
40
20
REDUX 501
REDUX 408
0
100
25
75
50
50
75
25
100
0
REDUX 410NA
REDUX 501
REDUX 408

FIG: 103

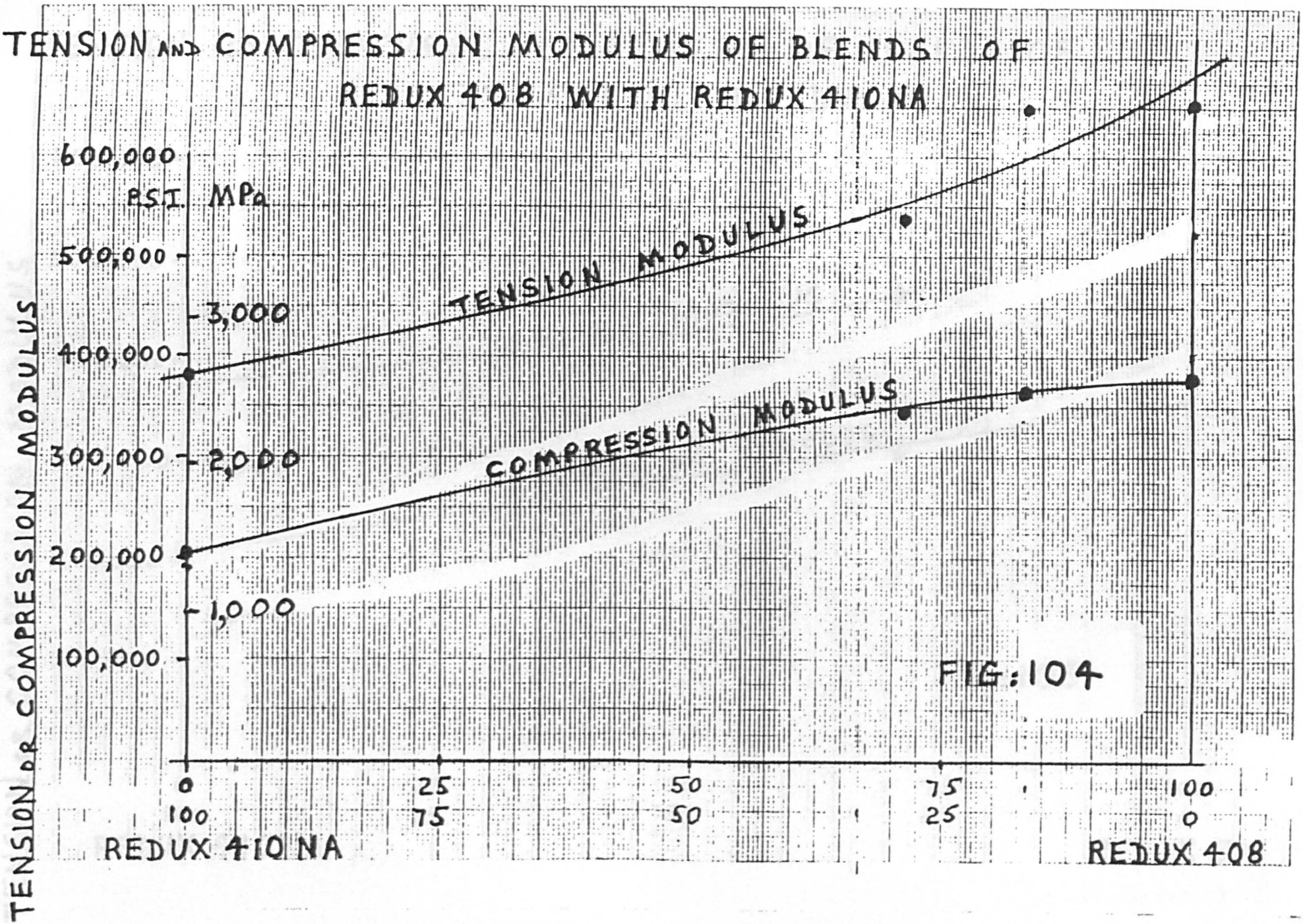

TENSION AND COMPRESSION MODULUS OF BLENDS OF REDUX 408 WITH REDUX 410NA
TENSION OR COMPRESSION MODULUS
PSI
MPa
600,000
500,000
400,000
300,000
200,000
100,000
3,000
2,000
1,000
TENSION MODULUS
COMPRESSION MODULUS
0
25
50
75
100
100
75
50
25
0
REDUX 410 NA
REDUX 408

FIG: 104

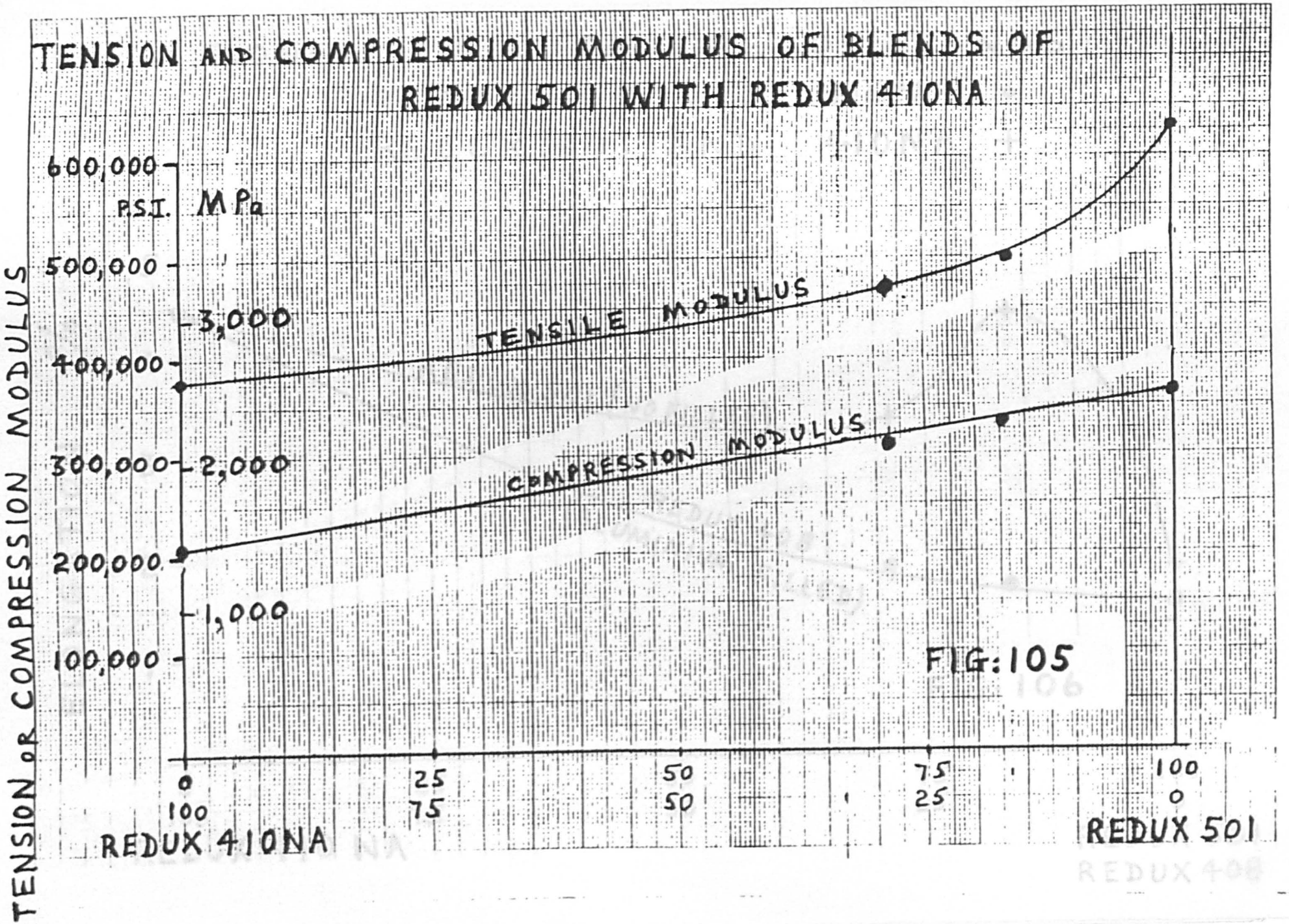

TENSION AND COMPRESSION MODULUS OF BLENDS OF REDUX 501 WITH REDUX 410NA
TENSION OR COMPRESSION MODULUS
600,000
P.S.I.
MPa
500,000
3,000
400,000
TENSILE MODULUS
COMPRESSION MODULUS
300,000
2,000
200,000
1,000
100,000
0
100
25
75
50
50
75
25
100
0
REDUX 410NA
REDUX 501

FIG:105

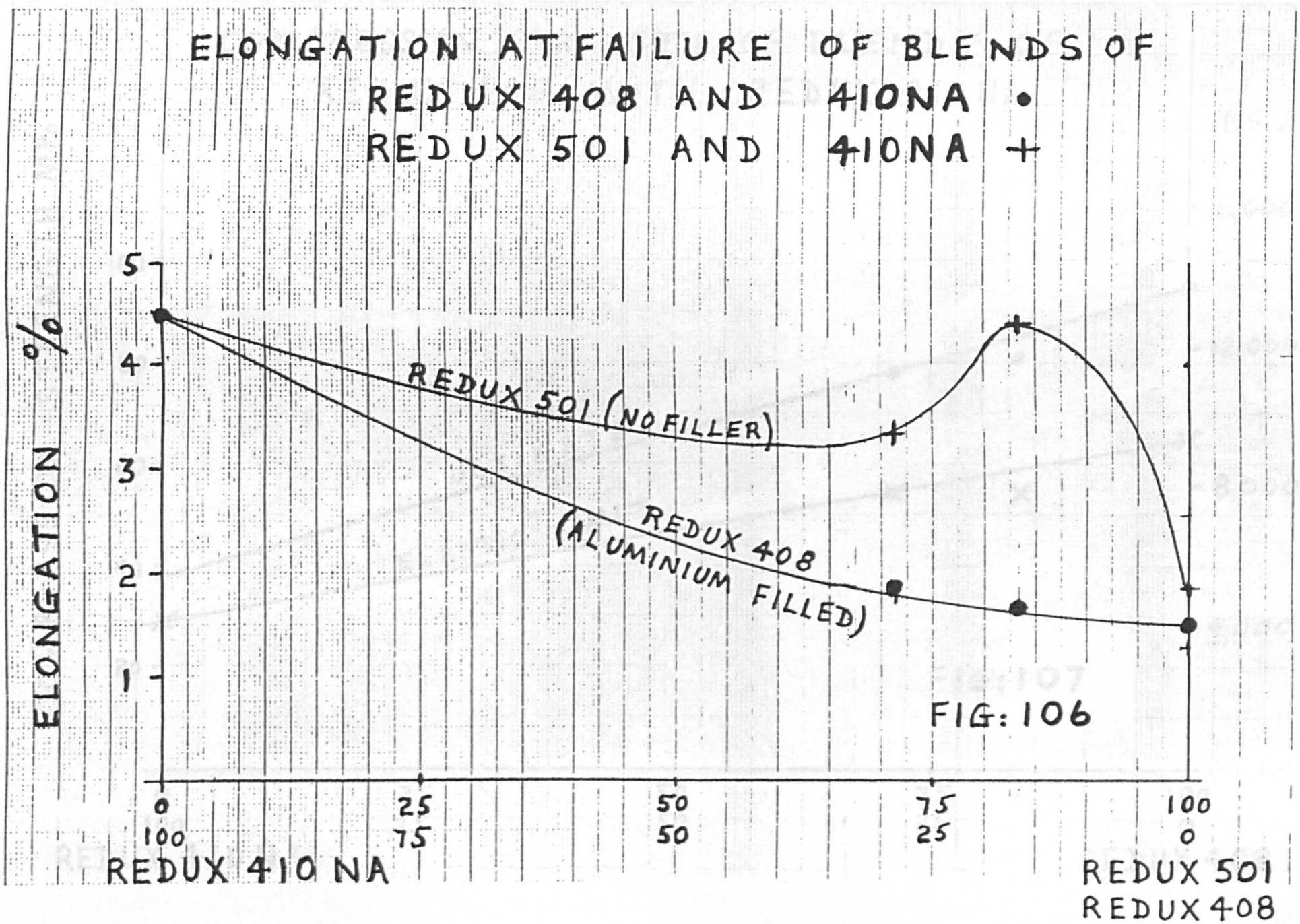

ELONGATION AT FAILURE OF BLENDS OF
REDUX 408 AND 410NA •
REDUX 501 AND 410NA +
ELONGATION %
5
4
3
2
1
REDUX 501 (NO FILLER)
REDUX 408
(ALUMINIUM FILLED)
0
100
25
75
50
50
75
25
100
0
REDUX 410 NA
REDUX 501
REDUX 408

FIG: 106

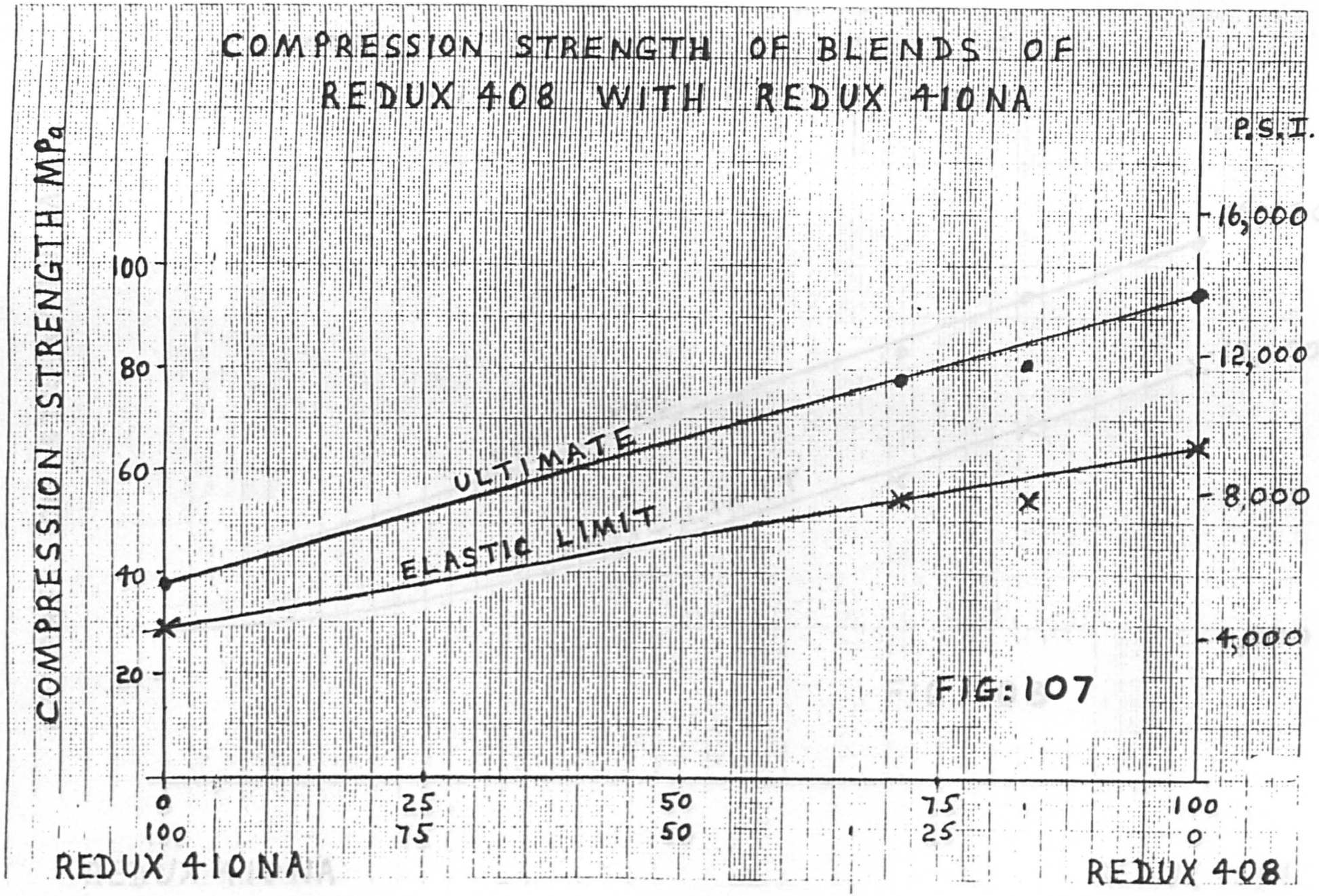

COMPRESSION STRENGTH OF BLENDS OF
REDUX 408 WITH REDUX 410NA
COMPRESSION STRENGTH MPa
P.S.I.
100
80
60
40
20
16,000
12,000
8,000
4,000
ULTIMATE
ELASTIC LIMIT
0
25
50
75
100
100
75
50
25
0
REDUX 410NA
REDUX 408

FIG:107

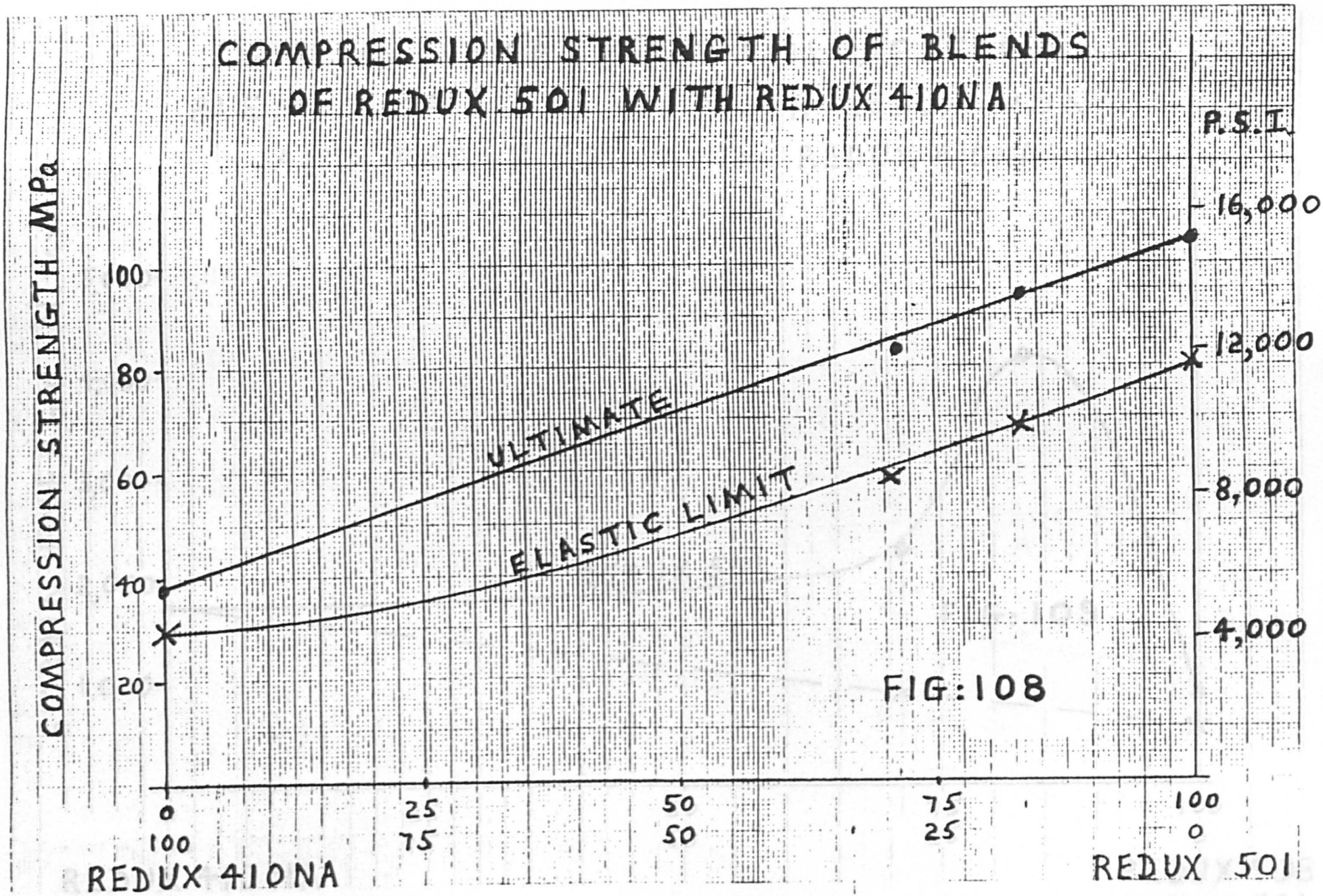

COMPRESSION STRENGTH OF BLENDS
OF REDUX 501 WITH REDUX 410NA
COMPRESSION STRENGTH MPa
P.S.I.
100
80
60
40
20
16,000
12,000
8,000
4,000
ULTIMATE
ELASTIC LIMIT
0
100
25
75
50
50
75
25
100
0
REDUX 410NA
REDUX 501

FIG:108

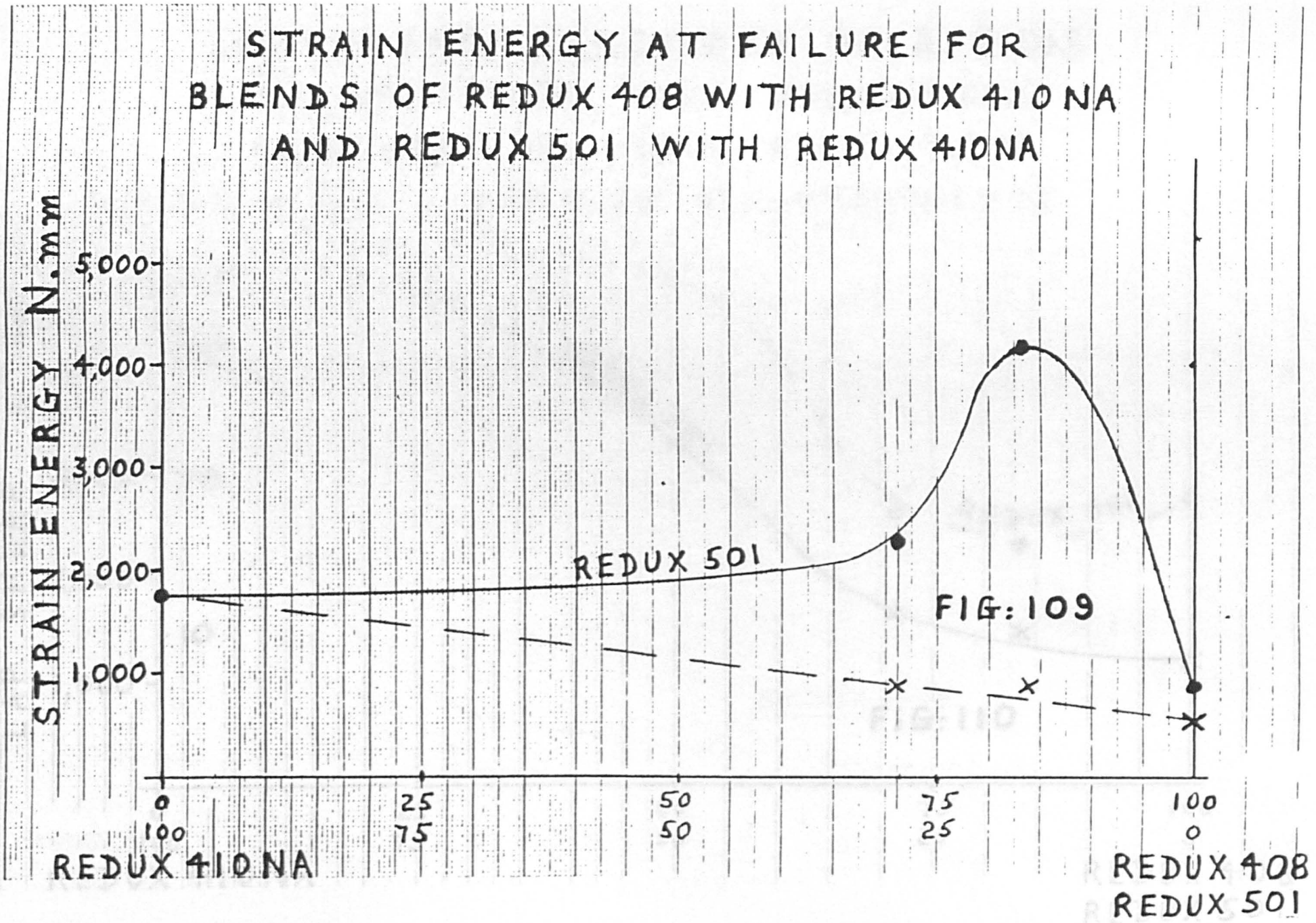

STRAIN ENERGY AT FAILURE FOR
BLENDS OF REDUX 408 WITH REDUX 410 NA
AND REDUX 501 WITH REDUX 410 NA
STRAIN ENERGY N.mm
5,000
4,000
3,000
2,000
1,000
REDUX 501
0
100
25
75
50
50
75
25
100
0
REDUX 410 NA
REDUX 408
REDUX 501

FIG: 109

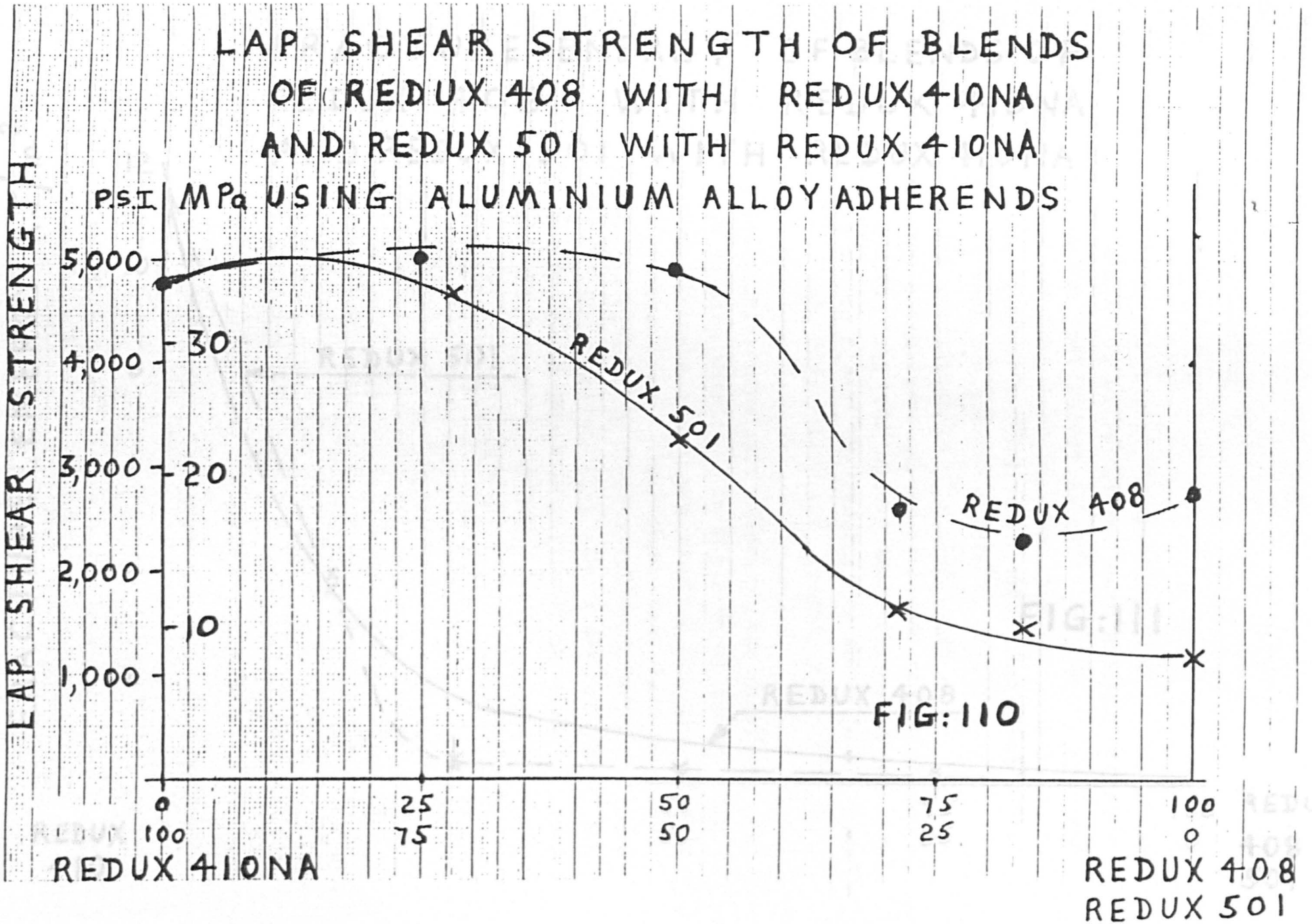

LAP SHEAR STRENGTH OF BLENDS
OF REDUX 408 WITH REDUX 410NA
AND REDUX 501 WITH REDUX 410NA
USING ALUMINIUM ALLOY ADHERENDS
LAP SHEAR STRENGTH
P.S.I
MPa
5,000
4,000
3,000
2,000
1,000
30
20
10
REDUX 501
REDUX 408
0
25
50
75
100
100
75
50
25
0
REDUX 410NA
REDUX 408
REDUX 501

FIG: 110

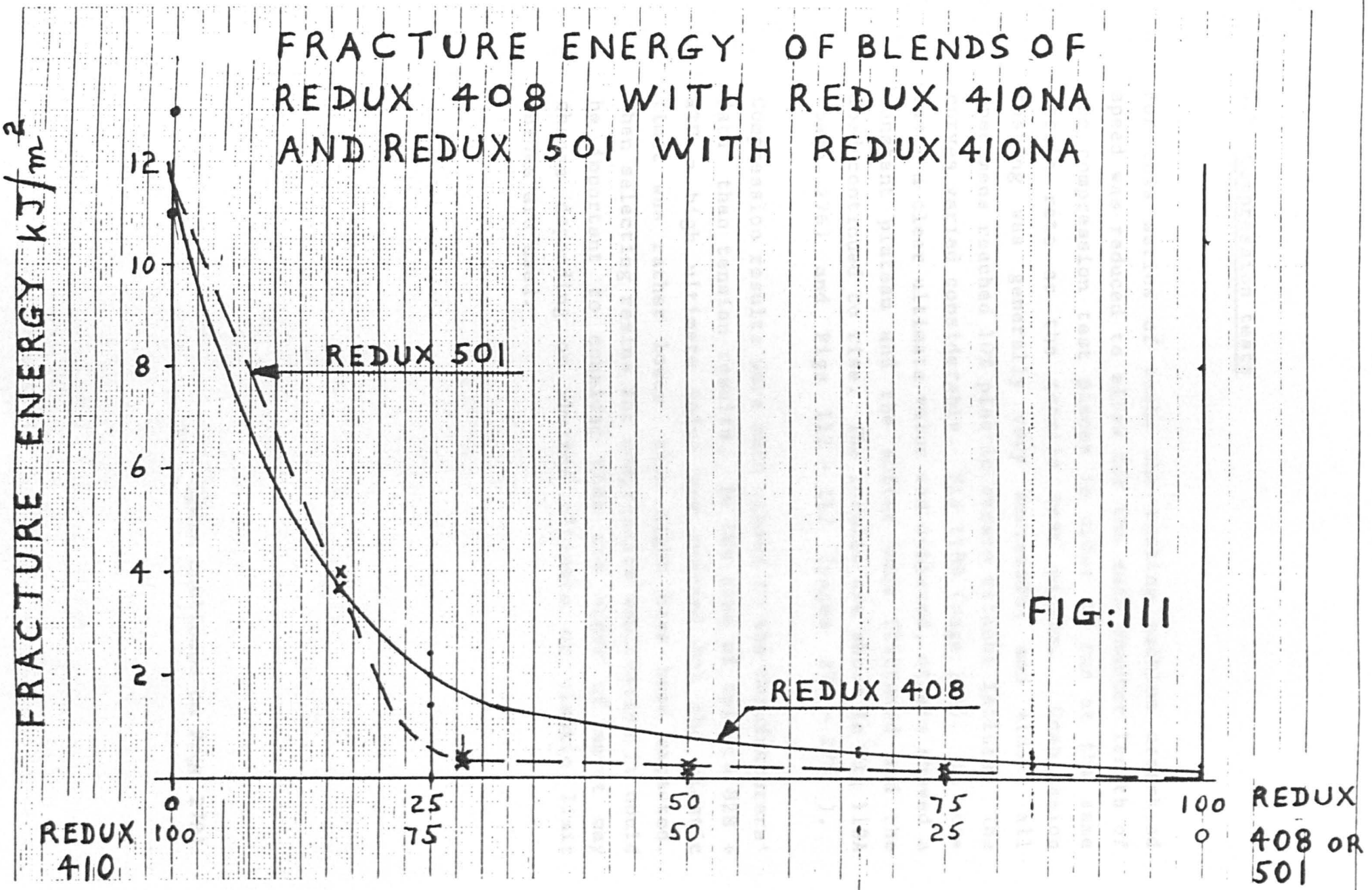

FRACTURE ENERGY OF BLENDS OF
REDUX 408 WITH REDUX 410NA
AND REDUX 501 WITH REDUX 410NA
FRACTURE ENERGY kJ/m²
12
10
8
6
4
2
REDUX 501
REDUX 408
0
25
50
75
100
REDUX 410
100
75
50
25
0
REDUX 408 OR 501

FIG:111

5.2 Compression tests

For this series of tests the testing machine crosshead speed was reduced to allow for the much shorter length of the compression test pieces in order to run at the same strain rate as the tensile test pieces. Compression testing was generally very successful and almost all specimens reached 10% plastic strain without failure. The curves varied considerably. Fig 118B (page 277). In some cases a clear ultimate value was achieved, others showed a constant plateau and the softer ones flattened and the load continued to rise. The results are shown in Fig 118A (page 276) and Figs 112 - 117 (pages 270 - 275).

Compression results were much closer to the Manufacturers' data than tension results. In the case of Epikote 828 + RTU a high ultimate value was reached but the elastic limit was rather lower than might have been expected. When selecting resins for compression application it could be important to consider that the order of merit may change depending on whether ultimate or elastic limit values are used.

(Text continues on Page 278)

COMPRESSIVE MODULUS OF ADHESIVES
MANUFACTURER'S DATA
HYSOL
COMPRESSIVE MODULUS P.S.I./MPa
P.S.I.
MPa
600,000
500,000
400,000
300,000
200,000
100,000
4,000
3,000
2,000
1,000
EA 9649
EA 9628
EA 9330
EA 9321
EA 9320
EA 9314
EA 9313
EA 9309.3 NA
EA 956
EA 934 NA
710

FIG:112

COMPRESSIVE MODULUS OF ADHESIVES
BRITISH AIRWAYS DATA
COMPRESSIVE MODULUS p.s.i./MPa
p.s.i.
MPa
600,000
500,000
400,000
300,000
200,000
100,000
4,000
3,000
2,000
1,000
REDUX 408
+20% 410NA
REDUX 408
+40% 410NA
REDUX 410NA
PERMABOND E34
PERMABOND E38
EC 2216
EC 9323
EA 9330
EA 9321
EA 9309.3NA
EA 9330 + 20% MICROBALLOONS
BOSTIK 5435/TM2

FIG:113

COMPRESSIVE MODULUS OF ADHESIVES
COMPOSITE MATRIX RESINS
BRITISH AIRWAYS DATA
COMPRESSIVE MODULUS P.S.I./MPa
P.S.I.
MPa
600,000
500,000
400,000
300,000
200,000
100,000
4,000
3,000
2,000
1,000
REDUX 501
REDUX 501+ 20% 410NA
REDUX 501+ 40% 410NA
SHELL 815+RTU
SHELL 815+ RTU 80°C POST CURE
SHELL 815+RTU 120°C POST CURE
SHELL 828+RTU
PERMABOND E37
FR 7020
ALL SAMPLES CURED AT ROOM TEMPERATURE
EXCEPT WHERE STATED

FIG:114

COMPRESSIVE STRENGTH OF ADHESIVES
MANUFACTURER'S DATA
HYSOL
COMPRESSIVE STRENGTH P.S.I./MPa
14,000
12,000
10,000
8,000
6,000
4,000
2,000
P.S.I.
80
70
60
50
40
30
20
10
MPa
EA 934 NA
EA 956
EA 9309.3NA
EA 9313
EA 9314
EA 9320
EA 9321
EA 9330
EA 9628
EA 9649
15,648
23,614
16,880
20,400

FIG:115

COMPRESSIVE STRENGTH OF ADHESIVES
BRITISH AIRWAYS DATA
ULTIMATE STRENGTH
ELASTIC LIMIT STRENGTH
COMPRESSIVE STRENGTH P.S.I./MPa
14,000
12,000
10,000
8,000
6,000
4,000
2,000
100
90
80
70
60
50
40
30
20
10
MPa
REDUX 408
REDUX 408 +20%
410 NA
REDUX 408 +40%
410 NA
REDUX 410 NA
PERMABOND E34
PERMABOND E38
FC 2216
EC 9323
EA 9330
EA 9321
EA 9309.3NA
EA 9330 + 20% MICROBALLOONS
BOSTIK 5435/TM2
* SAMPLE FLATTENED NO ULTIMATE VALUE FOUND
* SAMPLE FLATTENED NO ULTIMATE VALUE FOUND

FIG: 116

COMPRESSIVE STRENGTH OF ADHESIVES
COMPOSITE MATRIX RESINS
BRITISH AIRWAYS DATA
ULTIMATE STRENGTH
ELASTIC LIMIT
COMPRESSIVE STRENGTH P.S.I./MPa
14,000 - 100
12,000 - 80
10,000 - 70
8,000 - 60
6,000 - 50
4,000 - 40
2,000 - 30
- 20
- 10
REDUX 501
REDUX 501 + 20% 410NA
REDUX 501 + 40% 410NA
815 + RTU
815 + RTU 80°C POST CURE
815 + RTU 120°C POST CURE
828 + RTU
PERMABOND E37
FR 7020
ALL SAMPLES CURED AT ROOM TEMPERATURE
EXCEPT WHERE STATED

FIG: 117

TENSION AND COMPRESSION STRENGTHS
OF VARIOUS ADHESIVES
(ULTIMATE VALUES)
ROOM TEMPERATURE CURE
TWO-PART PASTES
HOT CURE FILMS
P.S.I
10,000
5,000
0
5,000
10,000
15,000
* REDUX 308A
* 3M-AF163
FR 7020
828+RTU
REDUX 501
REDUX 501 + 20% 410NA
REDUX 501 + 40% 410NA
REDUX 410
REDUX 408 + 40% 410NA
REDUX 408 + 20% 410NA
REDUX 408
E38 PERMABOND
60°C CURE
E37 PERMABOND
E34 PERMABOND
SHELL 815 + RTU
HYSOL EA9321
HYSOL EA9330
HYSOL EA9309.3
3M-EC9323
100
80
60
40
20
20
40
60
80
100
TENSION
MPa
COMPRESSION
* DUE TO FOAMING WHILE CURING A THICK BLOCK, EVEN UNDER
FIG:118A

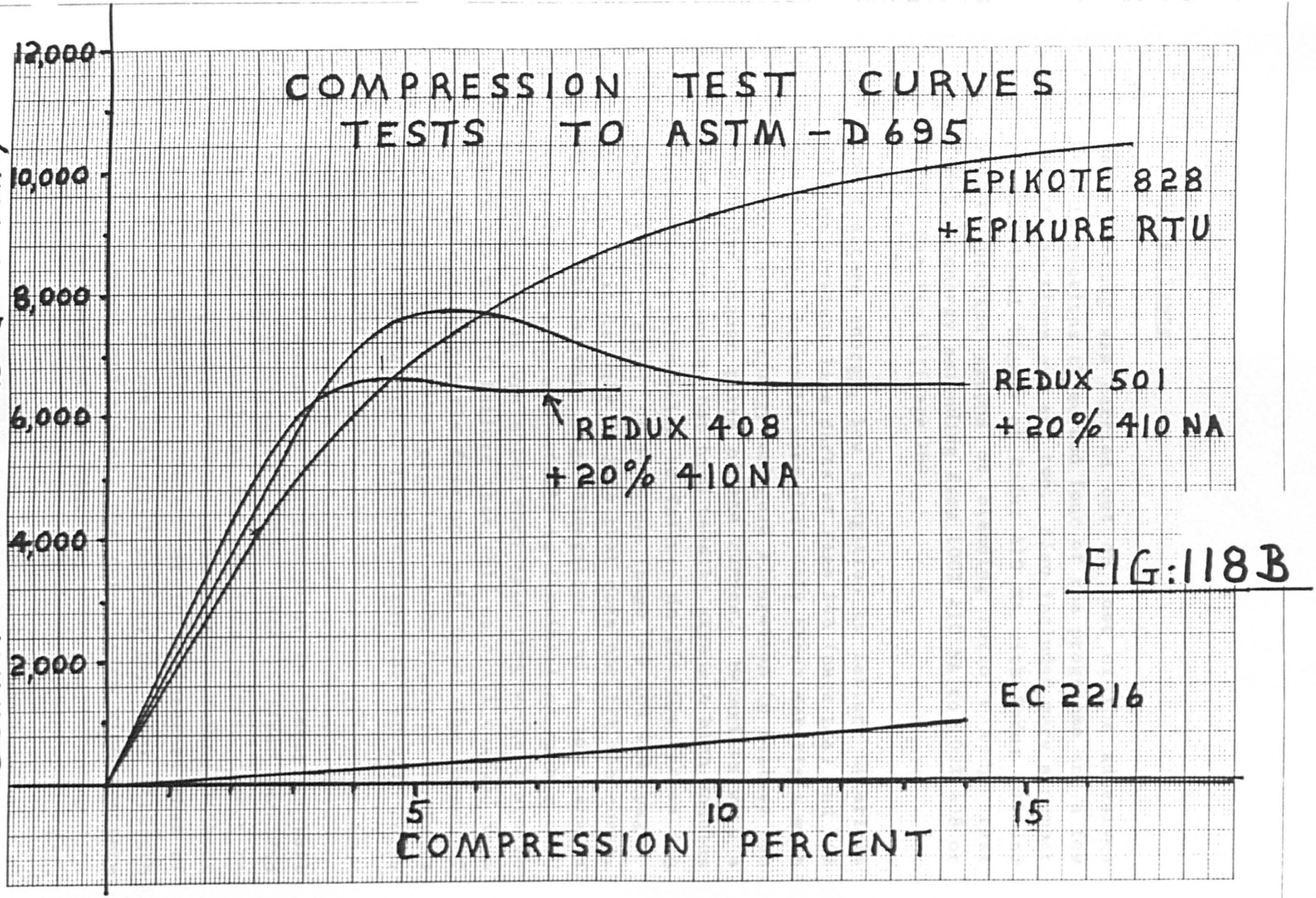


FIG:118B

5.3 Wedge Tests

Wedge testing was carried out on most of the adhesives used in sections three and four of the programme and a few used in sections one and two. Also included were a number of additional blends of Redux 410 NA with Redux 408 and 501 to provide graphs of blending ratio v wedge test fracture energy extending from 100% 410 NA to 100% 408 or 501. See Fig 111(page 268).

Low fracture energy, low elongation to failure materials fit the straight line parts of Figs 44A (page 144) and 44B (page 145). It would seem that only those materials with a high fracture energy and good elongation to failure can reach the higher parts of the curves. Materials with a low fracture energy but high tensile strength,high modulus and moderate elongation to failure do fit the curves (eg Epikote 815 + RTU). In Figs 44A (page 144) and 44B (page 145) it is only EC 2216 that does not fit the curve. EC 2216 has a very high elongation and a low tensile strength and modulus. EC2216 is flexibilised rather than toughened and it was noted when splitting wedge tests to check the mode of failure that this material changed from a ductile to a brittle fracture mode under the impact of splitting. In Fig 44D (page 147) where fracture energy is multiplied by modulus it is noteworthy that EC 2216 comes back on the curve.

When fracture energy is low the joint is likely to fail when the tensile strength of the resin is first exceeded at the ends of the joint and the local stress cannot be relieved by plastic strain, crazing or cracking without leading to immediate failure. It is of interest that of all the correlations attempted between lap shear strength and mechanical properties, the correlation with fracture toughness gives the best fit.

Experiment has shown that in some cases, when testing tough adhesives a 'ping' is heard as the 'spew' fails at the ends of a joint but this is usually only just before failure. The load does not increase much above this point before failure occurs.

Lap joints made with brittle adhesives fail with one bang and not in two or more stages. It would seem that brittle adhesives, with a high modulus, fail because the high stress at the ends of the joint cannot be relieved by plastic strain or crack growth because they have no plastic strain and the critical crack length is too short. On the other hand, tough adhesives are of lower modulus, exhibit some plastic strain and can tolerate a longer crack because of their higher fracture energy. Adams & Wake (1984) have shown that failure of brittle adhesives can be predicted by a maximum principal stress criterion whereas a maximum principal strain criterion was found more suitable for toughened adhesives. The crazing seen in EC 9323 and EA 9309.3 NA before failure would suggest that this is the case. Low strength, low modulus adhesives probably fail due to stress rather than strain.

Figs 44A (page 144) and 44B (page 145) indicate that some optimum combination of tensile modulus, tensile strength, elongation and fracture energy is required to give a high lap shear strength. Observation of lap joints under test showed an increasing rotation of the joint with increasing load indicating that some peel strength or fracture energy must be necessary.

The test pieces that failed at the highest loads suffered permanent deformation indicating that the yield point of 2024-T3 Aluminium Alloy had been exceeded. Adhesively bonded joints tend to fail when the yield strength of the adherend has been exceeded because of the additional

strain produced in the adhesive layer. Some of the adhesives that caused permanent deformation in the lap shear test also caused permanent deformation in the wedge test. The fracture energy values are probably too high because of this. Crack growth in water was probably too low for the same reason.

Fig 44C (page 146) shows a considerable drop in fracture energy after 10 days immersion in filtered water at room temperature. The value of fracture energy at which the curves level out would seem to be more important than the original dry values when comparing adhesives. Similar work by Arah et al (1989) studied durability of wet joints but they used stress-relaxation tests instead of fracture energy tests. Subsequent monitoring of tests in Fig 44C (page 146) which still continue at the time of writing has shown the vital importance of anodising as a surface preparation for Aluminium Alloys. These tests are continuing after 750 days immersion in water. No specimens have yet disbonded. By contrast similar specimens, given only a glasspaper abrade, disbonded completely in 24 hours!

The wedge test really brought out the difference between "adhesives" and "matrix resins". The former were always at the higher end of the fracture energy scale and the latter always at the lower.
In terms of fracture energy after a period of time dry, and especially after a period of time immersed in water, the difference between "flexibilised" resins and "toughened" resins could also be seen. Crack growth for "flexibilised" resins was always much greater. When splitting specimens to check the mode of failure it was found that a sharp hammer blow could change even EC 2216 from a tough to a brittle failure mode. All of the adhesives behaved in this way except the toughest, Redux

410NA and 3M-AF163-2K. This confirmed that driving the wedge in slowly in a controlled manner was the right approach. Adhesives for use in situations of impact loading need to be tested at appropriate loading rates to match the end use conditions.

It was also observed that although most of the failures were cohesive even with brittle materials, Redux 501 gave totally apparent adhesive failure. A blend of three parts Redux 501 and one part Redux 410 NA gave apparent adhesive failure for two thin glue lines but a totally cohesive failure for one thick glue line. See Kreiger (1973) who also found that glue line thickness could affect mode of failure. He attributed this to increased stress at the bond line which his formula shows to increase as the glue line thickness is reduced.

As the proportion of tough Redux 410 NA increased the proportion of cohesive failure increased although all specimens were made from the same sheet of Aluminium Alloy, anodised and bonded on the same day. It would seem that adhesive mechanical properties as well as good surface preparation can affect the achievement of cohesive failures. It was also noted that, within the limits recorded, a thicker glue line gave a higher fracture energy. See also Bascom and Cottington (1976), Bascom and Hunston (1982).

The results of wedge tests are shown in Figs 44A (page 144), 44B (page 145) and 44C (page 146) and also in Fig 111 (page 268). The work of Mall and Johnson is of interest as they have studied the effect of fracture energy in great detail. Johnson & Mall (1983) and Mall and Johnson (1988). They suggest that a no-growth threshold G_{TH} value of strain energy release rate may be an

important mechanical property. The wet value may be even more important. Johanneson and Blikstad (1985).

5.4 Lap Shear Tests

A number of lap shear tests were also carried out to ASTM-D-1002 on specimens made from the same variety of blends of Redux 410 NA with Redux 408 and Redux 501 used for the wedge tests described above. The tests were made to enable lap shear strength v fracture energy to be plotted. (Figs 44A (page 144) and 44B (page 145). Lap shear test pieces were all given a Chromic Acid anodise (unsealed) surface treatment immediately before bonding.

Other lap shear data quoted was obtained from Manufacturers' Data Sheets. It should be noted that in most cases it is possible to obtain results approaching those of the Manufacturers but experience over many years has shown that it never seems possible to reach or exceed them.

5.5 Water Uptake Tests

Water uptake tests using 40mm x 30mm specimens cut from the ends of tensile test pieces were run for all of the adhesives tested. The uptake curves are shown in Figs 17-43 (pages 109 - 141), Tg dry and wet in Table 1 (page 12) and Diffusion and Solubility coefficients in Table 4A (pages 125 - 126).

The water uptake work was done for the following reasons:-

1. Because water uptake was considered likely to relate to joint durability.
2. Because Tg and mechanical properties were expected to fall with increasing water content and to assess the rate of loss.
3. To obtain dry and wet Tg values
4. To obtain Diffusion Coefficients
5. To obtain Solubility Coefficients.

Table 4A (pages 125-126) shows that quite significant differences exist among the materials tested in both Diffusion and Solubility Coefficients and the data obtained is helpful to the selection of adhesives. The Diffusion Coefficient for Redux 775 cured at 100 psi is similar to the epoxies but the Diffusion Coefficient when cured at zero psi is higher by an order of magnitude. The Solubility Coefficients are very high compared with epoxies and make the durable performance of joints, made with Redux 775, difficult to explain. It is hoped that analysis of the water in each jar will help to clarify the situation.

Tests have shown that corrosion of Aluminium Alloy is most likely to be caused by high pH and the specific ions present and can occur with resins having low water uptakes. It would seem therefore that debonding may have a critical water content, Kinloch (1983) and corrosion a critical pH.

In the case of Aluminium Alloy corrosion occurs at both low and high pH. It is necessary therefore to remain within a safe band of pH. However, high water uptake of resins is of interest because it is likely to lead to debonding whether or not corrosion is involved. Ideally, resins need to be formulated to avoid both problems.

5.6 Diffusion of Water into Adhesives and Joints

Diffusion and Solubility Coefficients can be used in a practical way to assess the water content of the adhesive in a joint after a period of time. Comyn (1982), Comyn et al (1987). A computer programme for the diffusion of water into adhesively bonded metal lap joints was adapted from the work of Brewis et al (1979) to operate on an IBM

PC. Appendix 1 (page 310). This enables the diffusion of water into a lap joint with time to be calculated as a fraction of the total uptake for a particular resin.

Calculations were carried out for a standard 12.5mm x 25mm overlap test piece to ASTM D-1002 to estimate time to saturation under total immersion and also for a 38mm x 250mm joint to simulate a 1½" overlap commonly used when bonding thin metal skins during aircraft repairs. Only in wet areas of an aircraft would immersion be realistic but Fig 56 (page 208) shows the time to various fractional water uptakes for different diffusion coefficients at the centre of a 38mm overlap joint and Fig 9 (page 34) for a 12.5mm overlap. Fig 10 (page 35) shows the time for various levels of water uptake at a section across the centre of a 12.5mm joint for a diffusion coefficient of 10^{-12} m ^{2} s^{-1}.

Fig 11 (page 36) shows similar information for a 38mm joint. When these figures are related to the Diffusion Coefficients of commonly used adhesives it can be seen that in wet areas it is possible to get a rather wet joint after only a few years.

For thin composites (2mm or less) it must be assumed that equilibrium uptake will occur in quite a short time, probably less than one year. A figure of 1% is usually quoted for hot-cured pre-pregs although some authorities are suggesting an increase to 1.3%, Collings (1986). This reference suggests ageing at 84% RH at room temperature to simulate the worst world operating conditions.

A composite equilibrium uptake of 1.3% relates to an equilibrium uptake of the resin alone of about 5%. Resins with lower values than this are available. See Tables 2A - 2F (pages 37 - 46).

Wright (1979) suggests that Diffusion Coefficients for composites are about one order of magnitude less than those for neat resins. Other workers have studied moisture uptake of composites, Collings and Stone (1985) Collings (1986).

There is a need to develop adhesives for composite and bonded metal repairs and manufacture having lower Solubility Coefficients, whilst retaining all the desirable properties previously mentioned. Although Diffusion Coefficients are important and low values would be helpful to slow down the rate of moisture uptake, they would also reduce the speed of drying. For thin composites, which will always eventually reach equilibrium, the reduction of total uptake is probably much more important. This is also likely to be true for bonded metal joints where corrosion or debonding appears to take place when the water content exceeds some critical, but not yet well defined, value. Brewis et al (1979) and (1980) state that the strength of a joint has been correlated with its fractional water content. See also Nakamura (1987a) and (1987b).

Total moisture uptake in the service environment is important not only because of its effect on Tg and modulus for composites but also because above a critical value it governs the rate of debonding of steel/epoxy joints, Kinloch (1983) and by implication that of aluminium and other metal joints. Service experience with Aluminium Alloys and adhesives having a high water uptake has confirmed this. Unfortunately a unique critical water uptake cannot be defined because it varies with the adhesive, adherend and surface preparation combination selected. As mentioned earlier if the best surface preparation is used then the effect of water becomes very much less. This is confirmed by Alldredge and Holmquist (1985).

Wright (1979) states that the equilibrium moisture content depends more on relative humidity than temperature and that the diffusion coefficient depends more on temperature than relative humidity.

In the long run humidity in the area of operation would seem likely to be more important than temperature but tropical areas with high temperature and high humidity have been shown to be the worst for moisture uptake and durability in confirmation of the theory. While recognising, without question, that durability is affected by surface preparation more than by other factors, it is considered that, for a given surface preparation, durability is likely to be affected by the equilibrium water uptake of the resin used and therefore this uptake should be minimised.

Fokker have demonstrated by the excellent service of EC 2216, when used on an anodised surface primed with Redux 101, a hot-cured phenolic primer, that a water uptake of the resin of less than 5% is sufficient provided that the surface preparation is excellent. Schliekelmann (1985).It is probably also true to suggest that the lower the quality of surface preparation of metal surfaces, the lower the resin water uptake needs to be if long term durability is to be achieved. However, because of the reduction of Tg with water uptake it seems essential to aim for less than 4% water uptake for cold-setting epoxy matrix resins.

The choice of base resin and curing agent has a marked effect on moisture absorption. Tegg (1979) states "For the sorption of water by polar polymers, polar groups such as -OH, -COOH, $-NH_2$, may act as specific sorption sites and equilibrium sorption may depend not only on the quantity and nature of the polar groups, but also their

positions on the polymer chain". Danieley (1981) states that water uptake increases with the degree of cure because of the increase in the number of hydroxyl sites. Table 2A (page 37) shows that, in most cases, the water uptake is decreased by increasing the temperature of cure. From Tables 2A-2F and the literature it would seem that the chemistry can be adjusted, to some extent, to reduce water absorption. However, if polar groups are helpful to adhesion then the 'best' adhesives may be those that take up the most water. Shalash (1979) and Shen and Springer (1976).

Where long term adhesion is required it may well be better to start with less adhesion and retain it, than to start with more adhesion and lose it. For adhesion to carbon-fibre, where water does not displace the adhesive at the interface, the 'better' adhesive that absorbs more water may not be too much of a problem. Fig 119 (page 296) suggests that this is so. In this figure carbon-fibre lap shear test pieces, bonded with two different cold-setting epoxies are compared for strength after water immersion at room temperature for periods of two and three years.

The joints made with Hysol EA 9330 retained a good strength after two years of total immersion at which point the last available test piece was tested. The joints made with Shell Epikote 815 + Epikure RTU were still showing a good strength when the last test piece was tested after three years of total immersion. For Aluminium Alloy joints, experience with FM 1000, a nylon/epoxy film adhesive with a high water uptake, suggests that a resin with a low water uptake is the better choice. More recent experience with Hysol EA 9330 confirm this.

5.7 Corrosion tests

These tests were carried out on all the samples previously subjected to tensile testing. The results obtained after 130 days immersion were very interesting. It was found that no corrosion occurred until the pH of the water rose above 7. Conductivity and pH both rose with time and in most cases passed a peak after corrosion occurred and then began to fall. Peak values of pH are shown in Fig 45 (page 154). Redux 408 and 410 NA both contain an inhibitor and no corrosion occurred even at a pH of just above 7. Redux 308A produced a pH just above 7 but no corrosion in 130 days. Bostik 5435/TM2 gave no visible corrosion after 130 days and the pH was well below 7. Some corrosion was found after a longer time by RAE using a microscope. The pH after 130 days was 5.3.

FR 7020 was odd in that samples cured at RT and 50°C prevented corrosion in 130 days but the sample post-cured at 80°C did not prevent corrosion and Phenolic Redux 775 does not appear to contain anything chemical that prevents corrosion in the inhibition sense. Therefore it is considered that the greater durability of this adhesive, well-proven in service, must be attributed to chemical bonds with the oxide produced by anodising, which give greater resistance to hydrolysis. Brockmann (1986) believes this to be due to the production of surface chelate complexes with the metal oxide. He also states that phenolic resins guarantee a slightly acid medium in the boundary layer zone and should thus stabilise the oxide. Pocius et al (1984) state that phenolics are known to bond strongly to Aluminium oxide and that their acidic pH is helpful to this.

The fact that unclad 7075 - T6 corroded even faster in distilled water alone, than the samples containing a plate of adhesive, led to the original question being reversed. The original question was "Do adhesives in bonded joints actually cause corrosion?" While a few appear to make matters a little worse compared to distilled water alone the correct question would appear to be "Can adhesives be made to assist in the prevention of corrosion?" Except where undamaged cladding is used, or unbroken anodising, the corrosion of Aluminium Alloy can be expected to take place. Parts should, therefore, be cut to shape, drilled and countersunk before anodising treatment is given.

It is also true that many epoxy curing agents are corrosive alkaline materials. RTU, for example, has a pH of 11. It would seem, therefore, reasonable that epoxies used on Aluminium Alloys should have a natural cured pH of between 6 and 6.5 and that it should be normal to include corrosion inhibitors in the formulation.

The chromates in Redux 408 and 410 NA clearly work, the low pH of the Bostik 5435/TM2 acrylic adhesive would seem to be better than epoxies without inhibitors. The reason why Redux 308A prevents corrosion within the timescale of the test is under investigation.

There is a move to ban Chromates on health grounds so it is good to know that Matienzo, Shaffer, Moshier and Davis (1986) are working to develop safer corrosion inhibitors. Where a surface preparation of lower corrosion resistance than anodising is used it is even more important to use corrosion inhibited, low water uptake adhesives. Two other factors are worth mentioning -

1. Control samples of 7075 - T6 unclad, in distilled water only, corroded even faster than those immersed with an adhesive. The rise in pH was very rapid but the conductivity rose very little. Once severe corrosion had occurred the pH fell equally rapidly. After 44 days the pH was back to 7.2. The initial pH of the distilled water at the time of adding the Aluminium Alloy was only 5.1.

2. It was suggested by Dr Lees that the cheap soda lime glass bottles used for these tests might cause some rise in pH themselves. Two jars were filled with distilled water only and the pH monitored. It was confirmed that some alkali is leached from the glass alone as the pH did rise with time. It is therefore recommended that in any future work on these lines either 'Pyrex' glass jars should be used or other containers which will not themselves affect the results. Polythene bottles have also been tested and shown to have a much smaller effect than the glass jars.

CHAPTER SIX COMMENTS AND CONCLUSIONS

6.1 Comments

The above mentioned testing was carried out to assist selection of repair adhesives and matrix resins because the operating temperature of composites and bonded metal parts is limited by:

(a) The glass transition temperature of the resin

(b) The water uptake of the resin in service

Tg is affected by the choice of curing system and usually, but not always, by the temperature of cure.

Water uptake is dependent on the choice of curing agent and the degree of cure.

The in-service water uptake of an adhesive or composite matrix resin eventually reaches about 50% of the value obtained at saturation after immersion in water at room temperature. Tg falls by about 20°C for every 1% of water absorbed, Wright (1979).

Table 4A (pages 125 - 126)suggests that the reduction in Tg for cold-setting resins is much less than this.

The importance of resin Tg is much greater for repairs to composite skins than it is for metal lap joints or joints in composite parts. For joints it can be seen from Fig 99 (page 253) (Lap shear strength v resin modulus) that a considerable loss of modulus makes little difference to the joint strength and therefore short times under load, where creep is not a problem, are likely to be acceptable. However, for composites the compression strength of the skin has a direct relation to modulus below about 450,000 psi. (Fig 5, page 29). It is therefore, important to avoid loading composites at temperatures where the resin modulus falls below this figure.

The problem of selecting appropriate cold-setting resins for composite repairs is that the original parts are cured, most commonly at 180°C (350°F) and often at 120°C (250°F) in order to retain adequate hot/wet performance at 80°C (176°F).

The hottest air temperature in the world seldom exceeds 50°C and therefore even at the extreme an aircraft surface would be likely to have cooled to 50°C by the end of the take-off run. Problems arise in two particular circumstances:-

1. Aerodynamic heating of the surfaces of supersonic aircraft when the structure is under load.

2. High surface temperature (80°C) on upper surfaces when parked in the sun.

These conditions have to take into account the level of moisture uptake likely to have occurred in the resin matrix and the effect this has on Tg and the composite mechanical properties.

A resin for use as a composite matrix therefore requires the properties detailed by Palmer (1981) plus a Tg appropriate to the maximum in-service temperature in spite of its moisture content. A low water uptake will, therefore, be very helpful to achieving this.

For non-structural composite parts, lightly loaded parts and parts that are not loaded until an aircraft is airborne, a Tg of 50°C at 50% of the resin saturation water content would seem to be reasonable and Tg values of 40°C or lower would probably be acceptable. Fortunately the vast majority of the flight time of modern airliners is spent at high altitude where the air temperature can be

as low as -55°C and on rare occasions -76°C. As a result of a small amount of kinetic heating, skin temperatures are often around -25°C. One resin used for bonded metal repairs very successfully, except for long term corrosion, has a dry Tg of only 11°C. It has also been used successfully for a lightly loaded composite repair, which has now flown for five years with no signs of deterioration. This item is only loaded in flight.

For structural parts of supersonic aircraft, a Tg at 50% water content appropriate to the aircraft service temperature must be achieved. For lightly loaded parts the mechanical properties of the resin at the cruise temperature are probably more important than Tg.

Composite structural parts of subsonic aircraft that carry significant load, while heated by direct radiation from the sun, need to be made with resins having a Tg around 80°C at 50% of their saturation water content. These resins, whether cold-setting or not, will be post-cured at 80°C in service. Repairs can be made with resins of lower performance than the original, provided that extra layers of tape or fabric are used to restore the original compression strength Armstrong (1989b) and (1989c) and Fig 7 (page 31). This figure was derived simply as follows:

Working from data produced by Palmer (1981), Fig 5 (page 29), compression or flexural strength were tabulated against resin tensile modulus. Calculations for the increase in laminate thickness required were based on D^2 for flexure and D^3 for compression. For tensile moduli down to 300,000 psi the difference between the two was not great. Flexure data was used to plot Fig 7 (page 31) because it was the worst case.

A simple deflection test on a sheet of composite made from 4 layers of Marglass 7781 and with Epikote 815+ RTU as a matrix was compared with the same construction using Redux 410NA as the matrix. The sheet was approximately 20" x 10". The deflection was the same and therefore totally fibre dominated. This simple test suggests that the work of Palmer is valid for the test specimens used but probably not for other geometries. However, it does indicate that the reinforcement suggested in Fig 7 (page 31) is likely to be on the conservative side for some real life repairs.

It will be seen from Figs 98 - 102 (pages 252 to 257), 119 (page 296) and 120 (page 297) that metal bonding adhesives, in addition to composite matrix resins, can be more readily compared on the basis of fundamental mechanical properties than by comparison of lap shear tests alone. However, it must be said that lap shear testing should continue because lap joints are the most common joints. It would seem that the lap shear test does measure fracture toughness, though not quantitively, because only those adhesives with a good fracture energy achieve the highest lap shear performance.

From the data presented above it should now be possible for Engineers to tell their Chemist colleagues, fairly accurately, the mechanical and physical properties required of adhesives and matrix resins for specific end uses. It is not suggested that these properties will be easy to achieve. Finally it would also seem reasonable to suggest that the pH of a resin needs to be within a band suitable to the metal being bonded and that corrosion inhibitors suitable to the metal being bonded should be included in the resin formulation.

This programme of work has proved to be particularly interesting and its results are considered not only to aid selection but also to suggest guidelines for the development of improved adhesives and composite matrix resins. It has shown that the performance of adhesives in lap joints can be related to their fundamental mechanical properties in the same way as Palmer (1981) has shown that the performance of the matrix resin governs the performance of a composite using a particular fibre. The value of toughened matrix resins to improve damage tolerance is detailed in Aerospace Engineering (1987). Swartz (1986) and Ye (1989). Most new adhesives are of the toughened variety. (Lees (1986), Nakao (1987), Charnock (1985), Siebert et al (1986), St Clair and St Clair (1981).

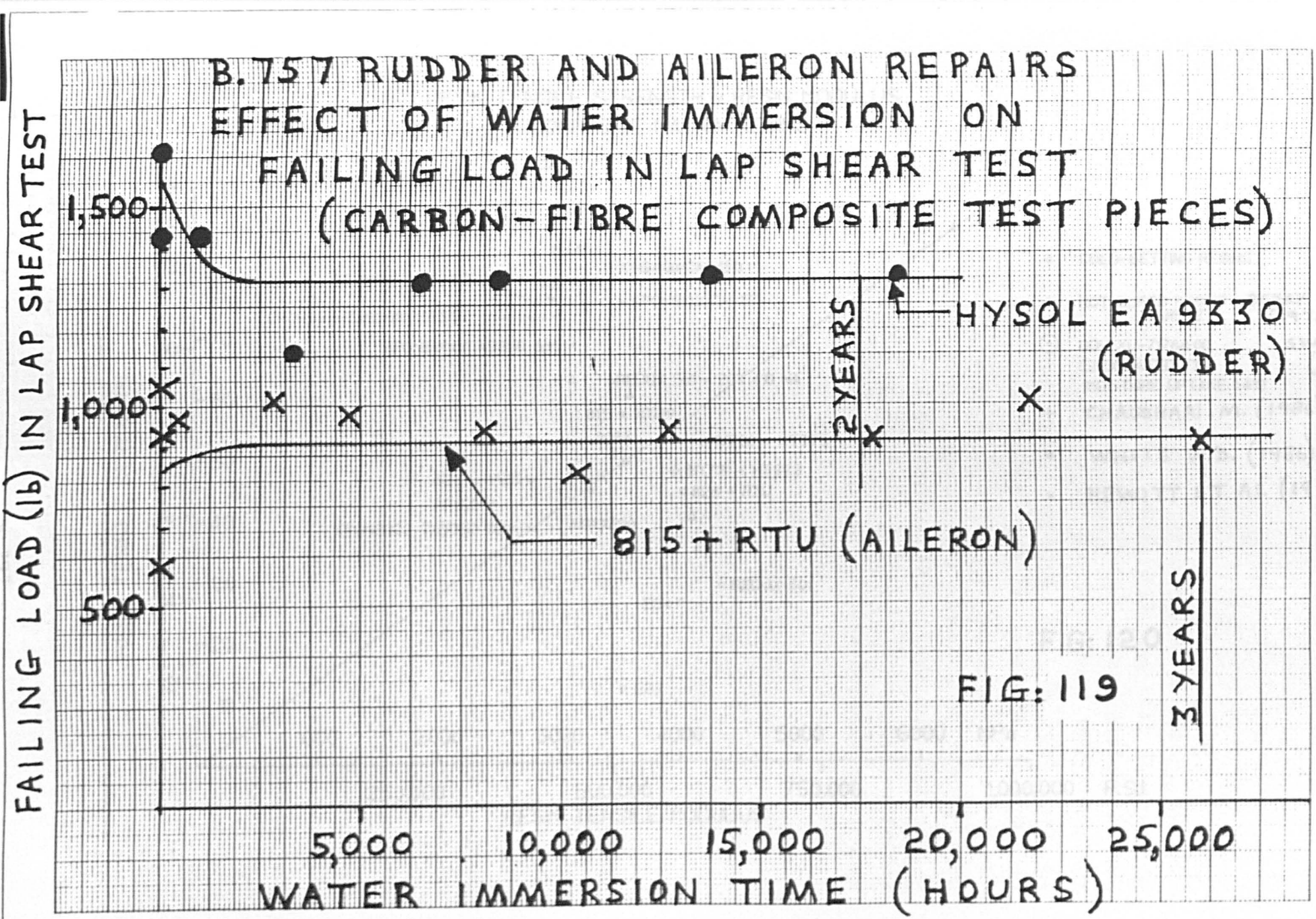

B.757 RUDDER AND AILERON REPAIRS
EFFECT OF WATER IMMERSION ON
FAILING LOAD IN LAP SHEAR TEST
(CARBON-FIBRE COMPOSITE TEST PIECES)
FAILING LOAD (lb) IN LAP SHEAR TEST
1,500
1,000
500
HYSOL EA 9330
(RUDDER)
815+RTU (AILERON)
2 YEARS
3 YEARS
5,000
10,000
15,000
20,000
25,000
WATER IMMERSION TIME (HOURS)

FIG: 119

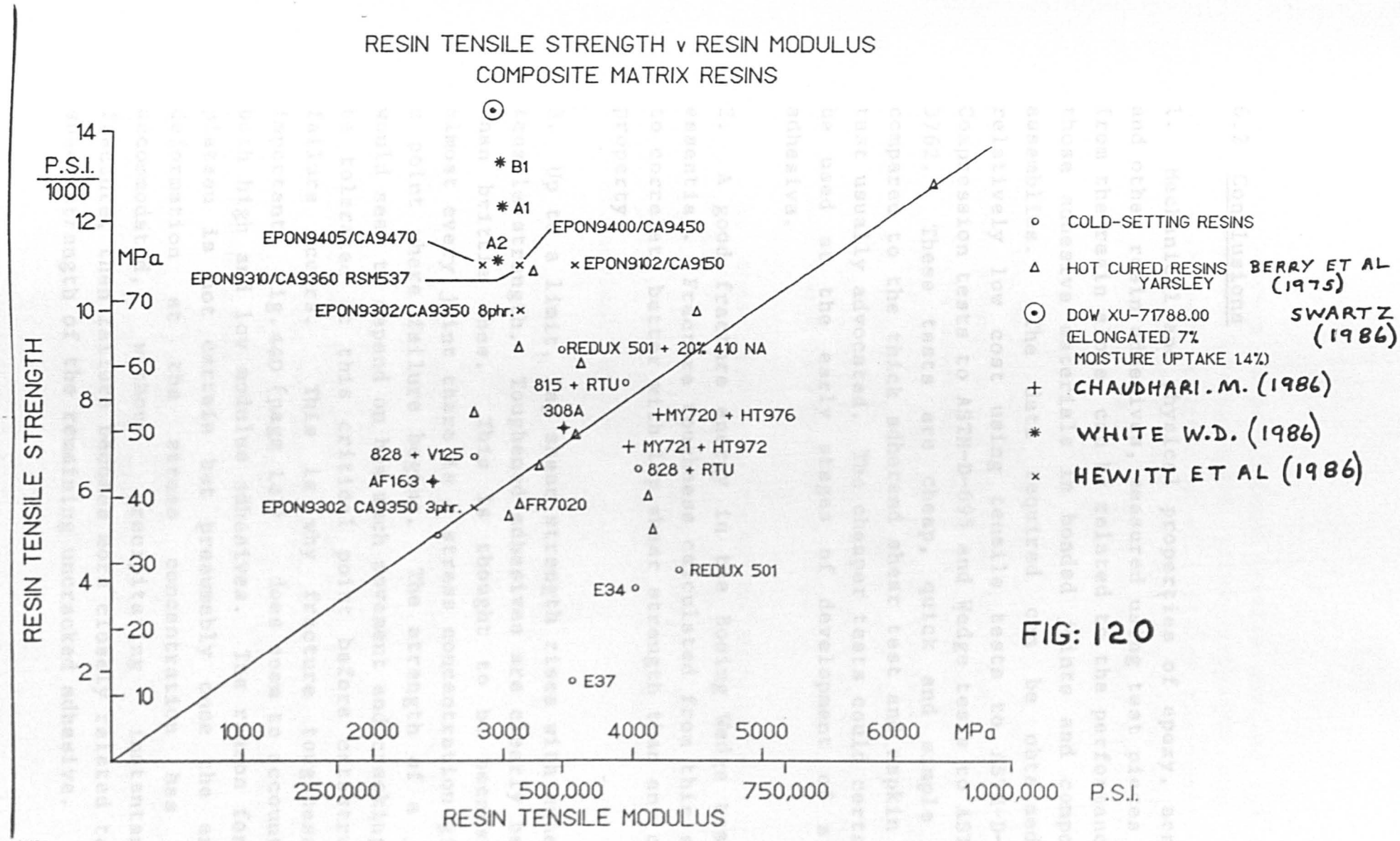

RESIN TENSILE STRENGTH v RESIN MODULUS
COMPOSITE MATRIX RESINS
RESIN TENSILE STRENGTH
P.S.I. / 1000
MPa
14
12
10
8
6
4
2
70
60
50
40
30
20
10
1000
2000
3000
4000
5000
6000
MPa
250,000
500,000
750,000
1,000,000
P.S.I.
RESIN TENSILE MODULUS
B1
A1
A2
EPON9405/CA9470
EPON9400/CA9450
EPON9310/CA9360 RSM537
EPON9102/CA9150
EPON9302/CA9350 8phr.
REDUX 501 + 20% 410 NA
815 + RTU
308A
+MY720 + HT976
+ MY721 + HT972
828 + V125
828 + RTU
AF163
EPON9302 CA9350 3phr.
FR7020
REDUX 501
E34
E37
COLD-SETTING RESINS
HOT CURED RESINS YARSLEY
BERRY ET AL (1975)
DOW XU-71788.00 (ELONGATED 7% MOISTURE UPTAKE 14%)
SWARTZ (1986)
CHAUDHARI. M. (1986)
WHITE W.D. (1986)
HEWITT ET AL (1986)

FIG: 120

6.2 Conclusions

1. Mechanical and physical properties of epoxy, acrylic and other resin adhesives, measured using test pieces made from the resin alone, can be related to the performance of those adhesive materials in bonded joints and composite assemblies. The data required can be obtained at relatively low cost using tensile tests to ASTM-D-638, Compression tests to ASTM-D-695 and Wedge tests to ASTM-D-3762. These tests are cheap, quick and simple when compared to the thick adherend shear test and napkin ring test usually advocated. The cheaper tests could certainly be used at the early stages of development of a new adhesive.

2. A good fracture energy in the Boeing Wedge test is essential. Fracture toughness calculated from this seems to correlate better with lap shear strength than any other property.

3. Up to a limit, lap shear strength rises with adhesive tensile strength. Toughened adhesives are clearly better than brittle ones. This is thought to be because in almost every joint there is a stress concentration giving a point where failure begins. The strength of a joint would seem to depend on how much movement and cracking can be tolerated at this critical point before catastrophic failure occurs. This is why fracture toughness is important. Fig. 44D (page 147) does seem to account for both high and low modulus adhesives. The reason for the plateau is not certain but presumably once the excess deformation at the stress concentration has been accommodated, without precipitating instantaneous fracture, then failure becomes more closely related to the shear strength of the remaining uncracked adhesive.

4. There appear to be optimum tensile modulus and shear modulus values giving good joint strength and creep strength although toughening will affect the position of an optimum. The achievement of improved impact resistance for composites may mean using tougher and lower modulus resins.

5. Figs 100A and 100B (pages 254 - 255) indicate that best joint strengths are obtained when the elongation to failure of the adhesive itself is about 5 to 10%. Joint strength falls quite sharply as the elongation to failure falls much below 5%. Strength and modulus usually increase with higher post-cure temperatures but elongation to failure would be expected to fall.

Good lap shear strength seems to require an optimum combination of resin tensile strength, modulus, elongation and in particular fracture energy. From the limited data available "T" peel strength would appear to require a similar combination.

6. Tg can be increased by warm curing to a useful extent in some cases.

7. Tg can be related to resin hardness to some extent.

8. Moisture uptake affects the modulus and Tg of a resin more than other properties. For most materials tested it had little effect on tensile strength. FR7020 and Epikote 815+RTU showed a significant loss of tensile strength and tensile elongation.

9. Post-curing is most likely to affect tensile strength. It may improve Tg and reduce water uptake slightly.

10. Blending a tougher resin with a brittle one can considerably improve tensile strength. The effect on moduli is likely to be in line with "The Rule of Mixtures". However, the amount of "tough" resin required to improve tensile strength is fairly small and the optimum amount only reduces modulus values very slightly.

11. Tg values need to be supplied by manufacturers. Ideally, they should be obtained using the torsion pendulum test to ASTM-D-2236 rather than Differential Scanning Calorimetry (DSC). DSC requires expert interpretation and standard runs usually go a long way above the actual Tg. This means that any re-run on the same sample is measuring a new material which has been:

(a) Dried to a lower water content

(b) Cured to a higher degree than the sample from which it was cut.

However, DSC is quicker, cheaper and can produce results from smaller samples of material.

12. The three major problems with cold-setting resins are:

(a) Low initial Tg because of choice of chemistry and low temperature of cure

(b) Loss of Tg and tensile strength in some cases due to water uptake. The loss is sometimes greater from a post-cure. See Table 1B (page 15).

(c) The tendency of many of them to assist, or fail to prevent,corrosion unless inhibitors are incorporated. This problem also applies to many hot-curing adhesives.

All adhesives likely to assist corrosion should contain suitable inhibitors. These may not be the same for all metals. The purification of base resins to remove Chlorine and any other corrosive ions could be helpful. Ideally

the use of corrosive ions in curing agents should also be avoided. Pocius et al (1984) state that dimethyl amine urea of p-chlorophenol isocyanate has long been used as an accelerator to allow di-cyandiamide to be used as a curing agent for epoxy systems cured at 120°C. Brockmann (1986) found during studies of corrosion at the edges of 2024 clad alloy bonded with EC.3924 primer and AF.163 that a brownish substance and corrosion products were found on unprotected edges near the bondline. FTIR analysis showed that this substance contained hydrolysis products of the hardener (dicyandiamide) which had emerged from the adhesive during the ageing process, thereby initiating primary corrosion on account of its hygroscopic behaviour. Adhesive joints can give off substances during ageing processes which then cause failures in their surroundings.

These aspects of adhesive behaviour need careful study and correction where possible. Brockmann et al (1986) suggest "Without a doubt improvements could result from the development of new, non-alkaline hardening systems for epoxy resins or even the return to phenolic resin adhesives which could now be produced as 120°C curing systems".

Where composites are used to repair metal parts the effects of water uptake and pH are likely to be more severe because water can penetrate the entire composite surface. The pH needs to be suitable for both the metal and the composite in this case. Glass-fibre is known to be sensitive to pH. Phillips (1989).
The need for this was confirmed when some composite repairs to Aluminium Alloy components using a particular resin did suffer corrosion. This adhesive was associated with corrosion in the tests mentioned above. It is also considered significant that the corroded areas had not been anodised.

13. The optimum adhesive modulus for a bonded joint, Fig 99 (page 253), is a little lower than the optimum modulus for making a composite. This suggests that if composite parts are assembled by co-curing, they should use a layer of toughened film adhesive to make the joints and not the same resin as that from which the composite itself is made. This could be particularly useful when composites are made using high modulus brittle resins.

14. Brittle resins, of high modulus, tend to have a low tensile strength because of a low fracture energy and high sensitivity to flaws and bubbles.

15. Compression strengths seem to vary from about the same as tensile strength to about 1.7 x tensile strength. This has been considered in detail and related to the effect of volumetric stress and strain components by Gali et al (1981). See also Table 12 (page 303) for data obtained from the literature.

16. Data for adhesives and composite matrix resins should, ideally, be provided in graphical form across the entire temperature range as typified by Fig 121 (page 304). This would greatly assist comparison and selection.

All temperature dependent properties could usefully be presented in this way. This data indicates that the fall in properties with temperature is seldom sudden and that some useful load can still be carried for short periods at temperatures a little above Tg.

A repeat of these curves using material at 50% of its saturation water uptake would help to indicate the performance of composites after a long period of outdoor service.

TABLE 12

COMPARISON OF TENSILE AND COMPRESSION MODULI FROM REF.13

RESIN	TENSILE MODULUS PSI	COMPRESSIVE MODULUS PSI	TENSILE COMPRESSIVE RATIO	REMARKS
FIBREDUX 914C	574,379	397,424	1.445	
CODE 69	594,685	424,983	1.4	
COURTAULDS 3501	600,487	388,721	1.54	
ERLA 416 + MPD	910,884	599,036	1.52	
828 + DDM	398,874	387,270	1.03	
828 + DDS	445,288	290,090	1.535	
DX210 + DX137	519,262	516,361	1.006	
DX210 + BF 400	488,802	272,685	1.79	

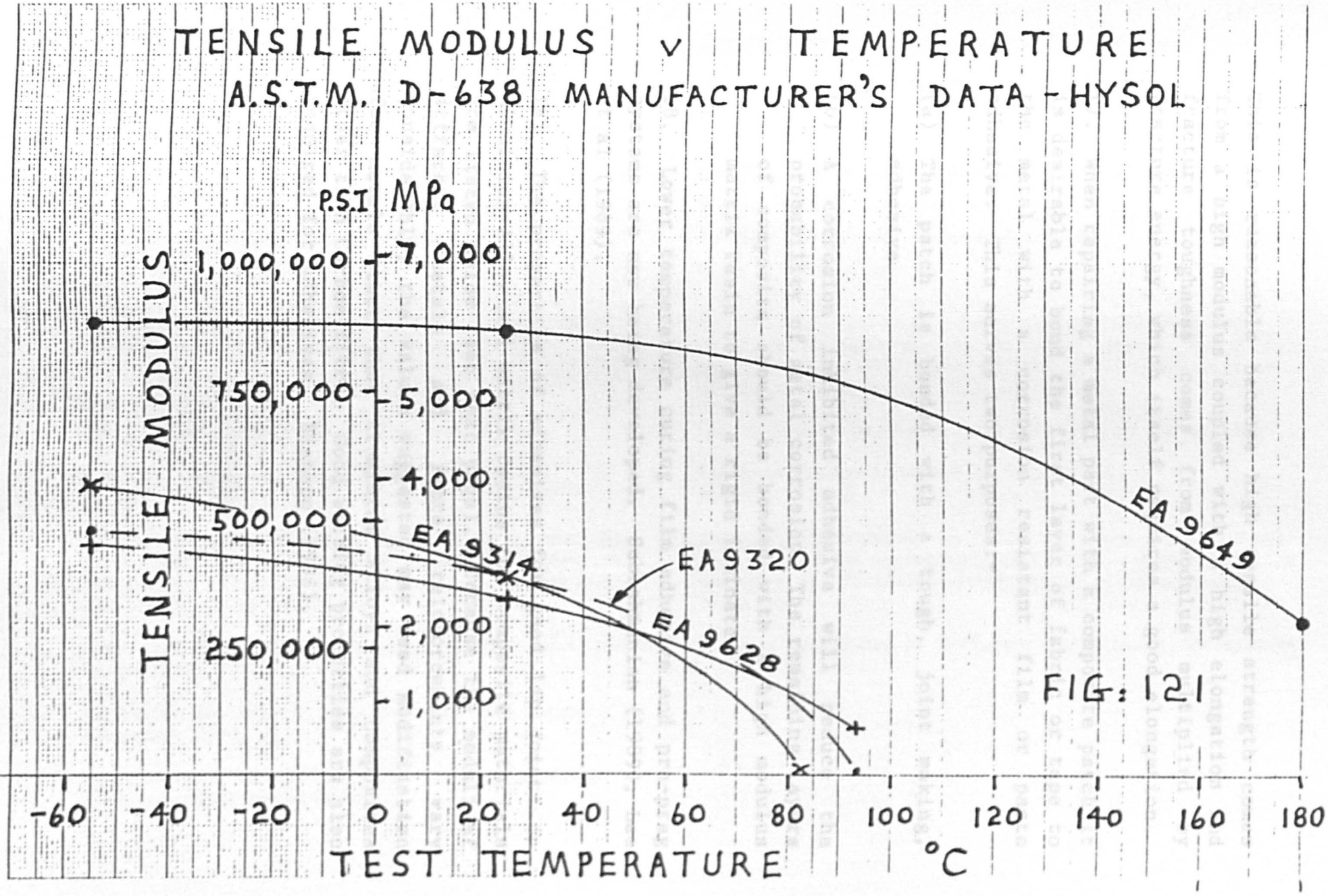

TENSILE MODULUS v TEMPERATURE
A.S.T.M. D-638 MANUFACTURER'S DATA - HYSOL
P.S.I
MPa
TENSILE MODULUS
1,000,000
7,000
750,000
5,000
4,000
500,000
2,000
250,000
1,000
EA 9649
EA 9320
EA 9314
EA 9628
-60
-40
-20
0
20
40
60
80
100
120
140
160
180
TEST TEMPERATURE °C

FIG: 121

This is reasonable because high tensile strength comes from a high modulus coupled with a high elongation and fracture toughness comes from modulus multiplied by fracture energy, which itself requires a good elongation.

17. When repairing a metal part with a composite patch it is desirable to bond the first layer of fabric or tape to the metal with a corrosion resistant film or paste adhesive. This serves two purposes:-

(a) The patch is bonded with a tough, joint making, adhesive

(b) A corrosion inhibited adhesive will reduce the probability of metal corrosion. The remaining layers of composite should be bonded with a high modulus matrix resin to give a rigid laminate.

18. Lower temperature curing film adhesive and pre-preg systems are now being developed. Subrahmanian (1989), Lee et al (1989).

19. The properties of adhesives for good lap joints on Aluminium Alloy and matrix resins for composite materials are listed below (see next page). Because the moduli of different metals and fibre reinforcements vary considerably, the values suggested may need modification for metals other than Aluminium Alloys and Composites other than Carbon-fibre. Good wetting properties are also required for adhesives. Bishopp (1986).

Lap Joint Adhesive Properties

A good lap joint resin for Aluminium Alloy should have the following properties. Optimum values may be different for other metals or composite materials.

Tensile Strength: 4,000 to 7,000 psi

Tensile Modulus: 350,000 - 500,000 psi

Tensile Elongation: Between 3 and 7%

Water Uptake: $< 4\%$

Tg sufficient to give 1000 psi lap shear strength at maximum service temperature.

pH of water soluble extract between 6.0 and 7

Fracture Energy in Wedge Test: > 1 KJ/m^2 to ASTM D-3762.

If greater shock or impact resistance is required then lower values of Tensile Strength and Modulus and higher values of elongation and fracture energy are likely to be beneficial

More attention needs to be paid to pH to give greater durability

Corrosion inhibitors should be included whenever it is necessary to do so.

The chemistry of the resin may need to be chosen to suit the metal being bonded.

Composite Resin Properties from Ref.7 Palmer

A good composite resin for carbon-fibre composites should have the following properties to give the best combination of impact and mechanical properties.

Tensile Strength: Between 8,000 and 10,000 psi

Tensile Modulus: Above 450,000 psi

Tensile Elongation: Between 5 and 6%

Water Uptake: $< 4\%$

Tg 40°C above maximum service temperature when dry to allow for reduction due to water uptake. For cold-setting resins 20°C above maximum service temperature may be sufficient.

Low viscosity to ensure good penetration and wetting

Fracture Energy in Wedge Test: > 0.5 KJ/m^2 to ASTM D-3762.

Increasing elongation to failure reduces impact damage area but lowers mechanical properties. Higher fracture energies are desirable where impact resistance is required

Optimum values may be different for other fibre systems

CHAPTER SEVEN FUTURE WORK

7.1 Standard Data Sheets for Adhesives

Considerable efforts have been made to persuade Adhesive Manufacturers to provide neat resin mechanical properties, derived using their more precise methods. These should be presented on standardised data sheets. Data is also required over the full range of service temperatures.

There is a need for International Standard Organisation (I.S.O) Data Sheets having a standard layout so that alternative materials can be more easily compared.

7.2 Need to increase Tg from room-temperature cure

Further work needs to be done to find methods of raising the Tg of cold-setting resins, either from a room temperature cure or by warm curing.

7.3 Reduced water uptake

Development of cold-setting and hot-curing resins could usefully concentrate on achieving a low water uptake without loss of the required mechanical properties.

7.4 Need for pH control

The preliminary work on corrosion mentioned above suggests that the durability of adhesive bonds to Aluminium Alloy and probably other metals could be significantly dependent on the pH of the resin and/or any extracts from it by leaching with water or other fluids. The effect of pH on the bonding of composites and composite joint durability could be a useful study especially for glass-fibre. Curing agents need to be found to give a cured pH in the

band 6.0 to 6.5 for adhesives for Aluminium Alloys and to give a complete cure to minimise leaching.

7.5 A more detailed study of the effect of resin mechanical properties on joint strength.

A more detailed study of the relative contributions of tensile strength, modulus, elongation at failure and fracture energy to lap joint strength could help to optimise the performance of new adhesives still further.

7.6 Portable surface preparation equipment

As surface preparation is the over-riding factor governing durability, once a good adhesive has been selected; considerable research effort could usefully be directed towards the development of portable equipment for the application of good surface preparation methods, in-situ, during the manufacture or repair of aircraft and other vehicles. For example, Selectrons Ltd. produce portable equipment that allows chromic acid anodising of local areas on an aircraft. The Boeing PANTA process (Phosphoric Acid Non-tank anodise) does the same sort of job. Portable grit blast is also available. Methods for local hot curing of phenolic primers would be useful. Portable methods could find applications in other industries. The taking of good surface preparation methods to the job is more likely to be successful than attempts to develop adhesives that do not require a good surface preparation.

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APPENDIX 1

COMPUTER PROGRAMME - 'WATERDIS'

The original programme for the calculation of the water distribution in an adhesively bonded joint was obtained from Leicester Polytechnic. The programme below is a version modified by British Airways Information Management Group to suit an IBM PC in the Structures Development Group. The B.A. version was found to be very "user friendly".

```
100 REM -  This is purely a remark.  Calc of water dist in a joint.
200 PRINT  "What is the value of the diffusion coefficient";
300 INPUT  D
400 PRINT  "What is the value of T in hours";
500 INPUT  A
600 LET T  = A: Let T=T*3600
700 PRINT  "What are the dimensions of the joint in X and Y Directions"
800 INPUT L1, L2
900  LET  L1=L1/1000
1000 LET  L2=L2/1000
1100 DIM  FZER (10,1)
1200 DIM  GZER (1,10)
1300 DIM  MZER (10,10)
1400 DIM  M1CON (10,10)
3200 'The following 3 lines mean nothing in today's PC basic
3300 'DIM print using 3600, M1
3400 'DIM print using 3600, F
3500 'DIM print using 3600, G
3700 REM calculation of total water content of a joint
3701 PRINT "D= ";D; "A= "; A; "HOURS ";"T=" T;" SECS":"X="; L1;"Y=";L2
3800 LET P=0: LET R=0
3900 LET V1=(-D*3.14159*3.14159*T)/(L1*L1)
4000 LET V2=(-D*3.14159*3.14159*T)/(L2*L2)
4100 LET K8=8/(3.14159*3.14159)
4110 PRINT "V1= ";V1;" V2= "; V2" K8= ";K8
4200 FOR N = 0 to 5
4250 'IN THE FOLLOWING FORMULAE (2*N+1) SQUARED CANCELS OUT !!!!
4300 LET P=P+K8*EXP(V1*(2*N+1)*(2*N+1))/((2*N+1)*(2*N+1))
4400 LET R=R+K8*EXP(V2*(2*N+1)*(2*N+1))/((2*N+1)*(2*N+1))
4410 PRINT "P= ";P;" R= "; R
4500 NEXT N
4600 LET C=1-(P*R)
4700 PRINT "THE TOTAL WATER CONTENT IS":C
4800 END
```

APPENDIX 2

Calculation of reference length of test piece shown in Fig 28A.
The formula from DIN 53455 is as follows:-

$$L_{ref} = b \left(\frac{L_s}{b} + \frac{2L_m}{b_m} + \frac{2L_e}{b_e} \right)$$

where $b_m = \dfrac{L_m}{\dfrac{a}{\sqrt{a^2 - 1}} \arctan (a+1) \tan \left(\tfrac{1}{2} \arcsin \dfrac{L_m}{r} \right) \Big/ \sqrt{a^2 - 1} - \tfrac{1}{2} \arcsin \dfrac{L_m}{r}}$

$$a = 1 + \frac{b}{2r} \qquad L = L_s + 2L_m + 2be$$

for BA Specimen Fig. 28A

$L = 100 + 71.4 + 6 = 177.4$

$L_s = 100$ mm

$L_m = 35.7$ mm

$L_e = 3$ mm (Depends on precise location of specimen in grips)

$b_m =$

$be = 40$ mm

$b = 10$ mm

$a = 1.1$ mm

$r = 50$ mm

$$b_m = \frac{35.7}{\dfrac{1.1}{\sqrt{1.1^2 - 1}} \arctan 2.1 \tan \left(\tfrac{1}{2} \arcsin \dfrac{L_m}{r} \right) \Big/ \sqrt{1.1^2 - 1} - \tfrac{1}{2} \arcsin \dfrac{L_m}{r}}$$

$$b_m = \frac{35.7}{2.4 \arctan \frac{2.1 \tan \left(\frac{1}{2} \arcsin \frac{L_m}{r}\right)}{.45826} - \frac{1}{2} \arcsin \frac{L_m}{r}}$$

$\frac{1}{2} \arcsin \frac{L_m}{r}$ = $\frac{1}{2}$ angle in radians whose sin is $\frac{L_m}{r}$

$\sin \frac{L_m}{r} = .714$ . . Angle = 45.56°

$\frac{1}{2}$ angle = 22.78°

$\frac{22.78}{57.3} = .3976$ radian

$$b_m = \frac{35.7}{2.4 \arctan \frac{2.1 \tan 22.78^\circ}{.45826} - .3976}$$

$$b_m = \frac{35.7}{2.4 \arctan \frac{2.1 \times .42}{.45826} - .3976}$$

$$= \frac{35.7}{2.4 \arctan 1.9244 - .3976}$$

The Angle in radians whose tangent is 1.9244 = 62.54°

$\frac{62.54}{57.3}$ = 1.0914 radians

$$b_m = \frac{35.7}{(2.4 \times 1.0914) - .3976}$$

$$b_m = \frac{35.7}{(2.4 \times 1.0914) - .3976}$$

$$b_m = 16.07 \text{ mm}$$

$$L_{ref} = 10 \left(\frac{100}{10} + \frac{2 \times 35.7}{16.07} + \frac{6}{40} \right)$$

$$= 10 \times 14.593 = 145.93 \text{ mm}$$

Original gauge length was 100 mm. Therefore all previous strain to failure values need to be divided by 1.4593.

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