(NASA-CR-166283) GRAPHITE POLYSTYRYL PYRIDINE (PSP) STRUCTURAL COMPOSITES Final Report (Societe Nationale des Poudres et Explosifs) 57 p HC A04/MF A01 CSCL 11D

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SNPE

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Groupe Technique Matériaux.

D.c./1

N.T. N° 27/81/CRB/NP
du 18 FEVRIER 1981
NASA : NASW - 3251

B. MALASSINE

Graphite Polystyryl Pyridine (PSP)

Structural composites

D.c./2

S.N.P.E.

CENTRE DE RECHERCHES DU BOUCHET

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		CLASSIFICATION	
		Secret Militaire	Secret Industriel
		Numéro du Contrat	Organisme Client
NT N° - 27/81/CRB/NP	Dc/Mb	NASW - 3251	NASA

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Service : RC	Contractuel		NOMBRE		
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TITRE : Graphite Polystyryl Pyridine (PSP5 Structural Composites.

AUTEUR (S) : M.B. MALASSINE.

RESUME DE L'AUTEUR :

PSP 6022 M resin, PSP 6024 M resin and W 133 Thormel T 300 graphite fabric reinforced panels have been fabricated and provided to NASA.Ames Research Center.

PSP 6022 et PSP 6024 caracteristics, process specifications for the fabrication of prepregs and of laminates are detailed.

Mechanical properties , thermomechanical properties and moisture resistance have been evaluated.

PSP 6022 et PSP 6024 appear as high performance thermostable systems, very easy to process , being soluble in MEK for prepregging, and being cured at no more than 250°C, and even 200°C.

DESCRIPTEURS : Matériau composite, ruban préimprégné, polymère hétérocyclique, résine thermostable, PSP, Fibre carbone, propriétés mécaniques, propriétés thermomécaniques, influence, humidité, procédé fabrication, imprégnation, laminage, note technique.

DIFFUSION INTERNE

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S.T.P.E. : M. LAMY

D.R.E.T. : Mme CORVINO.

COMPOSITES HORIZONS : MM. PETKER
STERN.

Contractuel

- NASA Ames : M.KOURTIDES
(6 ex).
- NASA Scientific et
Technical Information
Facility : (3 ex).

PREFACE

This is the final report of the SNPE-CRB effort on NASA contract No. NASW-3251, NASA - Ames Research Center, Dr D.A. KOURTIDES, Project Manager, covering the period from June, 1979 to September, 1980. The objective of this effort is to provide composites by using Polystyryl Pyridine (PSP) resin and commercially available graphite fabric. These composites are valuable to many potential commercial ventures where flammability protection or high temperature capabilities are required.

Report n° : NASW- 3251

Title : Graphite Polystyryl Pyridine (PSP) Structural Composites.

Authors : Dr B. MALASSINE.

Performing Organization Name and Address :

Société Nationale des Poudres et Explosifs
Centre de Recherches du Bouchet

BP N° 2 - 91710 - VERT-LE-PETIT. - FRANCE -.

Performing Organization Report No

NT 27 /81/CRB/NP

Sponsoring Agency Name and Address

National Aeronautics and Space Administration
Washington D.C. 20 546

Type of Report and Period Covered

Contractor final report
June 26, 1979 - September 30, 1980.

Supplementary Notes

Project Manager, Dr. D.A. KOURTIDES
Chemical Research Projects Office
NASA/Armes Research Center
Moffett Field, California 94035.

ABSTRACT

PSP 6022 M resin, PSP 6024 M resin and W133 Thormel T300 graphite fabric reinforced panels have been fabricated and provided to NASA Ames Research Center.

PSP 6022 et PSP 6024 caracteristics, process specifications for the fabrication of prepregs and of laminates are detailed.

Mechanical properties thermomechanical properties and moisture resistance have been evaluated.

PSP 6022 et PSP 6024 appear as high performance thermostable systems, very easy to process, being soluble in MEK for prepregging, and being cured at no more than 250°C, and even 200°C.

KEY WORDS

Graphite fiber
Polystyryl pyridine (PSP) resin
Structural Composites
Thermostable resins.

DISTRIBUTION STATEMENT

Unclassified, unlimited.

SECURITY CLASSIFICATION

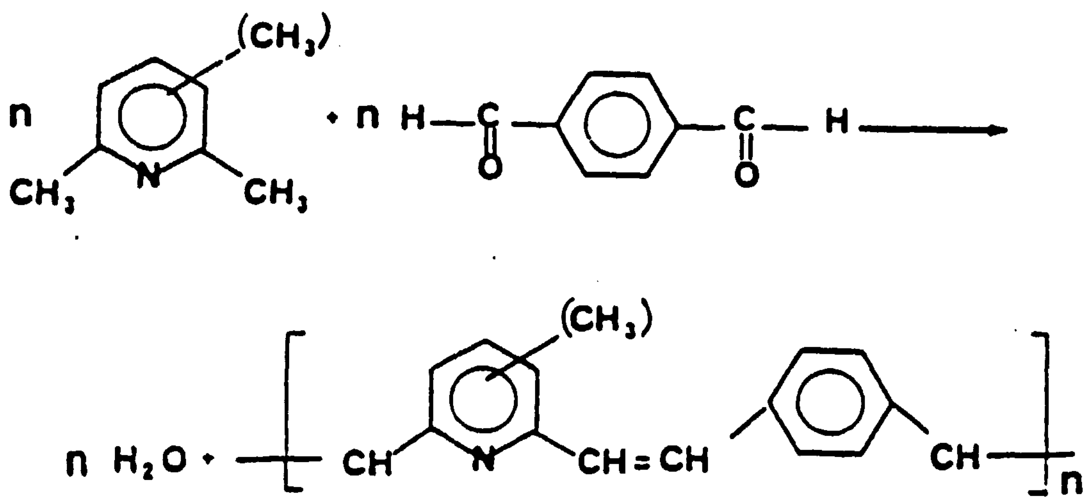
Unclassified.

CONTENTS

Part I - POLYSTYRYLPYRIDINE (PSP) RESINS

1.1 - PSP system

Polystyrylpyridine (PSP) Resins are heterocyclic aromatic thermostable polymers developed by SNPE (1), synthesized by condensation of aromatic aldehydes with methylated derivatives of pyridine.



The wholly aromatic structure results in a high level of thermostability and flame resistance, and it seems that double bond reactions are occuring at high temperatures, giving extraordinary flame thermal resistance at more than 300°C.

Raw materials are common products, resulting in low cost of neat resins called PSP 6022.

PSP 6022 resins are currently available from SNPE. Typical products are PSP 6022 M, 6022 P, 6022 PC described as following which differ by the condensation level in the prepolymers.

(1) - Patented by ONERA and by SNPE.

1.2 - PSP available resins

PSP 6022 M

Solution for impregnation
Solid content : 75 % weight
Solvent : Methyl Ethyl Cetone
Viscosity : 200 mPas at 25°C.

Gel begins after about 1 hr at 200°C or 3 hrs at 180°C and is complete after about 3 hrs at 200°C or 10 hrs at 180°C.

PSP 6022 P

Viscous resin for non solvent impregnation or injection
Volatiles (after 2 hrs at 200°C) : 8 %
Viscosity : 1 000 to 3 000 mPas at 100°C
Soluble in CH_2 Cl_2 and in MEC (with heating)

Gel conditions are like for PSP 6022 M.

PSP 6022 PC

Solid for molding compounds or injection
Volatiles (after 2 hrs at 200°C) : 3 %
Viscosity : 500 to 2 000 mPas at 180°C
Soluble in CH_2 Cl_2

Gel times are about half of those of PSP 6022 M.

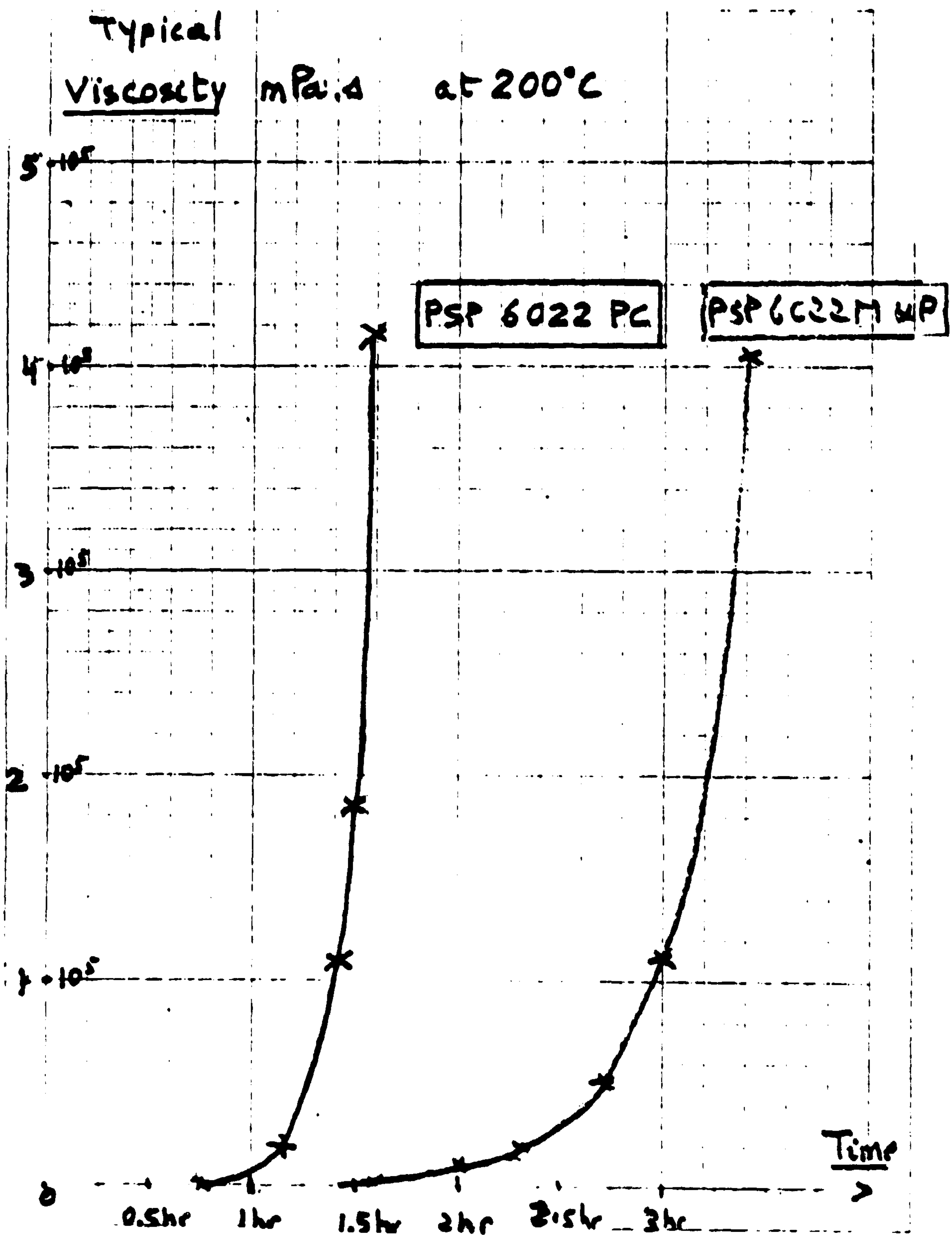
Other formulations can be prepared, depending on the application. For the present effort, another PSP resin has been used by comparison with PSP 6022 M :

PSP 6024 M

Solution for impregnation
Solid content : 70 % weight
Solvent : Methyl Ethyl Cetone
Viscosity : 2 000 mPas at 25°C

PSP 6024 M differs from PSP 6022 Mby raw materials, and is supposed to lead to higher condensed networks in cured resin.

Typical viscosity curves evolution at 200°C are enclosed, as measured in an Haake viscotester (X mobile, coef. 57.15).


Typical
Viscosity mPa.s at 200°C
5·10⁵
4·10⁵
3·10⁵
2·10⁵
1·10⁵
0
PSP 6022 PC
PSP 6022M WP
Time
0.5hr
1hr
1.5hr
2hr
2.5hr
3hr

1.3 - PSP 6022 neat resin curing conditions

Samples of cured neat PSP 6022 resins may be molded as follows :

- precure in an oven, at 200°C, for 1 hr to 3 hrs at 200°C; time depends on the type of resin and is about 1 hr to 2 hrs for PSP 6022 PC, 2 hrs to 3 hrs for PSP 6022 P or M without solvent ; precure is stopped when the resin viscosity begins to increase at this temperature. Volatils evolved are supposed to be 3 to 5 %.

- pound the resin in a powder form

- put the powder in a standard compression mold (usual for thermosets), of internal dimensions for example of 8 cm X 3 cm X 1 cm, preheated at 250°C

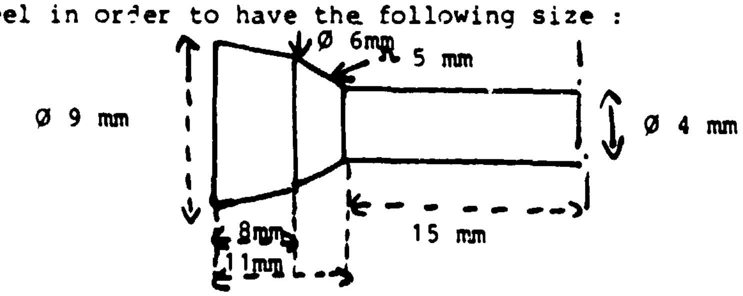
- apply 3 MPa progressively

- hold at 250°C for 1 hr to 2 hrs

- post cure may be done at 250°C ; time of post cure will depend on thermomechanical properties requested : generally 4 hrs are enough for good properties at 250°C, and 16 hrs for more than 250°C properties.

In all cases, cool slowly from cure or post cure temperature to room temperature.

For tensile properties measurements, it has been found (2) that the best mean to avoid microcracks is to prepare injected samples as 9 mm diameter cylindres, and then machining roughly by turning and rectifying cautiously with a diamond polishing wheel in order to have the following size :



Before injection , PSP 6022 M solvent is evaporated by heating under vacuum up to 200°C and holding 20 min at 200°C. Injection mold is preheated at 165°C. Curing conditions under 16 MPa pressure, are, for PSP 6022 PC or evaporated PSP 6022 M :

- heat from 165°C to 180°C at 1°C/min.

- heat from 180°C to 250°C at 0.1°C/min.

- hold at 250°C for 6 hrs.

(2) - work done in ONERA laboratories.

1.4 - PSP neat resin properties

Physical properties

Density : 1.14

Thermal expansion coefficient : $55\text{-}60.10^{-6}$ °/C

Mechanical properties

They depend on cure conditions. Following data (2) are presented as an example. ( ) : variation.

	Tensile strength (MPa)	Elongation to break (%)	Tensile Modulus (MPa)	No of Samples
6022 PC				
Cure A	58,7 (6,1)	2,98 (0,42)	2326 (30)	9
Cure B	50,9 (3,7)	2,43 (0,23)	2375 (62)	11
Cure B + PC	41,2 (1,7)	1,85 (0,1)	2397 (39)	2
6022 M				
Cure B	48,0 (8,3)	1,75 (0,31)	3004 (212)	4
Cure B + PC	55,0 (12,3)	2,06 (0,55)	2972 (115)	4

Cure conditions of injected samples, under 1.6 MPa :

Cure A : 160°C ↗ 180°C at 1°C/mn
180°C ↗ 200°C at 0,5 °C/mn
Hold 3 hrs at 200°C
200°C ↗ 250°C at 0,1°C/mn
Hold 2 hrs 40 mn at 250°C.

Cure B : 160°C ↗ 250°C at 0,1°C/mn
Hold 6 hrs at 250°C.

PC : Post cure 16 hrs at 250°C.

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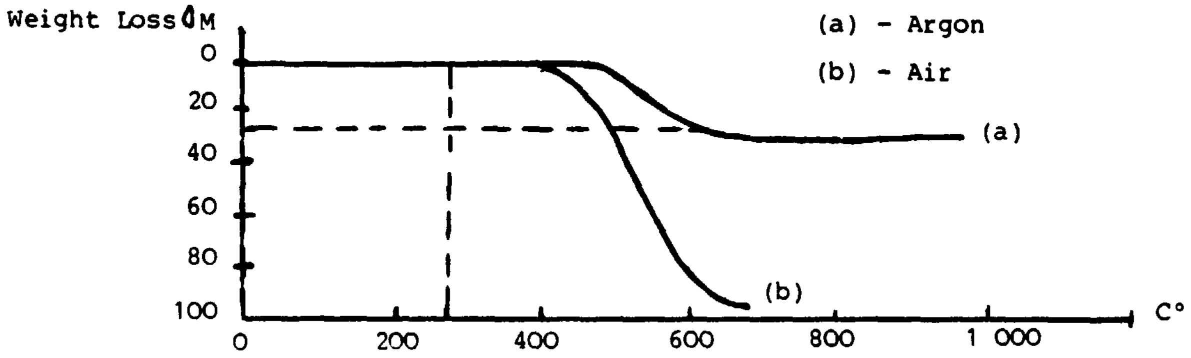
(2) - ONERA - C. Le Ripec, June 1980.

Thermostability properties

Thermal aging properties have been measured in air on PSP 6022 M, PSP 6022 PC and PSP 6024 M neat resins : weight less is about 2 % after 1200 hrs at 250°C.

Thermogravimetric analysis shows the very high percent char yield obtained with PSP 6022 : 96 % at 430°C, 72 % at 650°C, 68 % at 750°C (3).

Pyrolysis of PSP resin in non exidative atmosphere gives a char yield of about 65 % at 1 000°C, with good mechanical resistance.



Dielectrical properties

PSP 6022 PC was cured 2 hrs at 250°C under 3 MPa (see instructions), without any post cure.

Dielectrical properties were measured at about 9 GHz (X) at 20°C.

Dielectrical constant : 2.3 to 2.5.

Losstangent : $0.9.10^{-2}$.

(3) - W.J. Gilwee et R.H. Fish, NASA Ames R.C., NASA Technical memorandum 81179, February 1980.

1.5 - Material Safety Data

Acute oral toxicity

Toxicity has been measured on 2 batches of ten male rats, 190 g and 132 g body weight. Resin is introduced by intubation, and there is a 15 day observation period of the survivors after the test.

Resin used was PSP 6022 M, batch LDG 705. with 25 % MEK solvent (note that MEK has an acute oral LD 50 rat of 3.3 g/kg and methylderivatives of pyridine 0.7 to 1.5 g/kg). There was only 1 dead for 10 rats with 10 ml/kg, and the is no anormal symptom for 8 ml/kg at which dose PSP 6022 M is atoxic.

LD 50 > 10 ml/kg

Draize Primary Irritation

Six "New - Zealand white" rabbits are used , hair clipped from back with angora clippers in two areas 10 cm, appart. One area abraded by four epidermal incisions, two perpendicular and two others in the area of patch. One area is left intact ; patch is 3 cm square. 0.5 ml test substance is put under patch, clear plastic trunk bands outside. There is a twenty-four hour exposure period. Reaction is evaluated at 24 hours and at 72 hours.

The primary dermal irritation score found with PSP 6022 M (25 % MEK solvent) was 2-66, referenced as moderately irritating. (Note that MEK has an acute dermal LD 50, rabbit, of 8 ml/kg).

Recommendations for handling

Recommended practices for handling should be the same as for epoxy resins, related and auxiliary chemicals.

PSP 6022 M, PSP 6022 P, and PSP 6024 M have about the same condensation level and they may contain some unreacted methylpyridine derivatives, giving a strong odor when heated. Adequate ventilation must be provided both in the mixing and application areas. Fresh air ventilation and/or exhaust ventilation may be used. Equipement should be designed and installed such that the vapors are pulled away from the worker. To avoid adverse health effects, workers must not be exposed to air levels of contaminates in excess of the Threshold limit Values (ACGIH) or the Permissible Exposure Limits (OSHA).

TWA (Threshold Limit Values for Substances in workroom Air, issued by the ACGIH) are, for pyridine : 5 ppmand 15 mg/m3 (guidance note EH 15/77). LCLO, the lowest concentrations of substance in air, which have been reported to have caused death on humans or animals by inhalation, are 500 ppm/ 4 hrs to 4 000 ppm/4 hrs for methyl derivatives of pyridine.

1.6 - Caracteristics of batches of PSP used

Following batches have been used for this effort :

PSP 6022 M

- LDG 591 et 593 (same batch, without and with 1 % silica gel), used for laminates,

- LDG 647 et 677, (same batch, without and with 1 % silica gel), used for laminates ; 10 kg of each have been delivered to NASA Ames on January 1980.

PSP 6024 M

- LDG 672 et 673 (same batch , without and with MEK solvent) ; used for laminates ; 15 kg have been delivered to NASA Ames on January, 1980.

Batch controls

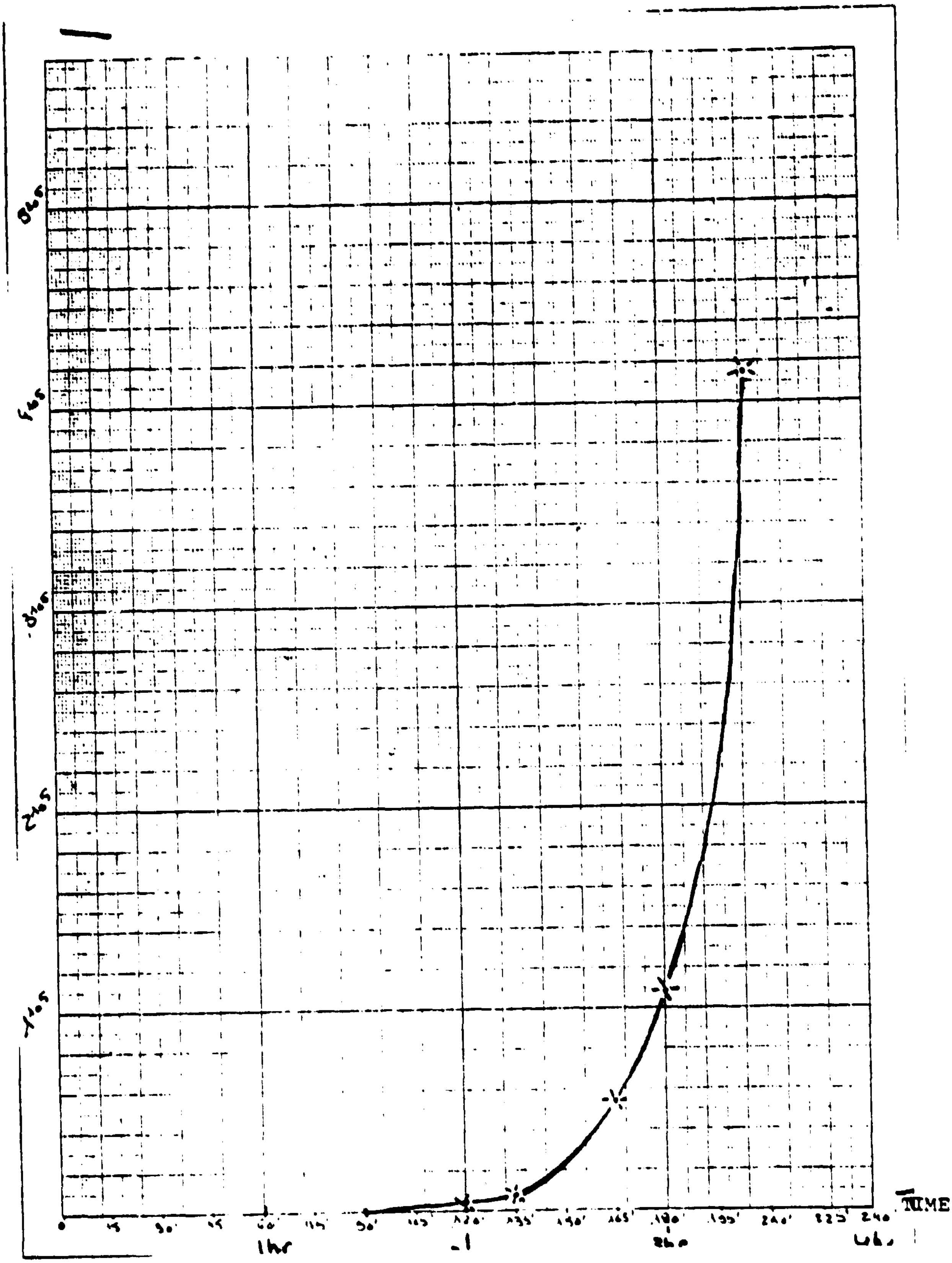
Following data are enclosed, fo each of the 3 batches :

- I.R. spectra

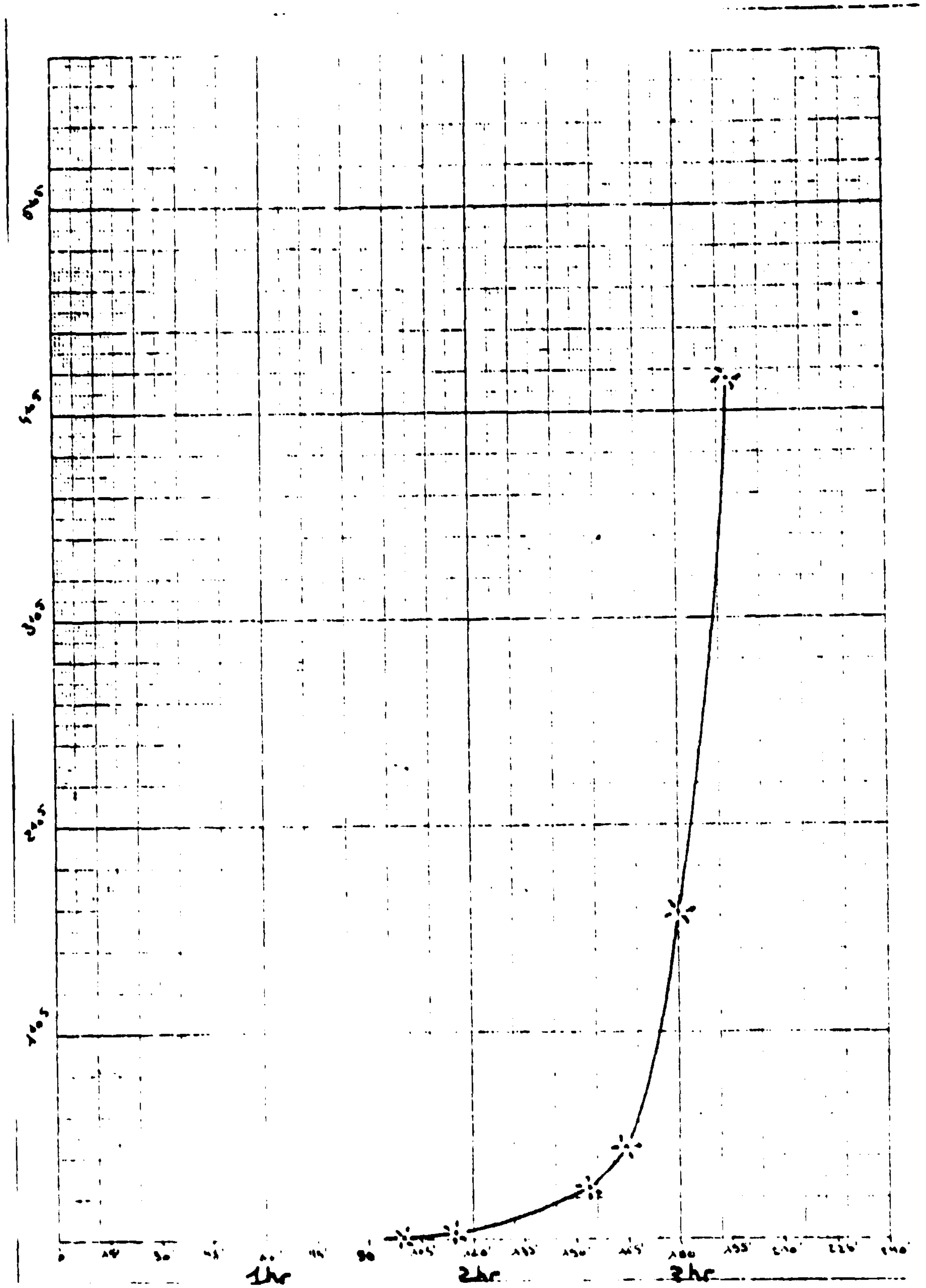
- G.P.C. spectra

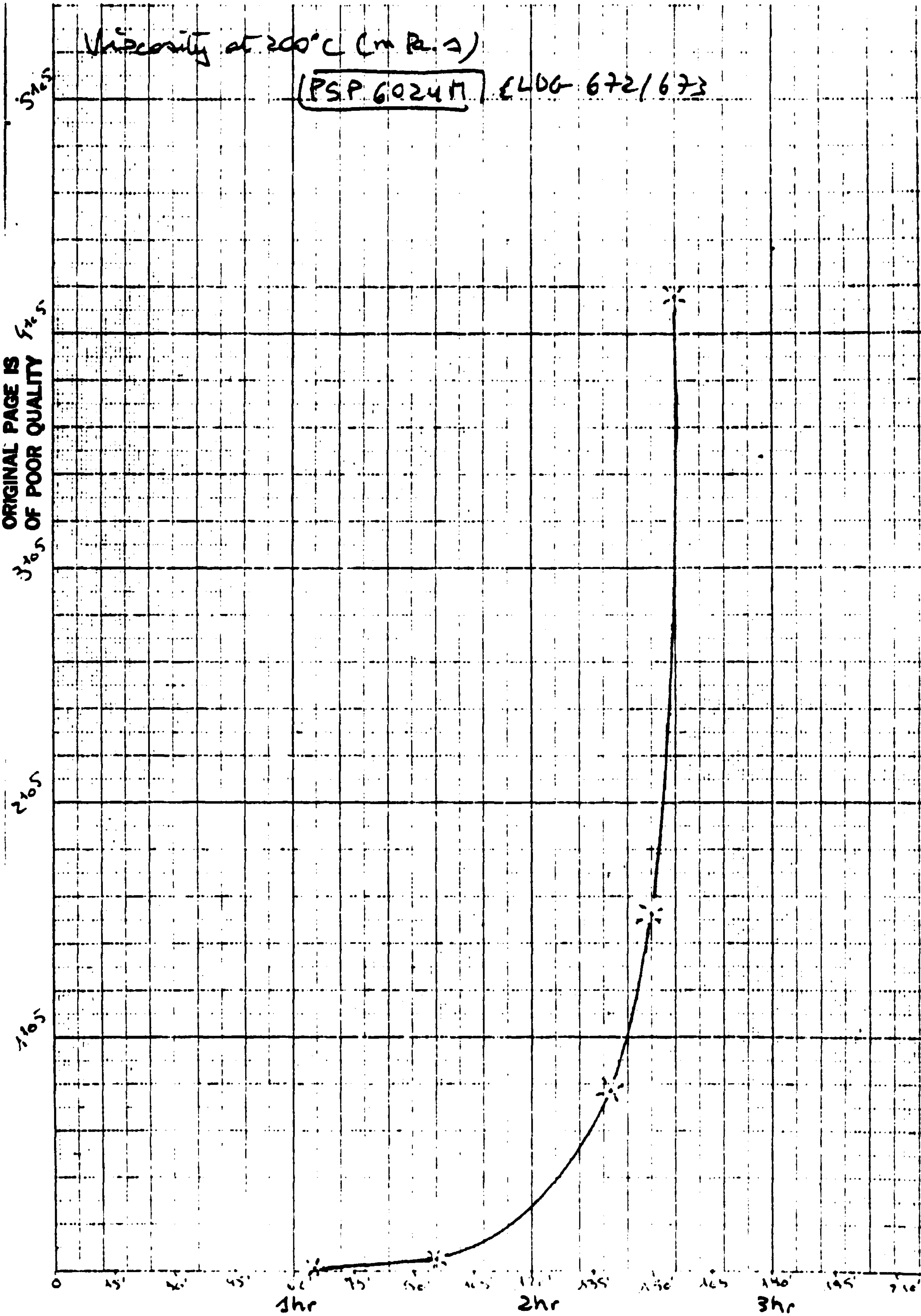
- viscosity evolution at 200°C, as measured in a Haake viscotester (X mobile, coef 57-15) on 200 g samples. This test is not fully representative of gel time, which seems to depend on pressure and air exposure. Weight loss at 200°C on 50 g samples of PSP 6022 M or PSP 6024 M, after solvent removing , is about 4.5 to 5 % after 4 hrs ; this test also is not fully representative because of possible removing, in such conditions, of reactive components.

Viscosity at 200°C (mPa.s)



Viscosity at 200°C (mPa.s)




Viscosity at 200°C (m Pa.s)
PSP 6024M {LOG 672/673}
0
1hr
2hr
3hr

Part II - PREPARATION OF PREPREGS WITH PSP RESINS

Impregnation of continuous fibers (tapes or fabrics) is very easy to realise with PSP 6022, particulary in solvent process with PSP 6022 M (or PSP 6024 M) solutions in MEK.

Condensation rates of PSP 6022 M, PSP 6022 P, and PSP 6024 M have been choosed to give excellent tape and drape prepregs, the prepolymers without solvent being very viscous or semi-solid at room temperature.

Long storage times are allowed for the prepregs by the stability of the resin at room temperature : several months storage at 25°C does not affect the properties of the prepregs.

2.1 - Industrial impregnations have been made with carbon fibers in 34 cm width unidirectional tape or in 1,2 m width fabrics (carbon, glass, Kevlar, silica) using PSP 6022 M solution.

For unidirectinal tape impregnation viscosity is fitted to 26 seconds, # 4 ford cup at 20°C (65 mPa-s) by addition of MEK. Solvent is removed by passing during about 4,5 to 5 min through an oven heated with pulsed air at about 100°C.

Quite the same conditions are used in fabrics industrial impregnation, but removing of solvent is made during about 7 min through an oven heated with pulsed air at about 90°C.

Prepreg areal weight is controlled, and fiber areal weight checked after dissolution of resin in MEK. It is not representative to measure volatiles contents, due to some residual reactive reactants, but a measurement is usually made after 1 hr at 125°C, giving less than 5 % volatils. Typical data sheet is enclosed.

2.2 - Laboratory impregnation of W 133 graphite fabric

For this effort it was asked to use style 133 satin finish Thornel T300 graphite fabric. Experiments have been runned in SNPE laboratories with different styles of fabrics :

- Fiberite W 133 : 8 Harness satin, 366 g/m2
- Stevens Genin 40830 : 8 Harness satin, 339 g/m2
- Stevens Genin 43377 : 5 Harness satin, 290 g/m2.

The specific task of delivering fabric laminates, has been subcontracted to Composites Horizons (4). The impregnation has been made as following, with PSP 6022 M and PSP 6024 M.

(4) - Composites Horizons, 2303 West Valley Boulevard, POMONA California 91768.

Impregnation of W133 graphite fabric with PSP resins (4)

- Cover a flat surface on which the impregnation is to take place with F.E.P. Tape edges so that F.E.P. is flat and slightly stretched.

- Cut length of W 133 graphite fabric to be impregnated and determine fabric weight.

- Place over F.E.P. , pull flat and tape to F.E.P. so that no uneveness remains in fabric.

- Calculate required amount of resin solids to obtain desired resin content (36 - 40 % weight).

- Weigh-out resin into three (3) batches -1 st batch to contain 50 % of total required resin ; 2nd batch to contain 30 % of total required resin ; 3rd batch to contain 20 % of total required resin.

- Dilute each batch of resin to a 3:2 resin to reagent M.E.K. solution.

- Spread resin with a teflon or urethane paddle so that no resin pooling remains and appearance is consistant. Work 25 to 30 gm of resin solution at a time until all the resin batch is consumed.

- Allow surface to become dry to the touch before applying next batch.

- Allow prepreg to dry for at least 24 hours at room temperature before cutting into panels.

- Place panels onto mylar film with F.E.P. side up and allow to dry another 24 hours at room temperature after removing the FEP film.

- Turn and dry for 24 hours two more times before curing.

NOTE : FEP is a.0005 inch film used as a strippable support.

In SNPE experiments, drying of prepregs was realized by heating 10 min at 120°C in an oven.

(4) - Composites Horizons.

2.3 - Technical data sheets

PSP 6022 preimpregnated products

AVAILABILITY

Most usual types of prepregs are available with PSP 6022 M (solvent process) or P (hot melt process).

Rovings

Kevlar , glass , carbone/PSP 6022 rovings for filament winding are available on request.

Unidirectional tapes

Carbon tape can be supplied in rolls up to 400 m long in standard width 340 mm. Tapes in widths between 10 mm an 340 mm are available on request.

Standard nominal moulded ply thickness at 60 % by volume of carbon fibre are 0.100 mm, 0.125 mm and 0.150 mm. Other thickness between 0.085 mm and 0.300 mm are available on request.

Tape is also available with glass scrim : a standard prepreg is : 120 g/m2 carbone plus 44 g/m2 glass.

Standard resin contents on carbone prepregs are :

- 38 $\pm$ 2 % wt
- 42 $\pm$ 2 % wt.

Volatiles content is $\leqslant$ 8 % (1hr at 120°C) ; most of these volatiles are reactive during curing process.

Woven fabric

A range of glass, Kevlar, Silica, Thermoproof (Genin), carbon fabrics impregnated with PSP 6022 is available on request.

Prepregs shelf life

Tack life when stored in sealed plastic bag is :

- 3 months at 20°C
- 6 months at 0°C
- 1 year at -18°C.

SAFETY INFORMATION

Observe the same safety precautions in hanlding prepreg material as in hanlding any epoxy resin. Work areas should be adequately ventilated. Avoid prolonged or repeated contact with the skin.

For pure resin, see health hazard data.

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SPECTRUM NO ______

DATE ______

SAMPLE ______

SOURCE ______

STRUCTURE ______

PSP6022M

PATH ______ mm ______

SOLVENT ______

CONCENTRATION ______

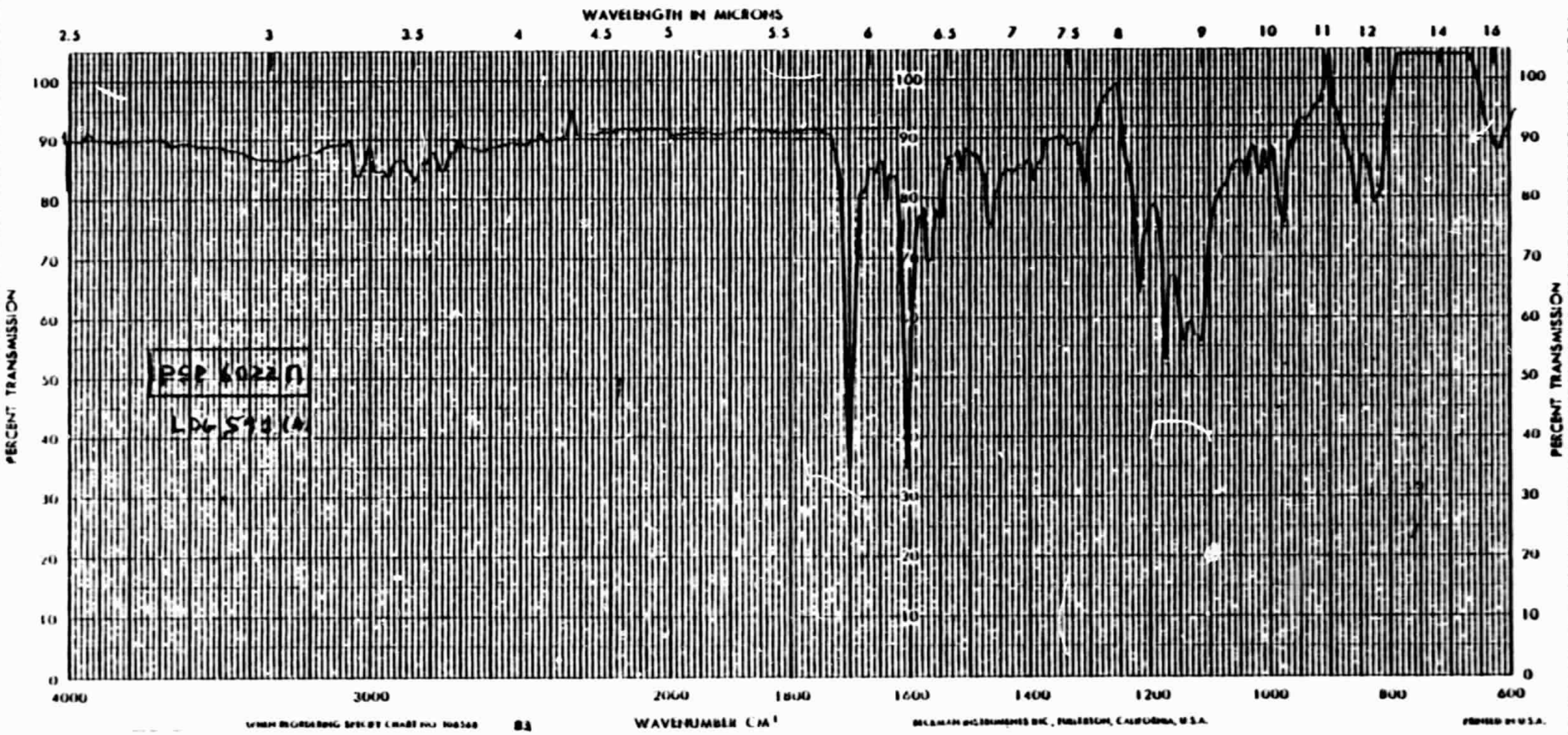
PHASE ______

COMMENTS ______

ANALYST ______

Beckman®

INFRARED SPECTROPHOTOMETER



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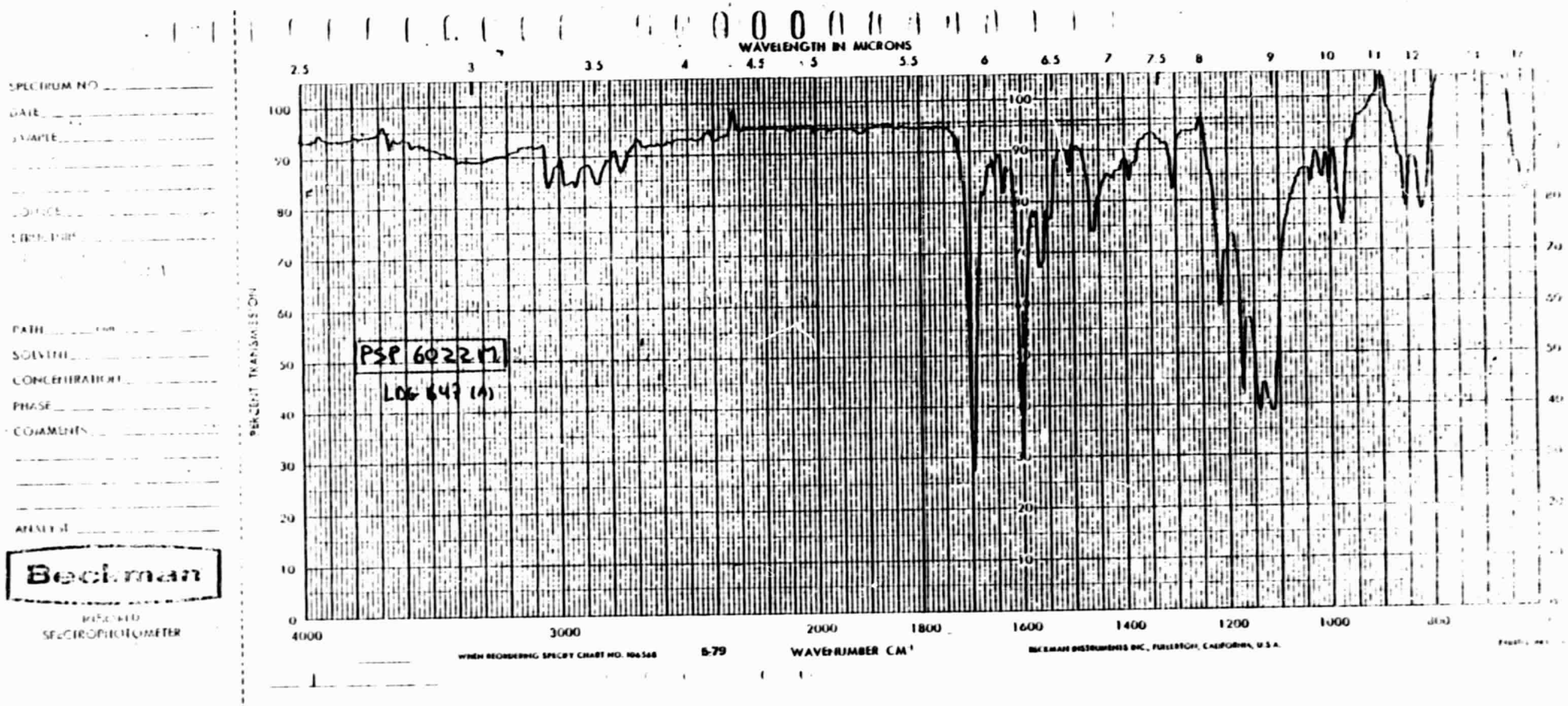


SPECTRUM NO ______

DATE ______

SAMPLE ______

SOURCE ______

STRUCTURE ______

6014
LOG 673

PATH ______ mm ______

SOLVENT ______

CONCENTRATION ______

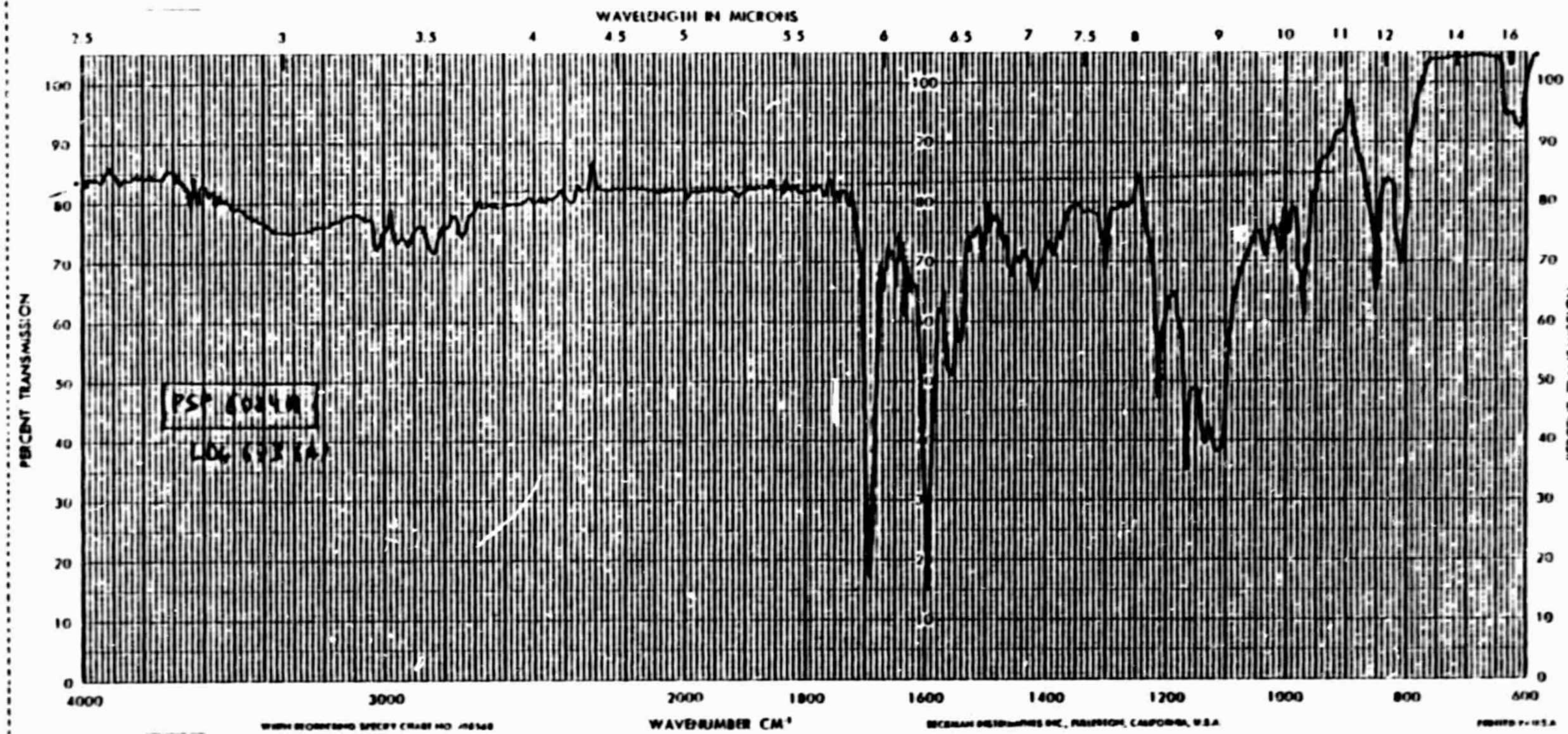
PHASE ______

COMMENTS ______

ANALYST ______

Beckman®

INFRARED
SPECTROPHOTOMETER



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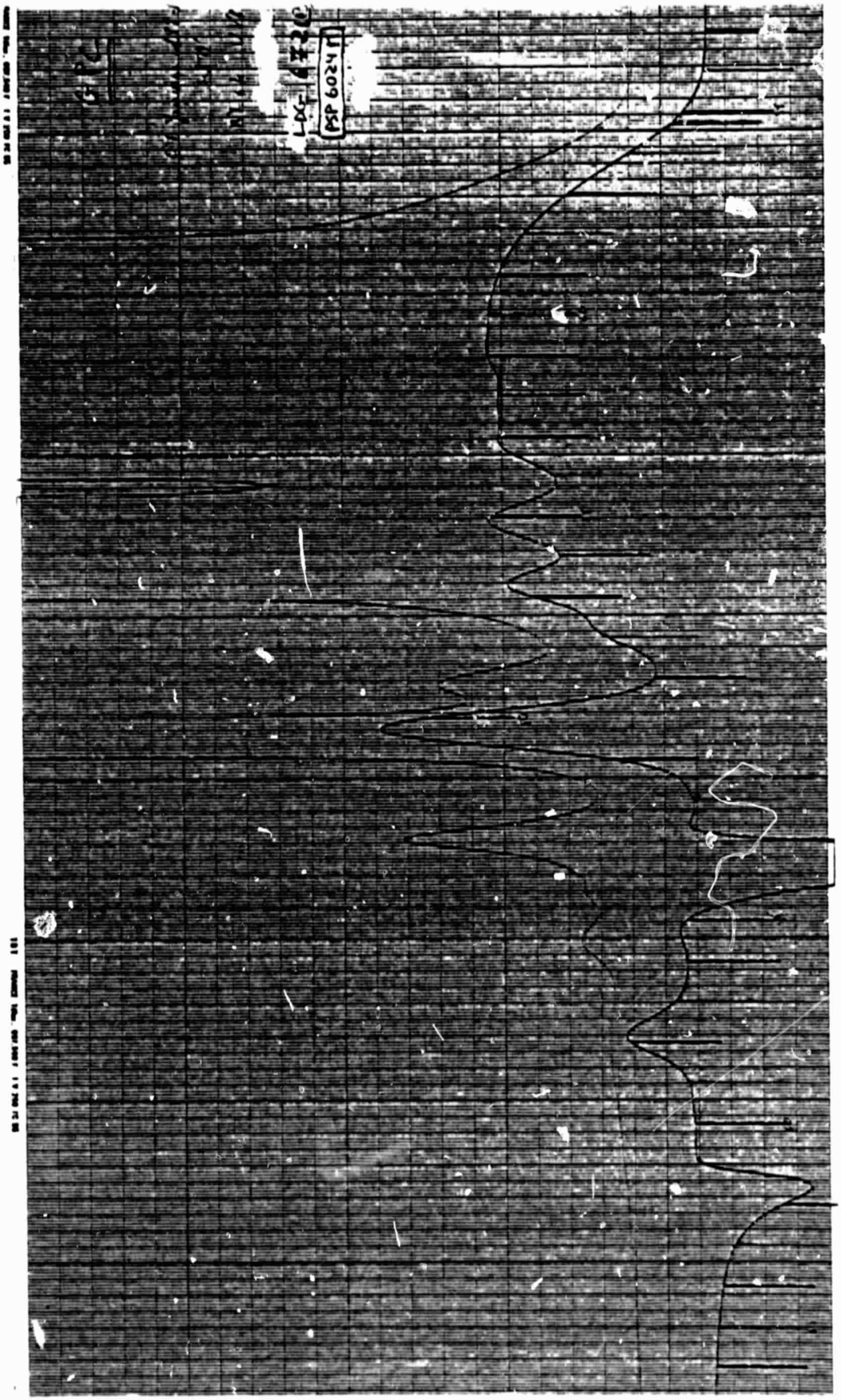
GPC
PSP 6024T

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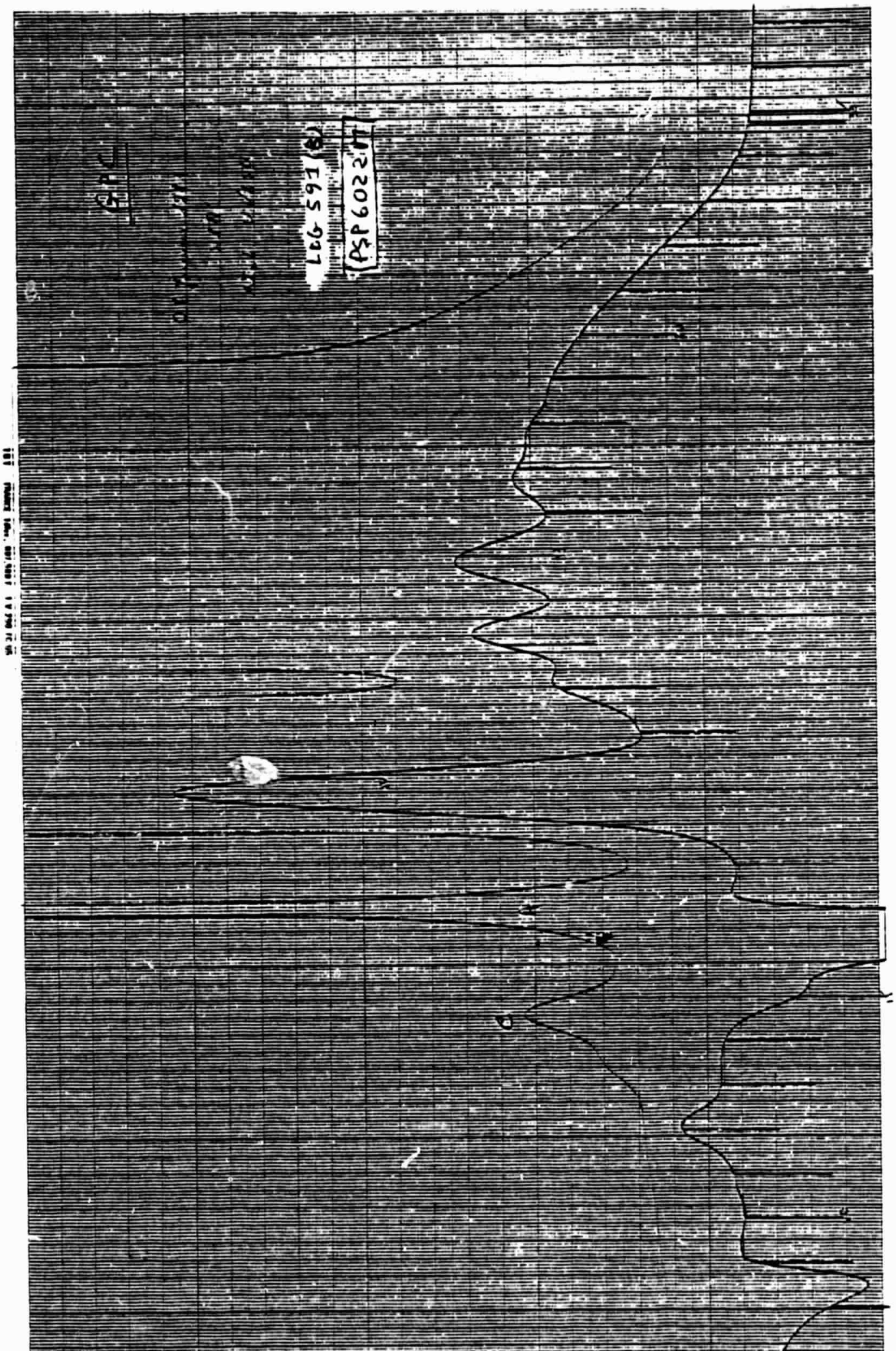
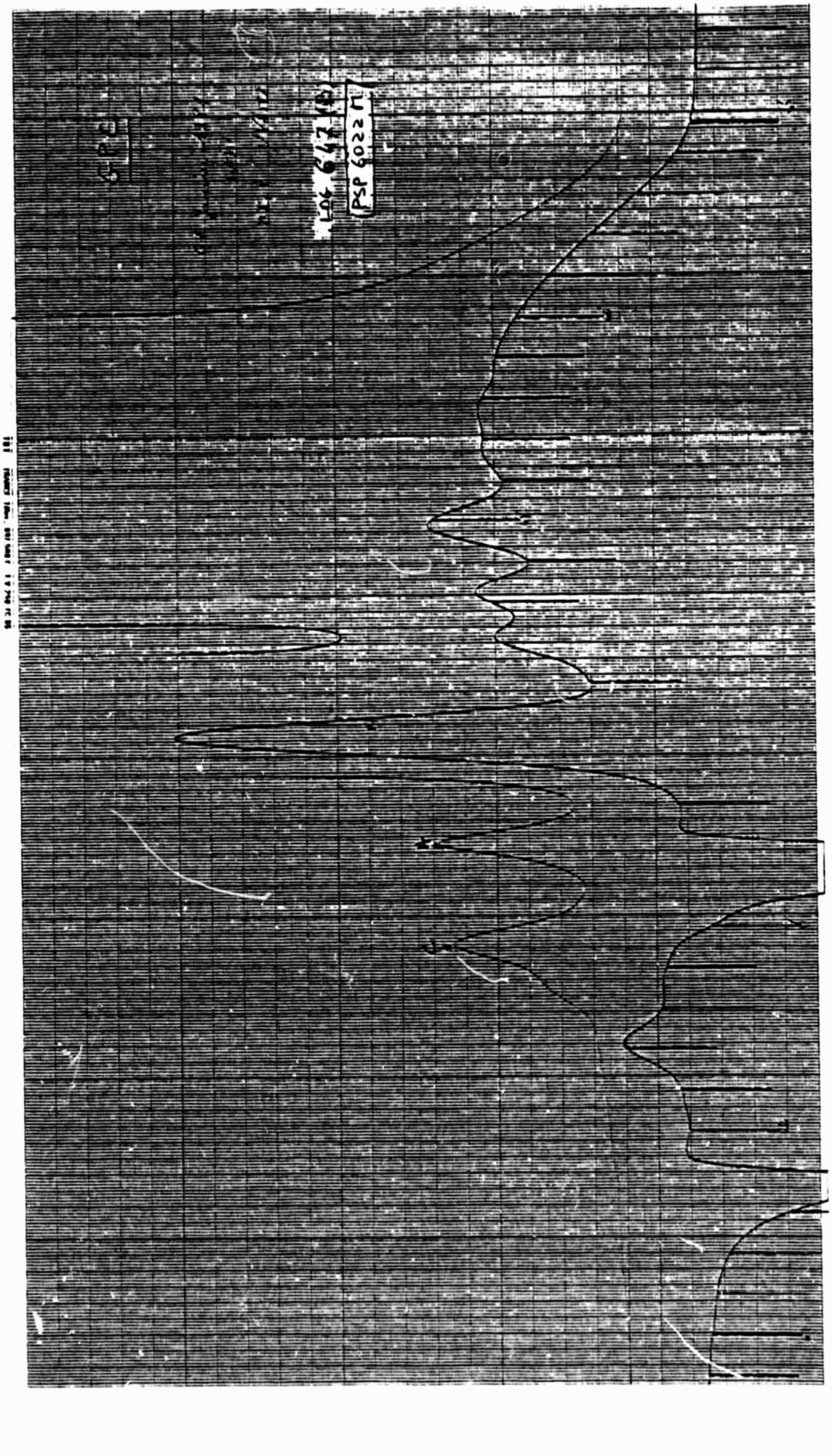



LOT 647 (B)
PSP 6022

Product : Carbon/6022 M prepreg tape Date : Réf : C.T.S.$_3$ - 13

Composition prepreg	FIBER CARBON	FIBER TYPE T 300	NB. FIL. 6 K	RESIN 6022 M
Typical Prepreg Characteristics	Areal weight, fiber 130 ± 5 g/m2	Resin content (weight) 42 ± 3 %	volatiles (weight) ≤ 5 %	Areal weight, prepreg 225 ± 15 g/m2
Typical Composite Characteristics	Flexural Strength ≥ 1 300 MPa	Flexural Modulus ≥ 100 000 MPa	Tensile Strength ≥ 1 200 MPa	Short Beam Shear Strength 20°C : ≥ 90 MPa 300°C : ≥ 50 MPa
Cure	Suggested press and autoclave cure cycle are enclosed in technical data sheet.			
Shelf life	25°C > 3 months	+ 5°C > 6 months	- 18°C > 1 year	
Remarks	Volatiles : after 1 hr at 125°C Order Batch Sample			

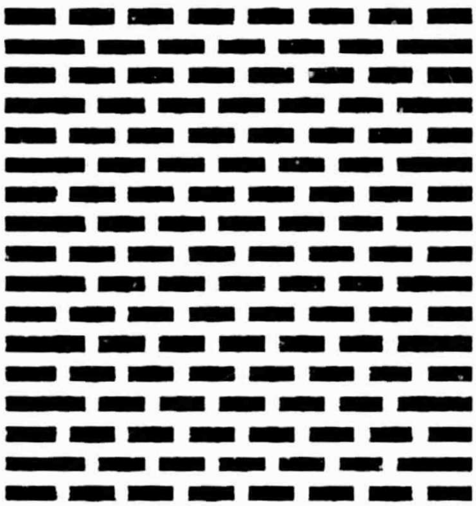
SNPE Office : 12 quai HENRI IV
75181 - PARIS CEDEX 04 - FRANCE
Tél. (1) 277.15.70

Plant : C.R.B., BP N° 2
91710 - VERT-LE-PETIT - FRANCE
Tél. (1) 493.39.39

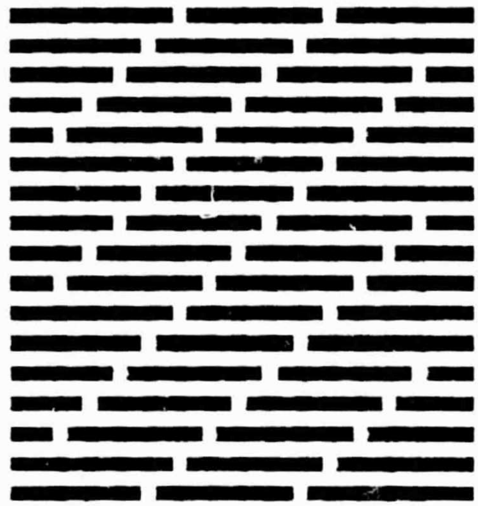
POPULAR WEAVE STYLES

Weave style is a critical component in many applications. If a part has curvatures or angles, a looser weave (such as the 8HS) would be used because of its good drapability characteristics. However, if a relatively flat part is to be produced, a plain weave would suffice. It is typically less drapable due to every other yarn being crossed.

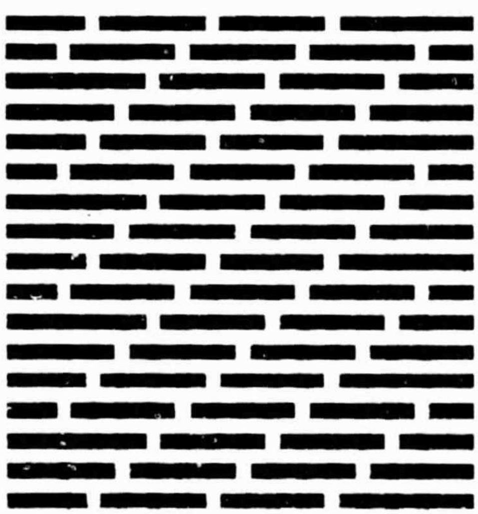
Shown below are four common weave styles. Keep in mind that each can have different properties depending on the amount of yarns per inch in the construction.



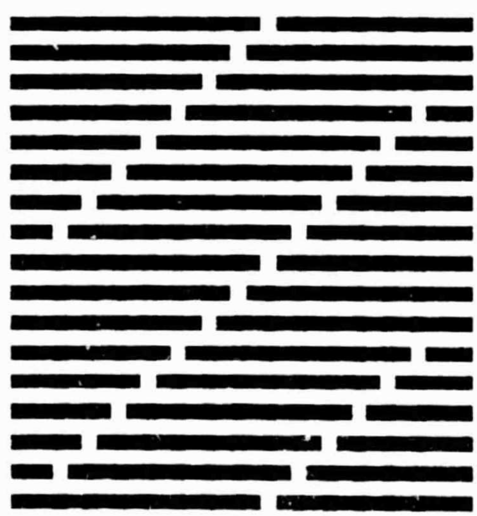
Plain Weave (P)
(over 1, under 1)



5 Harness Satin Weave (5HS)
(over 4, under 1)



Crowfoot Satin Weave (CFS)
(over 3, under 1)



8 Harness Satin Weave (8HS)
(over 7, under 1)

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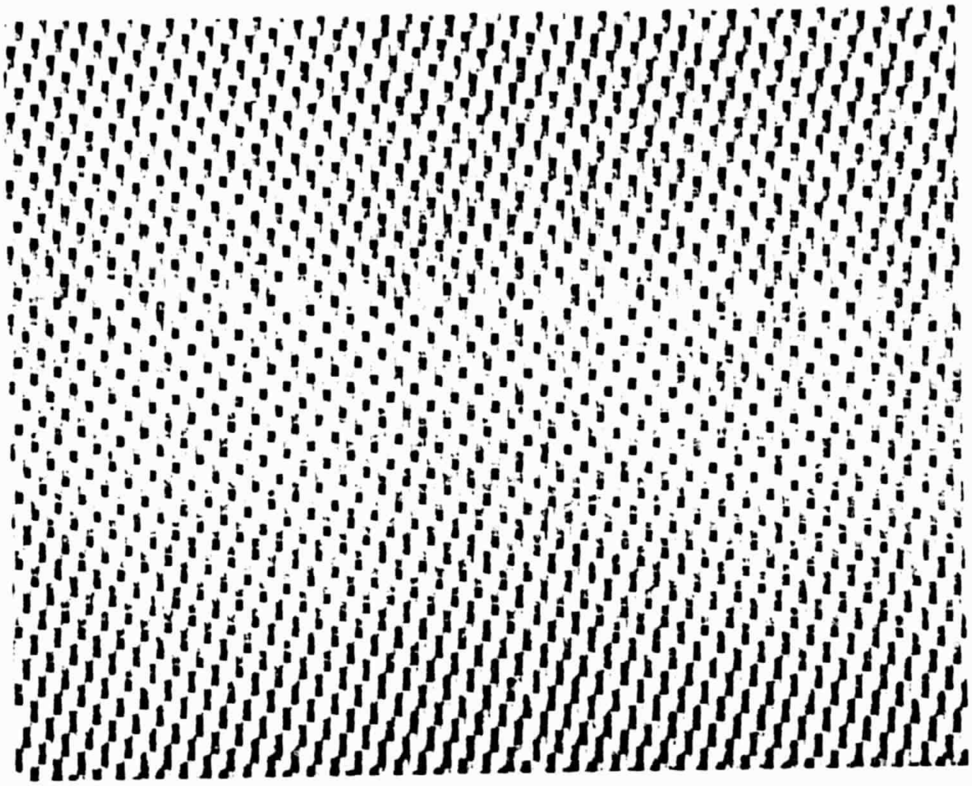
WOVEN FABRIC

hmf
By FIBERITE



FABRIC STYLE W-133

FABRIC DESCRIPTION

Thickness (mils) (ASTM-D-1777)	17.0	Warp Yarn	T-300 (3K)
Weight (oz/yd²) (ASTM-D-1910)	10.80	Filling Yarn	T-300 (3K)
Weave	8 HARNESS SATIN	Tracer Yarns:	
Thread Count:		Warp	2 INCH CENTERS
Warp x Filling	24 x 23	Filling	6 INCH CENTERS

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FABRIC DESCRIPTION

COMPANY	FIBERITE (U.S.A.)	STEVENS GENIN (FRANCE)	
Reference	W 133	40 830	43 377
Weave	8 Harness Satin	8 Harness Satin	5 Harness Satin
Weight (g/m2)	366	340	290
Warp Yarn	T 300 - 3 K	T 300 A - 3 K	T 300 A - 3 K
Filling Yarn	T 300 - 3 K	T 300 A - 3 K	T 300 A - 3 K
Thread count on			
- warp	9,5	8,5	7
- filling	9	8	7
Thickness (μ m) (cured ply , 60 % Vf).	330	300	250

Part III - LAMINATE FABRICATION

Typical cure procedure

Details of processing conditions may depend of course on the type of resin, resin content, laving up configurations or apparatus. Typical schedules are given for PSP 6022 M.

3.1- Press cure schedule

- heat the plates of the press at 200°C

- put the cast form (opened on 2 sides) , with wished number of plies between the plates ; temperature of the cast form reaches 200°C within about 10 to 15 minutes

- put the top plate to contact, without pressure, to avoid air contact on the upper ply

- hold at 200°C for 1 hr 30 to 1 hr 45

- apply for 1 MPa over 15 minutes

- hold for 1 hr 30 under 1 MPa

- heat to 250°C and hold for 2 hrs at 250°C under 1 MPa

- cool to 60°C under pressure.

For high temperature resistance, post cure of 4 hrs at 250°C is recommended.

3.2- Bag molding schedule

A silicon bag is used to transmit pressure by means pressurized air, on prepreg plies layed up in a cast form heated at 200°C with a radiant panel. Pressure (0.4 to 0.5 MPa) is applied after 1 hr 45 min, and total heating is 8 hrs at 200°C. There is no vaccum in the bag.

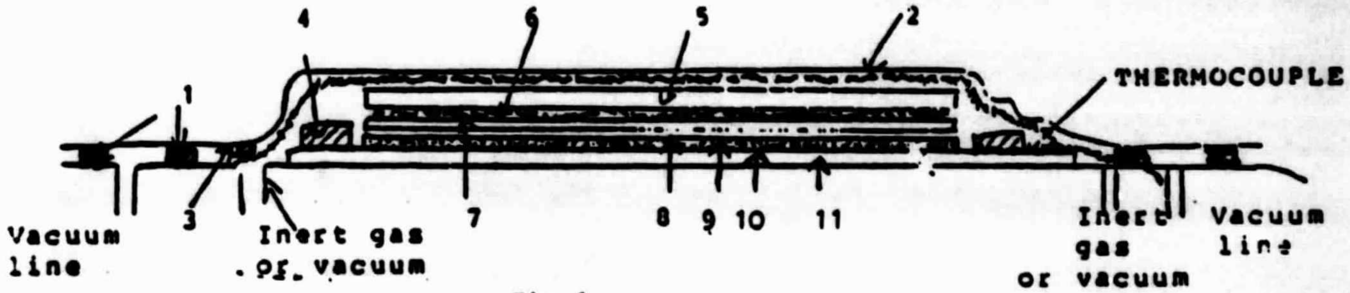
A post cure from 4 hrs to 16 hrs at 250°C is recommended for high temperature resistance.

3.3- Autoclave molding

Usual arrangements for controlled bleed lay-up procedure may be used, as in following examples.

331 - LAY UP PROCEDURE

Lay up procedure example 1 (controlled bleed) for molding PSP prepregs



- Fig 1.

1 - Bag sealant (ex : Dapcoseal 2010-2)

2 - Vacuum bag (ex : silicon bags, Vacallory D D)

3 - Breather (ex : fiberglass)

4 - Edge dam, 2 mm thickness for expected 2 mm thickness laminate, tighty close to prepreg (ex : silicon RTV)

5 - Pressure plate (optional)

6 - Solid FEP film, to stop bleed (ex : Armalon TG 4052, e 0.13 mm)

7 - Surface bleeder : 4 plies of type 181 glass bleed for 2 mm nominal cured thickness of laminate

8 - Perforated FEP (ex : Armalon TG 0003, e 0.08 mm)

9 - Prepreg part

10- FEP film (ex : Armalon TG 4052) or release agent

11- Tool plate.

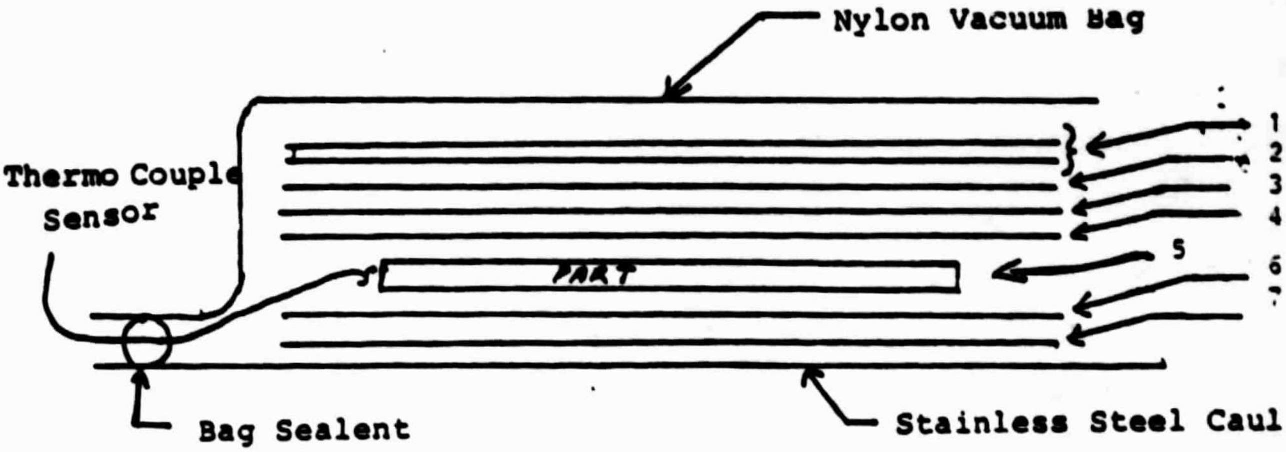
NOTE : in some cure procedures there is no vacuum in the bag. In such cases the bag sealing is maintained either by a vacuum line as shown on fig.1., or simplier a steel strap "picture frame" tool aid may be used to edge seal the bag during cure, "C" clamps providing pressure against the sealant.

.../...

LAY UP PROCEDURE - example 2 for molding PSP prepregs

(*)

- After drying place plies together in pairs (2ply) such that warp sides of plies face each other
- stack together pairs to obtain required number of plies such that warp fibers of all plies run parallel
- On a stainless steel caul which has previously been released with RAM 225, lay-up panels as follows :



- Fig 2. -

1 - 120 glass vent cloth, 2 plies

2 - Solid Teflon film, 0.15 mm (to stop bleed)

3 - Bleeder : 120 glass, 1 ply

4 - Porous Teflon (Pallflex TX 1040)

5 - Prepreg part

6 - Porous Teflon (Pallflex TX 1040)

7 - Solid Teflon film, 0.15 mm

Note : apply 635 mm Hg (minimum) on part for at least 30 minutes before starting cure.

(*) Preferred for lower than 40 % prepreg resin content.

332 - CURING CONDITIONS OF PSP 6022 M/P LAMINATES

It has been found that air contact on the surface of prepreg during curing process may induce lower properties on laminates ; this is the reason why it is recommended to put the top plate to contact during press cure schedule.

In autoclave molding the best mean to avoid air contact at 200°C would be to flow inert gas in the bag by the adequate line shown on figure 1, but it appears that as good laminates are obtained with no vacuum nor flow in the bag.

Too high vacuum would result in bad results, due to too much flow because of the very low viscosity of the resin at 200°C before gelation, and due to possible elimination of unreacted reactive monomers remaining in the preprolymer . So a no vacuum procedure (vacuum line open to air) is preferred when possible, or it is recommended to use an as slight as possible vacuum between 100°C and 200°C, at least up to gelation occured.

Examples of curing conditions at 200°C, and 250° maximum are following : all of them give good laminates between 20°C and at least 200°C. Higher thermomechanical performance or flame resistance are obtained by post cure of 4 hrs to 16 hrs at 225°C to 250°C, depending on initial curing conditions and degree of high temperature resistance required. Examples and typical properties are reported as followed.

Curing at 200°C - Example 1 (IRCA - 1 cure cycle) (Fig 3)

Lay up procedure used is detailed in example 1, fig 1 There is no vacuum in the bag (bag vented to atmosphere), with sealing maintained with or without vacuum on the edges.

- heat up to 200°C at 1.5 to 2°C/minute
- dwell at 200°C for 90 min
- apply 750 ± 50 kPa over 15 min
- hold for 6 hrs 15 mn at 200°C under pressure
- cool to less than 90°C under pressure.

Post-cure : 4 hrs to 16 hrs at 250°C, depending on required performanc above 250°C.

Curing at 200°C - Example 2 (1105 - 2 cure cycle) (fig 4)

Lay up procedure used is detailed in example 2, fig 2

- after vacuum system and lay-up in autoclave have been determined to be leak-free, reduce vacuum on part to 76 mm Hg

.../...

- heat-up autoclave to 163 °C using 1.5 to 2°C/min heat rise
- when part reaches 163°C ± 3°C, dwell for 90 minutes
- increase part temperature to 176°C using 1.5 to 2°C/mn heat rise
- dwell at part temperature of 176°C ± 3°C for 15 min
- increase part temperature to 200°C using 2°C/min heat rise
- dwell at part temperature of 176°C ± 3°C for 15 min
- apply 635 mm Hg (minimum) to part and dwell for 5 min
- add pressure at a rate of 70 kPa /min to 1 MPa
- cure at 200°C and 1 MPa for 16 hours
- cool to less than 93°C under pressure.

No post cure is necessary, glasstransition temperature in laminates being in excess of 370°C.

Curing at 250°C - Example 1 (MUCA 1 cure cycle) (fig 5)

Lay up procedure used is detailed in example 1, fig 1.

- apply 100 mm Hg vacuum
- heat-up to 200°C at 1.5 to 2°C/min
- dwell at 200°C ± 3°C for 90 ± 10 min
- apply 750 kPa ± 50 kPa over 15 min
- hold for 30 min at 200°C under 750 kPa
- heat-up to 250°C
- hold for 3 hrs at 250°C under pressure
- cool to less than 90°C under pressure

Post cure may be recommended (16 hrs at 250°C) for 400°C capability.

Curing at 250°C - Example 2 (1105 - 1 cure cycle) (fig 6)

Lay up procedure used is detailed in example 2, fig 2

- apply 76 mm Hg vacuum
- heat-up to 204°C at 1.5 to 2°C/min
- dwell at 204°C ± 3°C for 40 ± 10 min
- apply 635 mm Hg (minimum) to part and dwell for 5 min
- add pressure at a rate of 70 kPa /min to 1 MPa
- cure at 200°C and 1 MPa for 3 hrs 15 min
- increase part temperature to 250°C using 2°C/min heat rise
- cure at 250°C and 1MPa for 2 hrs
- cool to less than 93°C under pressure.

No post cure is necessary, glass transition temperature in laminates being in excess of 370°C.

FIGURE 3 : IRCA - 1 cure cycle

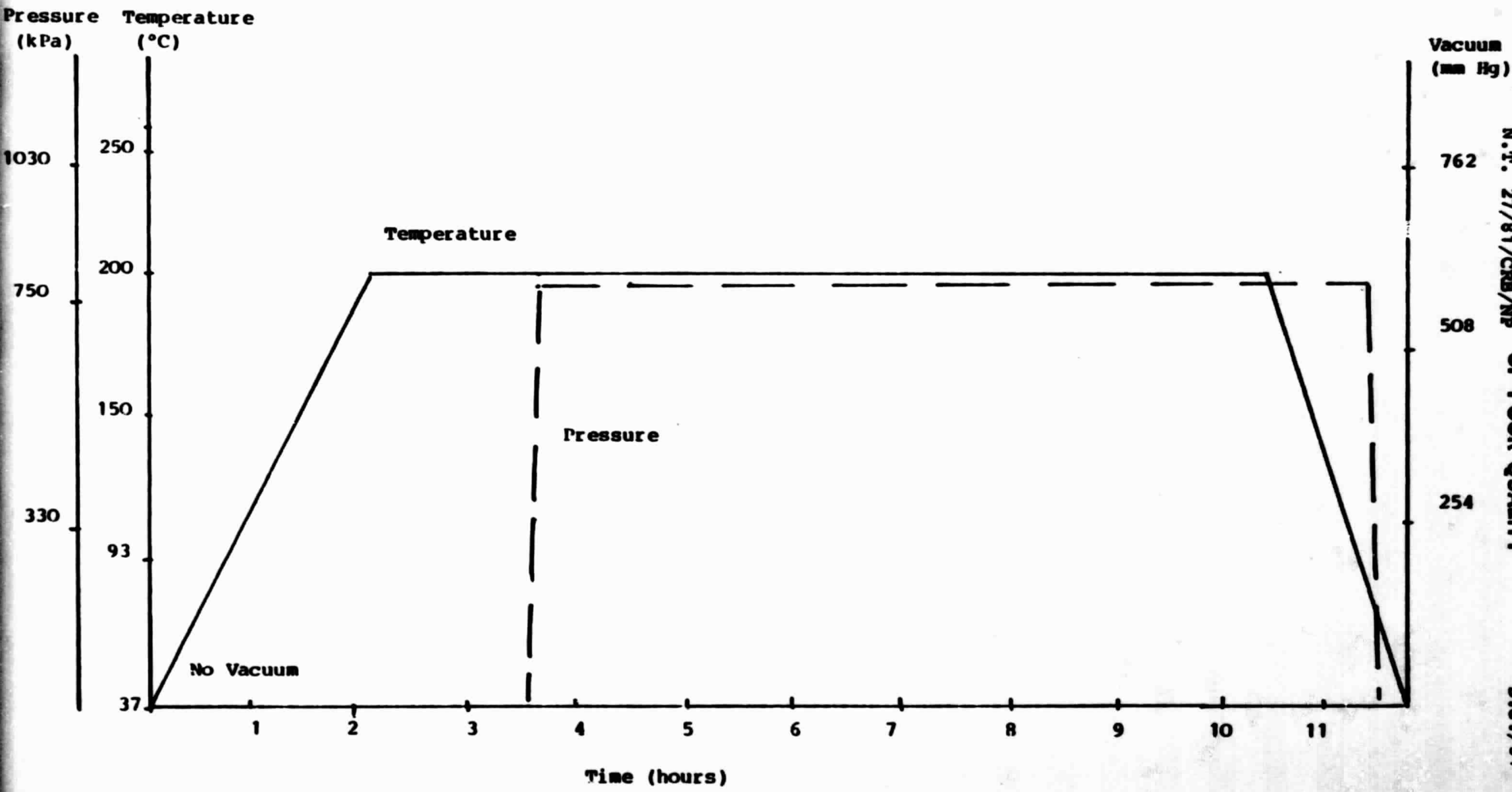


FIGURE 4 : 1105-2 cure cycle

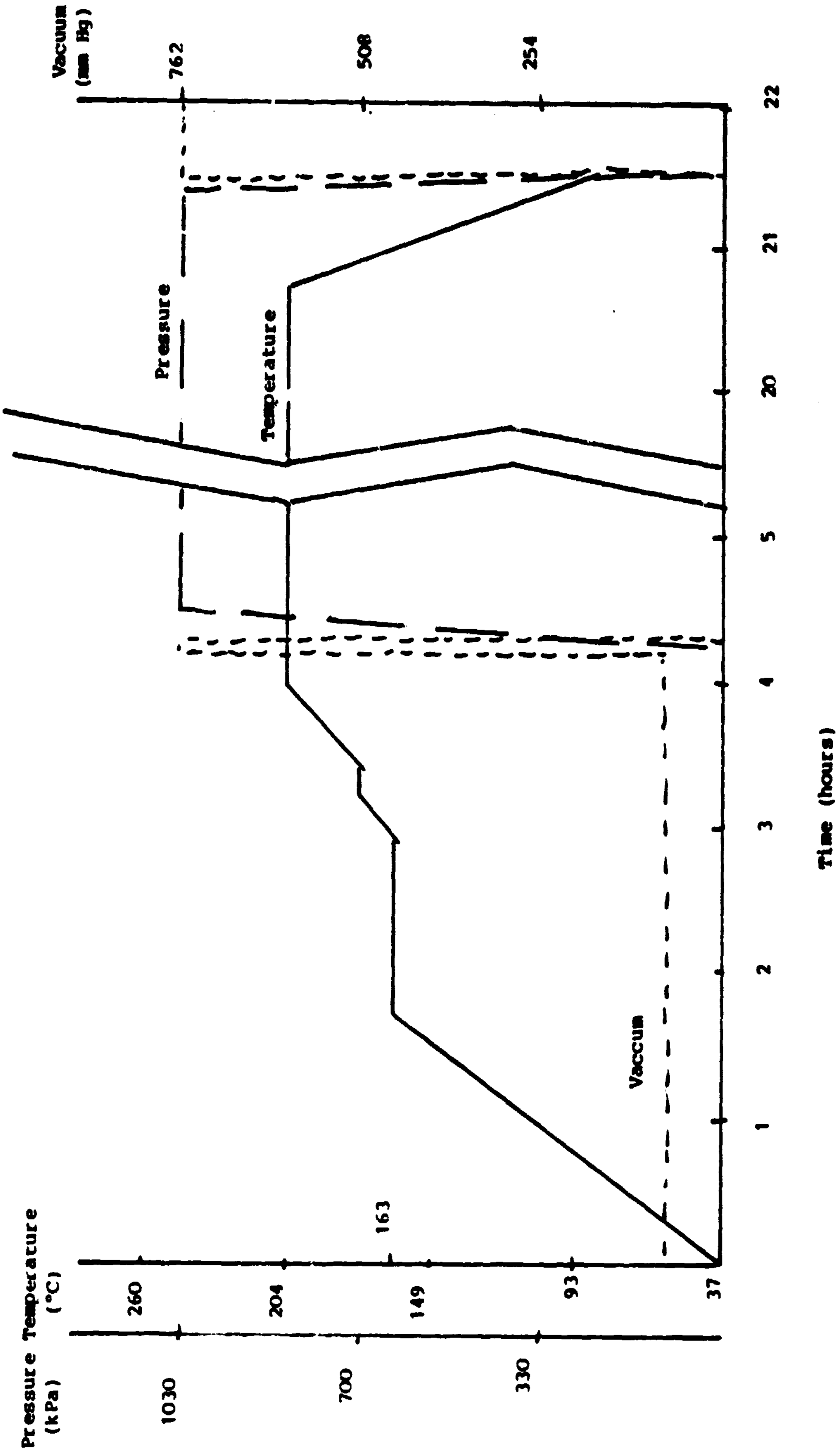


FIGURE 5 : MIKA - 1 cure cycle

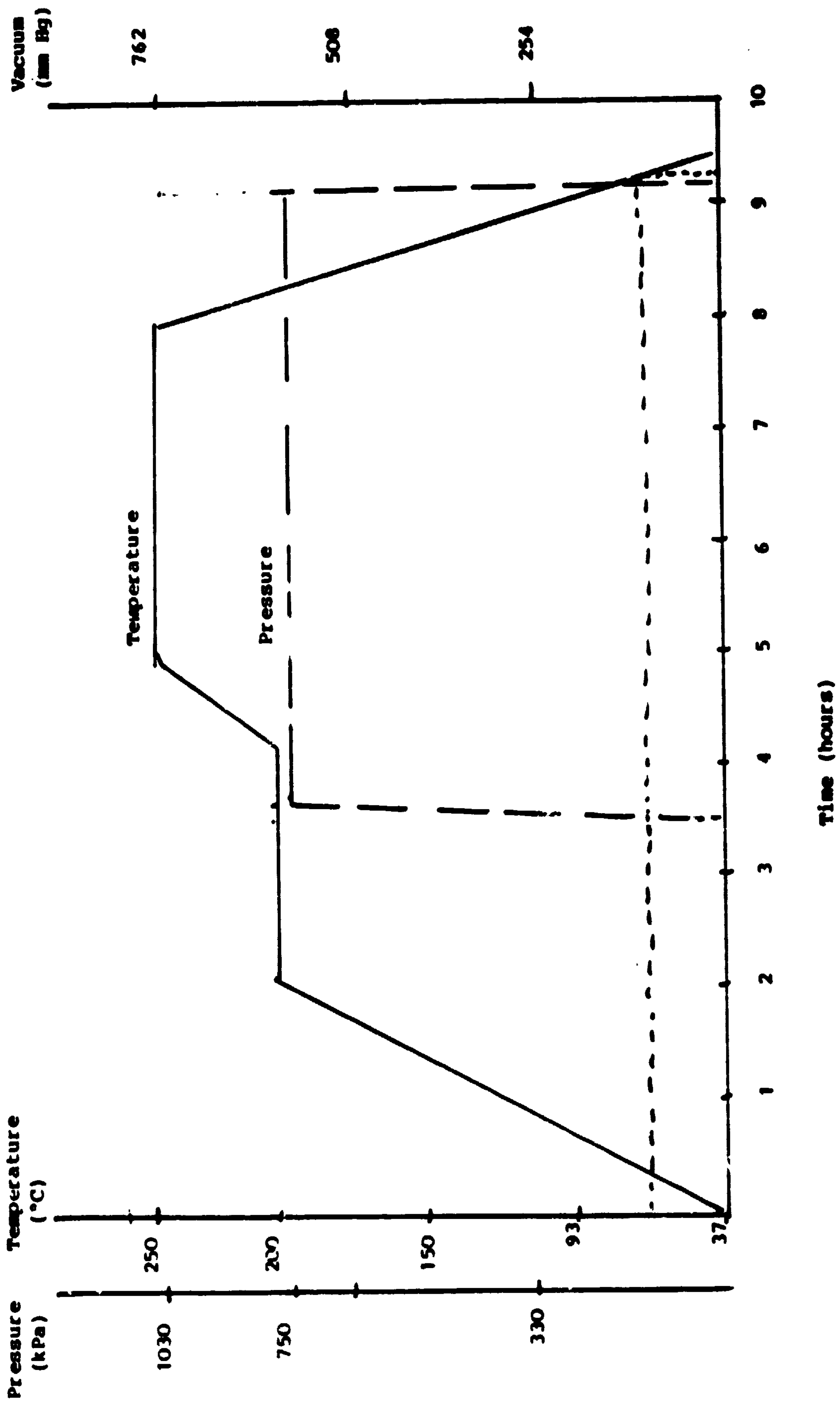
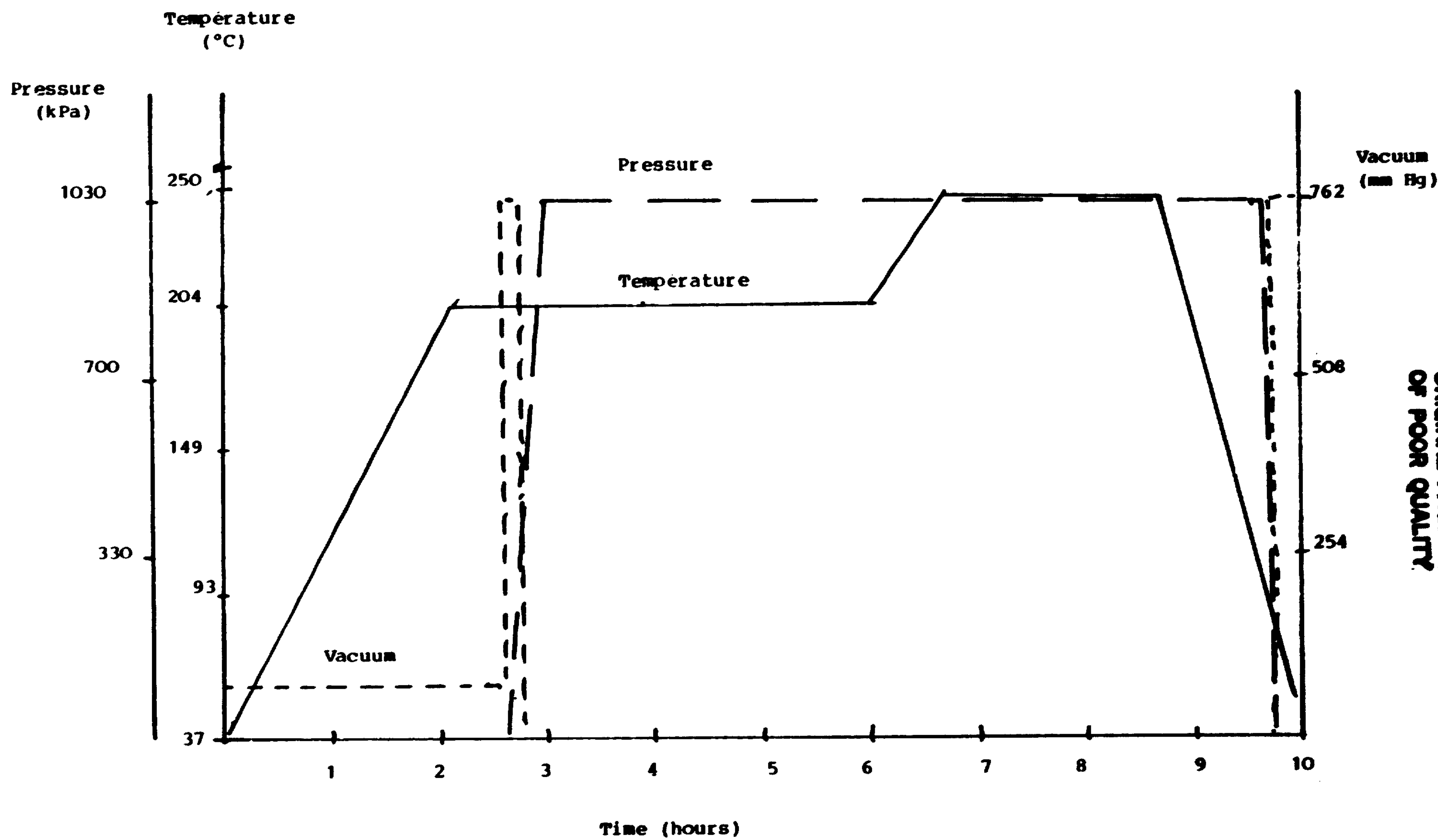


FIGURE 6 : 1105 - 1 cure cycle



4.1 - Usual reinforced PSP 6022 properties

Most usual reinforced PSP 6022 properties have been described in recent international symposiums (see réf. 1 to 8) :

Mechanical properties

PSP 6022 matrix reinforced laminates have mechanical performances as high as epoxy laminates . Typical room temperature interlaminar shear strength is 90 MPa to 100 MPa for unidirectional carbon PSP 6022 composites and is only slightly affected by post cure. Cross plied and carbon or glass fabric reinforced laminates give also satisfactory values.

Thermomechanical properties

Very high levels of mechanical properties have been found, up to 400°C, with unidirectional carbon reinforcement, as measured after 15 min at the test temperature : flexural modulus does not change, flexural strength loss is 10 to 20 % at 350°C and 400°C and ILSS at 400°C is 40 % of the value at room temperature. Good values are also obtained with glass fabrics.

Thermal aging

Measurements have been made on test samples, in air at 250°C with unidirectional carbon T 300 reinforced PSP 6022. Loss of more than 20 % of shear strength at 20°C and 250°C begins to appear after 1000 hrs at 250°C, even for laminates cured at 200°C only, without post cure. It seems that thermooxidative stability of T 300 carbon fibers may have significant effect as measured on unimpregnated fibers.

Thermal and mechanical fatigue

It had been shown (1) that carbon reinforced PSP were not sensitive to cyclic thermal shocks (2000 cycles of 5 min 225°C/20°C).

Mechanical fatigue resistance has been examined on unidirectional T 300/PSP 6022 laminates, with a flexural 3 points pulsated bending test at 25 Hz at 60 % of the ultimate flexural strength (0.9 % strain). Flexural strength and modulus remain unchanged after 10^7 cycles (there was about 10 % loss on a T 300/epoxy laminate properties tested for comparison).

Moisture resistance

The extraordinaty moisture resistance of carbon/PSP laminates, previously reported for HTS/PSP 6030 (1), has been confirmed on carbon T300/PSP 6022 unidirectional laminates ; there is only a slight loss of interlaminar shear strength at 200°C after 1000 hrs in boiling water on laminates cured in autoclave at no more than 225°C, with no post cure . Moisture pick up is 0.7 % after 100 hrs immersion in boiling water (8 hrs 200°C curing, 16 hrs post cure at 225°C) and 0.6 % after 750 hrs at 75°C and 95 % relative humididy (8 hrs 200°C curing, 8 hrs 250°C post curing).

.../...

Flammability properties

They have been measured on selected material composites of PSP 6022 resin and various reinforcements, and have been previously reported (2) (3) (5) :

Resistance to combusion has been determined by LOI, the limiting oxygen idex, wich is the minimum oxygen concentration required to support flamingcombustion. LOI of neat cured resin in ASTM-D 2863-70 test conditions is 26 %, and LOI of various reinforced PSP 6022 laminates are on less than 1 mm tickness ≥ 60 % vol fabric/PSP 6022 laminates , about 40 % with Kevlar, 70 % with carbon and 100 % with E glass (sizing A 1100).

The smoke generation properties have been determined in an NBS chamber (2) and a similar apparatus with a radiant heating of 2.5 W/cm2 (5) Glass and carbon reinforced PSP 6022 give impressive performances in terms of very low smoke emission in both flaming and non flaming conditions.

The toxicity of smoke gases emitted from glass reinforced PSP resins has been found expecially low by measurement of gas composition in NBS chamber (2) and stated as apparent lethal concentration 50 by pyrolysis of glass reinforced laminates (2).

Energy released from PSP 6022 reinforced laminates exposed to radiant energy levels of about 5 W/cm2 have been found very low, speciallywith carbon reinforcement (5).

Protection against flame had been also evaluted under severe conditions, with a plasma gun exposure at about 1800°C (0.5 kw/cm2) during 0.5 min on glass fabric reinforced PSP resin or at about 3000°C (2 kw/cm2 gas speed Mach 0.2-0.3) during 2 min, on Genin Thermoproof fabric/PSP laminate : PSP matrix appeared more performant than other resins in the same conditions (3).

Electromagnetical properties

The thermostructural and electromagnetical performances of glass reinforced PSP 6022 radomes have also been demonstrated at temperatures up to 400°C (7) : dielectrical constant is about 4.5 with E glass and less tangent is less than 2.10^{-2} from 20°C to 400°C.

4.2 - Resin batches controls

Both of the 6022 M batches used for the task and the 6024 batch have been controlled by making carbon T 300 unidirectional reinforced laminates, checking shear strength at room temperature and 300°C, after 8 hrs curing at 200°C (IRCA -1 cure cycle) and 16 hrs post cure at 250°C usual data have been obtained:

ILSS $\geqslant$ 90 MPa at 20°C
$\geqslant$ 50 MPa at 300°C

One of the PSP 6022 M resin batches (LDG 593) has been extensively evaluated in different US and european laboratories , with an industrial prepreg from SNPE, T300-6K reinforced. Some of the results are reported in table 1.

The incidence of silica gel on laminate properties has also been checked with the same LDG 591/593 PSP 6022 M batch : it does not appear any significant modification on room temperature shear strength resistance and flexural properties. It is usually preferred to have 1 % silica gel for unidirectional prepregs, to prevent too much flow during cure cycle (all published results on unidirectional laminates have been obtained like that)

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TABLE 1

Thermomechanical properties
of unidirectional carbon T 300/PSP 6022 M laminates.

CURING CONDITIONS POST CURING	MUCA-1 CURE CYCLE 16 HRS - 250°C			IRCA-1 CURE CYCLE 16 HRS - 260°C			IRCA-1 CURE CYCLE 8 HRS 250°C	IRCA-1 CURE CYCLE 16 HRS 250°C
TEMPERATURE	FLEXURAL Strength (MPa)	FLEXURAL Modulus (GPa)	I.L.S.S. (MPa)	FLEXURAL Strength (MPa)	FLEXURAL Modulus (GPa)	I.L.S.S. (MPa)	I.L.S.S. (MPa)	I.L.S.S.* (MPa)
20°C	1500	120	90	2000	178	84	90	103
150°C	1400	120	75	-	-	-	73	-
250°C/260°C	1150	120	62	2100	198	61	61	75
300°C	-	-	-	-	-	-	51	70
400°C	1150	115	40	-	-	-	-	-

NOTA : Laminates made in 3 laboratories with the same batch of prepreg from S.N.P.E. E 311

T 300-6000/PSP 6022 M - Batch prepreg = E 331 - Nominal Thickness 0.125 mm
Batch resin = LDG 593.

But (*) : made with T 300-3000 ans PSP 6022 M, batch LDG 856.

4.3 - Preliminary Carbon fabric /PSP 6022 M curing study

A preliminary study was done to know the effect of some parameters on carbon fabric/PSP 6022 Mlaminates . Detailed r'esults are reported in tables 2 to 5 ; The same batch of PSP 6022 M(LDG 593) has been used for this task

- Table 2 : effect of prepreg resin content, with W 133 fabric and PSP 6022 M (40 %, 47.5 %, 55 %) on shear strength and flexural properties of laminates cured in the same conditions (bag molding at 200°C 4 hrs post cure at 250°C). Probably due to the flow, there is no significant effect in these conditions.

- Table 3 : effect of dwell time before pressure applied (90 min to 165 min), on shear strength and flexural properties of Genin 43377 T 300 fabric/PSP 6022 M, with the same curing and post cure that previously . There also, probably due to the flow, no significant differences appear.

- Table 4 : effect of dwell time before pressure applied (75 min to 105 min) on shear strength of W 133/PSP 6022 M laminates, with the same curing but 2 different post cure conditions. It is not easy to conclude, with highly dispersed values, but it seems that 16 hrs at 225°C post cure give higher ILSS than 4 hrs at 250°C.

- Table 5 : effect of fabric type and supplier on shear strength and flexural properties of PSP 6022 M laminates at room temperature and 250°C with the same curing and post-cure conditios.

Three fabrics have been evaluated all with T 300 - 3 K fiber :

- Fiberite W 133 : 8 Harness satin, 366 g/m2
- Stevens Genin 40830 : 8 Harness satin, 339 g/m2
- Stevens Genin 43377 : 5 Harness satin, 290 g/m2

It seems that Genin 40830 fives slightly higher performances, and that W 133 and Genin 43377, though of different styles, give the same flexural properties, with higher ILSS obtained with Genin 43377. These differences have not been noted with an SNPE epoxy system.

- TABLE 2 -

Carbon fabric satin 8 (Fiberite W 133
366 g/m2)

Values at room temperature

Effect of resin content in prepreg

PSP 6022 M W 133 fabric

- 6 plies - cure 8 hrs 200°C
- hold 90 mn before pressure
- P.C. 4 hrs at 250°C

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Resin content in prepreg (% wt)	Average tickness (mm)	Resin content in laminate (calculated from tickness) (% wt)	I.L.S.S. Lowest / Highest	I.L.S.S. Average (MPa)	Flexural Strength Lowest / Highest	Flexural Strength Average (MPa)	Flexural modulus (MPa)
40	1.912	25.2	23.6 / 27.7	26.3	472 / 522	502	61.600
	1.936	25.9	24.6 / 27.5	26.1	487 / 517	505	47,160
47,5	1.932	25.8	24.7 / 30.3	26.8	471 / 600	531	53,010
	1.920	25.4	24.1 / 28.0	26.2	471 / 516	494	59,050
55	1.948	26.2	23.9 / 32.9	27.0	539 / 647	581	61,160
	1.914	25.2	21.2 / 33.3	26.7	472 / 509	489	61,500

D.c./40

* Batch LDG 593.

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Table 3

Effect of dwell time
PSP 6022 M* graphite fabric

Carbon fabric satin 5 (Genin 43377, 290 g/m2)

- Prepreg 47,5 % not resin
- 8 plies - Cure 8 hrs 200°C
- P.C. 4 hrs 250°C

Values at room temperature

dwell time before pressure application (min)	Average thickness (mm)	Resin content (calculated from thickness (% wt)	Experimental	I.L.S.S. (MPa) Lowest / Highest	I.L.S.S. Average	Flexural strength (MPa) Lowest / Highest	Flexural strength Average	Flexural Modulus (MPa)
90	2.01	25.0		28.0 / 29.8	29.0	480 / 628	550	53 900
105	2.01	25.0		25.6 / 32.8	29.4	480 / 539	510	54800
120	2,04	25.8		27.7 / 30.9	28.4	470 / 578	540	56000
150	2.10	27.4	29.1	27.5 / 31.9	29.6	481 / 775	647	58400
165	2.18	29.4	33.5	26.8 / 32.4	29.5	510 / 598	540	55400

* Assuming porosity is nil. * Batch LDC 593

- **TABLE 4** -

Effect of dwell time
PSP 6022 M*/W 133 fabric

Carbon fabric satin 8 (Fiberite W 133 366 g/m2)

- prepreg 47.5 % wt resin
- 6 plies - cure 8 hrs 200°C

Values at room temperature

Dwell time before pressure (min)	Average Thickness (mm)	Resin content (a) (% wt)	I.L.S.S (MPa) lowest highest	I.L.S.S (MPa) Average	I.L.S.S. (MPa) lowest highest	I.L.S.S. (MPa) Average
75	1.92	25.4	23.8 23.0	28.6	23.7 37.1	31.7
	1.89	24.6	22.8 33.9	26.8	24.2 32.7	28.5
90	1.90	24.9	26.2 33.9	30.0	22.0 35.0	30.7
	1.86	23.7	24.0 32.8	28.6	29.0 36.2	33.4
	1.90	24.9	22.3 27.6	25.5	19.6 36.4	27.5
	1.93	25.7	32.9 35.9	34.5	31.2 40.2	35.7
105	1.96	26.6	26.5 35.7	31.6	25.9 38.6	32.3
	1.93	25.7	24.7 32.5	27.9	20.3 35.0	27.8

* Batch LDG 593

(a) Calculated from thickness, assuming porosity is nil.

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- TABLE 5 -

Effect of fabric
PSP 6022 M */carbon fabric

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W 133 : satin 8, 366 g/m2
40830 : satin 8, 339 g/m2
43377 : satin 5, 290 g/m2

- Cure 8 hrs 200°C, pressure after 90 min, post cure 4 hrs at 250°C.
- Fiber content, volume 65-66 %.

FABRIC	THICKNESS (mm)	At room temperature			At 250°C		
		I.L.S.S. (MPa)	Flexural strength (MPa)	Flexural modulus (GPa)	I.L.S.S. (MPa)	Flexural Strength (MPa)	Flexural modulus (GPa)
Fiberite W 133 (6 ply)	1.93	24.7 30.3 26.8	471 600 531	53.0	25.7 29.5 27.7	426 484 451	52.7 56.0 53.8
Genin 40830 (7 ply)	2.06	26.8 33.0 30.0	550 677 608	60.1	28.2 30.5 29.1	423 496 451	59.8 63.5 61.3
Genin 43377 (8 ply)	2.01	28.0 29.8 29.0	480 628 549	53.9	28.8 31.0 29.6	457 509 480	55.4 58.9 57.8

* Batch LDG 593.

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4.4 - Fabrication and characterization of W 133/PSP 6022 M laminates (4)

All laminates have been cured in autoclave, from 1 m by 0.3 m cut W 133. T 300 fabric impregnated as described in item 2.2. There were 2 panels, 10 ply, 1 m by 0.3 m cured at the same time in the autoclave, referenced A et B, and panels were cutted each in 3 part 0.3 m by 0.3 m referenced 1,2,3.

4.4.1. - Material identification

References of panels, lots of W 133 fabric and of PSP 6022 M or PSP 6024 M resins, is given in table 6.

4.4.2. - Curing schedule

It was asked to cure at no more than 200°C . Lay-up procedure is detailed in item 3.3.1. example 2. Curing conditions are those described in item 3.3.2. : "curing at 200°C - example 2 - 1105-2 cure cycle". Initial curing time at 200°C and 1 MPa was only 8 hours and not 16 hours as in 1105-2 cure cycle and attempts were made to use post cure at 225°C or 250°C, but it appeared better to have longer cure at 200°C. Cure schedules used for this task are described in table 7 and cure history at 200°C for referenced panels is reported in table 6.

(4) - Subcontracted to Composites Horizons.

- TABLE 6 -

MATERIAL IDENTIFICATION FOR NASW-3251 DELIVERY

Panel No.	W133 Graphite Fabric lot No./Roll No.	PSP Resin Lot No.	Hours at 200°C
7A - 1,2,3	376/53	6022M LDG593	9
7B - 1	376/53	6024M LDG673	9
8A - 1,2,3	376/53	6022M LDG593	8.75
8B - 1,2,3	376/53	6024M LDG673	8.75
9A - 1,2,3	376/53	6024M LDG673	16
9B - 1,2,3	376/53	6024M LDG673	16
10A - 1,2,3	376/53	6024M LDG673	11
10B - 1,2,3	376/53	6024M LDG673	11
11A - 1,2,3	376/53	6022M LDG593	10.5
11B - 1,2,3	376/53	6024M LDG673	10.5
12A - 1,2,3	376/53	6022M LDG593	13
12B - 1,2,3	376/53	6022M LDG647	13
13A - 1,2,3	376/53 et 376/53A	6022M LDG647	14
14A - 1,2,3	476/35	6022M LDG647	14
14B - 1,2,3	476/35	6024M LDG673	15
15A - 1,2,3	476/35	6022M LDG647	15

- TABLE 7 -

CURE SCHEDULE FOR PSP 6022 M et 6024 M LAMINATES

FOR NASW - 3251 DELIVERY

NOTA : - impregnation procedure described in item 2.2.
- lay-up procedure described in item 3.3.1. example 2.

Initial cure schedule

- After vacuum system and lay-up in autoclave have been determined to be leak-free, reduce vacuum on part to 76 mm Hg
- Heat-up autoclave to 163°C using 1.5 to 2°C min. heat rise
- When part reaches 163°C ± 3°C, dwell for 90 minutes
- Increase part temperature to 176°C using 1.5 to 2°C min heat rise
- Dwell at part temperature of 176°C ± 3°C for 15 min
- Increase part temperature to 200°C using 2°C/min heat rise
- Dwell at part temperature of 200°C ± 3°C for 15 min
- Apply 635 mm Hg (minimum) to part and dwell for 5 min
- Add pressure at a rate of 70 kPa /min to 1 MPa
- Cure at 200°C and 1 MPa for 8 hours.

Modified cure schedule

Cure has been made at 200°C so that cure history of panels appears as reported in table 6, with time at 200°C and 1 MPa between 8 hours and 16 hours.

Post cure

First experiments have been made with the initial cure schedule and post cure, either 8 hours at 225°C or 4 hours at 250°C. For panels delivery (ref. 7 to 16) there was no post cure.

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4.4.3. - Testing Conditions

All mechanical testing is done on an Instron Universal Testing Machine. The testing includes short beam shear and flexural at room temperature and 232°C (after 30 min. soar) before and after humidity conditioning (exposing samples to 95-100 % humidity at 82°C until a constant weight is obtained). Schematics for both short beam shear and flexural test are shown in figures 7 and 8 resp. cross head speeds are 1.27 mm/min for shear and 2.54 mm/min for flexurals. All specimen lengths are cut in the warp fiber direction. Note that shears are tested at 4.1 span to depth ratio and flexes are tested at 32.' span to depth ratio.

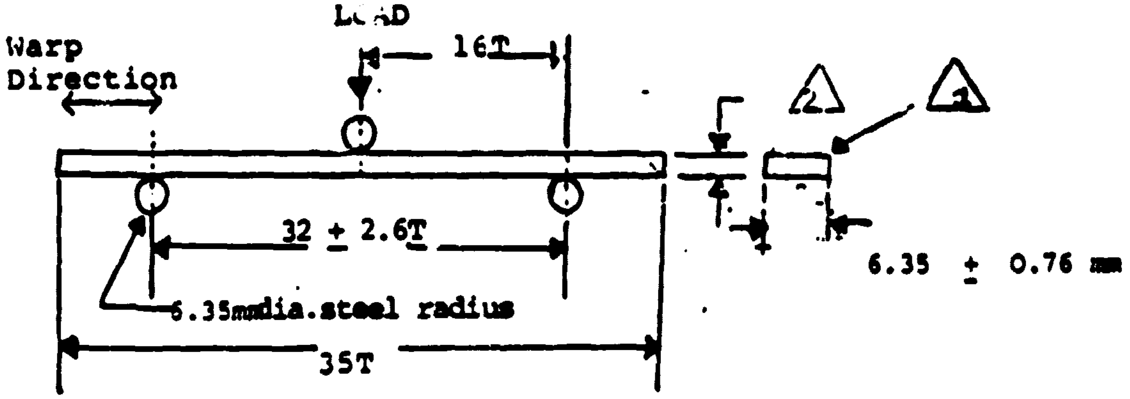
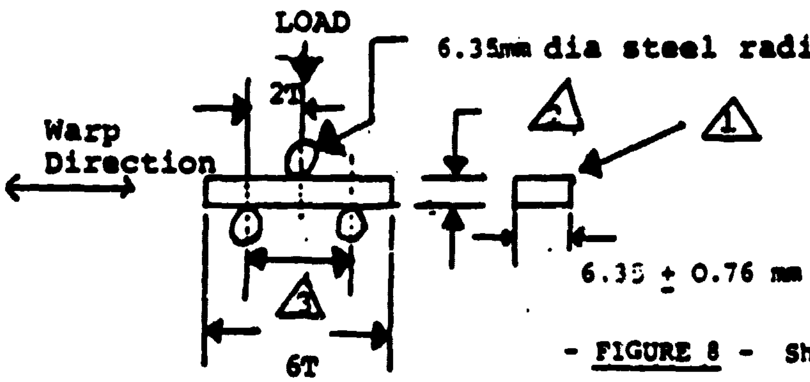


Figure 7: Flexural Test Specimens



- FIGURE 8 - Short Beam Test Specimens.

NOTES : Figures 7 and 8.

1. Specimen edges shall be parallel within 0.127 mm
2. Specimen thickness shall not vary more than ± 0.076 mm
3. Span of supports will be 4(± 0.3) T, short beam shear
4. Span of supports will be 32 (± 2.6) T, flexure.

4.4.4. - Laminate properties - Preliminary tests

First experiments have been made with the cure schedule with 8 hours at 200°C and 1 MPa, with the PSP 6022 M resin, batch LDG 593.

Laminates have been evaluated at 20°C and 200°C, without post cure and after post cure 8 hrs at 225°C or 4 hrs at 250°C. Data are reported in table 8.

- TABLE 8 -

PRELIMINARY TEST DATA ON W 133/PSP 6022 M LAMINATES FOR NASW-3251 DELIVERY.

POST CURE	TEST CONDITIONS	SHORT BEAM SHEAR (MPa)	FLEX. STRENGTH (MPa)	FLEX.MODULUS (GPa)
No post cure	20°C 200°C	28.7 29.5	660 479	46.7 43.7
8 hrs - 225°C	20°C 200°C	22,6 29,2	507 516	45.0 43.4
4 hrs - 250°C	20°C 200°C	21.3 26,2	457 550	43,2 44,1

Photomicropraphs show no void and there is no microcrack after cure 8 hrs at 200°C, but microcracks appear after 8 hrs at 225°C or 4 hrs at 250°C post cure , so that longer cure at no more than 200°C was decided , with no post cure.

4.4.5. - Laminate thermomechanical properties for NASA delivery

Tests as described in fig 7 et 8, have been runned on threee W133/PSP 6022 M panels and three W133/PSP 6024 M panels, at room temperature and 232°C. Date are reported in table 9.

- TABLE 9 -

TEST DATA ON W 133/PSP 6022 ET 6024 LAMINATES FOR SHIPMENT TO NASA.

Panel No	Cure (hours at 200°C)	test temperature (°C)	Short Beam Shear (MPa)	Flex strength (MPa)	Flex modulus (GPa)
PSP 6022 M 07 - AS	9 hrs	20°C 232°C	34.0 28.0	654.5 227.0	46.9 36.8
PSP 6022 M 08 - AS	8,75 hrs	20°C 232°C	32.1 23.3	547.0 390.5	48.7 46.4
PSP 6022 M 13 - AS	14 hrs	20°C 232°C	28.0 23.2	649 338	49.9 46.7
PSP 6024 M 08 - AS	8,75 hrs	20°C 232°C	32.4 23.4	662.0 442.0	48.7 45.0
PSP 6024 M 11 - BS	10 hrs	20°C 232°C	27.3 28.8	521 463	50.3 49.6
PSP 6024 M 09	16 hrs	20°C 232°C	30.4 25.8	625 441	51.2 47.4

4.4.6. - Moisture resistance

Moisture resistance has been examined after humidity conditioning, exposing shear and flex specimens to 95 - 100 % humidity at 82°C, in a sealed container over water, until a constant weight is obtained. With PSP 6022 M and PSP 6024 M this test has been runned during 30 days.

Data are reported in table 10, and compared to initial values, at room temperature and 232°C.

It is confirmed that PSP laminates have a very good moisture resistance, in such a test where moisture pick up of the best epoxy laminates would be twice or three times higher. There are little changes in R.T. short beam or flexural properties , but these properties decrease at 232°C as follows ; for both PSP 6022 Met PSP 6024 M laminates, depending on curing conditions (9 hrs at 200°C to 14 hrs at 200°C) :

- short beam shear : - 38 % to - 50 %
- flexural strength : - 25 % to - 54 %
- flexural modulus : - 8 % to - 21 %

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MOISTURE RESISTANCE OF W133/PSP 6022 ET PSP 6024 LAMINATES TO NASW-3251 DELIVERY.

Panel No	Cure (hours at 200°C)	Test temperature	Before humidity aging			After 30 days - 82°C - 95 % RH.			
			Short beam Shear (MPa)	Flex.Strength (MPa)	Flex.Modulus (MPa)	Weight Gain	Short Beam Shear (MPa)	Flex. Strength (MPa)	Flex. modulus (MPa)
PSP 6022 M 07 - AS	9 hrs	20°C	34.0	654.5	46.9	1.37 %	31.1	714.9	48.1
		232°C	18.0	227.0	36.8		9.0	141.5	29.0
PSP 6022 M 13 - AS	14 hrs	20°C	28.0	649	49.9	1.27 %	29.2	649.9	51.3
		232°C	23.2	338	46.7		14.5	251.5	41.4
PSP 6024 M 08 - BS	8,75 hrs	20°C	32.4	662.0	48.7	1,17 %	30.7	699.2	49.9
		232°C	23.4	442.0	45.0		13.9	203.3	39.9
PSP 6024 M 11 - BS	10,5hrs	20°C	27.3	521	50.3	1,35 %	29.5	583.3	51.1
		232°C	28.8	463	49.6		17.8	339.0	45.4

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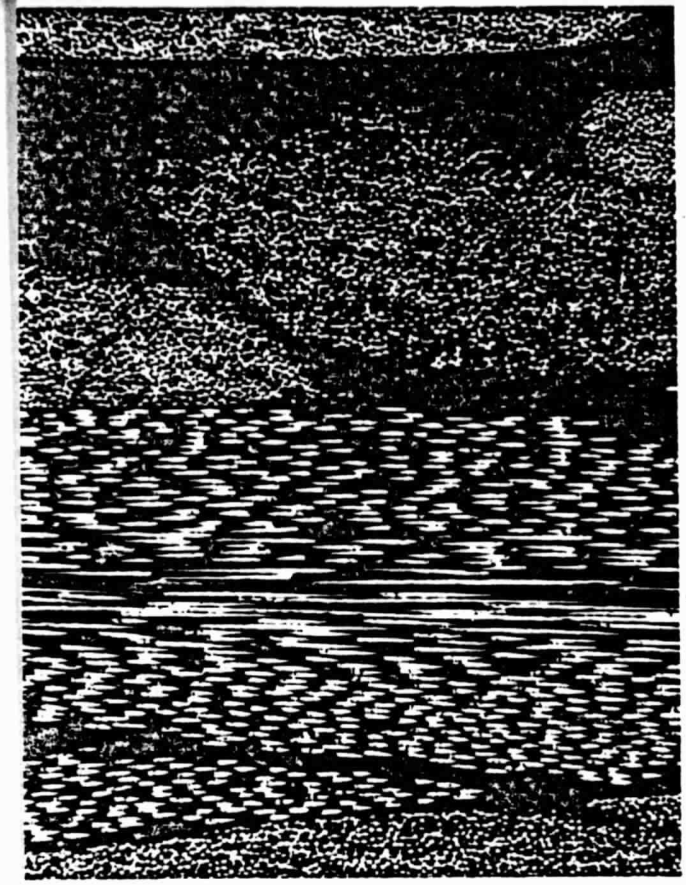
4.4.7. - Microphotographs

Enclosed are 4 photo-micrographs from separate panels two W133/PSP 6022 M and two W133/PSP 6024 M panels, which represente an area that was judged to be typical after examining a sample which ranged from 150 mm to 250 mm in length. Magnification is 150 X.

In examining these photo-micrographs it can be noted the absence of voids of either the interlaminer or intralaminer type. Estimated void content range from 0 % to 0.25 %, based on metallographic study. (When a void is observed, it usually is round and has a diameter similar to a fiber).

Most of the microcracking in the panels is transverse to the plies. Usually one or both ends of microcrack terminate in a fiber bundle.

It can be noted the presence of large resin pools between the fiber bundles. These result from the tows being held in place in the fabric. At points removed from the vicinity of these interstices, the tows are not held so rigidly, and therefore, the fibers have a chance to spread resulting in a better distribution of fibers in the resin. The photos are marked with arrows to indicate ply interfaces.



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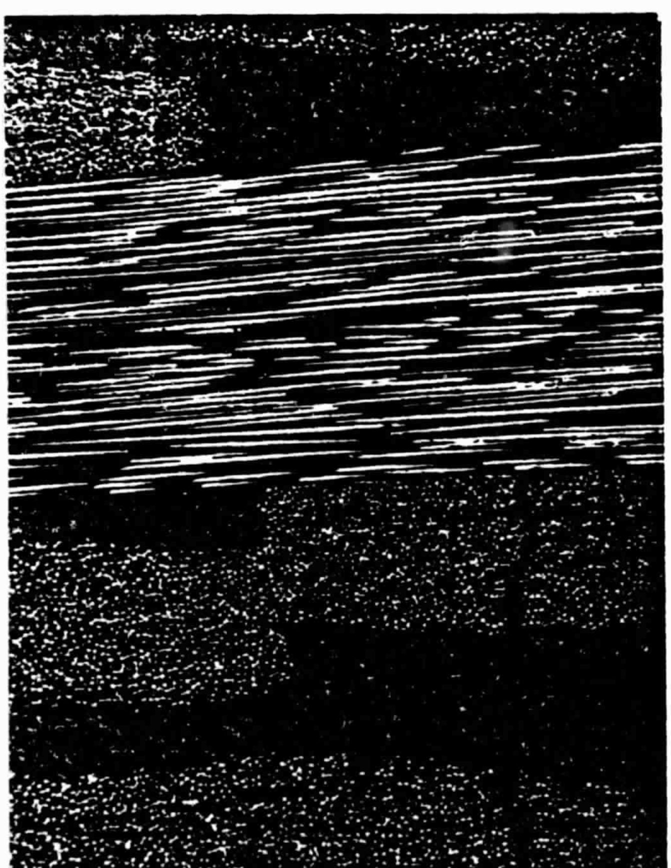

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4.4.8. - Laminates delivery to NASA

16 panels W133/6024 M and 13 panels W133/6022 M have been delivered from Composites Horizons to NASA Ames Research Center, on September 8 th, 1980.

4 panels W133/6024 M and 8 panels W133/6024 M have been delivered at the beginning of October 1980.

Material identification and curing condition of these panels have been reported in table 6.

4.5 - Conclusion

PSP 6022 M and PSP 6024 M reinforced with 8 Harness satin T300-3000 woven fabric have high thermomechanical performances, at least until 232°C, and very good moisture resistance, even with such cure conditions at no more than 200°C, which is quite unusual for thermostable resins.

It was the first time that carbon woven fabric was used as a reinforcement for PSP 6022 Mor PSP 6024 M resin and cure conditions were probably not yet fully optimized. Same work has been done after this task and it appears that much higher properties may be attained at room temperature, as good as with the best epoxy systems, but they are lowered after post cure in the same time as the 200°C and 250°C performances are entranced , so that an adjustement night have to be found depending on thermal performance expected. Some recent data are reported in table 11 and table 12.

PSP 6022 appear to be very high performance resins of use as matrix of reinforced composite materials ; high mechanical properties very high thermomechanical caracteristics up to 400°C and good thermo-stability at 250°C are similar to those of the best polyimide reinforced materials, moisture resistance is outstanding , and very good flame resistance, low smoke emission and very low toxicity of pyrolysis products are some of the most important benefits of the PSP systems, which can be attained with low temperature cure conditions (cure at no more than 200°C).

- TABLE 11 -

TEST DATA ON WOVEN T300/6022 M

MECHANICAL PROPERTIES.

Fabric Type	Genin 40830 8 Harness Satin	Genin 43377 5 Harness Satin
Cure	8 hrs 200°C 0.5 MPa after 90 min	5 hrs 200°C 0.7 MPa after 50 min
Flexural Strength (MPa)	860	830
Flexural modulus (GPa)	59	-
Shear Strength (MPa)	60	55

- TABLE 12 -

TEST DATA ON WOVEN T300/6022 M

THERMOMECHANICAL PROPERTIES.

WOVEN T300 used : Genin 43377 (5 Harness Satin, 290 g/m2)

Cure schedule : 8 hrs at 200°C in bag 0.5 MPa pressure added after 120 min, without vacuum in the bag.

	Short Beam (MPa)		
Temperature of the test	20°C	200°C	250°C
Without post cure	59	17	5
With post cure			
- 4 hrs at 210°C	57	28	15
- 4 hrs at 220°C	50	-	-
- 4 hrs at 230°C	45	43	29
- 4 hrs at 240°C	41	42	31
- 4 hrs at 250°C	29	36	36
- 16 hrs at 250°C	25	-	-

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Au Bouchet, le 18/02/1981

M.B. MALASSINE