1. INTRODUCTION

Bismaleimides are being used increasingly as high-temperature matrix resins for graphite fiber-reinforced composites. The monomers are cured by a thermally induced addition reaction to give highly crosslinked, void-free network polymers having good physical properties with high char yield, and higher thermal stability, better fire resistance, and lower water absorption than state-of-the-art epoxy systems.(1) However, there are problems with maleimide polymers, such as solvent retention in the prepregs, and high temperature often required for curing,(2) and brittleness of the polymers due to the high crosslink density obtained in network polymers. Recently, Technochemie GmbH-Verfahrestechnik developed a "hot-melt" solventless bismaleimide-type resin (H795)(3) to overcome the solvent retention problem, but this resin cures at a high temperature.

It is well known that vinyl monomers (such as styrene and divinylbenzene) readily copolymerize with maleimide double bonds at rather low temperatures (120-150°C). Vinyl monomers and a wide variety of vinylterminated oligomers are expected to act as reactive diluents or comonomers for bismaleimide resins. However, ordinary vinyl monomers would cause difficulties due to volatile losses and microvoid formation. If the vinyl linkage is in an aliphatic structure, the high-temperature performance of the modified maleimide polymer could be significantly decreased by depolymerization

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Development of New and Improved Polymer Matrix Resin Systems (Phase I)

M. S. Hsu

Prepared for
Ames Research Center
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National Aeronautics and
Space Administration

Ames Research Center
Moffett Field, California 94035

HC Chem Research & Service, Corp.

Report No. 1001

DEVELOPMENT OF NEW AND IMPROVED POLYMER MATRIX RESIN SYSTEMS (PHASE I)

FINAL REPORT

by

Ming-ta S. Hsu

Contract No. NAS2-11529

To: NASA Ames Research Center
Chemical Research Projects Office
Moffett Field, CA 94035
Technical Monitor: Dr. A. H. Heimbuch

December 1982 - December 1983

FOREWORD

This Phase I final report covers the work performed under NAS2-11529 from the period December 20, 1982 to December 19, 1983. Dr. Alvin H. Heimbuch at NASA Ames Research Center was the Project Monitor. Dr. Ming-ta S. Hsu of HC Chem Research & Service, Corp. was the Program Manager and Principal Investigator. Support activity was provided by Dr. Timothy S. Chen and David R. Liu.

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ABSTRACT

Vinylstilbazole (vinylstyrylpyridine) and vinylpolystyrylpyridine were prepared for the purpose of modifying bismaleimide composite resins. Cure studies of resin systems were investigated by differential scanning calorimetry. The vinylstyrylpyridine-modified bismaleimide composite resins were found to have lower cure and gel temperatures, and shorter cure times than the corresponding unmodified composite resins. The resin systems were reinforced with commercially available satin-weave carbon cloth. Prepregs were fabricated by solvent or hot melt techniques. Thermal stability, flammability, moisture absorption, and mechanical properties of the composites (such as flexural strength, modulus, tensile and short beam shear strength) were determined. Composite laminates showed substantial improvements in both processability and mechanical properties compared to the bismaleimide control systems.

The vinylstyrylpyridine modified bismaleimide resins can be used as advanced matrix resins for graphite secondary structures where ease of processing, fireworthiness and high temperature stability are required for aerospace applications.

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1. INTRODUCTION

Bismaleimides are being used increasingly as high-temperature matrix resins for graphite fiber-reinforced composites. The monomers are cured by a thermally induced addition reaction to give highly crosslinked, void-free network polymers having good physical properties with high char yield, and higher thermal stability, better fire resistance, and lower water absorption than state-of-the-art epoxy systems.(1) However, there are problems with maleimide polymers, such as solvent retention in the prepregs, and high temperature often required for curing,(2) and brittleness of the polymers due to the high crosslink density obtained in network polymers. Recently, Technochemie GmbH-Verfahrestechnik developed a "hot-melt" solventless bismaleimide-type resin (H795)(3) to overcome the solvent retention problem, but this resin cures at a high temperature.

It is well known that vinyl monomers (such as styrene and divinylbenzene) readily copolymerize with maleimide double bonds at rather low temperatures (120-150°C). Vinyl monomers and a wide variety of vinylterminated oligomers are expected to act as reactive diluents or comonomers for bismaleimide resins. However, ordinary vinyl monomers would cause difficulties due to volatile losses and microvoid formation. If the vinyl linkage is in an aliphatic structure, the high-temperature performance of the modified maleimide polymer could be significantly decreased by depolymerization and scission, thereby limiting the high temperature stability and reducing anaerobic char yield, and the flame-resistance.

It has been shown that graphite composites formulated from polystyrylpyridine matrix resins obtained from the condensation reaction of collidine and aromatic dialdehydes exhibit excellent fire resistance and high temperature stability.(4) Unfortunately, because the condensation curing reaction evolves water, void-free composites are difficult to obtain. Also, curing temperatures in excess of 250°C are required. At such high temperature, the matrix resin is stabilized by the presence and persistence of the vinylene double bond in the stilbazole moiety.

From model compound studies,(5) it appears that at temperatures in excess of 300°C the stilbazole group reacts in situ to give a highly crosslinked ring system, characterized by a char yield of 70% at 600-800°C in nitrogen. Advantage has been taken of these special thermal properties of the vinylene double bond in the design and synthesis of vinylstilbazole (VST) and vinylpolystyrylpyridine (VPSP) oligomers.

HC Chem Research & Service, Corp. has synthesized a vinyl terminated polystyrylpyridine (VPSP) and vinyl stilbazole (VST) by incorporating 5-vinyl-2-methyl pyridine with collidine and terephthaldicarboxaldehyde, or by reacting 5-vinyl-2-methyl pyridine with benzaldehyde. Preliminary data indicated that the reaction product of VST and H795 has shown significant improvements on processibility.

The objectives of this contract are:

(1) To study and improve the synthesis of vinylstilbazole (VST) and vinylpolystyrylpyridine (VPSP).

(2) To process these materials together with H795 and to evaluate the ability of these materials to form prepregs.

(3) To develop and evaluate the graphite composite panels, prepared with VST/VPSP and H795 in different ratios.

(4) To develop a light weight face sheet made with vinylstyrylpyridine modified bismaleimide resin for fire resistant sandwich aircraft interior panel.

2. SYNTHESIS AND CHARACTERIZATION OF VINYLSTYRYLPYRIDINE OLIGOMERS

2.1. Synthesis of Vinylstilbazole (VST).

Vinylstilbazole, or vinylstyrylpyridine, was synthesized by the condensation reaction of benzaldehyde and 2-methyl-5-vinylpyridine (MVP) in the presence of acetic acid and acetic anhydride at 100-120°C. (Fig. 1). 5-vinyl-2-methyl pyridine is an unstable compound. A series of experiments have been carried out to study the stability and reactivity of 5-vinyl-2-methyl pyridine under different reaction conditions. It was found that 5-vinyl-2-methyl pyridine polymerized rapidly through its double bond at temperature above 140°C, therefore prolong heating at temperature at 140°C would result a lot of poly-5-vinyl-2-methyl pyridine and reduce the yield of vinyl-stilbazole. On the other hand, if reaction temperature was below 100°C, most of the 5-vinyl-2-methyl pyridine did not react with benzaldehyde and the yield of vinyl-stilbazole was reduced with too much unreacted starting materials.

A typical reaction for synthesis of vinyl-stilbazole was carried out as follows: (see flow chart in Fig. 2)

50.0g (0.42 mole) of 5-vinyl-2-methyl pyridine, 44.6g (0.42 mole) of benzaldehyde, 25.2g (0.42 mole) of acetic acid, and 42.9g (0.42 mole) of acetic anhydride were placed in a 1000 ml, 3-necked round-bottom flask equipped with a mechanical stirrer and reflux condenser. The flask was immersed in an oil bath with a temperature control unit. The reaction solution was deoxygenated by nitrogen for 30 min.. The reaction solution was heated to 110°C and held at this temperature for seventy-two hours The reaction solution was then allowed to cool to room temperature and poured into a large beaker containing 1000 ml of 10% sodium hydroxide solution. The mixture was stirred for half an hour and the aqueous layer was decanted. The brownish viscous product was washed several times with de-ionized water until the water layer tested neutral. All the water was then discarded by decantation and the product was dissolved in 400 ml tetrahydrofuran (THF). The THF filtrate was then poured into large quantity of de-ionized water to precipitate out vinyl-stilbazole. This purification was repeated at least three times. Finally the brownish product was dried in vacuum, weighed and transfered into a storage container with or without THF as solvent.

2.2. Characterization of Vinyl-stilbazole

The synthesized vinylstilbazole was a low melting solid which contained some oligomers of VST. The infrared spectrum (Fig. 3) and nuclear magnetic resonance spectrum (Fig. 4) of the synthesized vinylstilbazole (HC 202) showed that it also contained some acetate and aliphatic hydrogens, and trace amount of unreacted starting materials. The acetate was derived from the acetic acid-acetic anhydride as acetate salt which was hard to remove by washing with water and base. The aliphatic hydrogens probably were derived from the addition product of the vinyl group.(oligomers of VST)

The dried material was also analyzed with mass spectrometry by means of direct insertion probe. The total ion intensity versus temperature (or time) is shown in Fig. 5. The major product was vinylstilbazole at 3.3 min.. Mass spectrum of the major product is shown in Fig. 6. Minor products were dimer of vinylstilbazole (m/e 413, M-1) and adduct of vinylstilbazole and 5-vinyl-2-methyl pyridine (m/e 325, M-1). Trace amount of starting materials were present in the dried crude product. Pure vinylstilbazole was isolated from the crude product by column chromatography packed with silica gel and eluted with chloroform/hexane= 1/4 mixture. The isolated solid was then recrystallized from methanol-water to give a light yellow crystalline pure VST. witha m.p. of 60°C. IR and NMR of the pure VST are shown in Fig. 7 and 8 respectively.

2.3. Synthesis of Vinylpolystyrylpyridine

It was reported that vinylpolystyrylpyridine(VPSP) could be prepared by reacting collidine, terephthalaldehyde and 2-methyl-5-vinyl pyridine in the presence of acetic anhydride and acetic acid at a temperature of 115°C to 120°C for 24 hours.(6) The same one step procedure was attempted to make VPSP. The resulting VPSP was a solid which was not very soluble in THF and had a softening temperature above 120°C. A two step process for preparing VPSP oligomers was developed (Fig. 9) to give a better VPSP product. The first step was to synthesize prepolymer of polystyrylpyridine (PSP) by reacting collidine with terephthalaldehyde at 150-170°C for a short period of time. The second step was the reaction of PSP prepolymer with MVP at low temperature (100-120°C) to avoid polymerization of MVP starting material and VPSP product. The resulting VPSP is soluble in THF and melts (softens) at about 100°C. A typical reaction for synthesis of vinylpolystyrypyridine was carried out as follows:

18.0g (0.3 mole) of acetic acid, 30.6g (0.3 mole) of acetic anhydride, 20.1g (0.15 mole) of terephthaldehyde, and 12.1g (0.1 mole) of collidine were placed in a 500 ml, 3-necked round bottom flask equipped with a mechanical stirrer and a reflux condenser. After the reaction solution was deoxygenated, the flask was immersed in an oil bath and the reaction solution was heated at 150°C to 170°C for 4 to 6 hours. The reaction solution was cooled to room temperature and 17.9g (0.15 mole) of 5-vinyl-2-methyl pyridine was added. The solution was degassed again and heated to 100°-120°C for 48 hours. The reaction mixture was then poured into 10% NaOH solution. The brownish viscous product was washed with 10% NaOH solution, then with de-ionized water until the aquous layer tested neutral. All the water was decanted and the product was dissolved in THF and filtered. The filtrate was then poured into large quantity of de-ionized water to precipitate out VPSP. This purification was repeated several times. Finally the product was dried in vacuum and stored as dry solid or in THF.

2.4. Characterization of Vinylpolystyrylpyridine

Vinylpolystyrylpyridine (VPSP) oligomer was characterized by infrared (IR) and nuclear magnetic resonance (NMR) spectrometry. Fig. 10 shows the infrared spectrum of VPSP. The aromatic C-H stretching is at 3000-3100 cm^{-1}. The carbonyl absorptions at 1750 and 1700 cm^{-1} are for acetate and unreacted aldehyde, respectively. The C=C stretching is in the 1600 - 1660 cm^{-1} region. Methyl bending is at 1380 cm^{-1}.

Trans stilbazole double bond bending is at 970 cm^{-1}. Vinyl double bond bending is at 910 cm^{-1}. NMR spectrum of VPSP in chloroform is shown in Fig. 11. Unreacted aldehyde proton is at 9.9 ppm. The aromatic and internal olefinic protons are at 6.4 - 8 ppm. Vinyl protons are at 5 - 6 ppm. The peak at 4.6 ppm is due to the trace amount of water present in the sample. The region between 2 - 3 ppm is due to methyl group resonance of acetate and collidine. The peaks at 3.7 and 1.8 ppm are due to tetrahydrofuran which was present in the sample.

Molecular weight of VPSP samples were measured using a Water Associates Model 202 Gel Permeation Chromatograph (GPC). The experimental conditions were as follows: Solvent, tetrahydrofuran; temperature, ambient; column, DuPont PSM 60S; sample concentration, 1%; flow rate, 1 ml/min; detector, refractive index. Fig. 12 is the GPC curve for a typical VPSP sample. The weight average molecular weight (M_w) was 3500, the number average molecular weight (M_n) was 950 using polystyrene standard curve multiplied with a factor of 1.5. The factor of 1.5 was derived by using 1,6-distyrylpyridine and 1,4,6-tristyrylpyridine standards.

3. CHEMICAL AND PHYSICAL PROPERTIES OF VINYLSTYRYLPYRIDINE-MODIFIED BISMALEIMIDE

Two batches of hot-melt H795 bismaleimide were supplied by NASA-Ames. The first batch M1268 cures at a temperature of 240-280°C. The second batch KT-148 cures at a lower temperature of 200-240°C. The differential scanning calorimetry (DSC) of the two batches are shown in Fig. 13 and 14 respectively. H795-KT148 contains some solvent (toluene) and starts to melt at about 70°C. H795-M1268 melts at about 120°C.

3.1. Copolymerization of VST and H795

Both VST and VPSP were easily thermally copolymerized with the hot-melt bismaleimide H795 over a wide range of comonomer ratios. Typical thermal processes occurring during copolymerizations are shown in the differential scanning calorimeter traces for VST and H795-M1268 in Fig. 13. It can be seen that VST exhibits a DSC melting temperature of 40-70°C with a slow and weak exothermic curing reaction occurring over a temperature range of 160-240°C due to thermal polymerization of the vinyl double bond of VST. In separate thin film infrared studies, it was found that the stilbazole double bond does not participate in that reaction. However, polymerization of the latter double bond probably occurs at higher temperature as suggested by the mild exotherm above 320°C. The DSC for H795 shows an endothermic melting point around 120°C, and a DSC cure temperature of 261°C typical of aromatic bismaleimides. The higher the VST/H795 weight ratio, the lower is the cure temperature until the optimum 1:1 weight ratio is reached. It can be seen that the blend with a VST/H795 weight ratio 1:4 (mole ratio of 1:2) begins to melt around 50°C and then polymerizes rapidly at 166°C; a cure temperature some 100°C below that of H795 alone. When blend has a weight ratio of 3:7, the polymerization temperature decreases to 159°C which is probably the temperature for a reaction of the vinyl group with the maleimido group. Similar reductions in melting points and cure temperatures are seen with VST/H795-KT148 (Fig. 14). Different batches of VST may show slightly different but similar DSC cures for the copolymer.

3.2. Copolymerization of VPSP and H795

Typical copolymerization of VPSP and H795 are shown in the DSC traces for VPSP/H795-M1268 blends in Fig. 15. VPSP melts around 80-130°C, the exotherm peak around 180°C is due to the addition reaction of vinyl group. The VPSP/H795-M1268 mixture melted around 100°C and then polymerized between 160-280°C depending on the amount of VPSP in the mixture, the more the amount of VPSP in the mixture the lower the cure temperature. Vinyl content of VPSP was very important, the higher the vinyl content the lower the cure temperature for the copolymer. Similar DSC curves were observed for VPSP/H795KT148 blends as shown in Fig. 16.

3.3. Thermogravimetric Analysis of Cured Resins

Thermogravimetric analysis (TGA) of cured H795, VST/H795, and VPSP/H795 blends was carried out in nitrogen and in air at 10°C/min.. Typical

TGA curves in nitrogen and in air are shown in Fig. 17 and 18 respectively. All resins decomposition temperatures are the same in nitrogen and in air. There is no char in air at temperatures above 600°C for all the resins tested.

The results obtained from thermochemical-physical characterization of H795 and copolymers are compared in Table 1. In all the copolymer ratios investigated, the cure temperatures are significantly reduced below that for the bismaleimide itself, and are less than that typically obtained for aerospace grade epoxy resin. The anaerobic thermal stability is as good as that of bismaleimide alone, as indicated by polymer decomposition temperatures in excess of 420°C. As predicted from studies on other stilbazole polymers, the anaerobic char yields are significantly higher than those obtainable from aerospace grade epoxy resins. With the exception of the VST/H795 ratio of 3:7, all the char yields for the various copolymers are substantially greater than that for the H795 bismaleimide alone. It is likely that the copolymer with the 3:7 ratio has too low a crosslink density to achieve an optimum char yield.

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TABLE 1: THERMOCHEMICAL-PHYSICAL PROPERTIES OF BISMALEIMIDE AND COPOLYMERS

RESIN SYSTEM	CURE TEMPERATURE (DSC PEAK), °C	T_g, °C	PDT (N_2), °C	CHAR YIELD at 800°C, %
EPOXY (MY720-DDS)	255	250	300	30
BISMALEIMIDE (H795)	261	> 400	> 420	42
COPOLYMERS:				
VST:H795 = 1:9	205	380	> 420	42
VST:H795 = 1:4	166	380	> 420	43
VST:H795 = 3:7	159	380	> 420	36
VPSP:H795 = 1:9	223	> 400	> 420	43
VPSP:H795 = 1:4	211	> 400	> 420	50
VPSP:H795 = 3:7	195	> 400	> 420	55
VPSP:H795 = 2:3	175	> 400	> 420	56

H795 is H795 M1268

4. PREPREG AND LAMINATE PREPARATION

A prepreg can be prepared by hot-melt or wet method using THF as a solvent. Viscosity data for H795 and copolymers are shown in Table 2.

4.1. Prepreg Preparation

Our prepregs were prepared by coating graphite cloth (8 harness satin weave cloth) with a THF solution of the resin. The prepregs were dried in an air oven at 80°C for 20 min.. The prepreg should be stored at -10°C to 15°C. The resin content of the prepreg should be 35±5% and volatile content less than 5%.

4.2. Cure Study of Prepreg

Isothermal cure study of the dried prepregs was performed using a Du Pont 981 dynamic mechanical analyzer. Isothermal DMA curves are shown in Fig. 19 and 20, with stiffness (modulus) of the prepreg plotted as a function of time at different temperatures. It is seen that the copolymers cure at a lower temperature and for a shorter time than does the bismaleimide H795-M1268. Similar DMA curves are shown in Fig. 21 - 23 for H795KT148 and modified H795KT148 at different isothermal temperatures, once again H795KT148 cures at lower temperature and shorter time than H795M1268. The modified resins also cure at lower temperature and shorter time than the bismaleimide alone. The resin blend of VPSP and H795 with the weight ratio of 3to 7 is likely to be the selected matrix resin for advanced composite due to its high char yield in nitrogen. At the same isothermal temperature, the prepreg made

Table 2 VISCOSITY OF H795 AND COPOLYMERS

MATERIALS	MELTING POINT	VISCOSITY,cps
H795 M1268	100 - 120°C	400 - 500 at 120°C 400 - 500 after 1 hr at 120°C
H795 KT148	70 - 100	2500 - 3000 at 100°C
VST 1 part H795 M1268, 4 parts	70 - 100	11,000 at 105°C 32,000 after ½ hr at 105°C
VPSP, 3 parts H795 M1268, 7 parts	70 - 100	3000 at 100°C 9000 after ½ hr at 100°C
VST 3 parts H795 M1268, 4 parts THF 5 parts		10 - 50 at ambient
VPSP 3 parts H795 M1268, 7 parts THF 10 parts		10 - 50 at ambient
VPSP 3 parts H795 KT148, 7 parts THF 1 part		3000 - 5000 at 70°C 5000 - 10000 ½ hr at 70°C 10000 - 16000 1 hr at 70°C

with VPSP modified H795 (3:7) can be cured even faster than VST modified H795 (1:4) as shown in Fig. 22 and 23.

4.3. Laminate Preparation

The dried prepreg (4 or 9 plies) was stacked and pressed between aluminum plates covered with Teflon film. The laminate was then cured in a flat platen press at 200°C at a pressure of 75-100 psi for 3.5-4 hr. Postcure of the laminate was not performed. Typical laminate preparation is shown in the molding procedure for VPSP/H795 resin.

4.3.1. Molding Procedures

a. In a flat platen load material at room temperature, apply contact pressure and heat to 160°C.

b. After 20 min, at 160°C, heat to 180°C and apply 75 psi for 10 min.

c. Heat to 200°C and 100 psi for 4 hrs.

c. Cool under pressure.

4.4. DMA Analysis of the Cured Laminate

Modulus curves of VST, VPSP modified and unmodified bismaleimide laminates are compared with MY720/DDS epoxy system as shown in Fig. 24. The bismaleimide H795M1268 sample was not completely cured, as indicated by the modulus dip in the temperature range of 100-300°C. However, the cure was completed after this was heated to 300°C. (The cure was completed under the same conditions as those for the copolymers which showed no modulus dip in the DMA curves.) From Fig. 24, it appears that the glass transition temperature of bismaleimide and copolymers is above 380°C, or

130-150°C higher than the glass transition temperature (~250°C) of epoxy resin.

4.5. Mechanical and Physical Properties of the Laminate

The laminates were tested for a number of physical properties: short beam shear (ASTM D 2344-76), flexural strength (ASTM D 790-70), and tensile strength (ASTM D 638-68). The flammability tests were performed with a Stanton-Redcroft Flammability Unit and the LOI was determined according to ASTM D 2863-74. The results are shown in Table 3. The flammability (LOI) of the composites based on the copolymers is equal to or better than that of the bismaleimide alone. In Table 3, it is also seen that the copolymers give better mechanical properties than the bismaleimide alone. The superior mechanical properties of the copolymers are probably due to the completion of the crosslinking reaction and/or better control on crosslinking density. The values for water absorption amounts to 1% or less. It was found that a comparable epoxy-graphite composite usually gives 2-3% water absorption under similar conditions. One may expect substantial improvement in the hot wet strength of these composites. Mechanical properties of laminate composite made with H795KT148 and modified H795KT148 are shown in Table 4.

4.6. Rubber Toughening Study

Laminates using VST/H795 and VPSP/H795 resins modified with liquid rubber CTBN have been prepared. Some mechanical properties of the composites made from CTBN modified resins have been measured. The mechanical properties of the composites were improved slightly by adding CTBN in the resin matrix as shown in Table 5. Thermogravimetric analysis of cured

TABLE 3 MECHANICAL PROPERTIES OF VST, VPSP/H795 COPOLYMER COMPARED WITH H795 GRAPHITE COMPOSITES

PHYSICAL & MECHANICAL PROPERTIES	RESIN SYSTEM WITH 9 PLY SATIN-WEAVE GRAPHITE FIBER					
	H795	VPSP/H795 1:4	VST/H795 1:4	VPSP/H795 3:7	VST/H795 3:7	VPSP
RESIN CONTENT, %	30.5	26	30	30.2	31.5	26
DENSITY, g/cc	1.55	1.43	1.39	1.4	1.39	1.44
LOI (4 PLY SAMPLE)	52	62	46	55	45	57
WATER ABSORPTION, % 2 hr BOILING WATER	0.72	1.17	0.99	1.20	0.86	1.36
SHORT BEAM SHEAR R.T. N/mm^2(KSI)	11.7(1.7)	20.3(2.95)	20.4(2.96)	18.8(2.7)	19.9(2.89)	21.7(3.15)
R.T. FLEXURAL MODULUS, KN/mm^2(msi)	53 (7.7)	54.5(7.9)	50 (7.3)	51 (7.4)	51 (7.4)	42.4(7.6)
STRENGTH, N/mm^2(ksi)	166(24)	337.9(49)	317(46)	331 (48)	282(41)	337.9(49)
ENERGY, ft. lb	3.1	8.3	8.8	8.7	7.3	12
R.T. TENSIL STRENGTH, N/mm^2(ksi)	248(36)	344.8(50)	289.7(42)	386.2(56)	275.8(40)	406.9(59)
MODULUS, KN/mm^2(msi)	13.8(2.0)	15.2(2.2)	17.2(2.5)	16.6(2.4)	11.7(1.7)	15.9(2.3)
ELONGATION-YIELD, %	2.3	4.5	3.3	4.9	3.9	4.7

*H795 is H795M1268

Table 4 PHYSICAL AND MECHANICAL PROPERTIES OF BMI (H795 KT148) and VST/VPSP MODIFIED BMI GRAPHITE FIBER COMPOSITE

PROPERTIES	RESIN SYSTEM WITH 8 HARNESS SATIN WEAVE GRAPHITE FIBER			
	H795 KT148	VPSP/H795KT148=1/4	VPSP/H795KT148=3/7	VST/H795KT148=1/4
RESIN CONTENT, %	22	22.5	22	25.5
DENSITY, g/ml	1.54	1.53	1.58	1.48
CHAR YIELD AT 800°C in N_2 %	48.5	52	51	47
LOI, %	59	65	63	50
SHORT BEAM SHEAR, R.T. N/mm^2(ksi)	15.2(2.2)	17.1(2.48)	16.6(2.41)	
FLEXURAL, R.T.				
STRENGTH, N/mm^2(ksi)	283(41)	276(40)	297(43)	393(57)
MODULUS, KN/mm^2(msi)	63.4(9.2)	62.8(9.1)	62(9.0)	64.8(9.4)
ENERGY, Ft-Lb	8.7	8.7	7.8	11.8
TENSILE, R.T.				
STRENGTH, N/mm^2(ksi)	531(77)	551(80)	517(75)	
MODULUS, KN/mm^2(msi)	19.3(2.8)	17.9(2.6)	17.9(2.6)	
ELONGATION %	4.5	4.5	3.5	

Table 5 PRELIMINARY PROPERTIES OF LIQUID RUBBER MODIFIED GRAPHITE FIBER COMPOSITE

PROPERTIES	RESIN SYSTEM WITH 8 HARNESS SATIN WEAVE GRAPHITE FIBER				
	VST/H795/CTBN 2/7/1	VPSP/H795/CTBN 2/7/1	H795/CTBN 9/1	VPSP/H795/CTBN 2/8/1	VST/H795/CTBN 2/8/1
RESIN CONTENT, %	29.8	27.5	24	23	24
CHAR YIELD, % at 800°C in N_2	37	40	37	35	35
FLEXURAL, R.T.					
STRENGTH, N/mm^2 (ksi)	327(47.3)	327(47.4)	461(66.9)	397(57.3)	410(58.3)
MODULUS, KN/mm^2 (msi)	53 (7.7)	56 (8.2)	67 (9.7)	58 (8.5)	58 (8.4)
ENERGY, FT-LB	10.38	11.18	13.96	11.99	14.51
SHORT BEAM SHEAR, R.T. N/mm^2 (ksi)	19.8(2.75)	19.4(2.82)	19.9(2.89)	17.4(2.52)	21.6(3.13)
TENSILE, R.T.					
STRENGTH N/mm^2 (ksi)			317(46)	310(45)	317(46)
MODULUS KN/mm^2 (msi)			13.1(1.9)	13.8(2.0)	15.2(2.2)
ELONGATION-YIELD			3.5	3.2	3.0

*H795 is H795M1268

CTBN modified resins have been determined in nitrogen at a heating rate of 10°C/min.. The char yield at 800°C for resins with CTBN was lower than those without CTBN reported previously. The less than 40% char yield of CTBN modified resins indicated that composite made from these resins may have poor fire resistance property.

5. FACE SHEET PREPARATION FOR INTERIOR SANDWICH PANEL

5.1. Material

It has been found that VPSP/H795 resin mixture with the weight ratio of 3 to 7 could be cured at a much lower temperature than H795 resin alone and also gave a composite with reasonably good physical and mechanical properties. This resin system has high char yield and good flame resistance property. Since H795KT148 cures at lower temperature than H795M1268, H795KT148 was used for face sheet preparation. Large scale synthesis of VPSP was performed by American Cyanamid according to our synthetic procedure, VPSP (Batch 179) was used for the face sheet preparation. Light weight carbon fiber (Hercules-A193A) was used for the face sheet. Some face sheet was also made with VPSP/H795 = 4/6 resin mixture.

5.2. Prepreg Preparation

Prepreg can be prepared by either hot-melt or wet method. The wet method was used for prepreg preparation. 10% solvent can be added in the resin system to improve the flow property for the hot-melt method.

5.2.1. Specification for VPSP/H795KT148 Prepreg of Face Sheet (Preliminary suggested Hot-melt Method)

1. Formulation of Prepreg Resin:

Part A. Vinyl polystyrylpyridine resin	30 parts
Part B. Bismaleimide, H795	70 parts
Part C. Tetrahydrofuran	10 parts

2. Properties of formulation

Viscosity, Brookfield LVT, spindle #4 at 70 degree C	3,000-5,000 cps

half hour at 70°C	5,000-10,000 cps
one hour at 70°C	10,000-16,000 cps

3. Preparation of prepreg

a. Coat carbon fiber (A193 P) by conventional hot melt method at 70°C.

b. Dry coated fiber at 80°C for 15 min.

c. Cool coated fiber to room temperature.

d. Store prepregs at -10 to 5°C in a plastic bag.

e. Resin content should be 45-50% and volatile content less than 5%.

5.2.2. Specification for VPSP/H795KT148 Prepreg of Face Sheet (Wet Method)

1. Formulation of Resin/Varnish:

Part A. Vinylpolystyrylpyridine Resin (VPSP)	30 parts
Part B. Bismaleimide Resin (H795 KT148)	70 parts
Part C. Tetrahydrofuran	70-150 parts

2. Properties of Formulation

Viscosity, Brookfield LVT, #3, 60 rpm	50-1000 cps
Weight per gallon	8.5-9.5 lb/gal

3. Preparation of Prepreg

a. Coat carbon fibers (A193 P) with varnish

b. Dry coated fiber for 60 min. at 25°C, coat the carbon fiber again, dry the coated fiber at 25°C for 60 min.

c. Dry the prepreg overnight at room temperature or 15 min. at 80°C.

d. Store prepreg at -10 to 5°C in a plastic bag.

e. Resin content should be 45-50% and volatile content less than 5%.

5.3. Face Sheet Molding Procedures

5.3.1. Face Sheet prepared from VPSP/H795 resin systems

The molding procedures for face sheet made from VPSP/H795 resin systems are:

a. In a flat polished platen load one ply prepreg (place one layer of release paper between platen and prepreg) at room temperature.

b. Apply 100 psi, heat to 160-200°C, then hold for 1 - 3 hrs.

c. Cool to room temperature slowly.

d. Resin content should be 30 - 40%.

5.3.2. The Molding Procedures for Face Sheet Made from H795 Resin

The following procedures was used to make H795 control face sheet.

a. In a flat polished platen load one ply prepreg (place one layer of release paper between platen and prepreg) at room temperature. Apply contact pressure and heat to 160°C for 10 min.

b. Apply 100 psi , heat to 180°C and hold for 1 - 3 hrs.

c. Cool to room temperature slowly.

d. Resin content should be 30-40%.

5.3.3. Face Sheet Made from Epoxy Resin

Face sheet using epoxy resin (MY720-DDS) was also prepared by the procedure described in 5.3.1.. The face sheet prepared by this procedure had low resin content and there were holes in the cured sheets. The best condition to mold the epoxy face sheet has not been achieved.

5.4. Evaluation of Face Sheet

5.4.1. Thermogravimetric Analysis

Various resin face sheets with or without postcure were examined by TGA in nitrogen at different heating rates. The results are shown in Table 6 and 7 for 177°C(350°F) cured resin and molded face sheet respectively.

5.4.2. Smoke Chamber Examination of Face Sheet

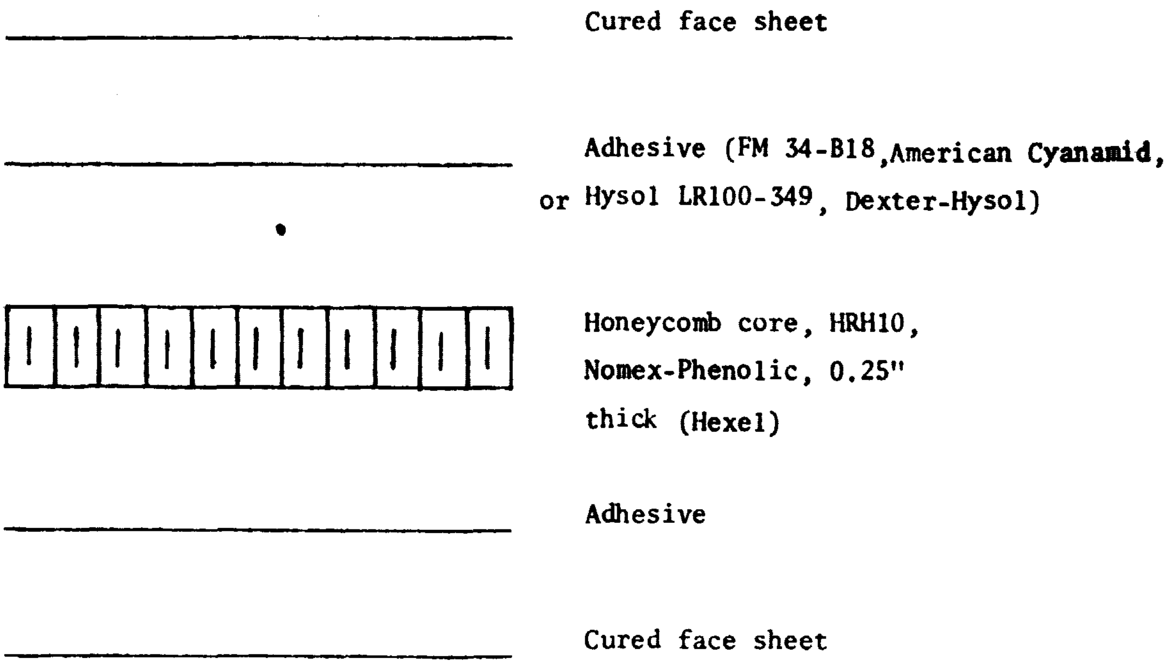
3" x 3" face sheet was placed in a smoke chamber and heated with 2.5 and 5 w/cm^2 heat flux. Mass change(% weight loss) and smoke density(DS) were measured. Mass optical density($DSMS = \Delta Ds/\Delta mass$), which is a correlating parameter for the NBS smoke density chamber[7], was also reported. The results for the face sheets made with VPSP/H795 (3/7,4/6), H795KT control and base line epoxy resins are shown in Figs. 25-33. The data indicated that face sheet made with VPSP/H795(3/7) resin gave lower weight loss, smoke density and DSMS than those made with VPSP/H795=4/6, H795 bismaleimide control or base line epoxy resin.

5.5 Preliminary Sandwich Panel Preparation

Sandwich panel was prepared by heating and pressing the face sheet, bond ply and honeycomb core together. Preparation of small 3"x3" panels using VPSP/H795, VST/H795 or H795 prepreg as adhesive has been attempted. The peel strength of the resulted panels was very weak.A small sandwich panel using Hysol LR100-349 as adhesive has shown good peel strength between face sheet and honeycomb core.

5.5.1. Preliminary Sandwich Panel Preparation Procedure

1. Fabricate the sandwich parel according to the construction shown in the following figure.



2. Panels shall be cured for a minimum of 1 hr at 177°C (350°F) under a vaccum pressure of 50.8 cm-Hg (20 in-Hg) or 25 psi.
3. Cool the panel slowly to room temperature.
4. Weight of the finished panel was 110 - 150 g/ft^2, which was less than the required 170 g/ft^2.

5.5.2. Evaluation of Sandwich Panel

Evaluation of sandwich panel will be the effort of Phase II of this contract.

Table 6 THERMOGRAVIMETRIC ANALYSIS OF VARIOUS RESINS FOR FACE SHEET IN N_2.

RESIN & CURE METHOD	HEATING RATE	DECOMPOSE TEMP.	CHAR YIELD (%)
H795KT148 cured at 177°C for 3 hrs	10 °C/min	423°C	44.5
	50	427	41.5
	100	450	41.2
H795KT148 cured at 177°C for 3 hrs plus 5 hrs post cure at 200°C	10	425	45.1
	50	446	41.3
	100	442	41.0
H795KT148 cured at 177°C for 3 hrs plus 5 hrs post cure at 250°C	10	408	47.0
	50	437	46.0
	100	435	44.3
H795KT148 cured at 177°C for 3 hrs plus 5 hrs post cure at 300°C	10	420	47.5
	50	468	45.4
	100	475	42.3
H795KT148/VPSP(7:3) cured at 177°C for 3 hrs	10	404	47.5
	50	439	44.9
	100	456	49.3
H795KT148/VPSP(7:3) cured at 177°C for 3 hrs plus 5 hrs post cure at 200°C	10	399	54.2
	50	458	52.6
	100	560	50.5
H795KT148/VPSP(7:3) cured at 177°C for 3 hrs plus 5 hrs post cure at 250°C	10	397	55.4
	50	415	53.6
	100	430	55.0
H795KT148/VPSP(7:3) cured at 177°C for 3 hrs plus 5 hrs post cure at 300°C	10	418	58.1
	50	450	55.4
	100	438	55.3

Table 6 (continue)

RESIN & CURE METHOD	HEATING RATE	DECOMPOSE TEMP	CHAR HIELD %
H795KT148/VST, cured at 177°C for 3 hrs (7:3)	10 °C/min	370°C	38.8
	50	407	36.7
	100	405	38.2
H795KT148/VST, cured at 177°C for 3 hrs, plus 5 hrs post cure at 200°C (7:3)	10	386	44.6
	50	421	40.0
	100	426	36.4
H795KT148/VST, cured at 177°C for 3 hrs, plus 5 hrs post cure at 250°C (7:3)	10	386	45.0
	50	436	38.9
	100	427	38.3
H795KT148/VST, cured at 177°C for 3 hrs, plus 5 hrs post cure at 300°C (7:3)	10	400	45.3
	50	430	53.0
	100	455	54.9
MY720 - DDS, cured at 177°C for 5 hrs.	10	335	26.4
	50	381	19.6
	100	394	22.8
MY720 - DDS, cured at 177°C for 5 hrs, plus 5 hrs post cure at 200°C	10	328	32.7
	50	385	27.4
	100	417	25.1
MY720 - DDS, cured at 177°C for 5 hrs, plus 5 hrs post cure at 250°C	10	341	36.1
	50	393	31.6
	100	400	29.5
MY720 - DDS, cured at 177°C for 5 hrs, plus 5 hrs post cure at 300°C	10	320	47.0
	50	385	46.5
	100	392	43.4

Table 7 THERMOGRAVIMETIC ANALYSIS OF VARIOUS FACE SHEET (CURED) IN N_2.

FACE SHEET NO.	RESIN	CURE METHOD	RESIN CONTENT	DECOMPOSE TEMPERATURE °C	CHAR YIELD %
FS5E	H795 KT	3 hrs at 177°C	45.71%	434.5	70.8
"	"	+5 hrs post cure at 200°C	43.84	419	71.3
"	"	+5 hrs post cure at 250°C	51.11	428	68.5
"	"	+5 hrs post cure at 300°C	45.81	431	71.0
FS2F	H795KT/ VPSP(7:3)	3 hrs at 177°C	37.13	405	74.9
"	"	+5 hrs post cure at 200°C	37.11	412	74.9
"	"	+5 hrs post cure at 250°C	36.40	410	74.9
"	"	+5 hrs post cure at 300°C	44.2	415	75.1
FS2H	H795KT/ VPSP/DCp (7:3:.5%)	3 hrs at 177°C	41.91	393	70.9
"		+5 hrs post cure at 200°C	45.41	397	65.7
"	"	+5 hrs post cure at 250°C	40.1	382	71.5
"	"	+5 hrs post cure at 300°c	45.71	416.5	76.3
FS4F	MY720/ DDS	3 hrs at 177°C	30.17	322	64.0

*DCp: Dicumyl peroxide

6. PREPARATION OF DELIVERABLES

Reports and preparation of selected resin and composite panel to be delivered to NASA was completed. The synthetic specification for vinyl-modified styrylpyridine monomer (5-vinyl-2-stilbazole) was delivered in April 1983. The synthetic specfication for vinyl/divinyl modified styrylpyridine oligomers was delivered in July 1983. The characterization of the selected matrix resins was delivered in October 1983. One pound of the selected matrix resin solution,which consisted 30 parts of VPSP, 70 parts of H795 KT148 and 100 parts of tetrahydrofuran, was delivered in November 1983. A 6' x 6' nine ply composite panel made from the selected resin (VPSP/H795 = 3/7) was delivered at the end of this phase of the contract.

7. CONCLUSIONS AND RECOMMENDATIONS

In the phase I study, HC Chem Research has demonstrated that VST/VPSP can be prepared by a simple synthesis procedure to give a low melt soluble material. VST/VPSP modified bismaleimides are low-temperature curing resins which: reduce water absorption, may be used without solvent or with low boiling solvents, give char yields consistent with optimum fire resistance, have long pot life, and service temperatures of 300°C or above. It is believed that the VPSP-modified bismaleimides described here represent a significant advance in matrix resins for graphite secondary structures where ease of processing, firewothtiness, and high-temperature stability are required. VPSP-modified bismaleimide resin composed of 3 parts of VPSP and 7 parts of H795 gave a matrix resin which can be used as light weight graphite fiber reinforced face sheet for aircraft interior panel.

It is recommended that a follow-on effort be initiated with the following objectives:

(1) Increase the vinyl content of VPSP.

(2) Examine the long term stability of VST and VPSP at room temperature.

(3) Examine the mechanism of copolymerization of VST/VPSP and bismaleimide resin by using model compounds.

(4) Prepare and evaluate light weight aircraft interior panel using VPSP/H795 face sheet and suitable high temperature bond ply.

(5) Develop a tougher bismaleimide resin system.

(6) Develop a resin matrix system which can be processed by filament winding method.

8. REFERENCES

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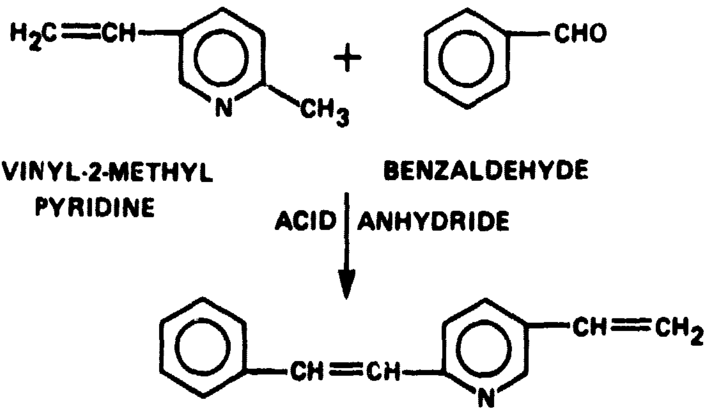
(6) J. J. Ratto and C. L. Hamermesh, US Patent 4,362,860 (1982).

(7) J. D. Seader and W. p. Chien, J. Fire & Flammability 5, 15 (1974)

FIG. 1 VINYL STILBAZOLE (VST) SYNTHESIS



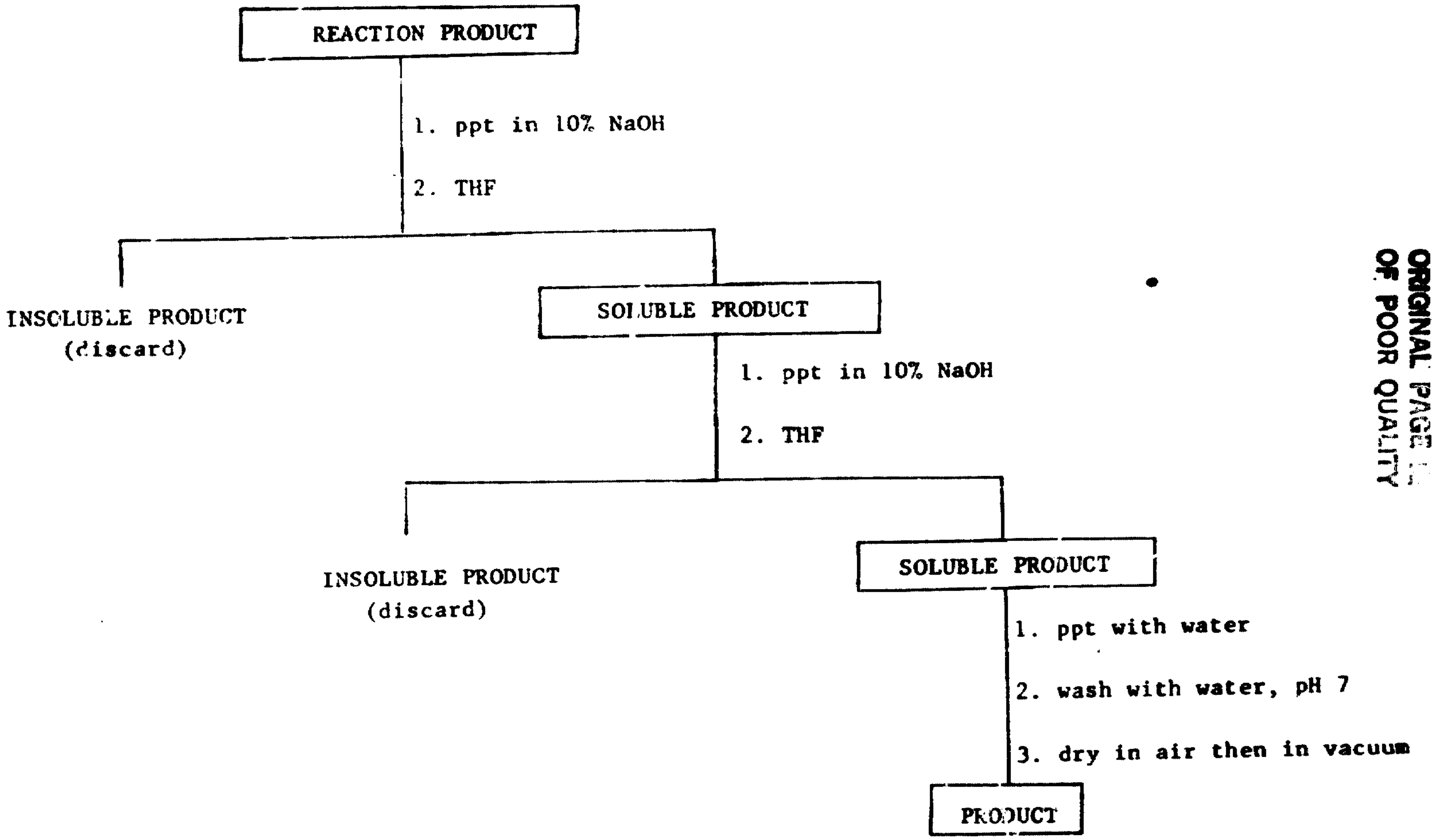


FIG.2 VST AND VPSP WORK-UP AND SEPARATION

FIG. 8 IR SPECTRUM OF VST

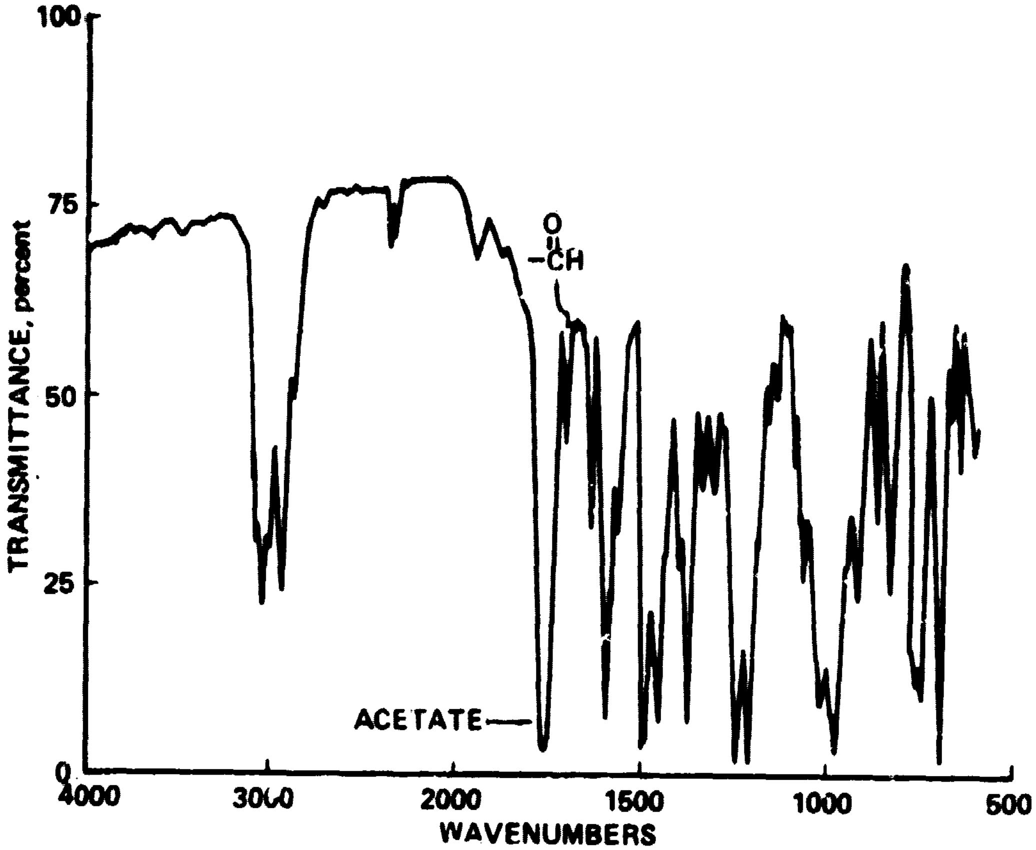


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FIG. 4 NMR OF 5 VINYL-2-STIL BAZOLE (VST)

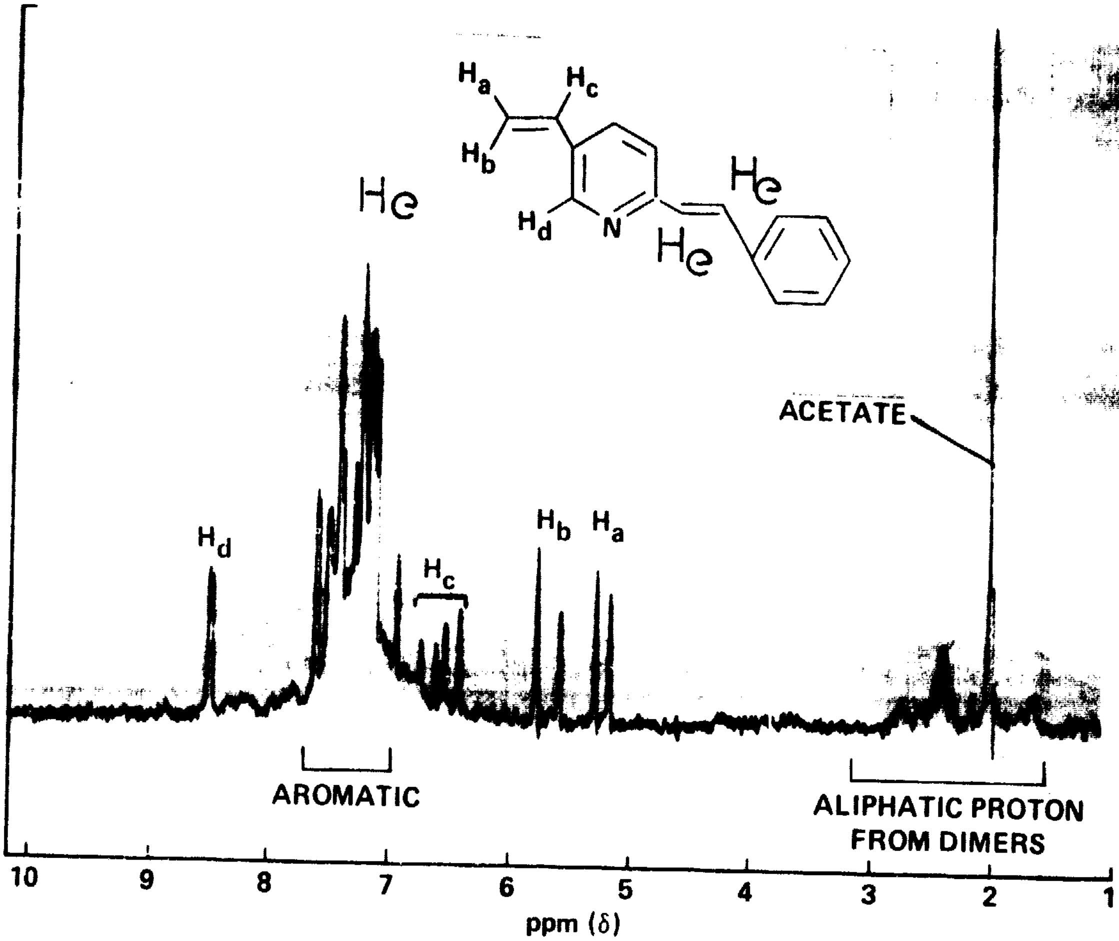
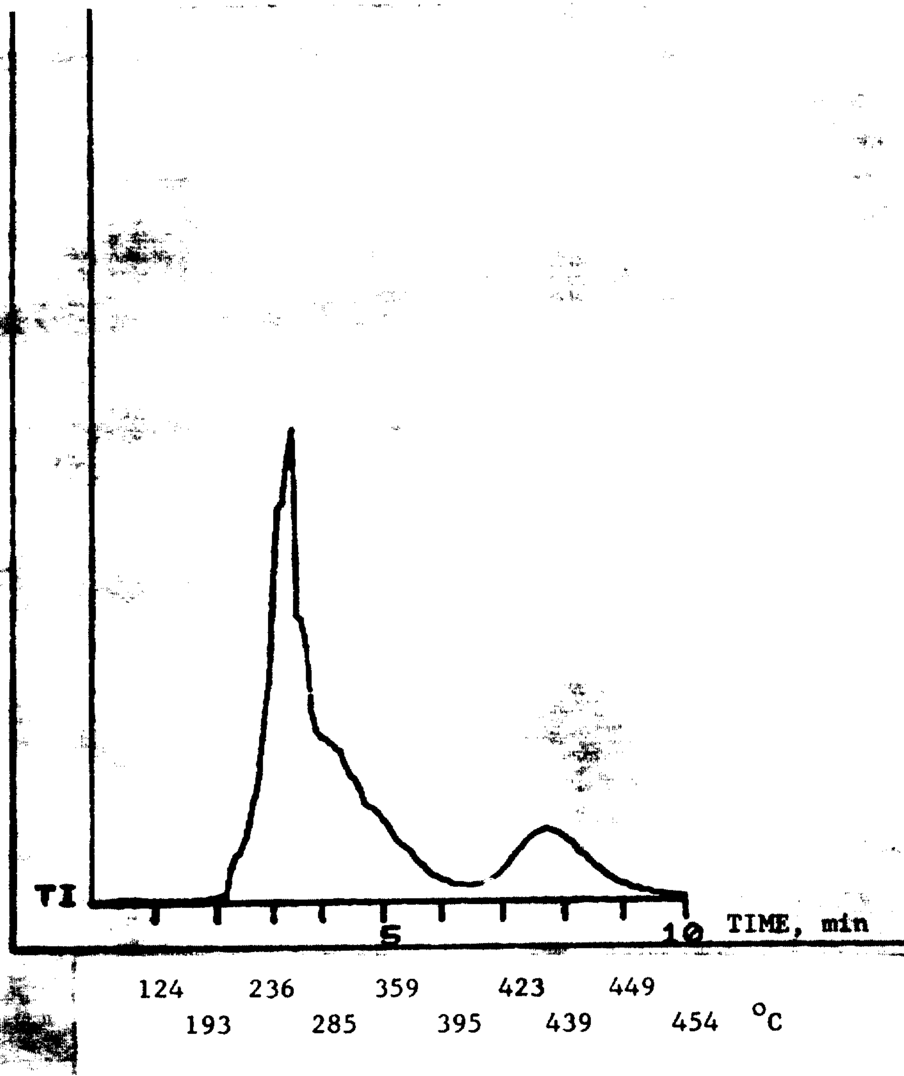


FIG. 5 TOTAL ION INTENSITY OF VST AT DIFFERENT TEMPERATURE AND TIME
(DIP RUN)



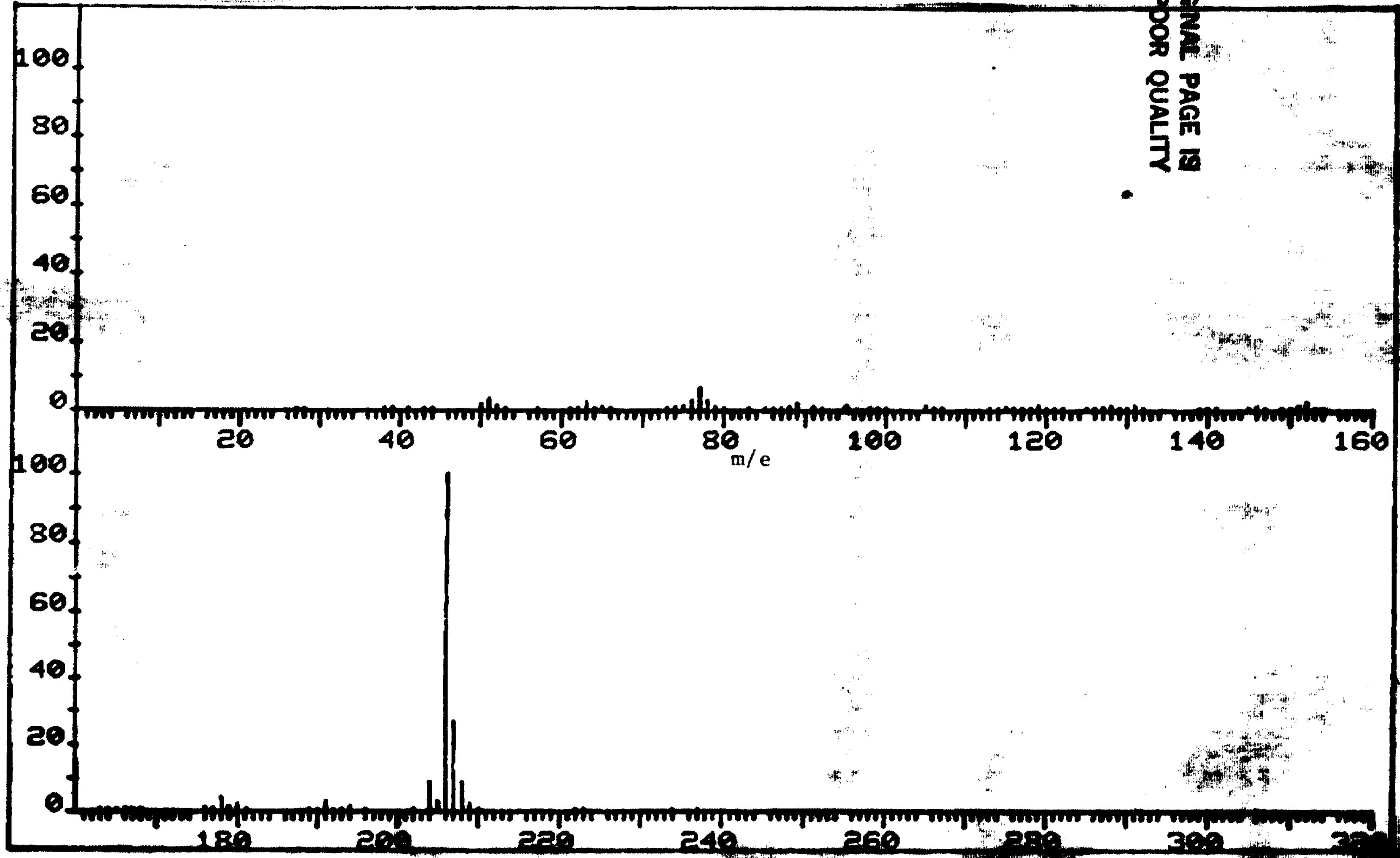


FIG. 6 MASS SPECTRUM OF VST

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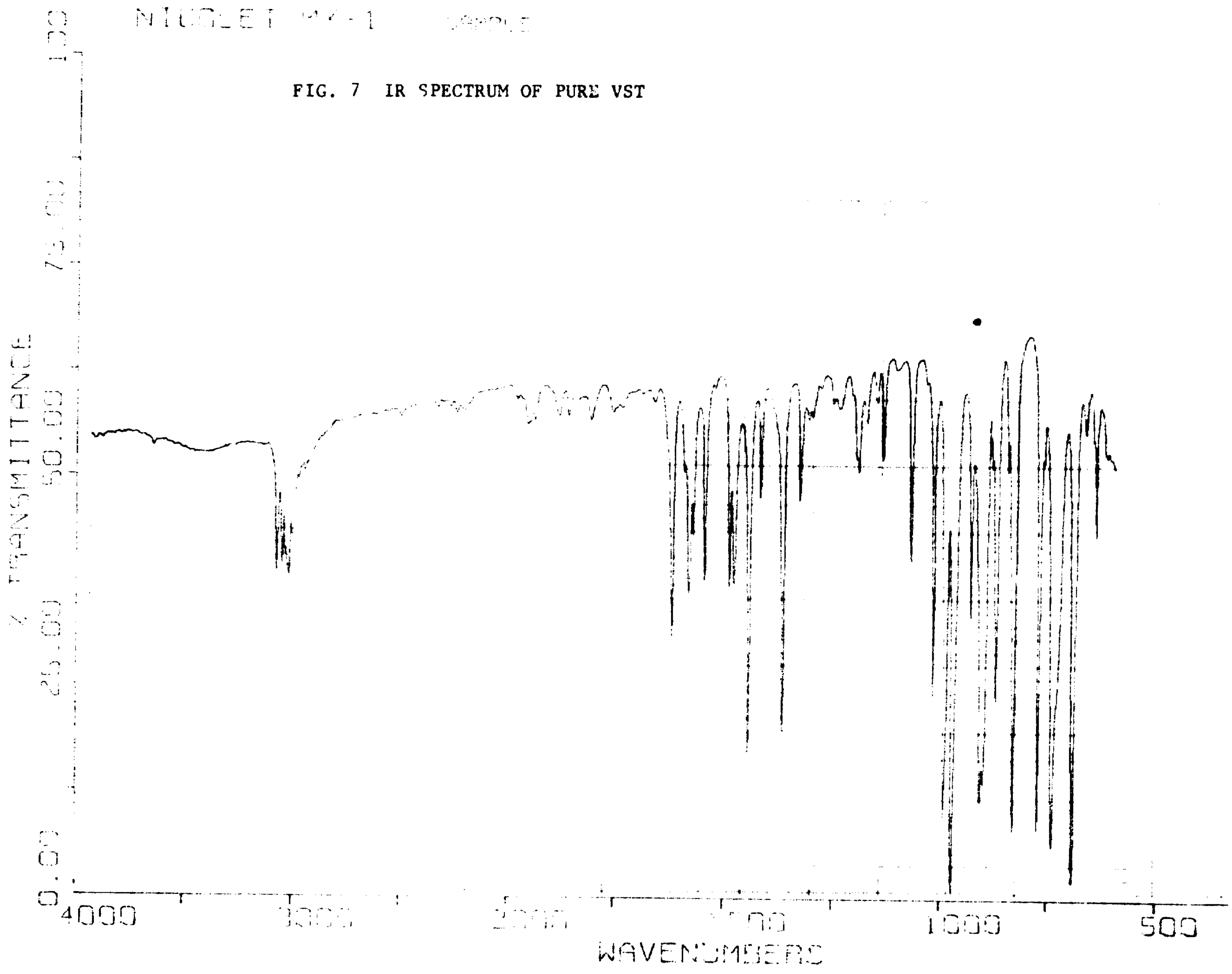

FIG. 7 IR SPECTRUM OF PURE VST

FIG. 8 NMR SPECTRUM OF PURE VST

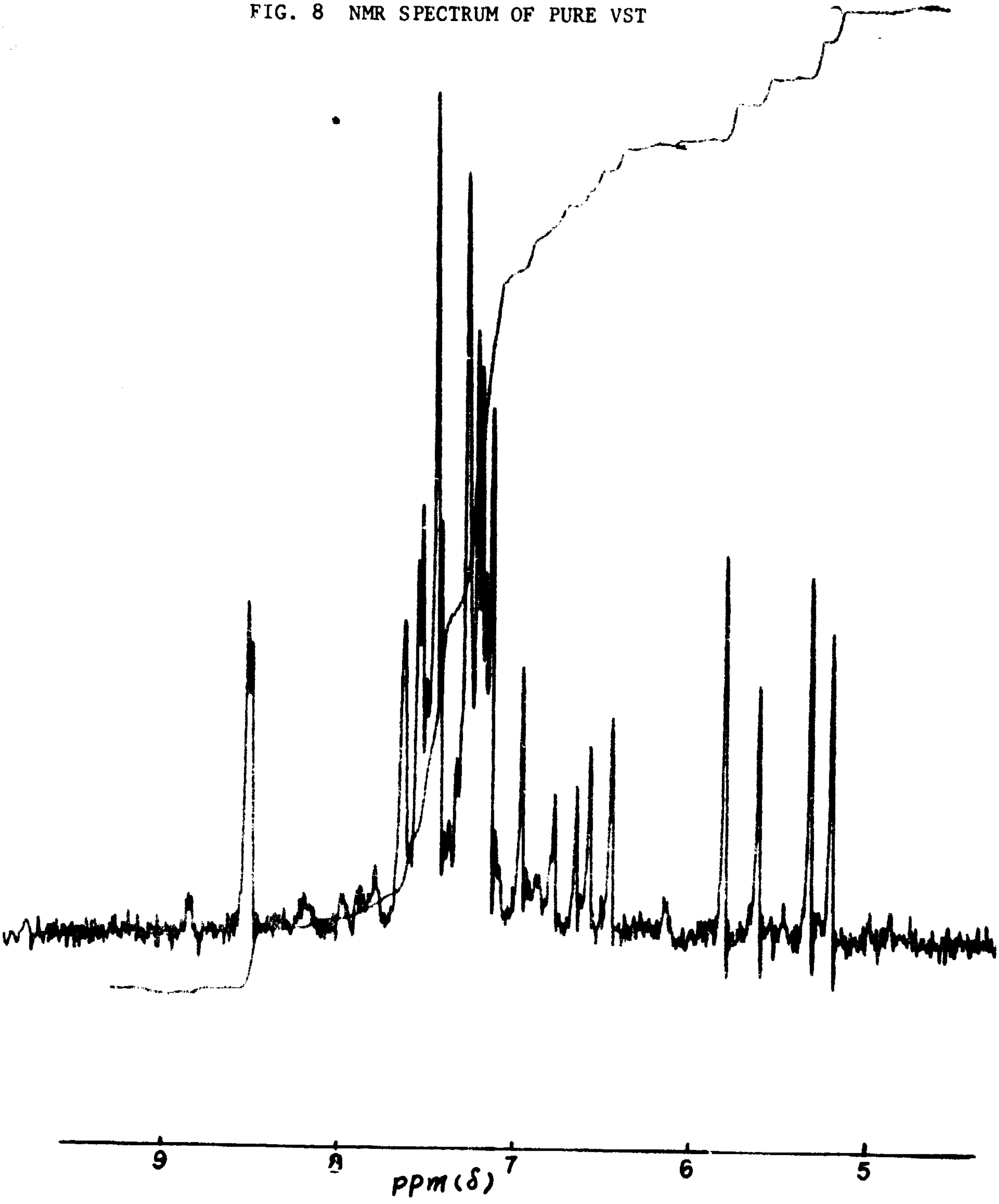

FIG. 9 VINYL STYRYLPYRIDINE (VPSP) SYNTHESIS

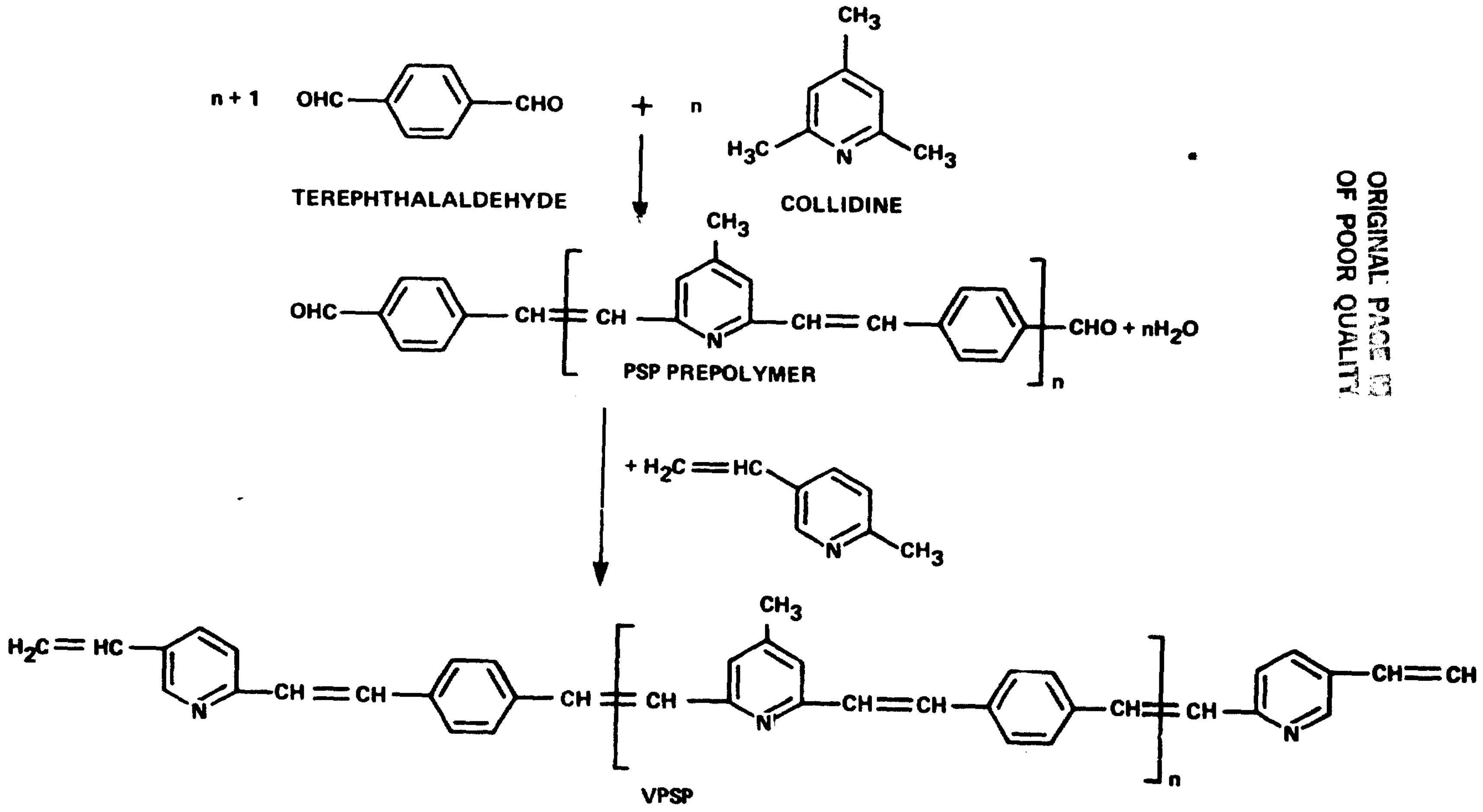

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FIG. 10 **IR SPECTRUM OF VPSP**

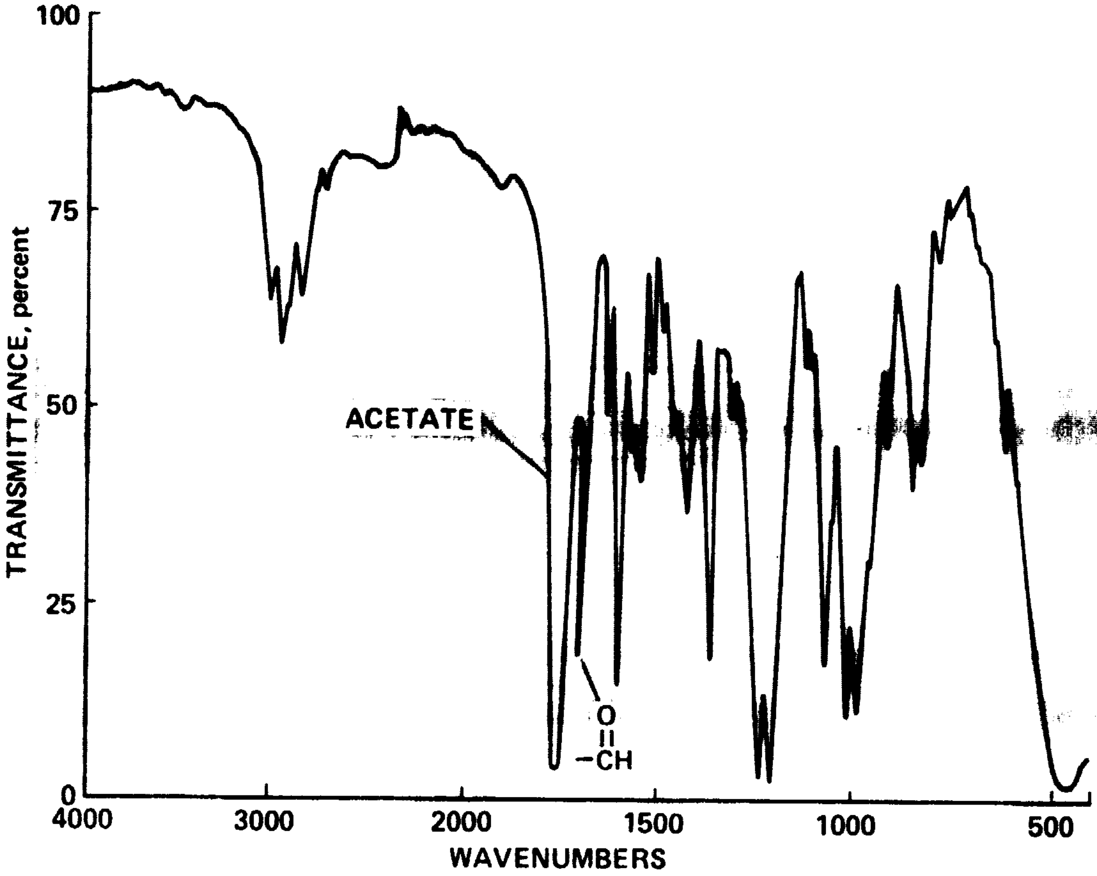

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FIG. 11 NMR OF VINYL POLYSTYRYL PYRIDINE (VPSP)

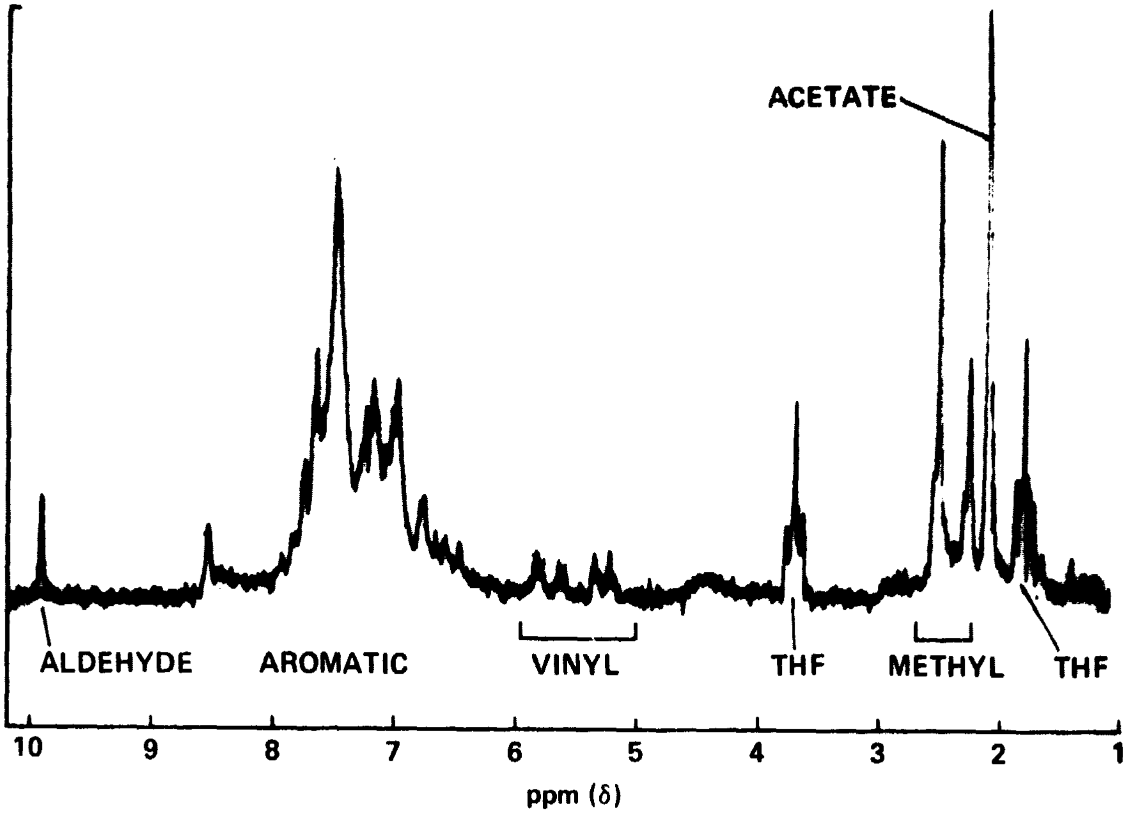
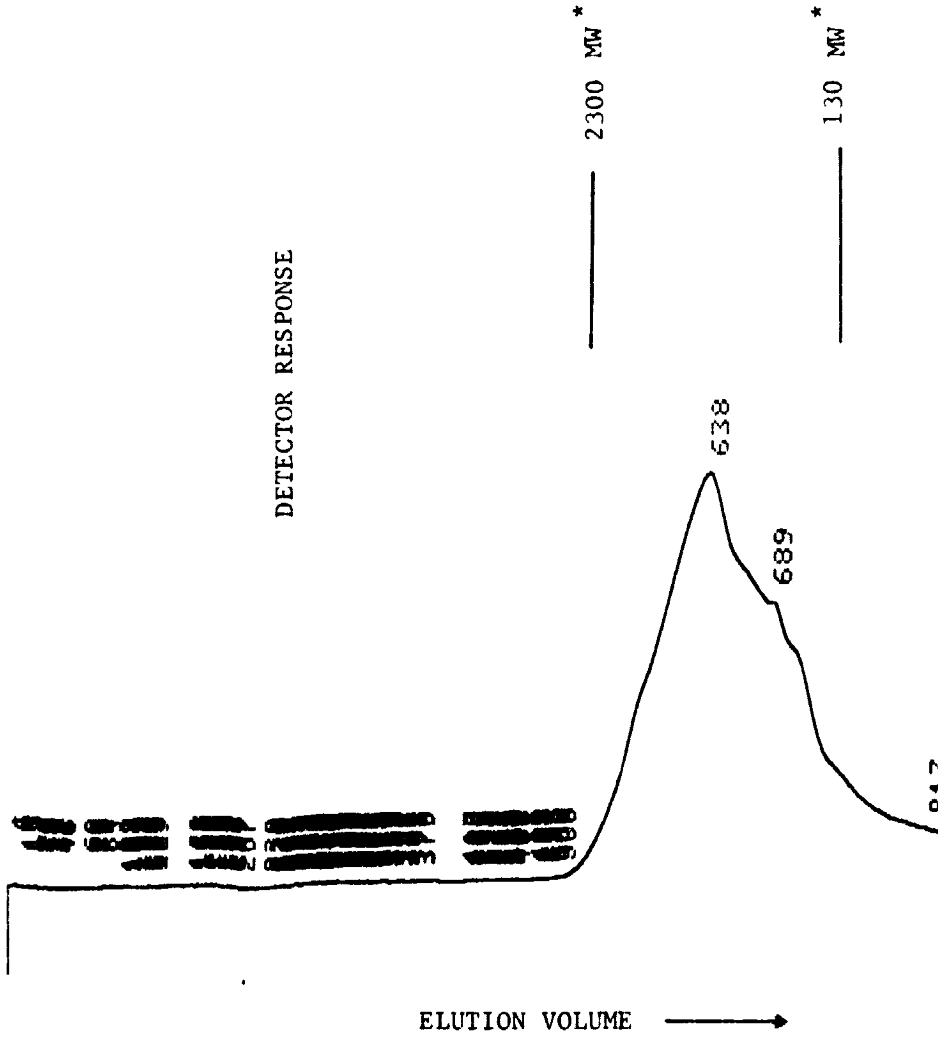


FIG. 12 SIZE EXCLUSION CHROMATOGRAM OF VPSP



Column: Du Pont PSM 60S
Solvent: THF
Detector: refractive index

*Molecular weight was corrected by a factor of 1.5 from polystyrene standard
M_n = 950 (corrected) M_n = 633 (uncorrected)
M_w = 3500 (corrected) M_w = 2333 (uncorrected)

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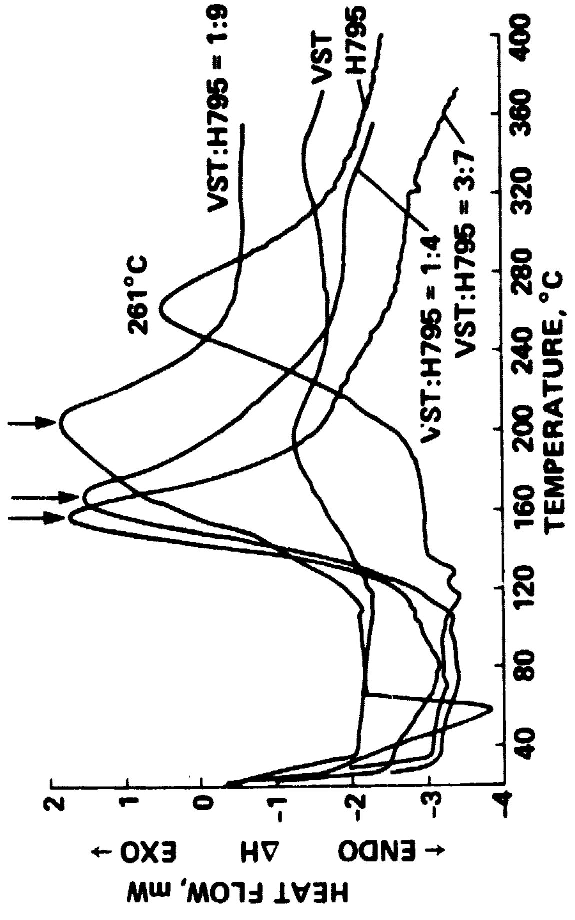
Fig. 13 DSC OF BISMALEIMIDE (H795), VST AND VST/H795 BLENDS



H795 is H795 M1268

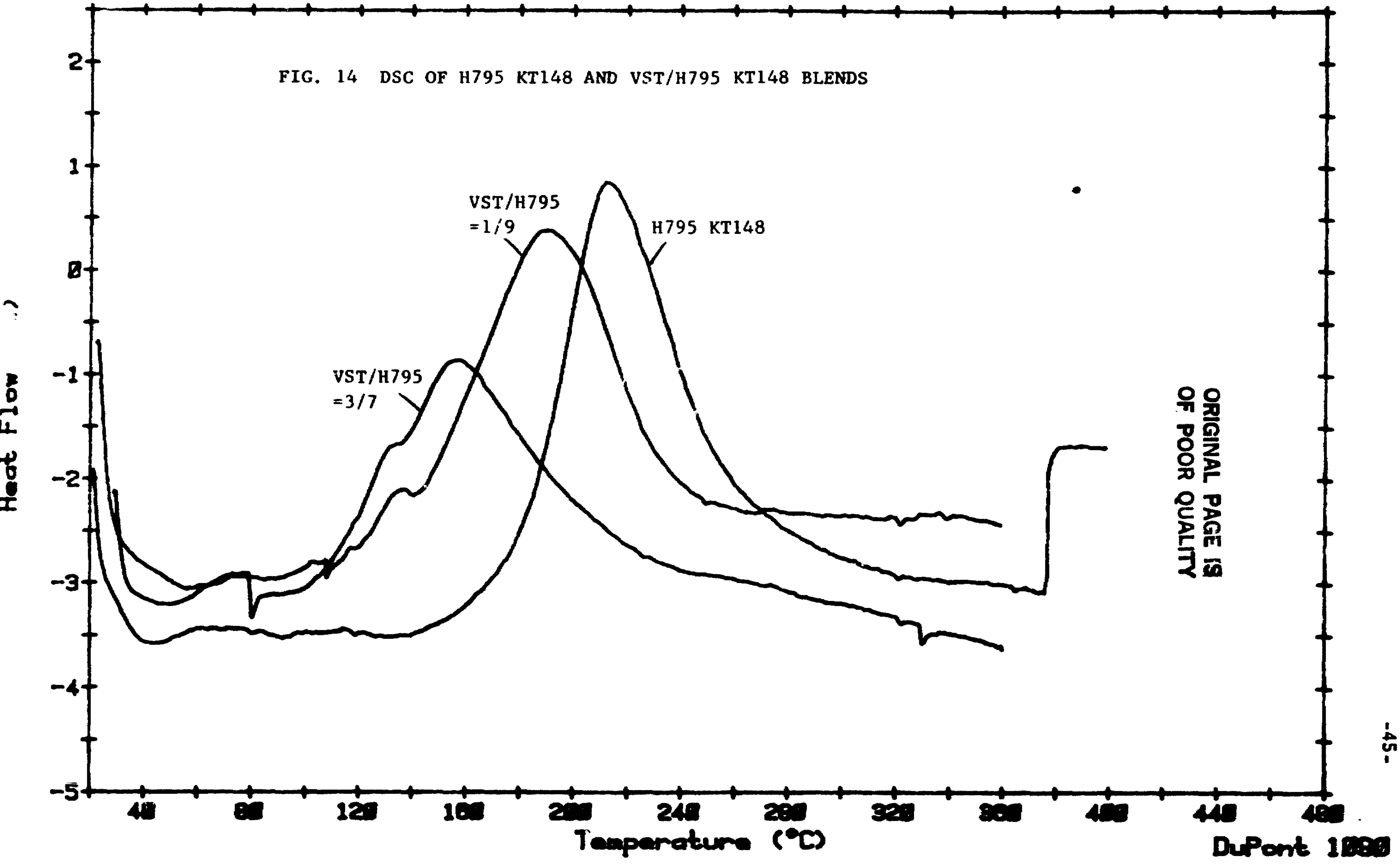
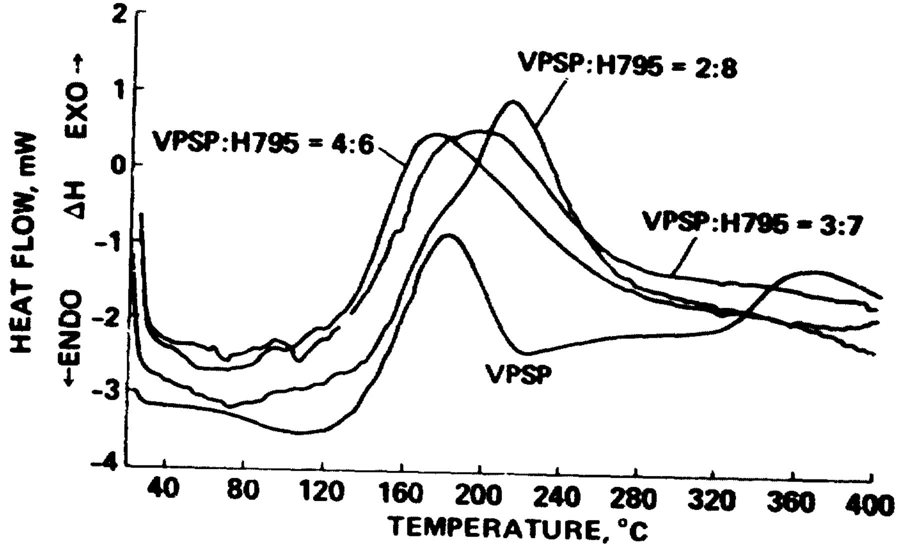


FIG. 14 DSC OF H795 KT148 AND VST/H795 KT148 BLENDS

Fig. 16 DSC OF VPSP AND VPSP/H795 BLENDS



H795 is H795 M1268

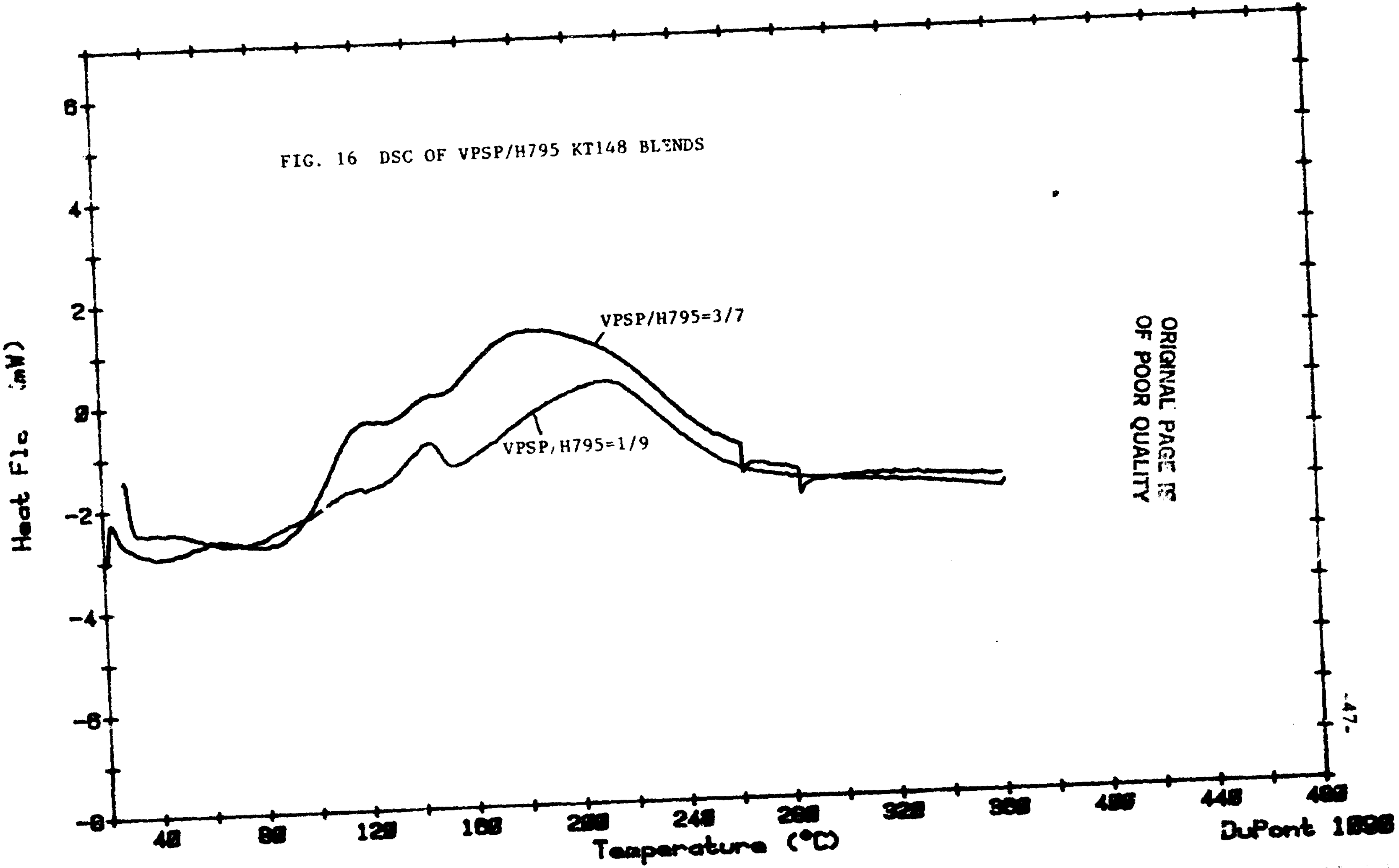


FIG. 16 DSC OF VPSP/H795 KT148 BLENDS

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FIG. 17 THERMOGRAVIMETRIC ANALYSIS OF VINYLSTYRYLPYRIDINE MODIFIED BISMALEIMIDE IN NITROGEN
10°C /min

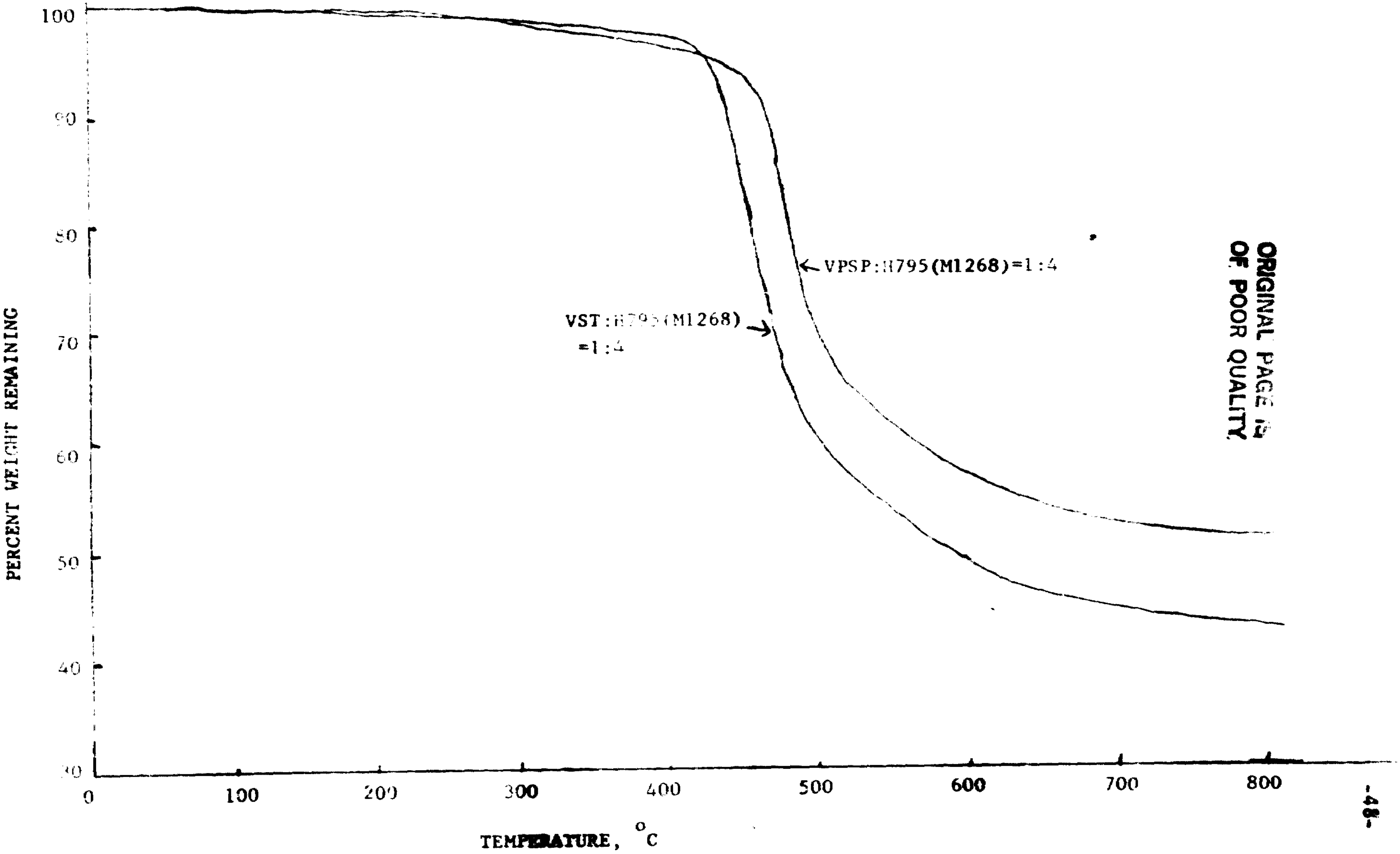


FIG. 18 TYPICAL THERMOGRAVIMETRIC ANALYSIS OF VINYLSTYRYLPYRIDINE MODIFIED BISMALEIMIDE IN AIR (10°C/min)

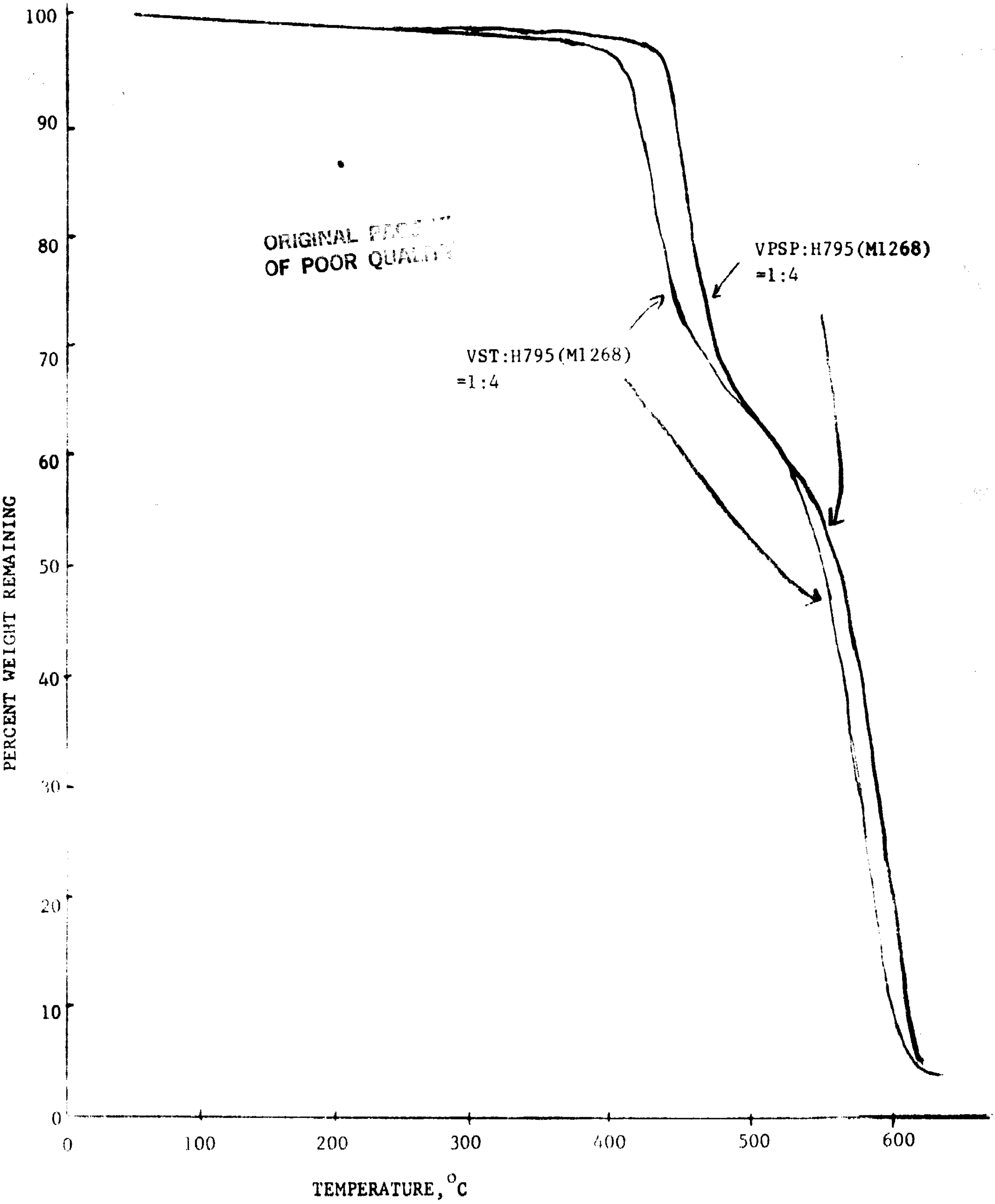
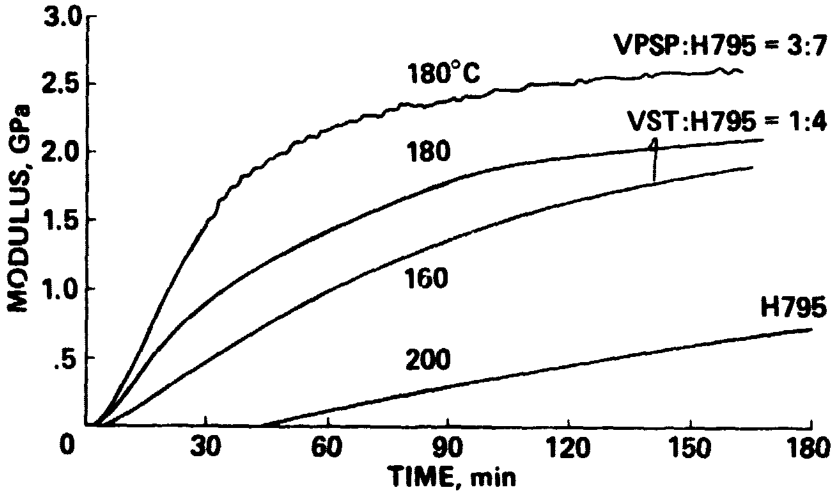


Fig. 19 ISOTHERMAL DMA OF MODIFIED AND UNMODIFIED BISMALEIMIDE PREPREG



H795 is H795 M1268

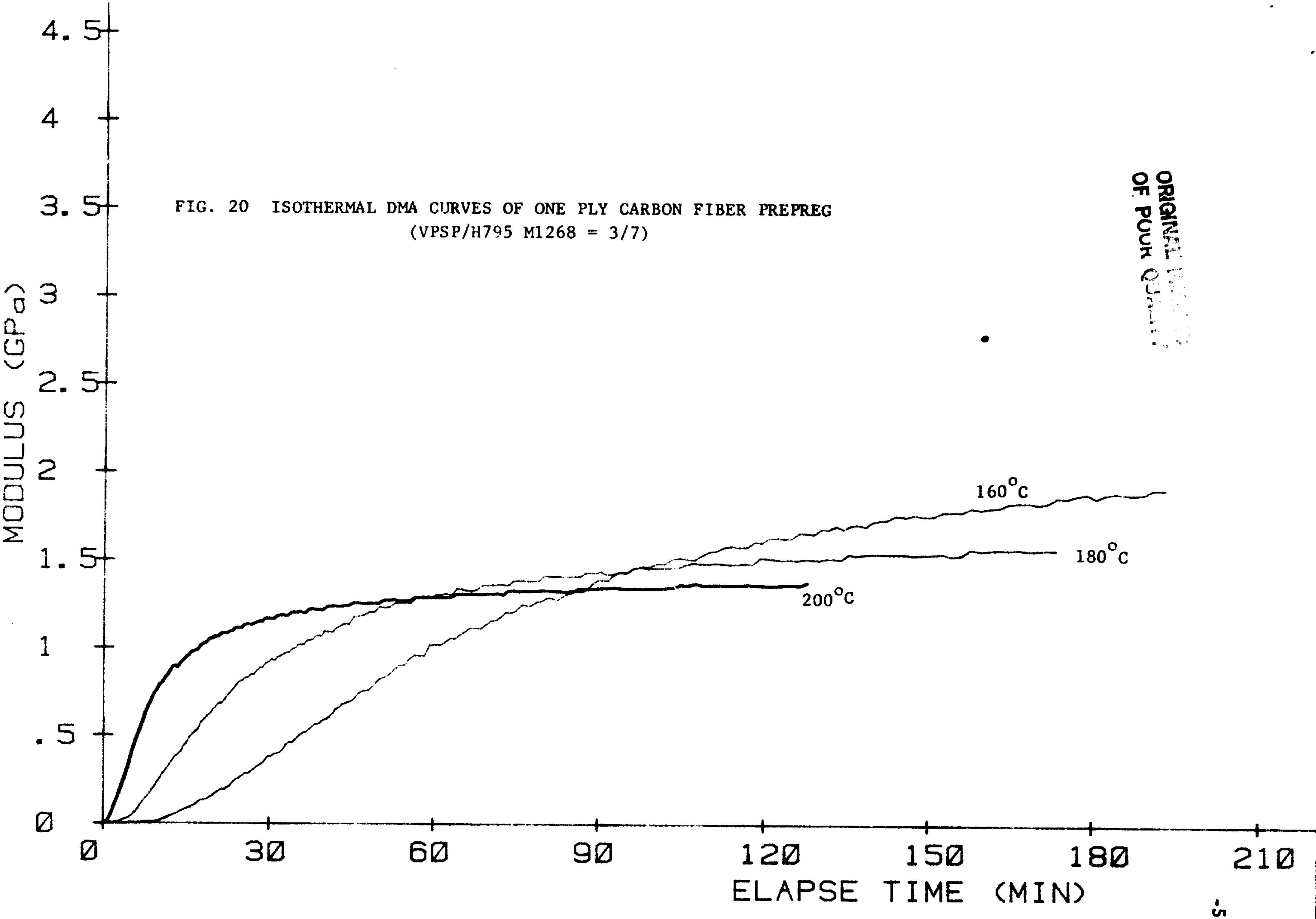


FIG. 20 ISOTHERMAL DMA CURVES OF ONE PLY CARBON FIBER PREPREG (VPSP/H795 M1268 = 3/7)

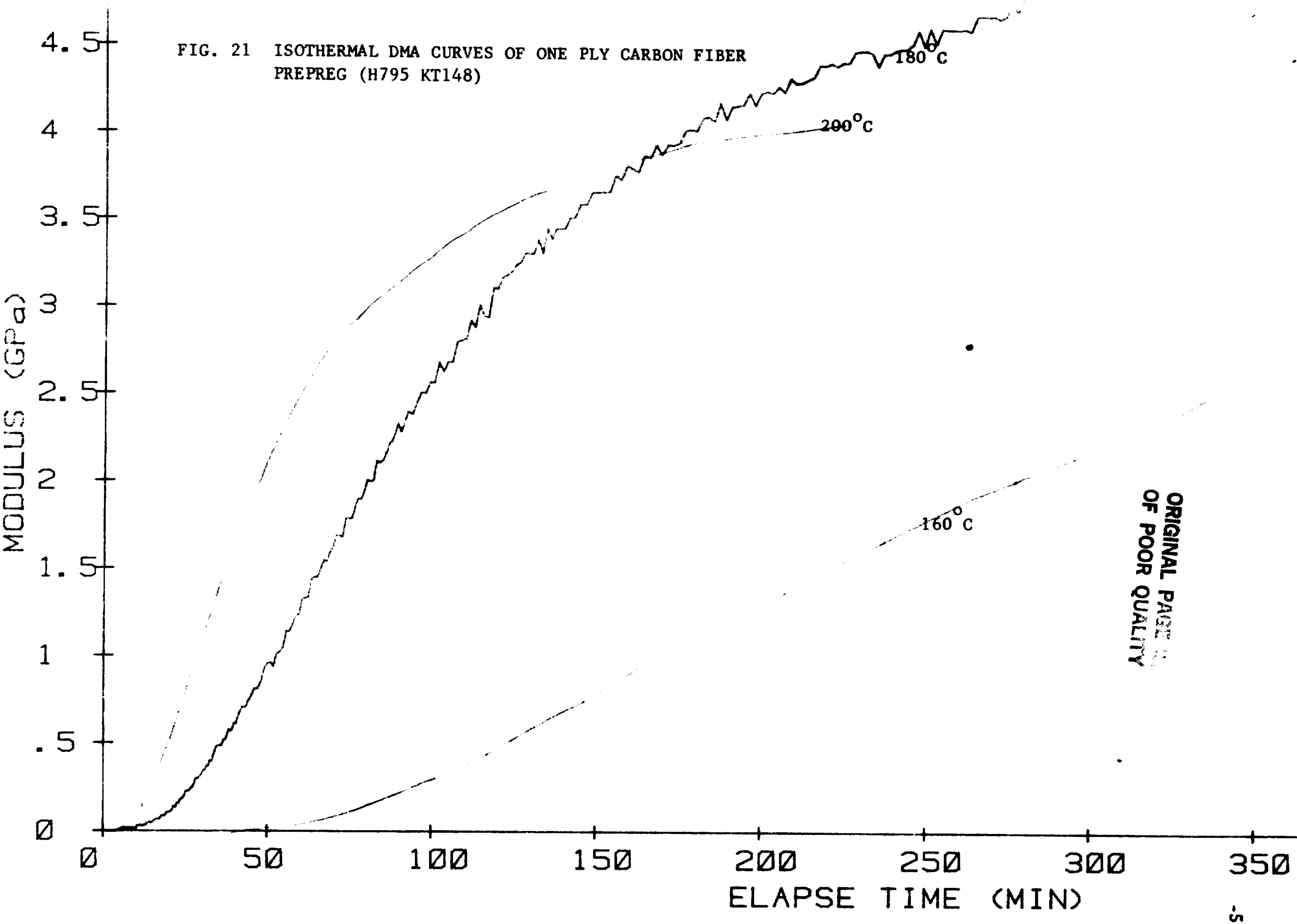


FIG. 21 ISOTHERMAL DMA CURVES OF ONE PLY CARBON FIBER PREPREG (H795 KT148)

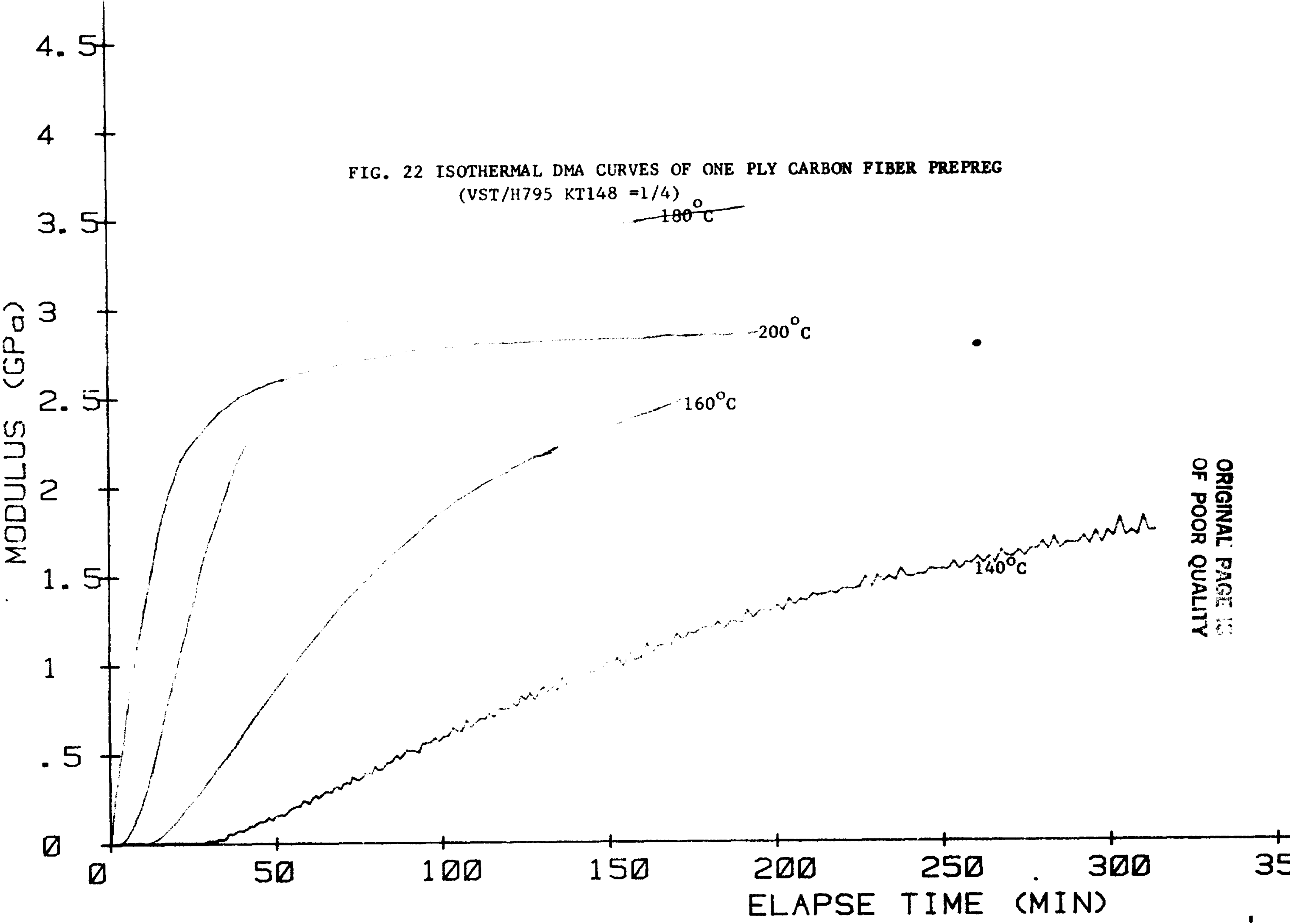


FIG. 22 ISOTHERMAL DMA CURVES OF ONE PLY CARBON FIBER PREPREG (VST/H795 KT148 =1/4)

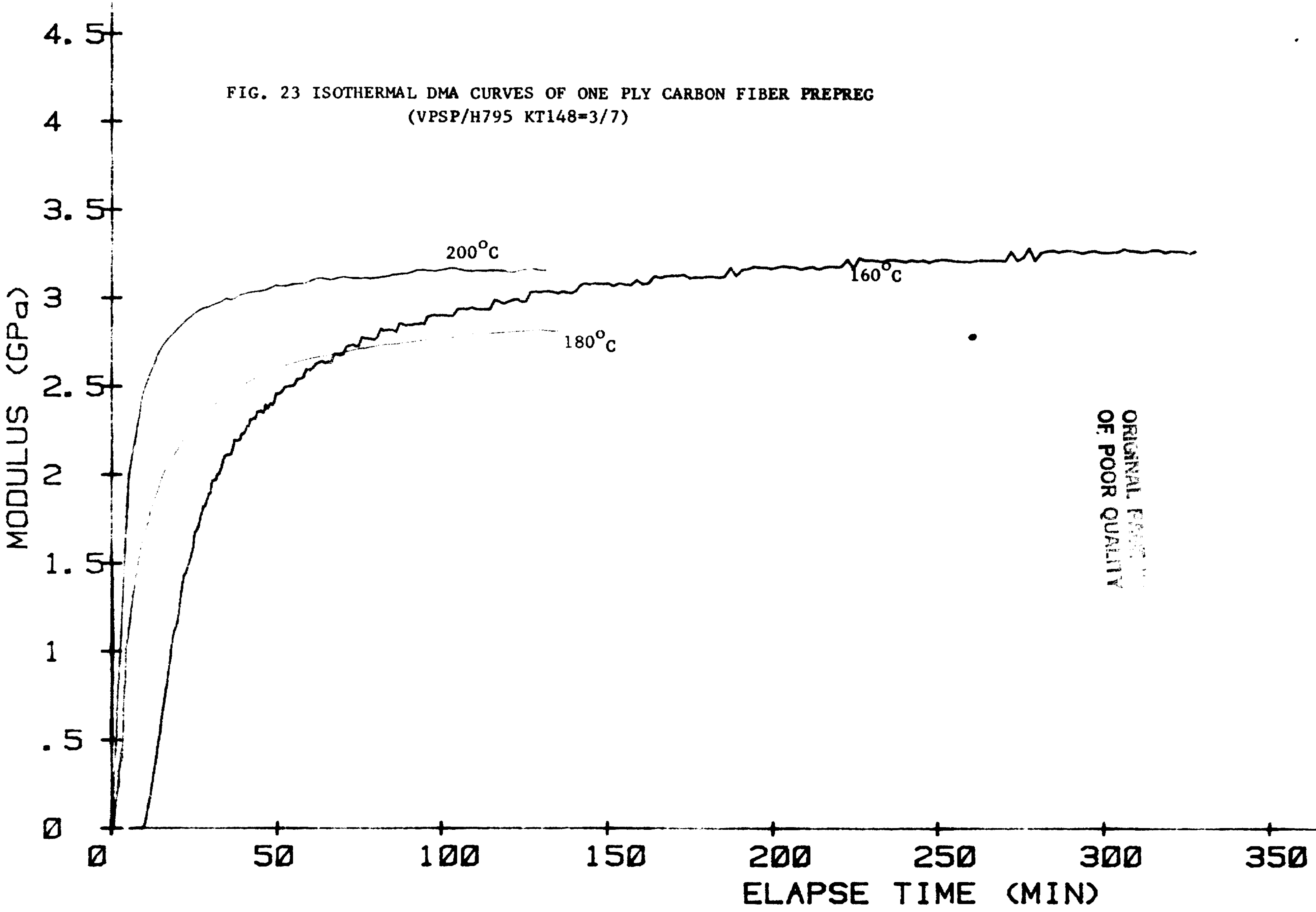
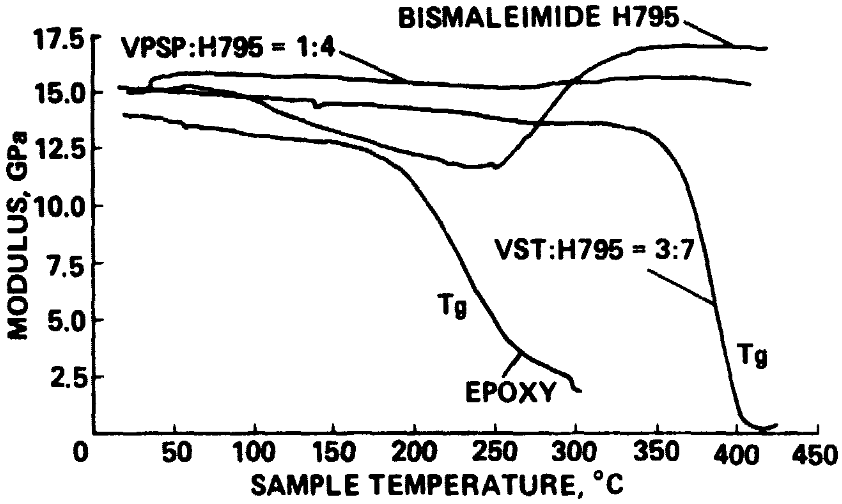


FIG. 23 ISOTHERMAL DMA CURVES OF ONE PLY CARBON FIBER PREPREG
(VPSP/H795 KT148=3/7)

Fig. 24 DMA OF VARIOUS COMPOSITES



H795 is H795 M1268

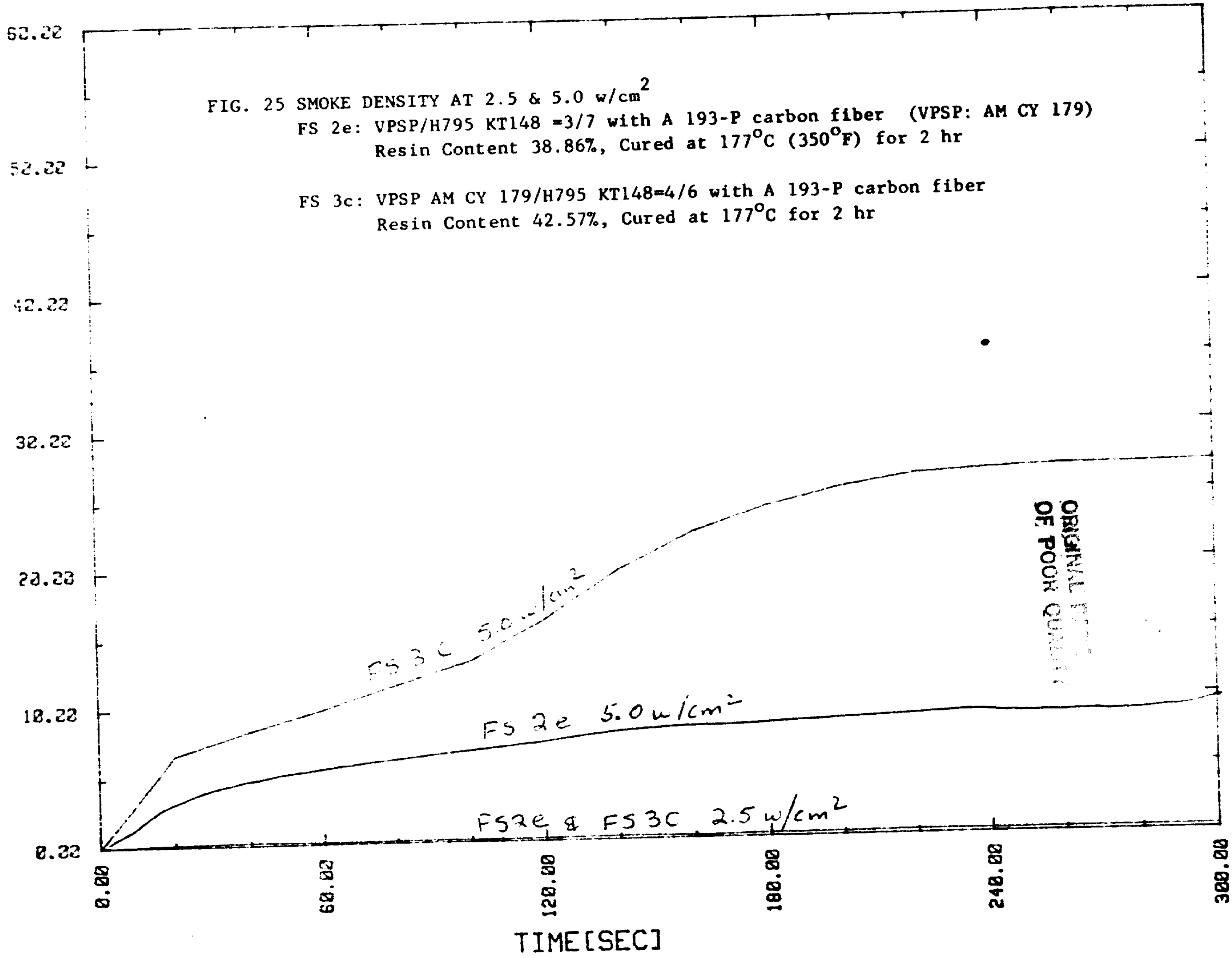


FIG. 25 SMOKE DENSITY AT 2.5 & 5.0 w/cm^2

FS 2e: VPSP/H795 KT148 =3/7 with A 193-P carbon fiber (VPSP: AM CY 179)
Resin Content 38.86%, Cured at 177°C (350°F) for 2 hr

FS 3c: VPSP AM CY 179/H795 KT148=4/6 with A 193-P carbon fiber
Resin Content 42.57%, Cured at 177°C for 2 hr

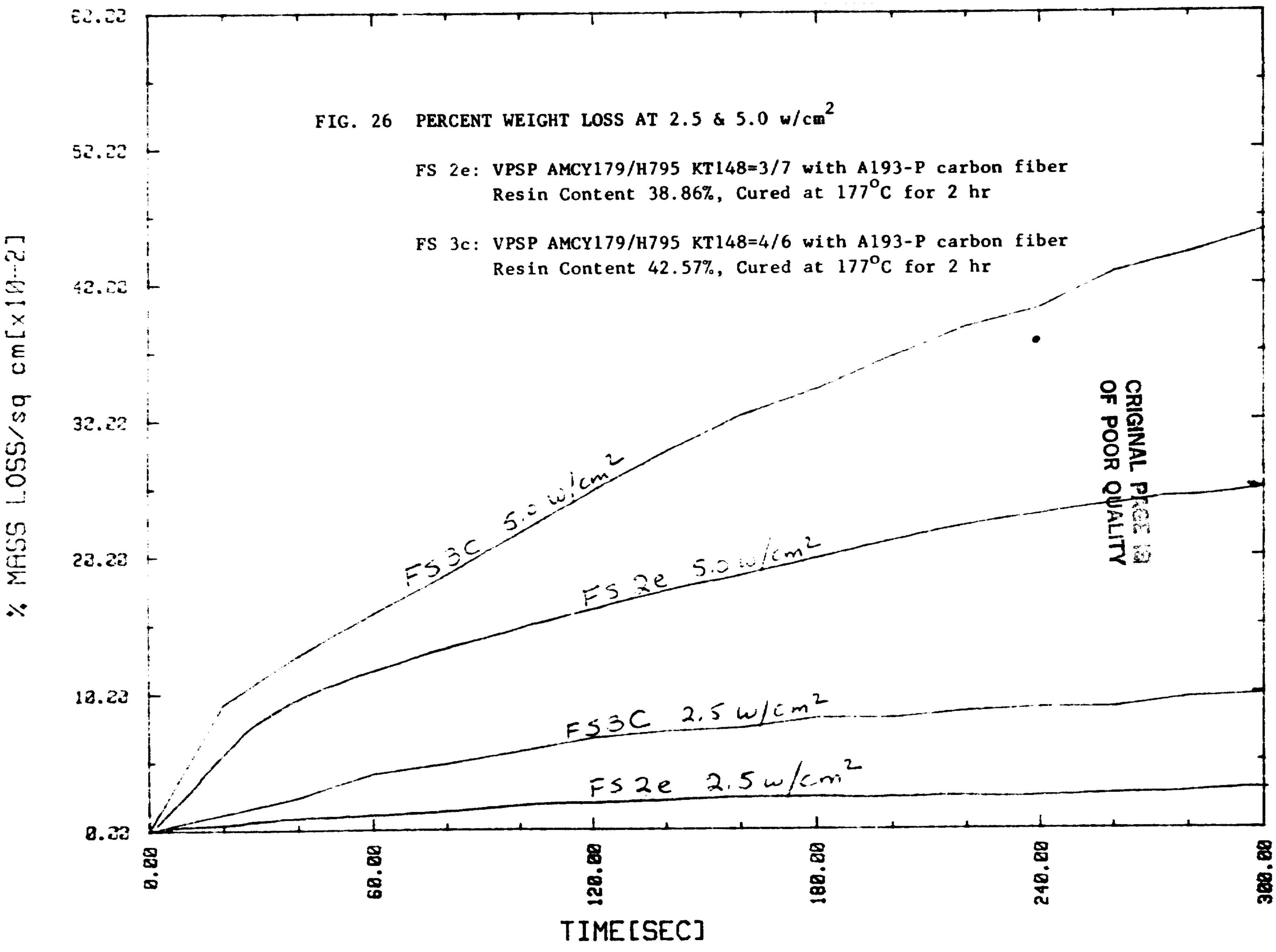


FIG. 26 PERCENT WEIGHT LOSS AT 2.5 & 5.0 w/cm^2

FS 2e: VPSP AMCY179/H795 KT148=3/7 with A193-P carbon fiber
Resin Content 38.86%, Cured at 177°C for 2 hr

FS 3c: VPSP AMCY179/H795 KT148=4/6 with A193-P carbon fiber
Resin Content 42.57%, Cured at 177°C for 2 hr

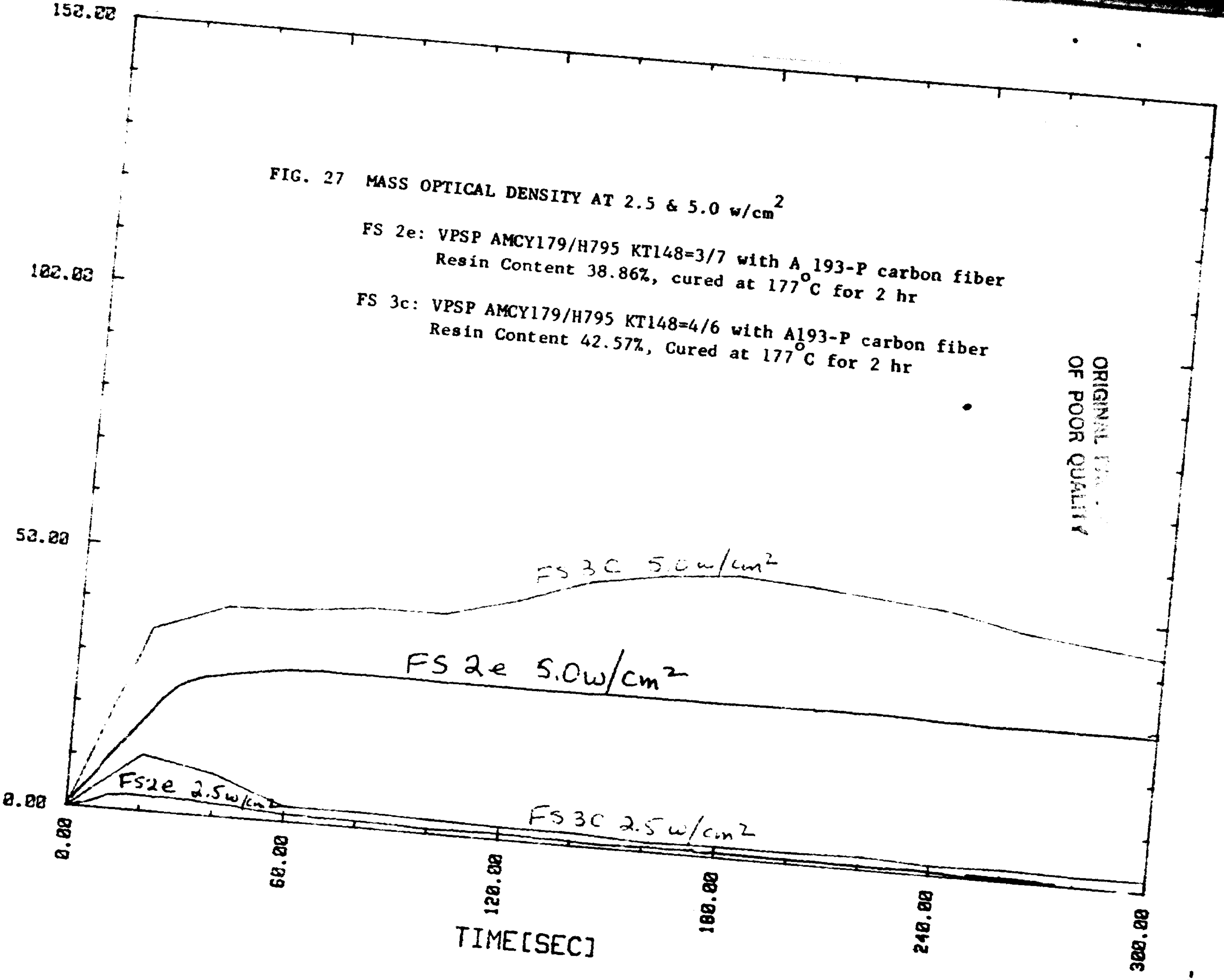


FIG. 27 MASS OPTICAL DENSITY AT 2.5 & 5.0 w/cm^2

FS 2e: VPSP AMCY179/H795 KT148=3/7 with A 193-P carbon fiber
Resin Content 38.86%, cured at 177°C for 2 hr

FS 3c: VPSP AMCY179/H795 KT148=4/6 with A193-P carbon fiber
Resin Content 42.57%, Cured at 177°C for 2 hr

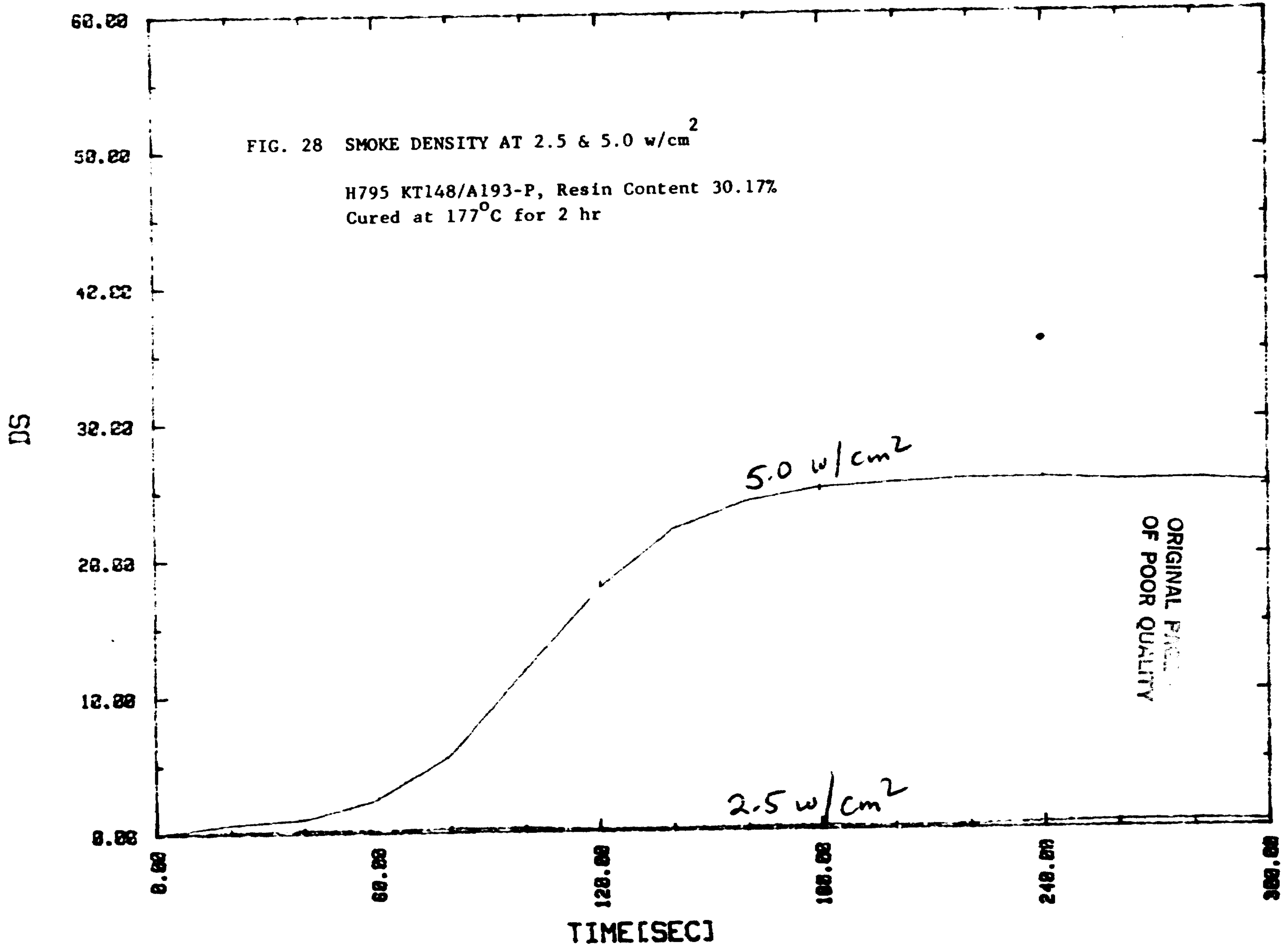


FIG. 28 SMOKE DENSITY AT 2.5 & 5.0 w/cm^2

H795 KT148/A193-P, Resin Content 30.17%
Cured at 177°C for 2 hr

ORIGINAL PAGE
OF POOR QUALITY

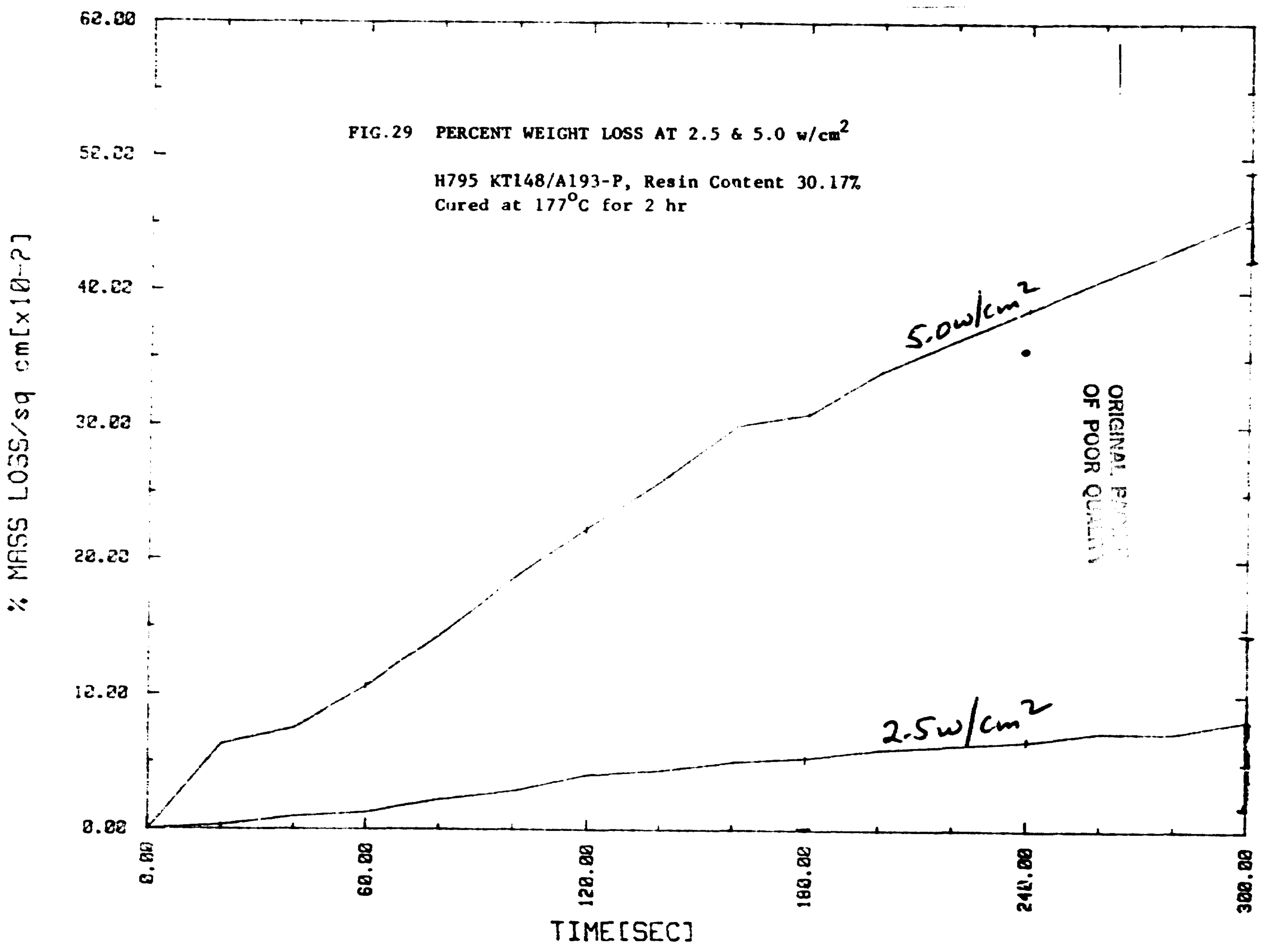


FIG.29 PERCENT WEIGHT LOSS AT 2.5 & 5.0 w/cm^2

H795 KT148/A193-P, Resin Content 30.17%
Cured at 177^{o}C for 2 hr

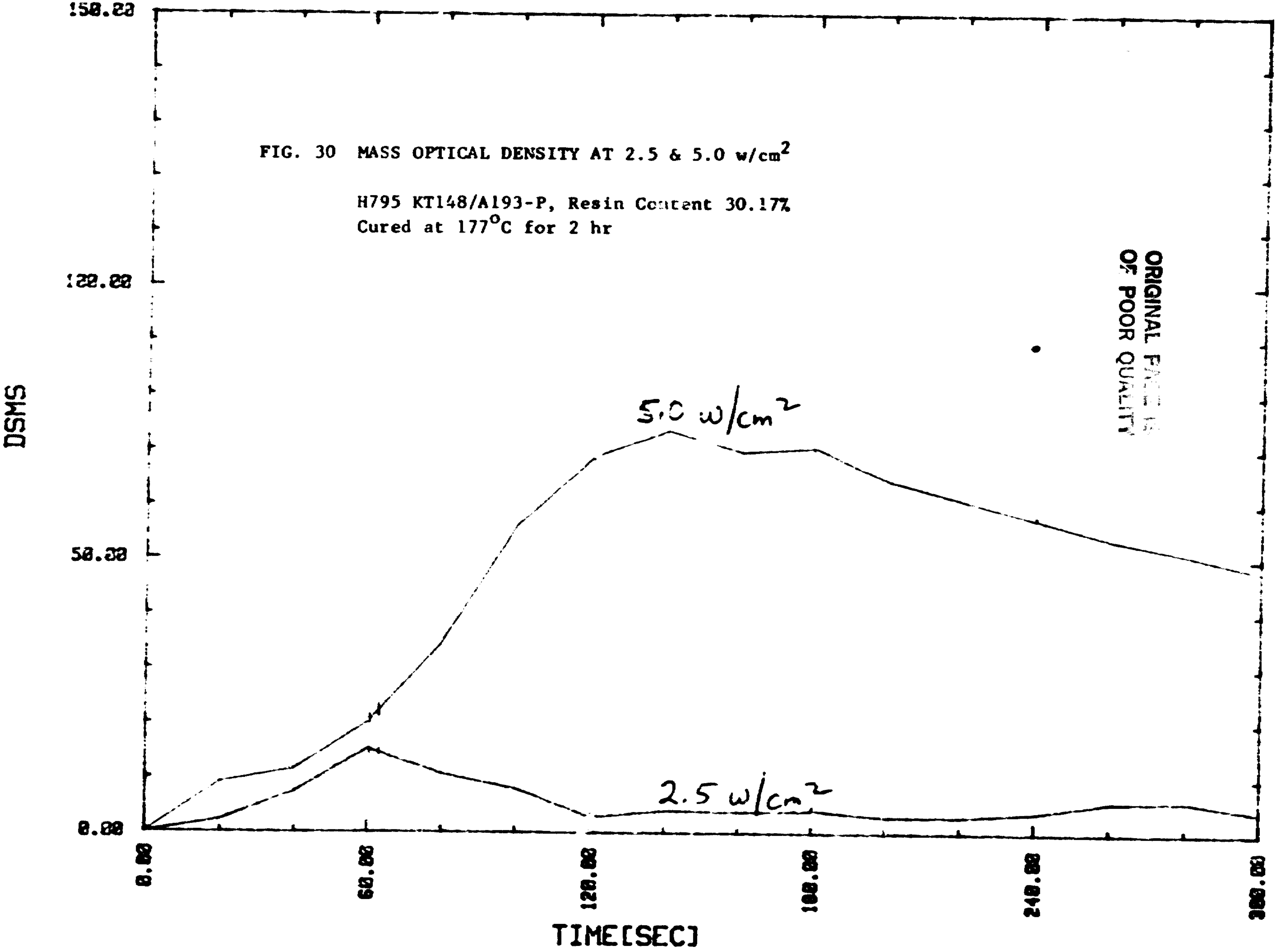


FIG. 30 MASS OPTICAL DENSITY AT 2.5 & 5.0 w/cm^2

H795 KT148/A193-P, Resin Content 30.17%
Cured at 177^{o}C for 2 hr

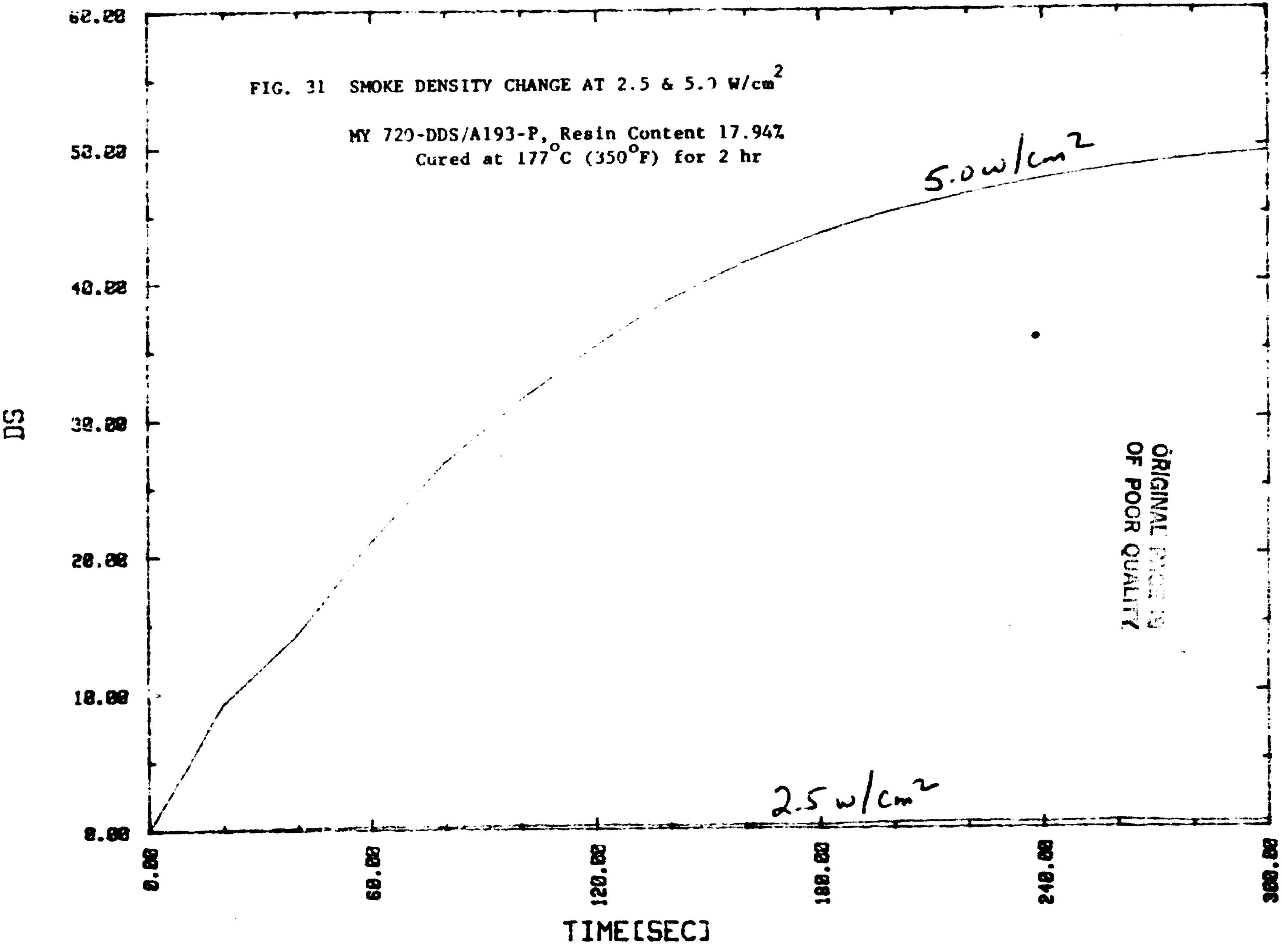


FIG. 31 SMOKE DENSITY CHANGE AT 2.5 & 5.0 W/cm^2

MY 720-DDS/A193-P, Resin Content 17.94%
Cured at 177°C (350°F) for 2 hr

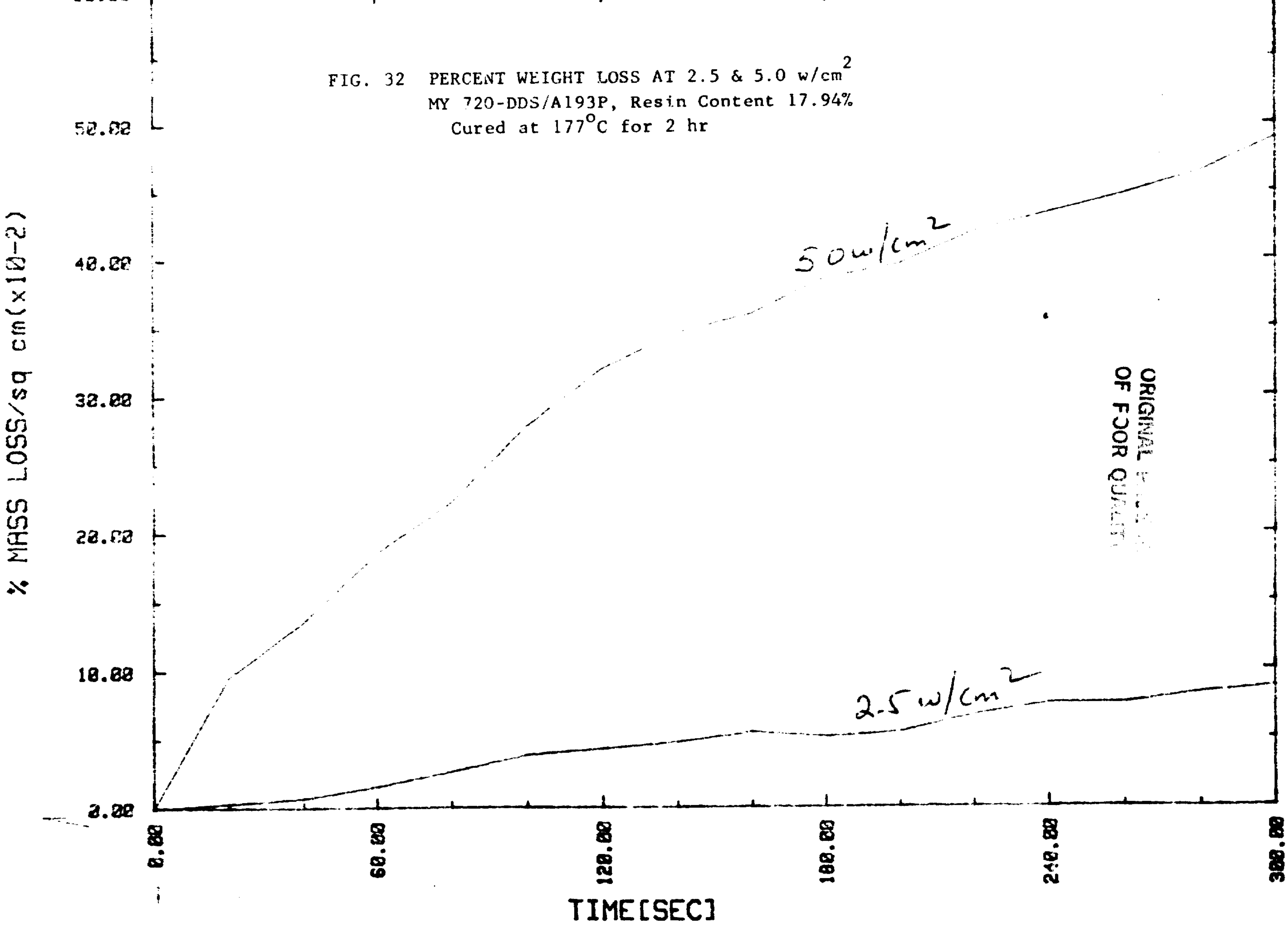


FIG. 32 PERCENT WEIGHT LOSS AT 2.5 & 5.0 w/cm^2
MY 720-DDS/A193P, Resin Content 17.94%
Cured at 177^{o}C for 2 hr

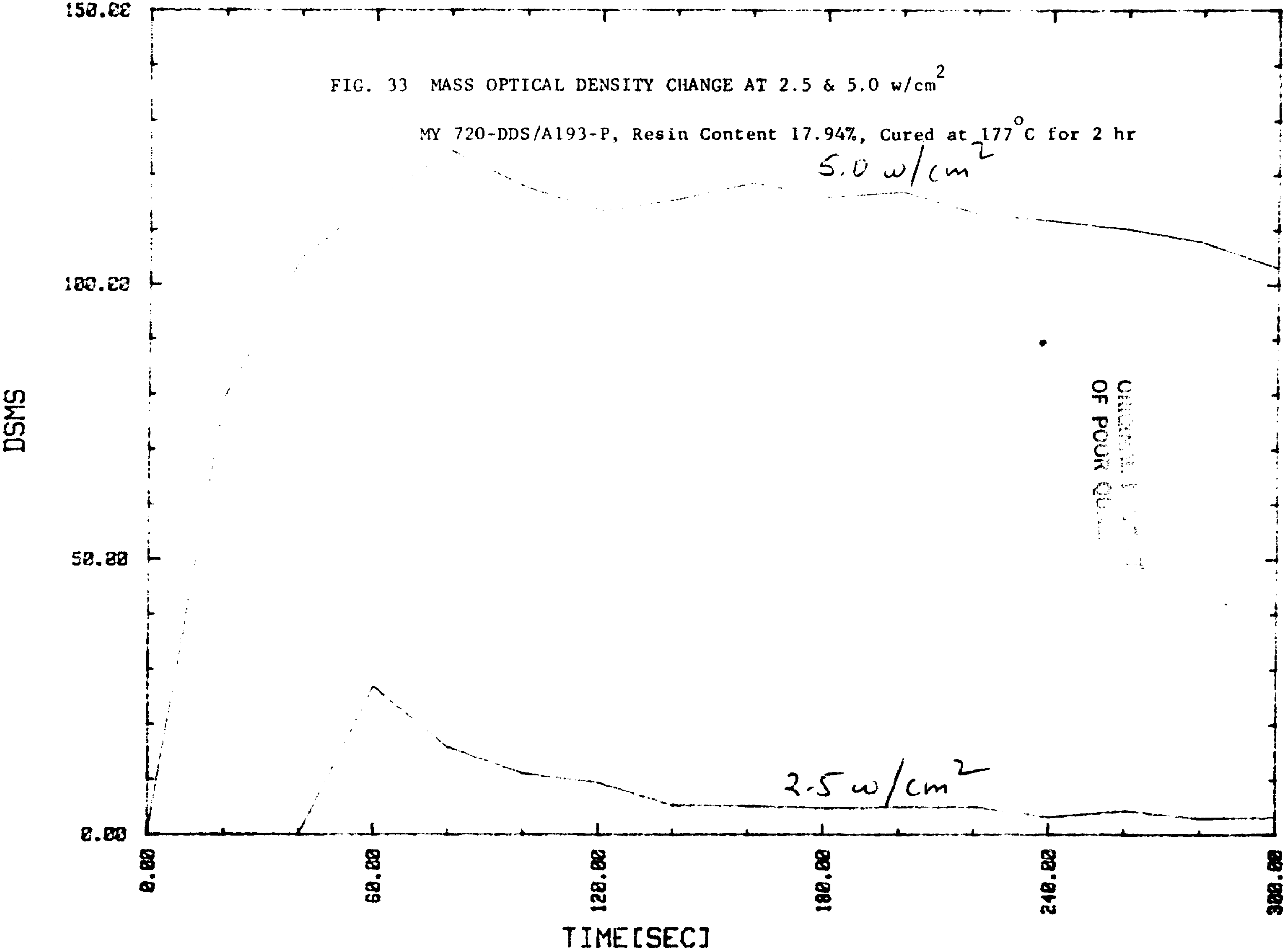


FIG. 33 MASS OPTICAL DENSITY CHANGE AT 2.5 & 5.0 w/cm^2

MY 720-DDS/A193-P, Resin Content 17.94%, Cured at 177°C for 2 hr