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FLAME RETARDANT POLYPHOSPHAZENES

Prepared by:

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ULTRASYSTEMS, INCORPORATED
Irvine, California

Prepared for:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center

Contract NAS3-17829

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16. Abstract <p>Three processes for the preparation of polyphosphazenes were investigated: (1) the reaction of bisphosphines with diazides, (2) the condensation of bisdichlorophosphoranes with diamines, and (3) the treatment of bisphosphines with diamines in the presence of carbon tetrachloride followed by base dehydrohalogenation. All products obtained were of low molecular weight; the degree of polymerization did not exceed twelve repeating units. However, several compositions exhibited good thermal stability. No weight loss was observed up to 390°C when heated in air at 5°C/min.</p> <p>Treatment of bisphosphines with either an excess of a diazide or an excess of a diamine in the presence of carbon tetrachloride resulted in the production of difunctional phosphazenes which were, respectively, azido and amino terminated. The reaction of these azido terminated "extended monomers" with bisphosphines did not produce high molecular weight materials.</p> <p>The bis-aminophosphazene prepared for the first time under this contract was successfully incorporated into a polyimide. A 3:2 mixture of 4,4'-methylenedianiline and the aminophosphazene was condensed with the dimethyl ester of benzophenonetetracarboxylic acid and the monomethyl ester of norbornene-dicarboxylic acid via the PMR process to yield a prepolymer of a formulated molecular weight of ~2400. Using this resin glass fabric reinforced laminates were produced and their mechanical properties and flammability characteristics compared with those of laminates prepared in an identical manner from prepolymer of formulated molecular weight of ~1500, which were free of aminophosphazene. The mechanical properties of the phosphazene modified laminates were inferior to those of the unmodified panels most likely due to the difference in formulated molecular weights and the not optimized processing conditions. When exposed to a stoichiometric natural gas/oxygen flame unmodified 3-ply laminates burned through within ~80 sec. With the modified laminates no burn-through occurred during 15 min exposure to the flame under otherwise identical conditions.</p>			
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FOREWORD

This Final Report describes the work performed by Ultrasystems, Inc. during the period 6 June 1975 through 9 July 1976 under Contract NAS3-17829 on Flame Retardant Polyphosphazenes. The investigations were carried out by K. L. Paciorek, D. W. Karle, and R. H. Kratzer, project manager, at the Chemicals and Materials Research Department, Irvine, California. The contract was administered by the NASA Lewis Research Center with Tito T. Serafini as the project manager.

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1. SUMMARY

This is the final report describing work performed by Ultra-systems, Inc. for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-17829.

The objective of the program was to prepare a series of polymeric compositions intended for use as laminating resins which would be flame retardant and would not produce toxic products on oxidative thermal degradation.

The feasibility of preparing such compositions was established under Contract NAS3-16768. The approach was to react aliphatic bisphosphines with triazine diazides whereby phosphazene units were formed which imparted the desired flame resistance to the end products. However, only low molecular weight oligomers were obtained and the aliphatic linkages reduced the thermal and oxidative stability of these materials. In addition, the triazine nuclei present in the backbone caused the formation of benzonitrile and hydrogen cyanide upon oxidative thermal degradation.

The goal of the current investigation was to develop a process yielding high molecular weight phosphazenes and to replace the aliphatic segments as well as the triazine rings by aromatic moieties free of heteroatoms. To achieve these objectives the following steps were taken: (1) the required monomeric species and prepolymers were synthesized, (2) selected model systems were prepared and studied, (3) three different processes for the production of high molecular weight phosphazenes were investigated, (4) the feasibility of producing phosphazene modified polyimides using the PMR technique was established, and (5) the oxidative thermal behavior, hydrolytic stability, and flammability characteristics were determined on representative compositions.

The monomers synthesized were 1,4-bis(diphenylphosphino)benzene, 4,4'-bis(diphenylphosphino)biphenyl, the respective bis-dichlorophosphoranes, mono-aminophosphazene, bis-aminophosphazene, bis-azidophosphazenes, and a model phosphazene,

$$\text{C}_6\text{H}_5\text{N}=\text{P}(\text{C}_6\text{H}_5)_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{P}(\text{C}_6\text{H}_5)_2=\text{N}\text{C}_6\text{H}_5.$$

Three polymerization processes leading to phosphazene systems were investigated: (a) diazide-bisphosphine interaction, (b) bis-dichlorophosphorane-diamine condensation, and (c) reaction of a diamine with a bisphosphine in the presence of carbon tetrachloride followed by base dehydrohalogenation.

The first process was originally studied under the previous contract, NAS3-16768; current work was directed at varying systematically reaction parameters with the ultimate goal of producing high molecular weight materials. Regardless of solvent, temperature, reaction periods, mode of addition, and stoichiometry the number of repeating units remained at 3-12. By adding the phosphine into an excess of an azide, azide terminated "monomeric" compounds were isolated in quantitative yields. These were characterized by derivatization and were employed as "extended" monomers or prepolymers in bulk polymerizations, however, the degree of polymerization did not exceed 7 units.

The polymerizations utilizing the aromatic diamines, p-phenylenediamine and 4,4'-methylenedianiline, and the bis-dichlorophosphoranes or the phosphine-carbon-tetrachloride system resulted only in low molecular weight compositions, 2-5 units. The products based on the aromatic bisphosphines exhibited high thermal stability, no weight loss up to 390°C, and a char yield of 47% at 600°C.

The phosphine-amine-carbon-tetrachloride process was modified to synthesize diaminophosphazenes as represented by

$H_2N-\phi-CH_2-\phi-N=P\phi_2-\phi-\phi-P\phi_2=N-\phi-CH_2-\phi-NH_2$ which were employed in conjunction with 4,4'-methylenedianiline, the monomethyl ester of norbornene-2,3-dicarboxylic and the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid to manufacture flame retardant polyimide laminates utilizing the PMR process.

2. INTRODUCTION

The flame retardant nature of phosphorus-nitrogen linkages in conjunction with their low potential for toxic product formation when subjected to thermal oxidative degradation, as exemplified in the extreme case by fire, has been fully discussed previously (ref. 1) and to a degree was substantiated by past investigations (ref. 1-3).

The previous investigations (ref. 1) were directed at forming the phosphorus-nitrogen linkages via oxidation of bisphosphines by diazides. The specific studies involving the reaction of triazine diazides and bis(diphenylphosphino)alkanes, e.g., 1,2-bis(diphenylphosphino)ethane and 1,4-bis(diphenylphosphino)butane failed to afford high molecular weight polymers. In addition, the presence of aliphatic moieties in the backbone imparted inherent oxidative instability, whereas the triazine nucleus was responsible for the traces of hydrogen cyanide liberated on thermal oxidative decomposition.

One of the objectives of the current program was to determine the conditions for the diazide-bisphosphine reaction leading to the formation of high molecular weight polymers. Another objective was to utilize a true condensation polymerization as, e.g., represented by a bis-dichlorophosphorane-diamine system to provide high molecular weight purely aromatic P-N materials free from triazine rings. The third objective was to synthesize difunctional monomeric phosphazenes for use as comonomers for the preparation of fire resistant polymers, which upon oxidative thermal degradation would form only minimal amounts of toxic products.

3. EXPERIMENTAL DETAILS AND PROCEDURES

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B) or under nitrogen by-pass. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

Molecular weights (MW) were determined in chloroform solutions using a Mechrolab Osmometer Model 302 at concentrations of 4-6 mg/ml. Infrared (IR) spectra were recorded on double mulls (Kel-F oil No. 10 and Nujol) using a Perkin-Elmer Corporation Infrared Spectrophotometer Model 21. Differential scanning calorimetry (DSC), differential thermal (DTA), and thermogravimetric analysis (TGA), were performed on a duPont 951/990 Thermal Analyzer.

All materials synthesized were dried at 100°C or higher in vacuo before physical and chemical characterization unless their melting point was lower than this temperature. The melting points of the monomers were determined in nitrogen filled or evacuated sealed capillaries, the softening and melting points of the polymers were obtained using a Fisher-Johns apparatus. The elemental analyses were performed by Schwarzkopf Micro-analytical Laboratory, Woodside, New York.

Since both the structural formulae and the appropriate chemical nomenclature for the monomers used during this program are complex and cumbersome, these compounds have been coded to aid in clarity of presentation throughout this report. The codes used are as follows:

TDA	$N_3-C_3N_3\phi-N_3$ 2,4-diazido-6-phenyl-s-triazine
DPPB	$\phi_2P-(CH_2)_4-P\phi_2$ 1,4-bis(diphenylphosphino)butane
BDBI	$\phi_2P-\phi-\phi-P\phi_2$ 4,4'-bis(diphenylphosphino)biphenyl
PDPB	$\phi_2P-\phi-P\phi_2$ 1,4-bis(diphenylphosphino)benzene
MDA	$H_2N-\phi CH_2 \phi-NH_2$ 4,4'-methylenedianiline
PPDA	$H_2N-\phi-NH_2$ p-phenylenediamine
PA	$H_2N-\phi CH_2 \phi-N=P\phi_2-\phi-\phi-P\phi_2=N-\phi CH_2 \phi-NH_2$ bis-aminophosphazene
NE	monomethyl ester of norbornene-2,3-dicarboxylic acid
BTDE	dimethyl ester of 3,3',4,4'-benzophenonetetra-carboxylic acid

3.1 MONOMER AND MODEL SYSTEM SYNTHESSES

2,4-Diazido-6-phenyl-s-triazine, TDA

This material was synthesized under the preceding contract wherein it is fully described (ref. 1).

1,4-Bis(diphenylphosphino)butane, DPPB

This monomer was purchased from Strem Chemicals, Inc., Danvers, Massachusetts and was used without further purification, mp 132-133°C, reported in literature mp 135-136°C (ref. 4).

Preparation of 4,4'-bis(diphenylphosphino)biphenyl, BDBI

Following the procedure of Baldwin and Cheng (ref. 5) 74.5 g (0.24 mol) of 4,4'-dibromobiphenyl were dissolved in 250 ml of dry tetrahydrofuran and 0.48 mol (145.9 g of a 20.9% solution in hexane) of n-butyllithium was added at -72°C over a period of 2 hr. After warming to 0°C and recooling to -70°C neat diphenylchlorophosphine (105.4 g, 0.48 mol) was added over a 2.75 hr period. All operations were carried out under strict exclusion of oxygen and moisture. After warming to room temperature the solids were filtered off under nitrogen and washed with water until a test for halide ion was negative. The remaining solid was digested under nitrogen with 500 ml methanol for 30 min, filtered, dried, and recrystallized from tetrahydrofuran giving pure BDBI (85.7 g, 68.3% yield), mp 192.1-192.9°C (ref. 6) (192.5-194°C). The DSC trace is presented in Figure 1.

Preparation of 1,4-bis(diphenylphosphino)benzene, PDPB

The procedure employed was essentially the same as that described by Baldwin and Cheng (ref. 5) for the preparation of 4,4'-bis(diphenylphosphino)biphenyl. Thus to 11.8 g (0.05 mol) of 1,4-dibromobenzene dissolved in ether (125 ml) was added under nitrogen by-pass 0.20 mol of n-butyllithium (64.8 g of 20.9% soln. in hexane; diluted with additional hexane to a total of 125 ml) at 4°C over a period of 45 min. This was followed by 3 hr reflux. Subsequently, the solution was cooled in an ice bath and diphenylchlorophosphine (22.1 g, 0.1 mol) was added over a period of 35 min. During addition, formation of

white solid was observed. After cooling this material was filtered off in an inert atmosphere enclosure giving 31.1 g of product. This material was then stirred with de-aerated water under nitrogen by-pass. This treatment was followed by stirring under reflux with methanol. The insoluble material was subsequently crystallized from benzene-heptane in an inert atmosphere enclosure giving 14.3 g (64% yield) of 1,4-bis(diphenylphosphino)benzene, mp 165.2-167°C (lit, ref. 6, 166-168°C). The DSC trace is presented in Figure 2.

Preparation of 4,4'-bis(diphenylphosphino)biphenyl-
bis-dichlorophosphorane

Under nitrogen by-pass to a stirred solution of BDBI (5.00 g, 9.568 mmol) in benzene (125 ml) cooled to 0°C was added a previously prepared solution of chlorine in carbon tetrachloride (30.3 g, containing 5.37 weight percent of chlorine) over a period of 30 min. The solid (6.24 g, 98% yield) which formed was filtered in the inert atmosphere enclosure. It was analyzed for chlorine using sodium hydroxide hydrolysis followed by Volhard titration. Analysis Found: Cl, 21.30 Calcd for $C_{36}H_{28}P_2Cl_4$: Cl, 21.34%. The infrared spectrum of the material formed on hydrolysis was identical with that of authentic BDBI bis-oxide.

Preparation of 1,4-bis(diphenylphosphino)benzene-
bis-dichlorophosphorane

Under a nitrogen by-pass a solution of 1,4-bis(diphenylphosphino)benzene (3.0 g, 6.719 mmol) in benzene (60 ml) was treated with a solution of chlorine in carbon tetrachloride until the yellow color of the chlorine solution persisted. After about half of the chlorine solution was added, the reaction mixture became opaque and when ~ 80% of the Cl_2 solution had been reacted, a white solid formed. The

reaction solution was then evaporated to dryness on the vacuum line in order to remove the excess chlorine. The resulting solid was washed with carbon tetrachloride in an inert atmosphere enclosure and then crystallized from acetonitrile to give 1.81 g (46% yield) of the bis-dichlorophosphorane. Anal. Calcd. for $C_{30}H_{24}Cl_4P_2$: Cl, 24.11. Found: Cl, 23.85.

Preparation of $N_3-C_3N_3(\Phi)-N=P\Phi_2(CH_2)_4P\Phi_2=N-(\Phi)C_3N_3-N_3$ via reaction of DPPB with TDA in 1:3 mole ratio

Under nitrogen by-pass to a stirred solution of TDA (3.37 g, 14.069 mmol) in chloroform (40 ml) was added a solution of DPPB (2.0 g, 4.690 mmol) in chloroform (20 ml) over a period of 1 hr. The precipitate started to form almost immediately. After stirring overnight the insoluble product (4.41 g, 111% yield assuming the structure $N_3-C_3N_3(\Phi)-N=P\Phi_2(CH_2)_4P\Phi_2=N-(\Phi)C_3N_3-N_3$) was filtered off.

The filtrate on evaporation afforded 1.06 g, (4.431 mmol) of pure unreacted TDA. Based on the bis-phosphine employed and the TDA recovered the ratio of the diazide to bis-phosphine in the product formed was 2.06 : 1.00; which agrees with the 111% yield realized.

The original precipitate could be crystallized from dimethyl formamide. However, crystallization was accompanied by what appears to be complex formation as evidenced by a band at 5.95μ in the infrared spectrum of the "crystallized" product. Washing with chloroform and heating at $100^\circ C$ in vacuo or boiling with benzene failed to remove the 5.95μ band in the infrared spectrum.

To remove the last traces of TDA, the original precipitate was boiled with toluene, filtered hot, and dried. The TGA analysis (Figure 3) of this treated material showed no weight loss up to $260^\circ C$, indicating the absence of TDA, which starts to decompose at $155^\circ C$. The toluene treated

product melted with decomposition at $\sim 260^{\circ}\text{C}$ in agreement with the TGA results, and its DSC analysis (Figure 4) showed no melting endotherm at 130°C , the melting point of TDA.

Reaction of $\text{N}_3\text{-C}_3\text{N}_3(\Phi)\text{-N=P}\Phi_2(\text{CH}_2)_4\text{P}\Phi_2\text{=N-(}\Phi\text{)C}_3\text{N}_3\text{-N}_3$ with $\text{P}\Phi_3$

To establish the structure and composition of $\text{N}_3\text{-C}_3\text{N}_3(\Phi)\text{-N=P}\Phi_2(\text{CH}_2)_4\text{P}\Phi_2\text{=N-(}\Phi\text{)C}_3\text{N}_3\text{-N}_3$, 398.7 mg (0.470 mmol) were placed into an ampoule with 2.016 g (7.685 mmol) of sublimed triphenylphosphine. After evacuation and sealing the ampoule was heated for 1.5 hr at $88\text{-}103^{\circ}\text{C}$ in an oil bath, during which time slight gassing was observed. This was followed by heating at 114°C in an oven for 16 hr. The ampoule was cooled and opened to a high vacuum system and the noncondensable gas, which had formed was collected in a Sprengel pump and identified as pure nitrogen by mass spectroscopy. The nitrogen yield was 0.892 mmol or 95.0% of theory. The solids in the ampoule were treated with hot heptane to remove the large excess of triphenylphosphine and the residue from this treatment was extracted three times with boiling benzene. The product thus obtained, mp $160\text{-}165^{\circ}\text{C}$, exhibited TGA given in Figure 5.

Anal. Calcd. for $\text{C}_{82}\text{H}_{68}\text{N}_{10}\text{P}_4$: C, 74.76%; H, 5.20%; N, 10.63%; P, 9.40%; MW, 1317.42. Found: C, 74.58%; H, 5.29%; N, 10.97%, P, 9.14%; MW, 1290.

Preparation of $\text{N}_3\text{-C}_3\text{N}_3(\Phi)\text{-N=P}\Phi_2\text{-}\Phi\text{-}\Phi\text{-P}\Phi_2\text{=N-(}\Phi\text{)C}_3\text{N}_3\text{-N}_3$ via reaction of BDBI with TDA in 1:3 mole ratio

In an inert atmosphere enclosure a solution of 4,4'-bis(diphenylphosphino)biphenyl (2.00 g, 3.827 mmol) in chloroform (35 ml) was added to a solution of 2,4-diazido-6-phenyl-s-triazine (2.75 g, 11.482 mmol) in chloroform (25 ml) at ambient conditions over a period of 1 hr. After addition was complete a solid formed. Stirring was continued for 18 hr,

the reaction mixture was filtered to give 3.43 g of insoluble material (94.8% yield, assuming the structure

$N_3-C_3N_3(\Phi)-N=P\Phi_2-\Phi-\Phi-P\Phi_2=N-C_3N_3(\Phi)-N_3$) which exhibited an azide absorption in the infrared. An aliquot (1.00 g) of the above material was boiled with toluene (25 ml), filtered hot and dried to give 0.75 g of material, which no longer exhibited an azide absorption in the infrared spectrum and had a melting point greater than 300°C.

Thermogravimetric analysis (Figure 6) showed a sharp weight loss at 258°C (corresponding to 7.5% of the original weight) which correlated with DTA (see Figure 7) exotherm at 249°C. If one assumes the structure shown above, the weight loss due to azide decomposition should be 5.9%.

Evaporation of the original reaction solution resulted in the recovery of 1.10 g of TDA contaminated with the "azide-terminated" product shown above, evaporation of the filtrate from the toluene treatment afforded 0.05 g of TDA.

Reaction of $N_3-C_3N_3(\Phi)-N=P\Phi_2-\Phi-\Phi-P\Phi_2=N-C_3N_3(\Phi)-N_3$ with $P\Phi_3$

To establish the structure and composition of

$N_3-C_3N_3(\Phi)-N=P\Phi_2-\Phi-\Phi-P\Phi_2=N-C_3N_3(\Phi)-N_3$, 805 mg (0.852 mmol) of this compound was treated with sublimed triphenylphosphine, (1.925 g, 7.340 mmol) *in vacuo* in a sealed ampoule at 139°C in an oven for 24 hr.

After cooling and opening to a vacuum system 1.595 mmol of nitrogen was collected using a Sprengel pump giving the ratio of

$N_3-C_3N_3(\Phi)-N=P\Phi_2-\Phi-\Phi-P\Phi_2=N-C_3N_3(\Phi)-N_3 : N_2 = 1:1.873$. Thus 93.6% of the expected nitrogen was evolved, proving the above postulated arrangement.

The solids in the ampoule were extracted, triturated with boiling heptane (4 x 75 ml) and filtered hot to remove the large excess

of triphenylphosphine resulting in 1.618 g of product. Two crystallizations from benzene-heptane afforded

$\text{C}_6\text{H}_5\text{P}=\text{N}-\text{C}_3\text{N}_3(\text{C}_6\text{H}_5)-\text{N}=\text{P}(\text{C}_6\text{H}_5)_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{P}(\text{C}_6\text{H}_5)_2=\text{N}-\text{C}_3\text{N}_3(\text{C}_6\text{H}_5)-\text{N}=\text{P}(\text{C}_6\text{H}_5)_3$, (0.351 g, 29.2% yield), mp 187-190°C, MW 1480 (Calcd. for $\text{C}_{90}\text{H}_{60}\text{N}_{10}\text{P}_4$: MW, 1413.50).

The DTA curve is given in Figure 8.

Preparation of $\text{C}_6\text{H}_5\text{N}=\text{P}(\text{C}_6\text{H}_5)_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{P}(\text{C}_6\text{H}_5)_2=\text{N}\text{C}_6\text{H}_5$

In an inert atmosphere enclosure, a solution of aniline (0.29 g, 3.114 mmol) in acetonitrile (12 ml) was added dropwise at room temperature to a stirred solution of 4,4'-bis(diphenylphosphino)biphenyl-bis-dichlorophosphorane (1.00 g, 1.505 mmol) in acetonitrile (50 ml) over a period of 12 min. After stirring at room temperature for 1.5 hr, triethylamine (0.63 g, 6.227 mmol) in acetonitrile (10 ml) was added over a period of 10 min and the solution was stirred for an additional 19.5 hr. Subsequent filtration afforded 0.96 g (90.5% yield) of a yellow solid which crystallized from benzene-heptane to give 0.84 g (79% yield) of product, mp 229-235°C. Two crystallizations from benzene-heptane resulted in pure $\text{C}_6\text{H}_5\text{N}=\text{P}(\text{C}_6\text{H}_5)_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{P}(\text{C}_6\text{H}_5)_2=\text{N}\text{C}_6\text{H}_5$, mp 235-237°C. Anal. Calcd. for $\text{C}_{48}\text{H}_{38}\text{N}_2\text{P}_2$: C, 81.80%; H, 5.43%; N, 3.97%; P, 8.79%, MW, 704.79. Found: C, 80.63%; H, 5.61%; N, 3.83%; P, 8.26%, MW, 770. The DTA curve is given in Figure 9 and the TGA trace is presented in Figure 10. The endotherm peaking at 238°C in the DTA corresponds to the observed melting point. Thermogravimetric analysis (Figure 10) shows an initial weight loss at 220°C, a constant weight after a loss of 2.5% up to 350°C, and a char yield of 47.5% at 500°C.

Preparation of $\Phi_3\text{P}=\text{N}-\Phi\text{CH}_2-\Phi-\text{NH}_2$ via reaction of tri-phenylphosphine with an excess of MDA, 1:5 molar ratio, in the presence of carbon tetrachloride followed by triethylamine treatment

Modifying the procedure of Appel and co-workers (ref. 7,8) under a nitrogen by-pass a solution of carbon tetrachloride (16.2 g, 105.3 mmol) in dichloromethane (25 ml) was added dropwise to a stirred solution of triphenylphosphine (25.0 g, 95.3 mmol) and 4,4'-methylenedianiline (94.2 g, 475 mmol) in dichloromethane (275 ml) over a period of 22 min. After stirring at room temperature for 46 hr, the reaction solution was heated under reflux for 2 hr. Filtration afforded 4.62 g of insoluble material identified as an amine hydrochloride by infrared spectral analysis. Removal by distillation of approximately 95% of the solvent from the reaction solution afforded a semi-solid, which on trituration with 90/10 mixture and 50/50 mixture of ether/acetonitrile and acetonitrile afforded 34.1 g (72.2% yield) of the solid intermediate, $[\Phi_3\text{P}-\text{NH}-\Phi\text{CH}_2-\Phi-\text{NH}_2]^+\cdot\text{Cl}^-$.

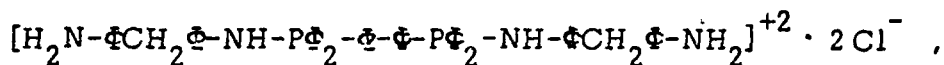
Subsequently, a mixture of the intermediate product (34.1 g, 68.9 mmol) and triethylamine (20.9 g, 207 mmol) in acetonitrile (250 ml) was stirred at room temperature for 16 hr under a nitrogen by-pass. Filtration removed 4.59 g (48.5% yield) of white solid identified as triethylamine hydrochloride by infrared spectroscopy. The reaction solution was evaporated on the rotary evaporator to give 33.9 g of solid which was dissolved in chloroform, washed with water, dried over sodium sulfate and precipitated into a 20-fold volume of petroleum ether. On standing the solution slowly deposited 5.80 g (9.6% overall yield) of crystalline $\Phi_3\text{P}=\text{N}-\Phi\text{CH}_2-\Phi-\text{NH}_2$, mp 143-148°C; crystallization from benzene-heptane gave mp, 146-147.5°C. Anal. Calcd. for $\text{C}_{48}\text{H}_{38}\text{N}_2\text{P}_2$: C, 81.20%; H, 5.94%; N, 6.11%; P, 6.75%; MW, 458.55. Found: C, 81.24%; H, 6.50%, N, 5.97%; P, 6.19%; MW, 460.

The DTA curve is given in Figure 11; the NMR trace is presented in Figure 12. The ratio of aromatic:aliphatic:amino protons was found to be 12:1:1 (theory, 11.5:1:1).

Preparation of $H_2N-C_6H_4-NH-PPh_2-C_6H_4-PPh_2-NH-C_6H_4-NH_2$ via reaction of BDBI with an excess of MDA, 1:10 molar ratio, in the presence of carbon tetrachloride followed by triethylamine treatment

Under a nitrogen by-pass, a solution of carbon tetrachloride (6.0 g, 39.01 mmol) in benzene (25 ml) was added dropwise at room temperature to a stirred solution of 4,4'-bis(diphenylphosphino)bi-phenyl (10.0 g, 19.14 mmol) and 4,4'-methylenedianiline (38.0 g, 191.7 mmol) in benzene (175 ml) over a period of 20 min. After stirring at room temperature for 5 days, the reaction mixture was heated under reflux for 1.5 hr. An oil formed immediately upon heating. After cooling the reaction solution was decanted from the oil adhering to the sides of the flask. The oil was then washed with benzene and the washings combined with the reaction solution. Evaporation of the benzene solutions gave 31.0 g of solid, identified by infrared spectral analysis as being mostly 4,4'-methylenedianiline.

The oil adhering to the sides of the flask was triturated and stirred with ether giving 15.05 g (79.6% yield) of the intermediate product,



which was stirred with triethylamine (24.30 g, 240.2 mmol) and chloroform (100 ml) at room temperature for 24 hr under nitrogen by-pass. This was followed by heating under reflux for 5 hr. The solution was subsequently washed with water and after drying over sodium sulfate it was precipitated into petroleum ether. The solid thus obtained was

treated with ethyl ether and dried in vacuo giving 6.31 g (36% overall yield) of the desired product,

$H_2N-\text{C}_6H_4-CH_2-\text{C}_6H_4-N=P(\text{C}_6H_5)_2-\text{C}_6H_4-\text{C}_6H_4-P(\text{C}_6H_5)_2=N-\text{C}_6H_4-CH_2-\text{C}_6H_4-NH_2$, mp 132-134°C. Anal. Calcd. for $C_{62}H_{52}N_4P_2$: C, 81.38%; H, 5.72%; N, 6.12%; P, 6.77%; MW, 915.07. Found: C, 79.62%; H, 5.85%; N, 5.51%; P, 7.07%; MW, 940. The NMR trace is presented in Figure 13. The ratio of aromatic:aliphatic:amino protons was found to be 11.9:1:1 (theory, 11.0:1:1).

Preparation of monomethyl ester of 5-norbornene-2,3-dicarboxylic acid

The monomethyl ester of 5-norbornene-2,3-dicarboxylic acid was prepared in 82.9% yield from 5-norbornene-2,3-dicarboxylic anhydride (97.75 g, 0.595 mol), and anhydrous methanol (26.26 g, 0.820 mol) using a slight modification of the method of Walton (ref. 9). The slight modification consisted of crystallization of the crude reaction product from benzene-petroleum ether. After thorough drying in vacuo for 12 hr at room temperature, the product had mp 98-100°C, (ref. 9), mp 102-103°C.

3.2 POLYMERIZATION STUDIES

3.2.1 Phosphine-Azide Solution Studies

All phosphine-TDA solution studies were conducted under a dry nitrogen atmosphere, either in an inert atmosphere enclosure or under a nitrogen by-pass. Equimolar and nonequimolar reactions were performed using normal and inverse addition modes. In the normal addition mode, azide solution was added to the phosphine solution; in the inverse addition mode, phosphine was added to the azide. A typical phosphine-azide reaction is described below. Specific reaction conditions, stoichiometries, addition modes, properties, yields, etc.,

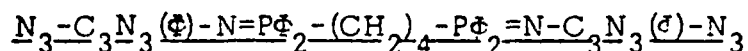
are listed in Tables I and II. The representative TGA curve of each of the systems studied are given in Figures 14-16.

Typical procedure for TDA-phosphine reactions

Inside the inert atmosphere chamber DPPB (2.0 g, 4.69 mmol) was placed in a 200 ml round bottom flask and dissolved in chloroform (20 ml). With stirring a solution of 1.12 g (4.69 mmol) of TDA in chloroform (20 ml) was added at room temperature over a 45 min period. Stirring at room temperature was continued for 3.5 hr before the product was precipitated (if required, after filtration of reaction medium insoluble material) by pouring the reaction mixture into 200 ml of dry n-heptane. The solid products collected by filtration were washed with two 20 ml portions of heptane and dried for a minimum 8 hr at 100°C on a high vacuum line.

3.2.2 Phosphine-Azide Bulk Reactions

Reactions of 1,4-bis(diphenylphosphino)butane with



a) Equimolar ratio. The reaction temperature was selected based on differential thermal analysis (DSC) of the mixture (see Figure 17) wherein a reaction exotherm with a maximum at 155°C is indicative of the occurrence of reaction. Accordingly, an ampoule was charged with DPPB (250 mg, 0.586 mmol) and $\text{N}_3\text{-C}_3\text{N}_3(\Phi)\text{-N=P}\Phi_2\text{-(CH}_2\text{)}_4\text{-P}\Phi_2\text{=N-C}_3\text{N}_3(\Phi)\text{-N}_3$ (500 mg, 0.589 mmol) in an inert atmosphere enclosure. The mixture was then evacuated and heated in vacuo at 151-165°C until gas evolution ceased (2 hr). The noncondensable gas was collected in a Sprengel pump and identified as pure nitrogen by mass spectroscopy. The nitrogen yield was 0.799 mmol (67.8% of theory), showing clearly that the reaction was incomplete.

The involatile product consisted of a mixture of white solid and a red brown glassy material. The white solid (99.5 mg), was mechanically separated from the mixture and identified by its infrared spectrum as unreacted $N_3-C_3N_3(\Phi)-N=P\Phi_2-(CH_2)_4-P\Phi_2=N-C_3N_3(\Phi)-N_3$. The red brown glassy solid (602.4 mg) was treated with chloroform (10 ml), filtered to remove additional 10.6 mg of unreacted diazide and precipitated into heptane. The solid thus obtained (374.2 mg, 66.8% yield), sp 140°C; mp 155-165°C; MW 4400 (corresponding to 7.3 units of repeating segment) exhibited an infrared spectrum and TGA curve typical of the products of the reaction of 2,4-diazo-6-phenyl-s-triazine and 1,4-bis(diphenylphosphino)butane.

The heptane filtrate on standing afforded 10 mg of the unreacted 1,4-bis(diphenylphosphino)butane in the form of its oxide. The yield of the "polymeric" product is in fairly good agreement with the evolved nitrogen (67.8%) and the incompleteness of the reaction is shown by starting materials recovery.

b) 3:2.1 Molar ratio. In an inert atmosphere an ampoule was charged with $N_3-C_3N_3(\Phi)-N=P\Phi_2-(CH_2)_4-P\Phi_2=N-C_3N_3(\Phi)-N_3$, (521.3 mg, 0.614 mmol), and DPPB (840 mg, 1.970 mmol). After evacuation on the vacuum line, the mixture was heated for 1.25 hr at 153-158°C until gas evolution ceased. The glassy amber product was then treated with chloroform (15 ml), filtered to remove a trace of insoluble material, precipitated into heptane and collected by filtration. The product obtained, 701 mg (93.6% yield; based on the azide employed), sp 118°C, mp 124-134°C, MW, 2400 (corresponding to 4 units of the repeating segment), exhibited an infrared spectrum and TGA trace closely related if not identical with those given by the material described in (a).

From the filtrate the excess of starting material, DPPB, was partially recovered in the form of its oxide (423 mg; 68% of the excess employed).

c) 10:1 Molar ratio. In an inert atmosphere an ampoule was charged with $\text{N}_3\text{-C}_3\text{N}_3(\Phi)\text{-N=P}\Phi_2\text{-(CH}_2)_4\text{-P}\Phi_2\text{=N-C}_3\text{N}_3(\Phi)\text{-N}_3$ (0.50 g, .589 mmol) and DPPB (2.55 g, 5.979 mmol). After evacuation on the vacuum line, the mixture was heated for 1.7 hr at 150-160°C until gas evolution ceased. To remove unreacted DPPB the hard glassy product was extracted and triturated with boiling heptane (4 x 75 ml) and filtered hot in an inert atmosphere. The heptane insoluble material (0.86 g, 88.8% yield) was then crystallized from benzene-heptane to give the desired extended bis-phosphine, mp 148-150°C; MW, 1620 (calcd. for $\text{C}_{102}\text{H}_{94}\text{N}_{10}\text{P}_6$: MW, 1645.79).

3.2.3 Dichlorophosphorane-Amine Reactions

Reactions of 4,4'-bis(diphenylphosphino)biphenyl-bis-dichlorophosphorane with 4,4'-methylenedianiline

Following are described two typical stoichiometric reactions (normal and inverse addition modes), of 4,4'-bis(diphenylphosphino)-biphenyl-bis-dichlorophosphorane with 4,4'-methylenedianiline. Specific reaction conditions, stoichiometries, addition modes, etc., are listed in Table III while physical constants, molecular weights, etc., are described in Table IV. The representative TGA scans are given in Figures 18-20.

a) Normal addition. A solution of 4,4'-methylenedianiline (0.299 g, 1.505 mmol) in acetonitrile (10 ml) was added dropwise to a stirred solution of 4,4'-bis(diphenylphosphino)biphenyl-bis-dichlorophosphorane (1.00 g, 1.505 mmol) in acetonitrile (40 ml) over a period of 10 min. A white solid formed immediately and the reaction solution became very viscous. Stirring was continued for 1.5 hr, then

triethylamine (0.61 g, 6.028 mmol) in acetonitrile (5 ml) was quickly added. A yellow solid formed immediately. The reaction mixture was stirred at room temperature for 0.75 hr and then heated under reflux for 1.5 hr under nitrogen by-pass. After cooling, filtration in an inert atmosphere enclosure afforded a yellow solid (0.93 g, 86.1% yield). Evaporation of the original reaction solution to dryness afforded an additional 0.64 g of a solid residue which consisted mostly of amine hydrochloride. The original insoluble yellow solid was stirred with water for 1 hr, collected, washed with additional water and dried to give 0.84 g (77.8% yield) of product. Only a trace (0.06 g, 5.4% yield) of reaction medium soluble material was obtained.

b) Inverse addition. A solution of 4,4'-bis(diphenylphosphino) biphenyl-bis-dichlorophosphorane (1.03 g, 1.550 mmol) in acetonitrile (50 ml) was added at room temperature dropwise to a stirred solution of 4,4'-methylenedianiline (0.370 g, 1.550 mmol) and triethylamine (0.81 g, 8.006 mmol) in benzene (25 ml) over a period of 1.5 hr. During the addition, an orange oil separated. After stirring at ambient conditions for 68.5 hr, the reaction solution was decanted from the orange oil and evaporated on the vacuum line. The residue was stirred with water, collected, and dried giving 0.56 g (50.3% yield) of product.

The orange oil was stirred with heptane (50 ml) in the inert atmosphere enclosure for 1 hr whereupon it solidified. Treatment with water following the procedure described above gave 0.27 g (26% yield) of product.

Reaction of 4,4'-bis(diphenylphosphino)biphenyl-bis-dichlorophosphorane with p-phenylenediamine in acetonitrile in the presence of triethylamine

In an inert atmosphere enclosure a solution of p-phenylenediamine (0.204 g, 1.887 mmol) in acetonitrile (15 ml) was added dropwise, at room temperature to a stirred solution of 4,4'-bis(diphenylphosphino)biphenyl-bis-dichlorophosphorane (1.25 g, 1.881 mmol) in acetonitrile (60 ml) over a period of 15 min. A tan solid slowly formed. After stirring at room temperature for 2.5 hr, triethylamine (0.77 g, 7.610 mmol) in acetonitrile (10 ml) was added over a period of 10 min. The reaction mixture was stirred at room temperature for 0.75 hr and then heated under reflux for 1.5 hr under a nitrogen bypass. A dark brown solid which formed was scraped out, stirred with water, and after drying gave 0.99 g (83.9% yield) of product, sp 240, mp 250-260°C, MW 3300, (corresponding to 5.2 units of the repeating segment, $\text{[-N} \langle \text{C}_6\text{H}_4 \text{N} = \text{P} \langle \text{C}_6\text{H}_4 \text{P} \langle \text{C}_6\text{H}_4 \text{P} \langle \text{C}_6\text{H}_4 \text{N}]_n$). The TGA curve presented in Figure 21 shows very slight weight gain in the 300-350°C region, an initial weight loss at 363°C, and a char yield of 65.7% at 500°C.

Reaction of 1,4-bis(diphenylphosphino)benzene-bis-dichlorophosphorane with 4,4'-methylenedianiline in acetonitrile in the presence of triethylamine

In an inert atmosphere enclosure, a solution of 4,4'-methylenedianiline (0.166 g, 0.839 mmol) in acetonitrile (15 ml) was added dropwise to a stirred solution of 1,4-bis(diphenylphosphino)benzene-bis-dichlorophosphorane (0.49 g, 0.833 mmol) in acetonitrile (50 ml) over a period of 10 min. A white solid formed immediately. After stirring for 2 hr, triethylamine (0.35 g, 3.459 mmol) in acetonitrile (10 ml) was added over a period of 5 min. A yellow solid formed immediately. The reaction mixture was stirred at room temperature for

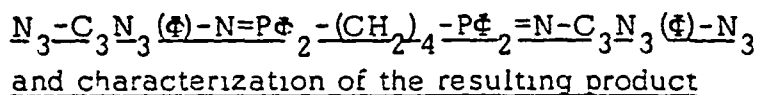
0.75 hr and then heated under reflux for 1.5 hr under nitrogen by-pass. The yellow solid was stirred with water and after drying, gave 0.37 g (69.3% yield) of material, η_{sp} 195 $^{\circ}$, mp 199-205 $^{\circ}$ C; MW, 2350 (which corresponds to 3.7 units of the repeating segment $\{N\text{-}\text{C}_6\text{H}_4\text{-CH}_2\text{-}\text{C}_6\text{H}_4\text{-N}=\text{P}\text{C}_6\text{H}_4\text{-}\text{C}_6\text{H}_4\text{-P}\text{C}_6\text{H}_4\}$). Thermogravimetric analysis (Figure 22) shows a slight weight gain in the 225-340 $^{\circ}$ C region, an initial weight loss at 340 $^{\circ}$ C and a char yield of 65% at 500 $^{\circ}$ C.

3.2.4 Reaction of 4,4'-bis(diphenylphosphino)biphenyl with 4,4'-methylenedianiline, 1:1 molar ratio: in the presence of carbon tetrachloride followed by triethylamine treatment

Under a nitrogen by-pass a solution of carbon tetrachloride (0.72 g, 4.7 mmol) in dichloromethane (7 ml) was added dropwise to a stirred solution of BDBI (1.00 g, 1.91 mmol) and MDA (0.38 g, 1.92 mmol) in dichloromethane (20 ml) over a period of 10 min. After stirring at room temperature for 74.5 hr, the reaction solution was evaporated to dryness and the yellow residue, 1.61 g, was stirred under nitrogen by-pass with triethylamine (1.08 g, 10.7 mmol) in acetonitrile (25 ml) for 42.5 hr at room temperature; this was followed by a 3 hr reflux. The solid product which separated out was washed with acetonitrile, dissolved in chloroform (25 ml), washed with water, dried over sodium sulfate, and precipitated into heptane to afford a light yellow solid (0.70 g, 48.3% yield), mp 177-183 $^{\circ}$ C; MW, 1800 (this corresponds to 2.5 units of the repeating segment $\{N\text{-}\text{C}_6\text{H}_4\text{-CH}_2\text{-}\text{C}_6\text{H}_4\text{-N}=\text{P}\text{C}_6\text{H}_4\text{-}\text{C}_6\text{H}_4\text{-P}\text{C}_6\text{H}_4\}$). Based on TGA trace and infrared spectral analysis the material is essentially the same as that isolated from the stoichiometric reactions of 4,4'-bis(diphenylphosphino)-biphenyl-bis-dichlorophosphorane with 4,4'-methylenedianiline.

3.3 DEGRADATION STUDIES

Thermal degradation of

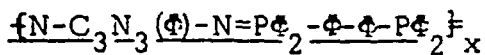


To determine the nature of the products formed during the sharp weight loss observed at $\sim 265^\circ\text{C}$ during thermogravimetric analysis of this bis-azide terminated intermediate (see Figure 3), a 580.0 mg (0.683 mmol) sample was placed in an ~ 25 ml ampoule equipped with constriction. After drying at 80°C under high vacuum for 1.5 hr to remove possibly adsorbed solvents or moisture the ampoule was sealed at the constriction and placed for 30 min into a furnace preheated to 275°C . The ampoule then was cooled with liquid nitrogen, opened to the high vacuum system, and 1.375 mmol of a noncondensable gas, identified as nitrogen by mass spectroscopy, were collected in a Sprengel pump. This corresponds to a ratio of N_2 : " $\text{N}_3\text{-x-N}_3$ " = $1.375:0.683 = 2.012:1$. In addition to the nitrogen, a 14.8 mg sample of a liquid condensable at -78°C was obtained, which consisted of $\sim 90\%$ chloroform and $\sim 10\%$ toluene, based on mass spectroscopy. Both of these materials had been used as solvents during preparation and purification of the sample, thus apparently have remained adsorbed despite the above described drying.

The residue remaining in the ampoule weighed 518.8 mg, which corresponds to a weight loss of 61.2 mg or 10.55%. This weight loss compares favorably to that observed in the TGA (Figure 3) of the bis-azide terminated material. The residue was a hard, black, glassy solid, sp 228, mp $244\text{-}250^\circ\text{C}$. It was soluble in hot chloroform and partially soluble in hot benzene, acetonitrile, and toluene. Its infrared spectrum showed similarities to the materials isolated from the normal reactions of 2,4-diazido-6-phenyl-s-triazine and 1,4-bis(diphenylphosphino)butane.

An aliquot (181.2 mg) of the residue was dissolved in chloroform, filtered, precipitated into heptane, collected by filtration giving after drying 36.4 mg (75.2% recovery) of material, mp 185-216°C, MW, 2600 (corresponding to 3.3 units of the repeating segment $\left[\text{N-C}_3\text{N}_3(\Phi)\text{-N=P}\Phi_2\text{-(CH}_2\text{)}_4\text{-P}\Phi_2\text{=N-C}_3\text{N}_3(\Phi)\text{-N}\Phi_x \right]$) exhibited a TGA curve (see Figure 23) which showed at 500°C a significantly larger char yield than the usual $\left[\text{P}\Phi_2\text{(CH}_2\text{)}_4\text{P}\Phi_2\text{=N-C}_3\text{N}_3(\Phi)\text{-N}\Phi_x \right]$ polymer e.g., 35% versus 21% (compare Figures 23 and 14). Based on infrared spectral analysis the material contains amino and possibly azido or nitrile groups.

Oxidative thermal decomposition of



Using the sealed tube technique (ref. 10) the medium insoluble phosphazene, prepared in Test No. 4, Table I, was subjected to oxidative thermal degradation. Thus, into the heating finger of the 2-liter flask were placed 1036.3 mg of the sample and the flask was evacuated. Then 52.5 mmoles of synthetic air (free of CO₂) were introduced and the flask closed, followed by heating at 420°C for 30 min. After cooling to room temperature the liquid nitrogen noncondensable gases were collected with a Sprengel pump and the room temperature volatile products were separated into fractions condensing at 0, -23, -78, and -196°C. Each fraction was quantitatively analyzed using infrared spectroscopy and combined gas chromatography-mass spectroscopy. The hard, black residue remaining in the finger amounted to 902.2 mg which corresponds to a 134.1 mg (12.94%) weight loss. The weight of the volatile products recovered was 112.9 mg, thus 84.2% of the total products formed were accounted for. The quantitative product distribution is given in Table V.

Hydrolytic stability of $\Phi N=P\Phi_2-\Phi-\Phi-P\Phi_2=N\Phi$

The model compound, $\Phi N=P\Phi_2-\Phi-\Phi-P\Phi_2=N\Phi$, (19.5 mg) was stirred with boiling water (10 ml) for 3 hr, collected and dried to give 16.4 mg (84%) of recovered material, which exhibited an infrared spectrum and DTA curve identical with that of the original sample.

3.4 POLYIMIDE COMPOSITE FABRICATION

The successful synthesis of an amino terminated phosphazene under this program provided the opportunity to prepare phosphazene modified polyimides which would be expected to be less flammable and should form smaller amounts of toxic products upon oxidative thermal degradation than compositions not containing the phosphazene units. The resin system chosen to determine the validity of this hypothesis was that composed of BTDE, NE, and MDA, which was prepared using the technique of polymerization of monomeric reactants (ref. 11-13). The formulated molecular weight (FMW) of the unmodified composition was 1500. The modified version was prepared by replacing a part of MDA by the amino terminated phosphazene PA, using throughout these studies a ratio of MDA:PA = 3:2. By employing the same molar ratios of tetraacid: diacid: diamine as in the unmodified composition, the FMW of the phosphazene modified system thus became 2387.

The amino terminated phosphazene PA and the monomethyl ester of nadic acid, NE, were prepared as described in Section 3.1. MDA was recrystallized three times inside an inert atmosphere chamber from benzene, adding charcoal in the first two crystallizations, mp 91-92.5°C of the purified material. The dimethylester of benzophenone tetracarboxylic acid, BTDE, was prepared freshly by refluxing for 2 hr a solution of benzophenone-tetracarboxylic dianhydride in such a quantity of methanol that the resulting solution contained 50% by weight of BTDE.

After cooling to room temperature to this solution of BTDE in methanol were added NE, MDA or a 3:2 molar mixture of MDA and PA and methanol to produce a 50% solution of the comonomers in the molar ratios BTDE:MDA:NE for the unmodified resin and BTDE: (3/5 MDA + 2/5 PA): NE for the phosphazene modified version of 2.087:3.087:2. The resulting mixtures were stirred until solution was complete and then used directly by pouring onto weighed 4" x 4" pieces of heat treated style 181 E-glass supported on Mylar film. The viscous solution was worked into the glass fabric with a wide spatula to produce prepregs of 30-40% resin content. The individual prepregs were then air dried for 1 hr at room temperature followed by drying in an air circulating oven at 120^oF for an additional 1 hr to reduce the volatiles content to 9-12% (see Table VI). The desired number of plies (3 or 12) was then placed into a preforming mold and imidized at 250^oF for 3 hr under an applied pressure of 0.1-0.3 psi. This treatment reduced the volatiles content to 2-5% (see Table VI) as determined by measuring the weight loss of a specimen during exposure to 600^oF in air for a period of 2 hr.

Composites were then molded (ref. 17) by placing the stack of imidized plies into a mold preheated to 450^oF. After a 10 min. dwell time to further reduce the volatiles content a pressure of 500 psi was applied and the temperature increased to 600^oF at a rate of 3^oF/min. This temperature and pressure were then maintained for 1 hr, after which time the temperature was lowered to 500^oF followed by reducing the pressure to 250 psi. After the platen temperature had dropped to 400^oF the pressure was released to contact pressure and the mold allowed to cool to room temperature. In this manner two 3-ply and three 12-ply laminates were prepared with each of the unmodified and modified resin systems (see Table VI).

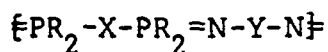
3.5 COMPOSITE TESTING

Flexural strength tests were performed using a 3 point loading fixture with a fixed span of 2 inches. The thicknesses of the laminates ranged from 0.070 to 0.085 inch. The resultant span/depth ratio used ranged from 24 to 29. The rate of center loading for flexural testing was 0.05 inch/min. Interlaminar shear strength tests were conducted at a constant span/depth ratio of 5. Elevated temperature tests were performed in an environmental heating chamber. For the flexural and shear tests the load was applied after a 15 minute soak at the test temperature. The results of the flexural strength and the interlaminar shear strength tests are summarized in Table VII. The data presented there are averages of 3 or more tests under each condition.

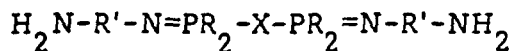
For the burn-through tests all 3-ply laminates prepared under this program (see Table VI, laminates No. 1 and 2 and No. 6 and 7) were mounted vertically and perpendicular to a natural gas/oxygen flame adjusted to 45 mm length. The distance between burner tip and test specimen surface was 35 mm, the largest flame diameter was ~ 6 mm. The natural gas/oxygen ratio was stoichiometric for all practical purposes; the adiabatic flame temperature was ~ 2700°C. Burn-through time was taken as the interval between exposure to the flame and the appearance of a brightly glowing pin hole on the backface of the specimen. In those cases where no burn-through occurred the duration of flame exposure was 15 min. The appearance of the laminates after the test is shown in Figure 29.

4. TECHNICAL DISCUSSION

The objective of this program was to produce flame retardant laminating resins which do not form highly toxic pyrolysis or combustion products. Such a resin could be based on "homo" polymers derived from a repeating segment as presented below:

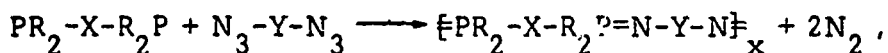


or on "hetero" polymers formed by substituting, e.g., some of the diamino compound employed in polyimide manufacture by a suitably phosphazene modified diamine, i.e.,

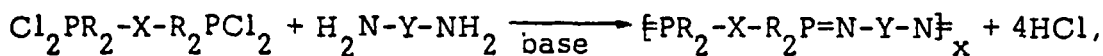


Three basic methods are known which conceivably could produce polymers of the general formula $\left[\text{PR}_2\text{-X-PR}_2\text{=N-Y-N} \right]_x$:

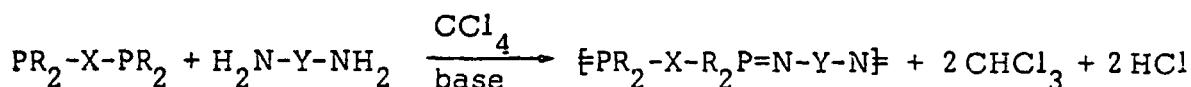
- a) oxidation of a bisphosphine by a diazide:



- b) interaction between a bis(dichlorophosphorane) and a diamine followed by base dehydrohalogenation:



- c) formation of pentavalent phosphorus nitrogen linkages by reaction of diamines with bisphosphines in the presence of carbon tetrachloride, again followed by base dehydrohalogenation:

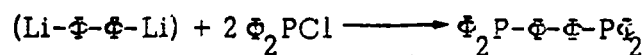
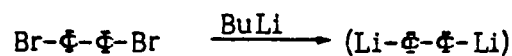


The diazido-bisphosphine process was studied previously (ref. 1) but only low molecular weight products were obtained. It was, however, believed that conditions could be identified for synthesis of high molecular weight compounds. The other two methods have been described in the literature, mainly to prepare monomeric species (ref. 7,8,14). The adaptability of these methods to polymer formation had to be determined. For the preparation of the functional phosphazenes of the general form, $H_2N-R'-N=PR_2-X-PR_2=N-R'-NH_2$, new techniques had to be developed.

The overall program thus consisted of: (1) monomer and model system synthesis, (2) polymerization studies embodying the three methods delineated above, (3) degradation studies, and (4) laminate fabrication and testing.

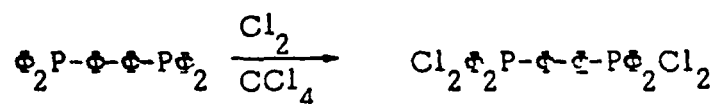
4.1 MONOMER AND MODEL SYSTEM SYNTHESIS

Under the previous program only bisphosphines were employed wherein the two phosphorus atoms were linked by aliphatic moieties. In view of the inherent thermal oxidative instability of aliphatic groupings, fully aromatic bisphosphines were essential. Since none are available commercially the two candidates, 4,4'-bis(diphenylphosphino)biphenyl (BDEI), and 1,4-bis(diphenylphosphino)benzene (PDPB) had to be synthesized. The procedure employed was a slight modification of the method of Baldwin and Cheng (ref. 5) wherein the dilithio derivative of 4,4'-dibromobiphenyl (in case of BDBI) is treated with diphenyl chlorophosphine according to the following equations:



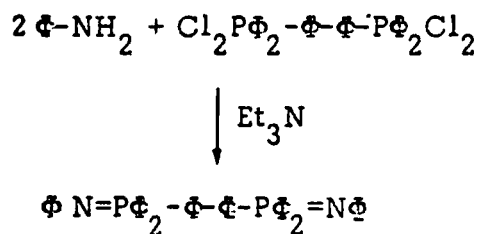
To prepare PDPB, $\text{C}_6\text{H}_5\text{P}(\text{C}_6\text{H}_5)\text{C}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2$, the dilithio derivative of 1,4-dibromobenzene was employed. Thus BDBI, mp 192-193°C, PDPB, mp 164-166°C, were obtained in 68 and 64% yields, respectively.

The corresponding bis-dichlorophosphoranes were synthesized via addition of a chlorine solution in carbon tetrachloride to a benzene solution of a given bisphosphine, i.e.,



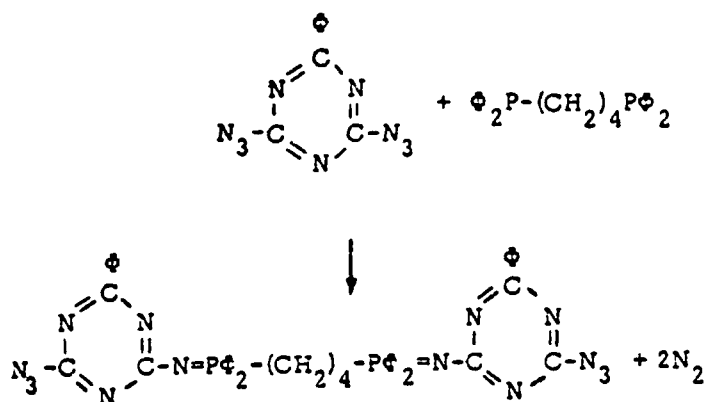
By this technique 4,4'-bis(diphenylphosphino) biphenyl-bis-dichlorophosphorane was prepared in 98% yield; the corresponding 1,4-bis(diphenylphosphino)benzene-bis-dichlorophosphorane was isolated in 46% yield.

To determine the reactivity of the bis-phosphoranes toward aromatic amines and to obtain a representative model system the BDBI-bis-dichlorophosphorane was treated with aniline in the presence of triethylamine, i.e.,



The phosphazene, $\text{C}_6\text{H}_5\text{N}=\text{P}(\text{C}_6\text{H}_5)_2-\text{C}_6\text{H}_4-\text{P}(\text{C}_6\text{H}_5)_2=\text{N}\text{C}_6\text{H}_5$, mp 232-234°C, was formed in 79% yield. Thermogravimetric analysis indicated that the material has good thermal stability with a char yield of 47.5% at 500°C (see Figure 10). Treatment of an aliquot with boiling water produced no change in the compound, indicating hydrolytic stability.

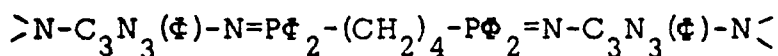
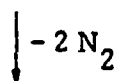
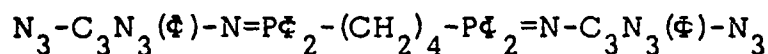
As was noted above one of the aims of the current program was to develop conditions giving high molecular weight polymers via the diazide-bisphosphine process. It was believed that the major reason for the failures encountered to date was preferential ring formation, which was apparently not hindered by the presence of rigid middle groups such as a triazine nucleus. To prevent ring formation, utilization of extended monomers offered an attractive avenue. A promising azido terminated compound was prepared by adding the (most available) bisphosphine into a three-fold excess of triazine diazide, i.e.,



The TGA curve of this compound (see Figure 3) showed a sharp weight loss at 260°C corresponding to 10.6% of the original weight. If one assumes the structural arrangement to be that given above and the weight loss to be due to azide decomposition then this value should be 6.6%.

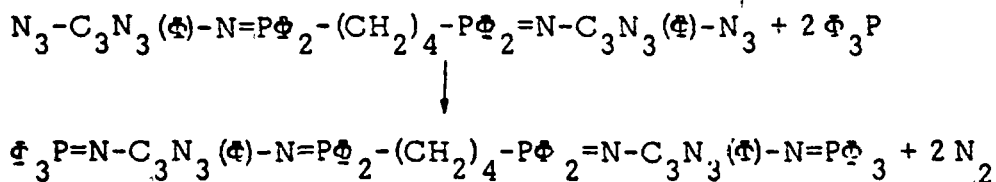
On the other hand, one cannot expect such a process to occur without complications and thus it is very likely that a side reaction, or reactions, taking place concurrently with azide decomposition are responsible for the observed value. The decomposition itself must be exothermic in nature as shown by the strong exotherm in the vicinity of 260°C in the DSC trace (see Figure 4).

Pyrolyzing the bisazide in an evacuated ampoule at 275°C for 30 min produced 2.06 mol of nitrogen per mol of azide in good agreement with the theoretically expected 2 mol:



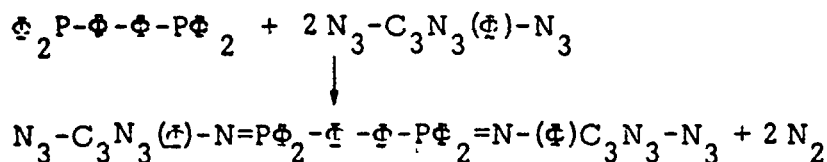
The black, hard, glassy residue was soluble in chloroform and after precipitation into heptane and drying had a molecular weight corresponding to ~ 3.3 repeating units of above structure. It is noteworthy that its TGA showed significantly higher char yield at 500°C than that observed for the usual $\text{P}\Phi_2-(\text{CH}_2)_4-\text{P}\Phi_2=\text{N}-\text{C}_3\text{N}_3(\Phi)-\text{N}$ polymers (35% versus 21%; compare Figures 23 and 14). This would tend to indicate that the pyrolysis product contains structural arrangements different from the diazide-bisphosphine reaction derived phosphazenes.

To prove the structure and composition of $\text{N}_3-\text{C}_3\text{N}_3(\Phi)-\text{N}=\text{P}\Phi_2-(\text{CH}_2)_4-\text{P}\Phi_2=\text{N}-\text{C}_3\text{N}_3(\Phi)-\text{N}_3$, it was treated with an excess of triphenylphosphine at 114°C; the temperature was selected based on DTA of the ingredient mixture wherein an exotherm was observed to start at ~ 110°C (see Figure 24)

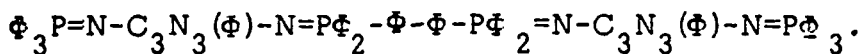


The yield of nitrogen was 95.0% of theory and the molecular weight and elemental analyses of the isolated phosphorane supported the postulated arrangement.

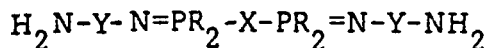
An "extended monomer" free from aliphatic groups was prepared in 77% yield from a 3:1 molar ratio reaction of TDA with 4,4'-bis(diphenylphosphino)biphenyl:



This material in analogy with the bis(diphenylphosphino)butane derived compound, exhibited in its TGA trace (see Figure 6) a sharp weight loss at 258°C (corresponding to 7.5% of the original weight) which correlated with a DTA exotherm at 249°C (see Figure 7). The structure was proven by forming the triphenylphosphine derivative,

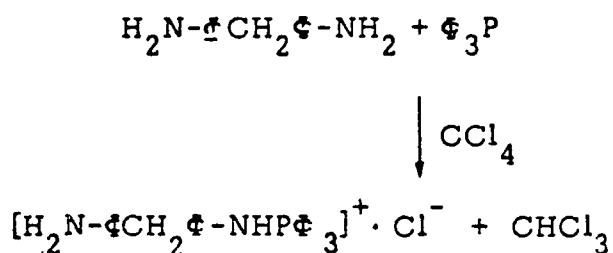


The synthesis of an amino-phosphazene of the general formula

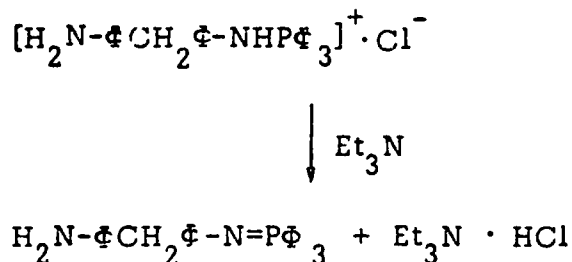


presented an entirely different challenge than the systems discussed above. The most obvious process would involve the interaction of bis-dichlorophosphorane with an excess of a suitable diamine. Unfortunately none of the desired product could be isolated. Appel and co-workers (ref. 7,8) produced nonfunctional phosphazenes by

reaction of monophosphines with diamines and by reaction of bis-phosphines with mono-amines in the presence of carbon tetrachloride. Syntheses of amino terminated phosphazenes using this technique have not been described in the literature. To evaluate the feasibility of such a process, triphenylphosphine was reacted with an excess of 4,4'-methylenedianiline in methylenedichloride-carbon tetrachloride medium, giving after purification ~ 72% yield of what appeared to be (based on infrared spectral analysis) an amine hydrochloride in agreement with the equation:



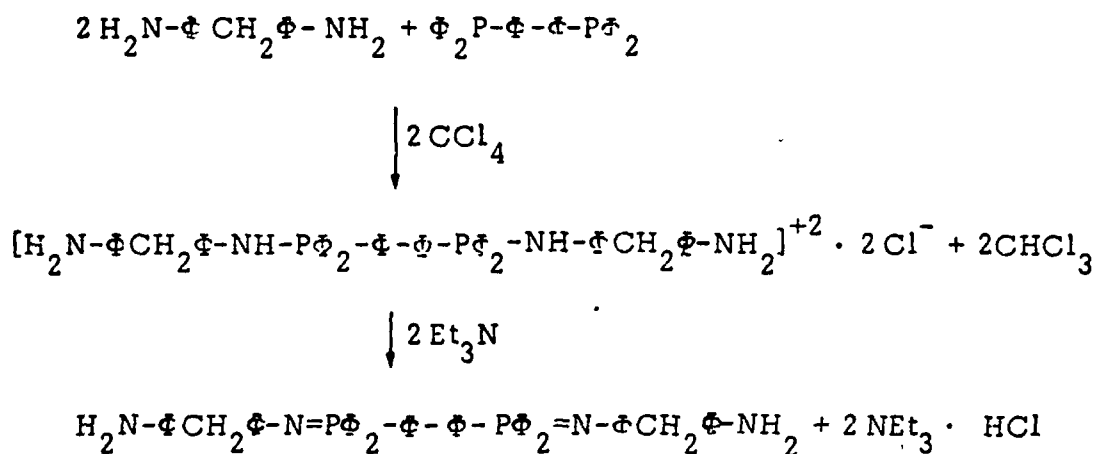
The free amine was subsequently obtained in ~ 56% yield using triethylamine-acetonitrile treatment:



The aminophosphazene, mp 146-148°C, was characterized by molecular weight determination and elemental analysis; in addition, its structural arrangement was unequivocally proven by NMR spectroscopy (see Figure 12) wherein the ratio of aromatic:aliphatic:amino protons was found to be 12:1:1, in agreement with the theoretical values of 11.5:1:1.

It is noteworthy that Appel and co-workers (ref. 7,8) in their reactions employed potassium amide in liquid ammonia as the dehydrohalogenating agent. In view of the above described results it is evident that triethylamine is a sufficiently strong base to perform this function.

The successful preparation of $\text{C}_6\text{H}_5\text{P}=\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$ showed that this process could very well be adaptable to the synthesis of di-aminophosphazenes. Interaction of 4,4'-bis(diphenylphosphino)-biphenyl with a tenfold excess of 4,4'-methylenedianiline gave the amine hydrochloride which on treatment with triethylamine afforded the desired product, $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{P}(\text{C}_6\text{H}_5)_2-\text{C}_6\text{H}_4-\text{P}(\text{C}_6\text{H}_5)_2=\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$, in an overall 36% yield. The sequence is depicted below:

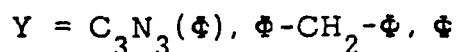
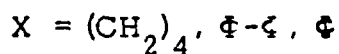


The reaction, however, did not proceed as readily as in the case of triphenylphosphine and to attain the yields finally realized the conditions had to be modified in a number of experiments. It was thus found that best results were obtained by performing the first step in benzene and then conducting the dehydrohalogenation in chloroform. The diamino-phosphazene was fully characterized by elemental analysis, molecular

weight, infrared spectroscopy, and NMR spectroscopy, wherein the ratio of aromatic:aliphatic:amino protons was found to be 11.9:1:1 in fairly good agreement with the theoretical values of 11.0:1:1.

4.2 POLYMERIZATION STUDIES

The basic polymeric system considered under this program can be best represented by: $\left[\text{PR}_2\text{-X-PR}_2\text{=N-Y-N} \right]_n$, wherein



To synthesize such a system a number of avenues were investigated. These involved: (a) phosphine oxidation by azide in solution, (b) bulk interaction of "extended-azide" with phosphine, (c) bis-dichlorophosphorane-diamine condensation, and (d) bisphosphine-diamine- CCl_4 reaction. In the following subsection the results obtained using these different approaches will be discussed.

4.2.1 Phosphine-Azide Solution Studies

The azide oxidation of bisphosphines, has been investigated previously (ref. 1) and the major objective in this area under this program was to study variations in reaction conditions to hopefully find a method of producing high molecular weight materials. In order to investigate the largest number of possible variations with a minimum expenditure of time only one reactant pair was employed in these studies, namely 1,4-bis(diphenylphosphino)butane and 2,4-diazido-6-phenyl-s-triazine. The former material is commercially available in a pure state, the latter was synthesized without difficulty using a previously developed procedure (ref. 1). The experiments carried out are summarized in Tables I and II.

The nature of the solvent constitutes one of the important variables. Benzene was extensively studied under a previous phase of this work (ref. 1) thus the current effort was limited to tetrahydrofuran, acetonitrile, the immiscible combination acetonitrile/n-heptane and chloroform. Using the first three solvents (see Run Nos. 1-3) soluble and insoluble products were formed in ratios of 1:3 to 1:9. All products obtained had practically identical infrared spectra, all softening points, and melting ranges were comparable (175-190 and 185-210°C, respectively); the thermograms were superimposable and identical with those obtained previously (ref. 1) (see Figure 14 for a representative TGA trace). In addition, the molecular weights of the soluble portions were within experimental error of a material consisting of three repeating units, e.g., $[=N-C_3N_3(\Phi)-N=P\Phi_2-(CH_2)_4-P\Phi_2=]_3$, MW, 1829. These results would indicate that the reaction of TDA and DPPB in these three solvents proceeds in the same way and that a variation of the total solids concentration and a change in reaction temperature has no effect on the molecular weights of the reaction medium soluble products. The fact that insoluble products were also obtained may, however, be an indication that higher molecular weight materials were produced.

Conducting the process in chloroform and employing the normal addition mode, namely adding TDA to a DPPB solution resulted in an absence of the medium insoluble products. The molecular weights of the materials obtained were definitely higher than three repeating units. Comparing Run Nos. 6 and 7 (Table I) it may be argued that higher solids concentration does increase molecular weight, whereas the employment of an excess of TDA (see Run Nos. 8 and 9, Table II) tends

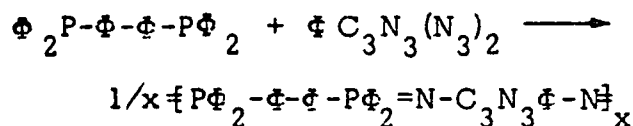
to lower the "degree of polymerization" despite the fact that the excess of azide is recovered unchanged. This latter aspect was proven unequivocally in Run No. 9, where TDA was reacted with DPPB in a 4:3 molar ratio. Of 6.27 mmoles of TDA employed for reaction with 4.69 mmoles of DPPB, 1.21 mmoles of TDA were recovered unchanged, thus making the ratio of DPPB to TDA consumed 1:1.08, which is within experimental error for a 1:1 composition. The isolated products exhibited identical infrared spectra and thermal analysis curves as the polymers isolated from the equimolar reactions in agreement with the recovery of excess TDA.

To investigate the effect of the mode of addition in the reaction of TDA with DPPB on the product molecular weights Run No. 9 (Table II) was repeated with the exception that a solution of DPPB was added to a solution of TDA. When comparing Run Nos. 9 and 10 it can be seen that inverse addition (DPPB added to TDA, Run No. 10) produced a chloroform insoluble material in 64% yield, furthermore the molecular weight of the soluble product corresponded to ~ 8 repeating units, whereas using normal addition (Run No. 9) gave material consisting of ~ 12 repeating units.

The insoluble product, sp 255°C, mp 265-275°C, exhibited an infrared spectrum completely different from those of the products obtained to date from the interaction of DPPB and TDA. Its TGA curve (see Figure 3) showed a sharp weight loss at 260°C corresponding to 10.6% of the original weight. If one assumes the structural arrangement to be $N_3-C_3N_3(\text{C}_6H_4)-N=P\text{C}_2(\text{CH}_2)_4P\text{C}_2=N-(\text{C}_6H_4)C_3N_3-N_3$ and the weight change to be due to azide decomposition then the weight loss should be 6.6%. The DSC of this product (see Figure 4) exhibited

a strong exotherm with an onset at ca 205°C and a peak at ca 260°C. The TGA, DSC, and melting behavior indicated an azido type of a moiety, however the absence of absorption at 4.7μ in the infrared spectrum was unexpected. By using 50% excess of the required TDA the desired "extended azide" $N_3-C_3N_3\phi-N=P\phi_2(CH_2)_4P\phi_2=N-C_3N_3\phi-N_3$ was obtained in essentially quantitative yield (see Run No. 13, Table II). In the same manner the BDBI analogue was prepared (see Run No. 14, Table II). The characterization and structure proof of these materials is fully described in Section 4.1.

To investigate the possibility of avoiding ring formation and producing a high molecular weight product via azide oxidation of an aromatic, more "rigid" bisphosphine a benzene solution of TDA was added at room temperature to a benzene solution of 4,4'-bis(diphenylphosphino)biphenyl according to:

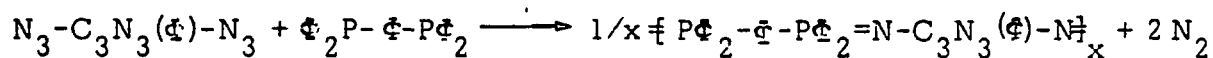


In this manner a 35.9% yield of benzene soluble and a 51.5% yield of benzene insoluble product was obtained. The benzene soluble material softened at 240°C, mp 247-253°C, and had a molecular weight of 3200 (x = 4.5). The product insoluble in benzene (but soluble in chloroform) softened at 195°C, mp 284-292°C, and showed a molecular weight of 8400 (x = 11.9). Thus it would appear that substitution of an aliphatic by an aromatic bisphosphine does not prevent ring formation (the products were free of azide). Longer reaction times (see Test No. 16) failed to affect the molecular weights and product ratios. However, the thermal stability in air of both the soluble and insoluble reaction products is remarkable. Programming at 5°C/min shows no weight loss

up to 390-400°C and the char yield at 600°C, ~ 47% is surprisingly high (a representative TGA curve is given in Figure 15).

To determine the oxidative thermal decomposition characteristics of polyphosphazenes derived from the reaction of BDBI with TDA, $\text{[N-C}_3\text{N}_3(\Phi)\text{-N=P}\Phi_2\text{-}\Phi\text{-}\Phi\text{-P}\Phi_2\text{]}_x$, (see Test No. 4, Table I) was subjected to degradation using the sealed tube technique (ref. 10). This sample thus was heated in air at 420°C for 30 min and the room temperature volatile products were quantitatively determined using combined gas chromatography/mass spectroscopy. A total of 109 mg of volatile products were formed per gram of phosphazene employed, which is in good agreement with the weight loss of ~ 6% in air at 420°C as measured by thermogravimetric analysis (see Figure 15). The slightly higher total weight loss in the sealed tube test, ~ 13%, is due to the longer residence time at temperature. The results of the analysis of the products formed are presented in Table V. As can be seen very few toxic products are formed and none in large quantities. The species of concern are CO, HCN, (CN)₂, benzene, phenol, and cresol, of which HCN and (CN)₂ almost certainly originate from the s-triazine ring present.

An analogous reaction using 1,4-bis(diphenylphosphino)benzene and TDA was carried out to determine whether higher molecular weight products of equally good thermal stability may be formed by this phosphine-azide pair. After a 96 hr reaction of equimolar amounts of PDPB and TDA in benzene at room temperature a 72% yield of a benzene insoluble solid and a 7% yield of benzene soluble product was obtained (see Table I, Run No. 12):



Both materials had identical infrared spectra and TGA curves. The latter (see Figure 16, for the TGA of the insoluble product) showed these products to be thermally less stable than the products from the BDBI-TDA reaction. The molecular weight of the benzene soluble product indicated ~ 4.4 repeating units, which is comparable to that found for the soluble material obtained in the corresponding BDBI-TDA system.

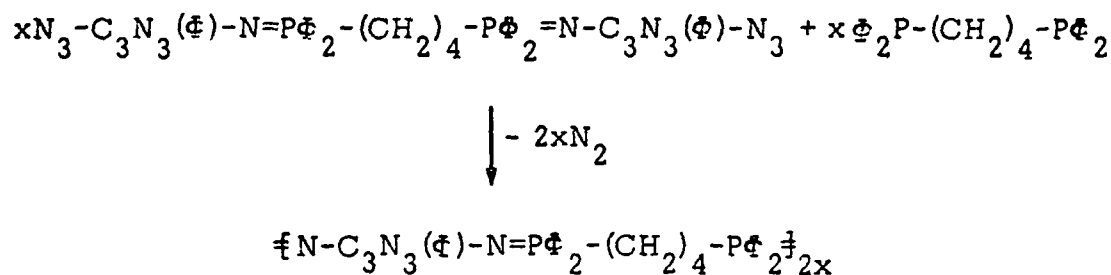
Based on the series of reactions discussed above, the following can be concluded: (a) the thermal stability of the products decreases in the order BDBI > PDPB > DPPB; (b) the "normal" addition of TDA to the bis-phosphine in 1:1 ratio regardless of solvent forms products of low molecular weight which possibly are of a cyclic nature; (c) the "inverse" addition of the bis-phosphine to TDA produces azide terminated intermediates which can be obtained in practically quantitative yield provided a large enough excess of TDA is employed.

It should be stressed that the structure of the low molecular weight "polymeric" materials obtained is unknown, the "degree of polymerization" of ~ 2 to 12 repeating units per molecule is within the same range as previously found by, e.g., Bilbo and Sharts, e.g., ~ 2 to 9 repeating units (ref. 15). Since so far no unreacted end groups, e.g., azido groups, could be detected in these products, it may be speculated that cyclic compounds are being formed. A similar conclusion was reached by Horn (ref. 16) who found the products of bis-phosphine-diazide reactions to contain 2 to 4 repeating units.

4.2.2 Phosphine-Azide Bulk Reactions

The extended azide $N_3-C_3N_3(\Phi)-N=P\Phi_2-(CH_2)_4-P\Phi_2=N-C_3N_3(\Phi)-N_3$ in view of its relatively extensive chain length seemed an ideal candidate to avoid the formation of cyclics and thus to lead to high molecular weight products or to provide longer chain phosphine terminated materials. Inasmuch as the extended azide was insoluble in conventional solvents and formed permanent complexes with liquids such as dimethylformamide the studies were necessarily limited to bulk reactions.

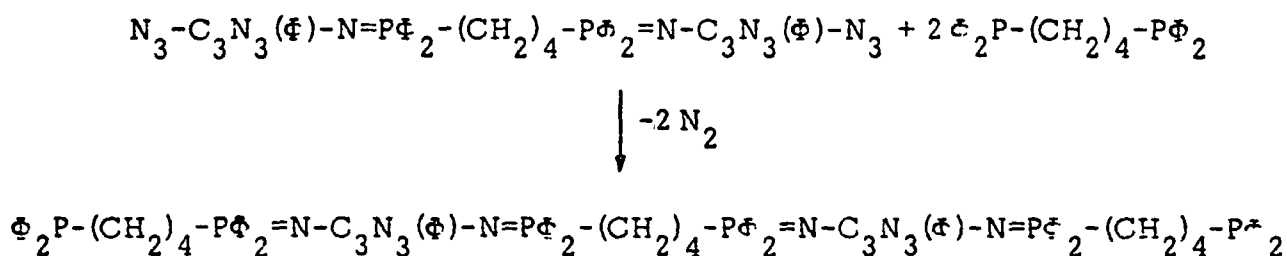
The equimolar reaction of the DPPB derived bisazide with DPPB in the absence of solvent at 151-165°C for 2 hr was according to the measurement of the evolved nitrogen only 68% complete. The incompleteness of the reaction was most likely due to poor mixing of the solids, which assumption is supported by the recovery of 22% of the unchanged diazide. The product obtained after dissolving the crude mixture in chloroform and precipitating into heptane amounted to 67% of the quantity expected on the basis of unrecovered bisazide, which is in good agreement with the amount of nitrogen evolved. The overall process therefore may be represented by the following equation:



The material thus isolated melted at 155-165°C, had a molecular weight of 4400 which corresponds to 7.3 of the above repeating units, and exhibited an infrared spectrum and TGA trace identical with those

of the products obtained in equimolar reactions of DPPB and TDA in chloroform at room temperature (see Table I). It must therefore be concluded that under the conditions studied the employment of "extended monomers" such as the DPPB derived diazide offers no advantage in regard to formation of high molecular weight materials over the direct interaction of the true monomers.

The reaction of DPPB with the DPPB derived diazide described above in an ~ 3:1 molar ratio was carried out to possibly extend the latter by two DPPB units and to obtain a phosphine terminated "extended monomer" via the following equation:



Heating the two reactants in the absence of solvent at 153-158°C for 1.25 hr, however, formed a product which exhibited essentially an identical infrared spectrum and TGA curve as the material obtained in the equimolar reaction. The molecular weight of 2400 corresponded to 4 units of the repeating segment. Thus it would seem that the desired product was not formed.

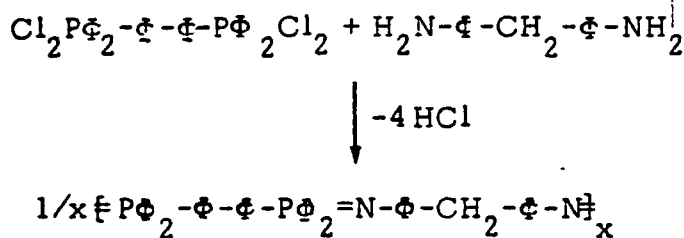
In order to improve the conditions for the formation of the phosphine terminated "extended monomer" depicted above, the DPPB derived diazide was reacted with DPPB in the absence of solvent in a 1:10 molar ratio. The product of this reaction, after extraction with heptane and crystallization from benzene-heptane, had a molecular weight of 1620, which agrees very well with the theoretically expected 1645.

Based on these limited investigations it can be concluded that the azide-phosphine reactions regardless of the conditions selected do not lend themselves to the production of polymeric materials. On the other hand, by careful stoichiometry selections linear compounds of relatively high molecular weight, insofar as monomers are concerned, with predetermined end groups can be obtained.

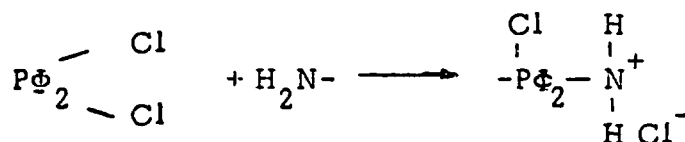
4.2.3 Dichlorophosphorane-Amine Reactions

In view of the low molecular weight products obtained via the azide-phosphine reaction it was thought that a condensation process involving dichlorophosphoranes and amines would be more likely to afford truly polymeric materials. Furthermore, the use of aromatic amines in conjunction with aromatic phosphines would give a fully aromatic system free from triazine rings which have been found to produce hydrogen cyanide on degradation (ref. 1).

The desired bis-dichlorophosphoranes were readily obtained from the respective bis-phosphines and their synthesis is discussed in Section 4.1. The major effort was centered on the interactions of the bis-dichlorophosphorane of BDBI with methylenedianiline. Prior to conducting the reactions the DSC curves of the bis-dichlorophosphorane (Figure 25), of MDA (Figure 26), and of their mixture (Figure 27) were determined. The DSC of the mixture indicates that a reaction occurs at about 90°C (strong exotherm), in the vicinity of the melting point of MDA. Thus an equimolar mixture of BDBI-bis-dichlorophosphorane and MDA was heated in the absence of solvent at $\sim 110^{\circ}\text{C}$ with the objective to achieve the following reaction:



However, no hydrogen chloride evolution was observed. The product of this heat treatment showed an infrared spectrum closely resembling that of the dichlorophosphorane, yet in its DSC (see Figure 28) the melting endotherm of MDA (compare Figure 26) was absent. Only an exotherm at $\sim 235^\circ\text{C}$ was present which could be correlated neither with the DSC of the chlorophosphorane of BDBI (Figure 25) nor with that of its mixture with MDA (Figure 27). These results may be interpreted by the formation of an intermediate hydrochloride, e.g.:

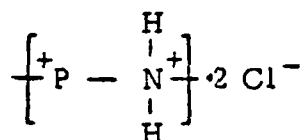


Heating this intermediate to 260°C , well above the temperature where the DSC (Figure 28) indicated an exothermic reaction, still produced no hydrogen chloride, only a black mass resulted. However, when the intermediate product was treated with triethylamine in refluxing benzene, a material could be isolated, the infrared spectrum of which clearly showed the presence of an amine hydrochloride. After removal of the amine hydrochloride with water, the product of this reaction had a molecular weight of 3500 which corresponds to an average 4.3 repeating units. Apparently, the desired reaction does not take place unless an acid acceptor such as triethylamine is employed.

To evaluate optimum conditions for preparing high molecular weight materials, the following solvent systems, concentration and type of base, temperature regimes and modes of addition were studied: (1) benzene/acetonitrile, excess triethylamine, room temperature and inverse addition (addition of bis-dichloro-phosphorane to-arylene diamine); (2) acetonitrile, excess triethylamine, room temperature and inverse addition; (3) chlorobenzene, stoichiometric triethylamine, reflux temperature, and normal addition; and (4) acetonitrile, excess pyridine, reflux temperature and inverse addition. These experiments are compiled in Table III.

All the materials formed (see Table IV) were essentially identical and of the same type as those obtained previously except for the insoluble products formed in chlorobenzene (Run No. 6) and pyridine (Run No. 7) which exhibited different infrared spectra and TGA curves. None of the reaction parameter variations had apparently any effect on the products' molecular weights which ranged from 1.5 to 4.9 repeating units. The TGA curves of all the products are very similar showing onset of major weight loss in air at 325-375°C and char yields at 600°C of 18-37% (see Figures 18-20) with the exception of the materials prepared in Run No. 4 and those of the insoluble products from Run Nos. 6 and 7. The latter two materials show indications in their infrared spectra of the presence of amino or hydroxy containing moieties, thus the different TGA curves are not surprising. The TGA curves of the products obtained in acetonitrile/benzene (Run No. 4), however, exhibit a so far not observed feature, namely a relatively large (~ 3%) weight gain in air at ~ 225-350°C (see Figure 20). It can be speculated that under these conditions oxidatively unstable compositions, possibly amino-terminated chains, were produced.

Based on the studies performed acetonitrile was found to be the most suitable solvent for the bis-dichlorophosphorane-MDA system. The reaction apparently proceeds via an ammonium-phosphonium bis-hydrochloride, e.g.:



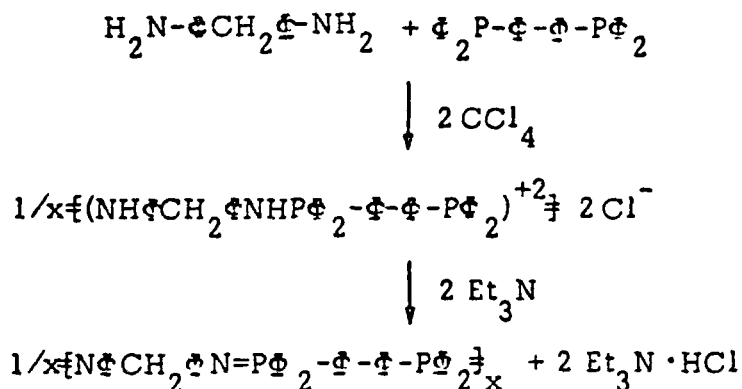
in view of the finding that no gaseous hydrogen chloride is evolved during reaction. On the other hand, the possibility that MDA hydrochloride or dihydrochloride is also present cannot be ignored. The phosphazene is subsequently liberated by addition of an acid acceptor as represented by triethylamine.

In order to evaluate the effects of other aromatic diamines on the product properties, the bis-dichlorophosphorane of 4,4'-bis(diphenylphosphino)biphenyl was reacted with an equimolar amount of p-phenylenediamine (PPDA) in acetonitrile solution in the presence of triethylamine. The product thus formed appeared to be the desired phosphazene. This composition exhibited a higher softening and melting point (sp 240°C, mp 250-260°C) than the materials obtained by reaction of BDBI with MDA, whereas the molecular weight (5.2 units of repeating segment) and the thermal stabilities (see Figure 21) of the two types of phosphazenes were comparable.

The reaction of 1,4-bis(diphenylphosphino)benzene-bis-dichlorophosphorane with an equimolar amount of 4,4'-methylenedianiline in acetonitrile solution in the presence of triethylamine formed a product which, based on the data available at present, is the desired phosphazene. The product exhibited a molecular weight and thermal stability comparable to those materials listed above (Table IV), e.g., a molecular weight of 2400 and a char yield of 65% at 500°C (see Figure 22).

4.2.4 Bisphosphine-Diamine-Carbon Tetrachloride Reactions

An alternate to the diamine-bis-dichlorophosphine process is the interaction of a bis-phosphine with a diamine in the presence of carbon tetrachloride followed by base treatment. The latter procedure was utilized by Appel and co-workers (ref. 7,8), specifically for the synthesis of non-functional mono-phosphazenes. An attempt to adapt this method to the preparation of polymers employing equimolar quantities of 4,4'-bis(diphenylphosphino)biphenyl and 4,4'-methylenedianiline, i.e.:



resulted unfortunately only in low molecular weight species (2.5 repeating units) which exhibited infrared spectra and TGA curves identical with those obtained on the products from the dichlorophosphorane reactions.

It is apparent from the above discussion that neither the bis-dichlorophosphorane-diamine, nor the bisphosphine-diamine-carbon tetrachloride systems offer a process leading to high molecular weight materials. The formation here of the insoluble salt-type-intermediate, is one of the factors which would be expected to prevent chain growth. On the other hand, considering the findings of the azide-phosphine investigation, it would seem that cyclics must be preferentially formed regardless of the process or monomers

involved. No parallel example of this type of an occurrence can be found in the usual polymerization chemistry. It is tempting to speculate that conditions could be discovered to promote chain growth, yet all the efforts expended to date failed to achieve this objective.

4.3 SYNTHESIS AND EVALUATION OF PHOSPHAZENE CONTAINING POLYIMIDES

The investigations described in Sections 4.2.2 and 4.2.4 above showed that under the conditions employed high molecular weight materials could not be produced. On the other hand, it was proven that by "off-setting" the reaction stoichiometry difunctional "extended monomers" can be obtained.

The successful synthesis of such difunctional materials thus provides the opportunity of improving the flame resistance of polymeric composition wherein one of the comonomers is, e.g., a diamine. This approach appears particularly attractive in view of the finding (ref. 2) that a relatively low concentration of PN units is capable of reducing considerably the flammability of a polymeric composition with the concurrent suppression of toxic product formation. The obvious resultant advantages are that both flameproofing and toxic product suppression can be achieved with minimum costs and a minimum change to the basic polymer structure so that the physical and mechanical properties of the final composition should closely resemble those of the unmodified material.

To prove the potentials of this approach the synthesis of a phosphazene modified polyimide was undertaken and its unmodified analogue prepared for comparison. The method employed for preparing both polyimides was the in situ polymerization of monomer reactants (PMR) (ref. 11) in view of the advantages this technique offers in

processing of fiber reinforced composites. The specific system chosen was that composed of the monomethylester of nadic acid (NE), the dimethylester of benzophenonetetracarboxylic acid (BTDE), and methylene dianiline (MDA), on which extensive investigations have been performed (ref. 12,13). Based on the finding that in this system a formulated molecular weight (FMW) of 1500 provides the best overall balance between processability and composite properties this formulation ratio (BTDE : MDA : NE = 2.087 : 3.087 : 2 moles) was employed for the fabrication of all unmodified composites. The monomeric reactants were dissolved in methanol to give solutions of 50% solids by weight; the reinforcing fabric was heat treated style 181 E-glass.

For the preparation of the phosphazene modified polyimide the same reactants and procedures were used and the same molar ratios of tetraacid:diamine: diacid were employed. The modification consisted in replacing a part of the MDA by the bis-aminophosphazene (PA) synthesized for the first time under this contract (see Section 3). The molar ratio of these two diamines was kept constant in all the composites prepared, namely MDA : PA = 3 : 2. Since the molecular weight of PA is much higher than that of MDA (915.1 versus 198.3; average molecular weight of a 3 : 2 mixture is thus 485.0) and since the above given molar ratios of BTDA : NE : total diamines was employed, the FMW of the modified polyimide was consequently considerably increased (to 2387). In this manner the average number of imide moieties between norbornyl end-groups (before curing) or the number of imide units between crosslinks was the same for the unmodified and the phosphazene modified polyimides, whereas the average "chain length" of the modified system was much greater than that of the

unmodified version. Consequently, a comparison of the unmodified and modified polyimides prepared under this contract must take under consideration that the crosslink density in the latter composition is much lower. This may be reflected in the excessive resin flow observed during fabrication of two 12-ply laminates with the phosphazene modified polyimide (see Table VI) which resulted in a considerably lower resin content than that aimed for.

Both the unmodified and phosphazene modified 3-ply laminates were subjected to burn-through tests, whereas for both the unmodified and modified 12-ply laminates the flexural strength and the interlaminar shear strength were determined. The results of the strength measurements are given in Table VII. The lower flexural strengths of the phosphazene containing laminates No. 8, 9, and 10 as compared to the unmodified panels 3, 4, and 5 (compare Table VI) and their failure in the elevated temperature interlaminar shear strength tests may be attributed to the not optimized processing conditions, but may also be due to the difference in formulated molecular weights between the unmodified and modified resins. The effect of exposing the 3-ply laminates No. 1, 2, 6, and 7 (see Table VI) to an approximately stoichiometric natural gas/oxygen flame (adiabatic flame temperature $\sim 2700^{\circ}\text{C}$) can be seen in Figure 29. The burn-through times for the unmodified laminates No. 1 and 2 were 76 and 83 sec, respectively. When impinging this flame onto the phosphazene modified laminates No. 6 and 7 under identical conditions for 15 min, no burn-through occurred.

5. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are conclusions and recommendations reached during the current investigations of flame retardant phosphazene laminating resin systems.

- 1) The phosphazenes as represented by $\text{R}_2\text{P-R}'\text{-PR}_2\text{=N-R}''\text{N}_x$, wherein R, R' and R'' are aromatic entities, have been synthesized and found to be thermally, oxidatively and hydrolytically stable, as well as flame resistant. No highly toxic products were formed on oxidative thermal degradation.
- 2) Variation of experimental parameters failed to identify conditions leading to high molecular weight species. The molecular weights attained corresponded to 2-12 units of a given repeating segment.
- 3) Unbalancing of the reactants stoichiometries led to the preparation of di-functional phosphazenes, i.e., diamino and diazido terminated materials, amenable to incorporation into conventional laminating resin systems. This approach was successfully proven in the manufacture via the PMR process of flame retardant polyimide laminates.
- 4) The synthesis of the diaminophosphazene (PA) prepared under this program should be scaled up to make sufficient quantities available for further evaluation. In addition to optimizing processing procedures and investigating compositions and formulated molecular weights other than those employed in this program, these evaluations should include a study of the possibility of using this comonomer in making other flame resistant polymers, e. g., polyamides or polyureas.

- 5) The feasibility of applying the process developed for the synthesis of the diaminophosphazene to the preparation of difunctional phosphazenes terminated by, e.g., -OH, -COOR, -N=C=O, or -CH=CH₂ moieties should be investigated. Furthermore, the advantages of replacing the biphenyl based bisphosphine employed in the synthesis of PA by, e.g., a bisphosphine derivative of benzene should be evaluated.
- 6) The fact that the condensation product of PA with two moles of NE will have a molecular weight of 1207 makes it intriguing to speculate that this monomer could be employed as the sole resin component. This compound could possibly be applied to reinforcement as a melt, thus making drying and removal of volatiles unnecessary and theoretically ensuring the production of truly void-free laminates.

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APPENDIX

TABLES AND FIGURES

TABLE I
SUMMARY OF EQUI-MOLAR TDA-PHOSPHINE REACTIONS^a

Run No.	Phosphine	Reaction Conditions			Reactant Quantities			Medium Soluble Polymer				Medium Insoluble Polymer			
		T °C	Time hr	Solv.	TDA g	P g	Solv. ml	Yield %	SP °C	MP °C	MW	Yield %	SP °C	MP °C	MW
1	DPPB	RT	22.5	THF	1.12	2.00	40	9.1	182	190-197	1900	80.4	185	197-210	-
2	DPPB	Reflux	5.0	CH ₃ CN	1.12	2.00	110	12.9	175	185-202	1700	63.6	181	189-197	-
3	DPPB	Reflux	6.0	CH ₃ CN/C ₇ H ₁₄	1.12	2.00	60/110	22.3	177	188-205	2000	68.5	178	185-197	-
4	BDBI	RT	26.5	C ₆ H ₆	0.92	2.00	55	35.9	240	247-253	3200	51.5	195	284-292	8400
5 ^a	DPPB	RT	5.0	CHCl ₃	1.12	2.00	40	52.1	186	197-207	4800	30.0	195	224-227	-
6	DPPB	RT	4.0	CHCl ₃	1.12	2.00	40	88.1	193	203-213	7100	0	-	-	-
7	DPPB	RT	168.0	CHCl ₃	0.57	1.00	40	88.0	190	195-202	4000	Trace	-	-	-
12	PDPB	RT	97.0	C ₆ H ₆	1.07	2.00	70	6.7	235	241-252	2800	72	265	272-282	-
15	DPPR	104	4.8	DMF	1.12	2.00	100	71.3	182	192-198	2800	0	-	-	-
16	BDBI	RT	114.0	C ₆ H ₆	0.91	2.00	65	34.3	226	246-257	3600	59.6	225	> 300	6300

^a In all the experiments with the exception of Run No. 5, the solution of the azide was added to the phosphine solution; inverse addition mode was employed in Run No. 5.

TABLE II
 SUMMARY OF NON-EQUIMOLAR PHOSPHINE-TDA REACTIONS CONDUCTED IN
 CHLOROFORM AT ROOM TEMPERATURE

Run No.	Phosphine	Reaction Conditions		Reactant Quantities				Medium Soluble Product				Medium Insoluble Product			
		Time hr	Addn. Mode	P g	TDA g	TDA/P g	Solv. ml	Yield %	SP °C	MP °C	MW	Yield %	SP °C	MP °C	MW
8	DPPB	117.0	N	2.00	1.23	1.1/1	40	83.9	196	206-226	5100	Trace	183	196-204	-
9	DPPB	24.5	N	2.00	1.50	1.3/1	40	96.2	186	191-197	4400	0	-	-	-
10 ^a	DPPB	42.5	I	2.00	1.50	1.3/1	40	46.0	180	186-203	-	54.0	255	265-275	-
11 ^b	DPPB	25.2	I	2.00	3.37	3/1	63	-	-	-	-	93.5	-	267-277	-
13 ^b	DPPB	72.0	I	4.00	6.75	3/1	130	-	-	-	-	100.0	-	267-277	-
14 ^b	BDBI	19.0	I	2.00	2.75	3/1	55	-	-	-	-	77.1	-	> 300	-

a In this test the insoluble product consisted predominantly of $N_3-C_3N_3P_2(CH_2)_4P_2=N-C_3N_3-N_3$; the "polymer" was present in the soluble portion.

b In tests 10-13 the insoluble product consisted of pure $N_3-C_3N_3-N=P_2RP_2=N-C_3N_3-N_3$.

TABLE III
 REACTIONS OF 4,4'-BIS(DIPHENYLPHOSPHINO)BIPHENYL-BIS-DICHLORO-
 PHOSPHORANE WITH 4,4'-METHYLENEDIANILINE

Run No.	X MDA		Y $(Cl_2P\phi)_2$		Z Et_3N		Molar Ratio X : Y : Z	Solvent ^a		Addition			Reaction	
	g	mmol	g	mmol	g	mmol		Type	ml	Mode ^b	Time hr	Temp °C	Time hr	Temp °C
1A ^d	0.597	3.010	2.00	3.010	-	-	1:1	-	-	-	-	17.5	77-111	
1B ^e	-	-	-	-	-	-	1:1	-	-	-	-	25.0	252-266	
1C ^f	-	-	-	-	0.23	2.287	1:1	B	15	N	O	RT ^c	Reflux	
2 ^g	0.597	3.010	2.00	3.010	1.23	12.146	1.1 4.04	B	25	N	0.1	RT	Reflux	
3 ^h	0.298	1.505	1.00	1.505	0.61	6.029	1.1 4.01	A	60	N	0.2	RT	Reflux	
4 ⁱ	0.370	1.550	1.03	1.550	0.81	8.006	1 1 5.17	A	50	I	1.5	RT	RT	
5 ^j	0.287	1.449	0.96	1.445	0.74	7.314	1 1 5.06	A	75	I	2.25	RT	RT	
6 ^k	0.303	1.529	1.01	1.520	0.62	6.080	1 1 4	CB	140	N	1.0	120-130	122-140	
7 ^l	0.271	1.377	0.91	1.370	-	-	1:1.453	P	50	I	1.5	RT	104-110	
8 ^m	0.874	4.409	0.97	1.460	0.62	6.128	3 1 4.20	A	100	I	0.75	RT	RT	

a A = acetonitrile, B = benzene, CB = chlorobenzene, P = pyridine.

b N = normal addition, MDA added to solution of $(Cl_2P\phi)_2$, I = inverse addition, $(Cl_2P\phi)_2$ added to solution of MDA

c RT = room temperature.

d Neat reaction, no apparent reaction.

e Used 1.00 g of 1A reaction mixture, no apparent reaction.

f Used 0.50 g of 1A reaction mixture.

g MDA added to $(Cl_2P\phi)_2/Et_3N$ mixture.

h Incremental addition of MDA and Et_3N .

i Add $(Cl_2P\phi)_2$ to mixture of MDA/ Et_3N or MDA/P.

k MDA/ Et_3N added to $(Cl_2P\phi)_2$ suspension.

l Used 49.1 g, 621 mmol of pyridine.

m To the mixture of MDA and $(Cl_2P\phi)_2$ in acetonitrile, Et_3N was added.

TABLE IV
 PRODUCTS FROM REACTIONS OF 4,4'-BIS(DIPHENYLPHOSPHINO)BIPHENYL-BIS-
 DICHLOROPHOSPHORANE WITH 4,4'-METHYLENEDIANILINE

Run ^a No.	Material	Yield		SP °C	MP °C	Molecular Weight		TGA Fig. No.
		g	%			Exp	Units ^b	
1	Soluble	0.08	19.3	143	165-180	1700	2.9	18
	Insoluble	0.20	48.9	182	195-213	3500	4.9	
2	Soluble	0.71	32.9	156	166-182	1800	2.6	19
	Insoluble	1.23	57.2	185	195-203	2400	3.3	
3	Soluble	0.06	5.4	124	145-155	1100	1.5	20
	Insoluble	0.84	77.4	197	203-212	3200	4.4	
4	Soluble	0.55	50.3	175	182-195	1900	2.7	20
	Insoluble	0.27	24.6	210	215-225	3300	4.6	
5	Soluble	-	-	-	-	-	-	20
	Insoluble	0.90	35.6	170	175-185	2400	3.4	
6	Soluble	0.62	56.6	178	185-196	1700	2.4	20
	Insoluble	0.39	-c	245	250-255	-	-	
7	Insoluble	0.51	-c	212	216-233	1200	-	
8 ^d	Insoluble	0.52	50.3	156	160-167	1700	2.3	

a See Table III for description of reactions.

b Based on $\text{FNC}_6\text{H}_4\text{N}=\text{P}(\text{C}_6\text{H}_5)_2-\text{C}_6\text{H}_4-\text{P}(\text{C}_6\text{H}_5)_2$.

c Yield was not calculated because the material formed was not the desired product.

d The reaction medium soluble product 2.23 g was a mixture of what appeared to be the amino-terminated phosphazene and MDA.

TABLE V
VOLATILE PRODUCTS OBTAINED ON THERMAL
OXIDATIVE DEGRADATION OF $\text{[NC}_3\text{N}_3(\text{C}_6\text{H}_5)_2\text{N=PC}_6\text{H}_4\text{-C}_6\text{H}_4\text{-PC}_6\text{H}_4\text{]}_x$ AT 420°C IN AIR *

Product	mg/g	Product	mg/g
H ₂	?	Xylenes	0.488
CO	2.73	Bromobenzene	0.003
CO ₂	3.87	Methyl chloride	0.041
HCN	0.842	Methyl bromide	0.015
C ₂ N ₂	T	Chloroform	1.332
C ₂ -species	0.273	Phenol	0.733
C ₃ -species	0.303	Cresol	0.646
C ₄ -species	0.197	Acetaldehyde	0.001
C ₅ -species	0.071	Acetone	0.056
C ₆ -species	0.078	2-Penten-4-one	T
n-Heptane	4.69	2-Hexanone	0.002
C ₈ -species	0.100	2-Heptanone	0.035
Benzene	11.6	Cyclopentanone	0.002
Toluene	1.29	Benzonitrile	79.6

* Amount of material employed, 1.0363 g; residue, 87%; weight loss, 134.1 mg; recovered in volatiles, 112.9 mg (84.2%). Identification and quantitation of species, 99.9%. At 420°C char yield from TGA, 95%.

TABLE VI
PMR POLYIMIDE/GLASS LAMINATES^a

Laminate No. ^b	Monomer Solution Composition	Ply No.	Prepreg ^c % Volatile		% Resin Content	Identification
			120° F	250° F		
1	NE/BTDE/MDA	3	-	-	40	1-76-43-1
2	"	3	11.9	3	32	1-76-46-1
3	"	12	-	-	33	1-76-13-1
4	"	12	-	-	34	1-76-48-1
5	"	12	12.2	2.5	37	1-76-56-1
6	NE/BTDE/(3 MDA: 2 PA)	3	11.0	-	33	1-76-52-1
7	"	3	11.3	-	33	1-76-53-1
8	"	12	9.4	4.2	32 ^d	1-76-58-1
9	"	12	8.9	3.8	24 ^d	1-76-61-1
10	"	12	11.2	5.0	27 ^d	1-76-63-1

a) Style 181 E-glass fabric, heat treated; 4" x 4", 0.21 mm/ply. For molding conditions see Section 3.4

b) Laminates 1-5: FMW = 1500; laminates 6-10: FMW = 2390.

c) Determined by measuring weight loss during 2 hr heating at 600° F in air furnace.

d) Excessive resin flow during molding.

TABLE VII
MECHANICAL PROPERTIES OF PMR POLYIMIDE/GLASS LAMINATES

Laminate No. ^a	Flexural Strength			Interlaminar Shear Strength		
	RT ^b	$N/m^2 \times 10^{-6}$ (psi $\times 10^{-3}$)		RT	$N/m^2 \times 10^{-6}$ (psi $\times 10^{-3}$)	
		204°C	316°C		204°C	316°C
3	362 (52.5)	265 (38.4)	226 (32.8)	46 (6.60)	32 (4.60)	22 (3.15)
4	368 (53.4)	311 (45.0)	317 (46.0)	35 (5.00)	35 (5.10)	32 (4.65)
5	366 (53.1)	328 (47.6)	338 (49.0)	53 (7.70)	37 (5.47)	31 (4.50)
8	207 (30.0)	104 (15.0)FP ^c	83 (12.0)FP	20 (4.06)	FP ^d	FP
9	207 (30.0)	104 (15.0)	55 (8.0)	19 (2.70)	F	F
10	207 (30.0)	90 (13.0)	52 (7.6)	18 (2.67)	F	F

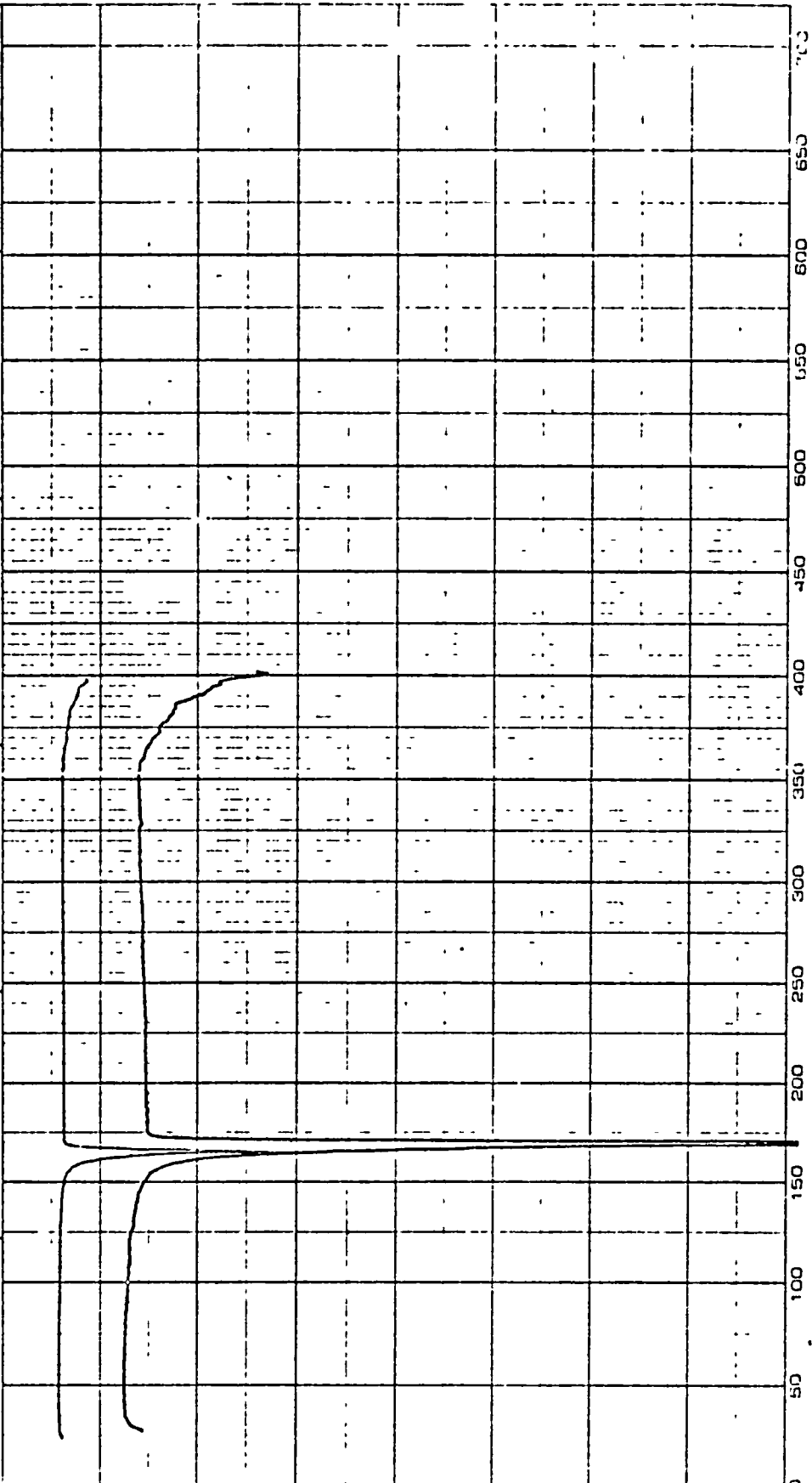
a) For sample identification see Table VI.

b) Room temperature.

c) Thermoplastic.

d) Thermoplastic failure.

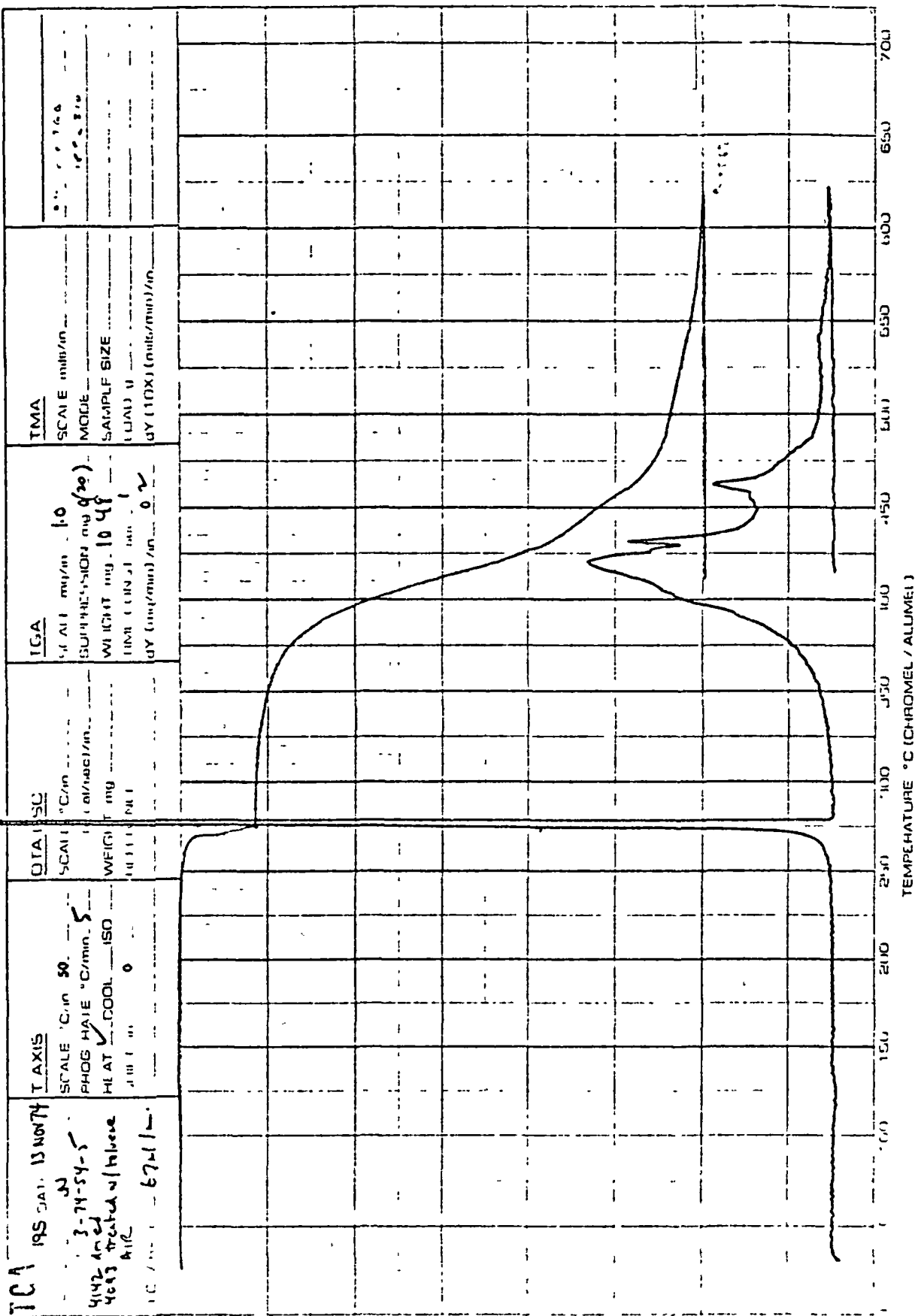
PSC
 DATE: 11 Sept 74
 OPERATOR: FS
 FILE: 3-11-34-2
 ID: 1016
 ATM: N₂
 FLOW RATE: 50 cc/min
T-AXIS
 SCALE °C/in.: 50
 PROG RATE °C/min: 5
 HEAT: COOL: ISO:
 SHIFT in: 0
DTA/DSC
 SCALE °C/in.: (mcal/acc)/in.
 WEIGHT mg: _____
 REFERENCE: Pd, 10 (mcal/acc)/in.
 Scan 0.2 (mcal/acc)/in.
TGA
 SCALE mg/in.: _____
 SUPPRESSION mg: _____
 WEIGHT mg: _____
 TIME CONST sec: _____
 dY (mg/min)/in.: _____
TMA
 SCALE mils/in.: _____
 MODE: _____
 SAMPLE SIZE: _____
 LOAD g: _____
 dY (10X) (mil/min)/in.: _____
 Baseline Slope: 505



TEMPERATURE °C (CHROMEL / ALUMEL)

Figure 2: DSC of $\Phi_2P-\Phi-Pd_2P$, Pd₂PB

PART NO 591288



PART NO 990088

OSI
 RUN NO 75 DATE 14 Nov 74
 OPERATOR FS
 SAMPLE 3-74-84-5
 ZERO none dried
 ATTN N₃ / 100% / 100% / 100%
 FLOW RATE 50 ml/min

T-AXIS
 SCALE °C/in 50
 PROG RATE °C/min 5
 MEAL COOL ISO
 SHIFT in 0

OSC
 L °C/in _____
 (mcal/sec)/in _____
 Wt mg _____
 REFERENCE _____
 A 0.2 (mcal/sec)/in
 B 0.2 (mcal/sec)/in

TGA
 SCALE mg/in _____
 SUPPRESSION mJ _____
 WEIGHT mg _____
 TIME CONST sec _____
 WY (mg/min)/in _____

TMA
 SCALE mils/in _____
 MODE _____
 SAMPLE SIZE _____
 LOAD g _____
 WY (10X) (mils/min)/in _____

Baseline 505

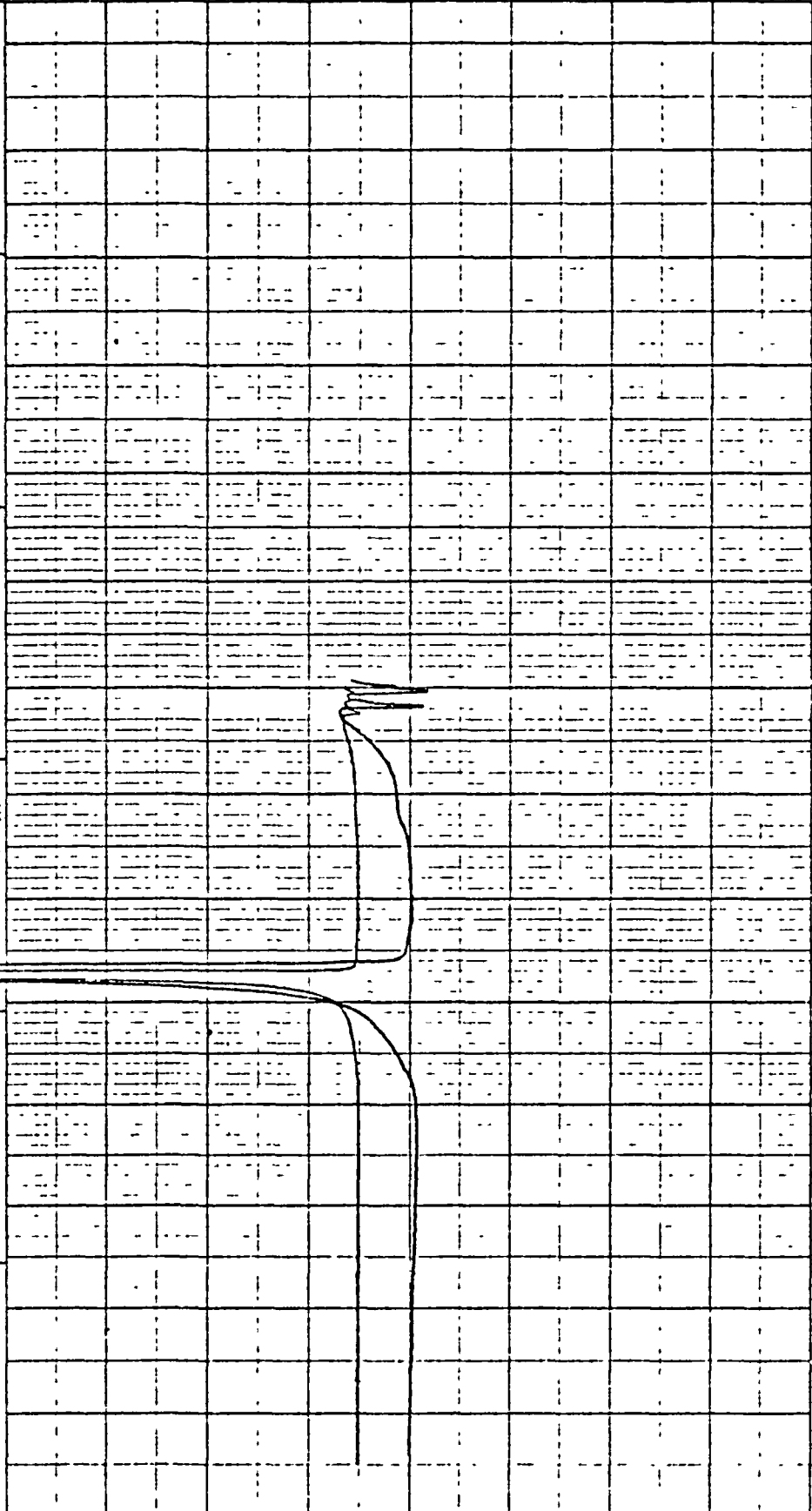


Figure 4: DSC of $N_3-C_3N_3-N=NO_2(CH_2)_4P\Phi_2=N-C_3N_3-N_3$

PART NO 990088

TGA RUN ID 213 / DATE 8 Jan 75 OPERATOR FS SAMPLE 3-14-62-2 @ 80°C IN 2103 Z-TM Air FLOW RATE 67 ml/min	T-AXIS SCALE °C/in 50 PROG RATE °C/min 5 HEAT COOL ISO SHIFT in 0	DTA/DSC SCALE °C/in (mt offset)/in WEIGHT mg REFERENCE	TGA SCALE mg/in 1.0 SUBSTRATE SECTION mg 0.0(0) WEIGHT mg 9.10 THERM CONST (mg/min)/in 0.1	TMA SCALE mils/in MODL SAMPLE SIZE LOAD g dY (10X) (mils/min)/in
--	--	---	---	--

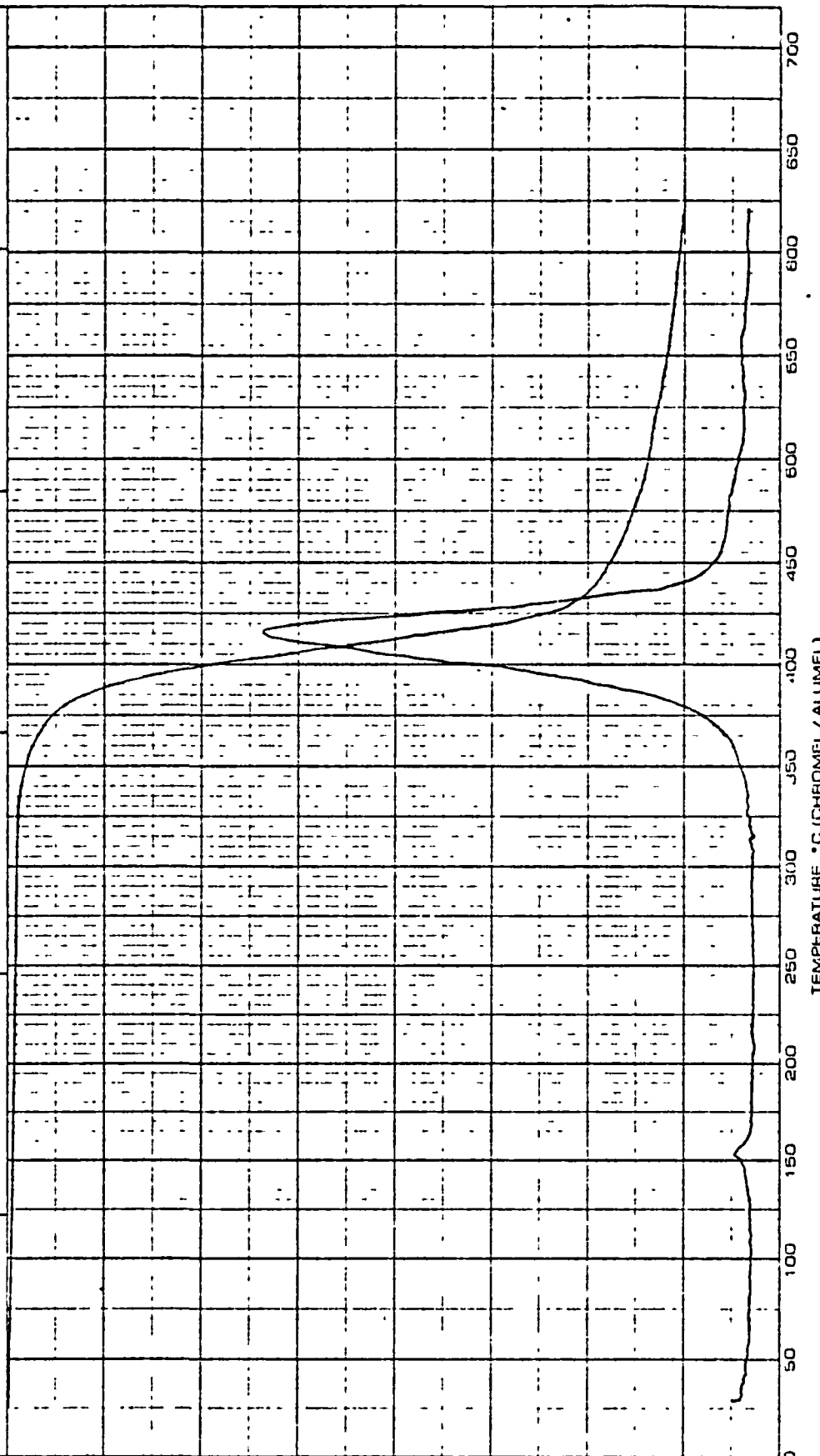


Figure 5: TGA of $\Phi_3\text{P}=\text{N}-\text{C}_3\text{N}_3(\Phi)-\text{N}=\text{P}\Phi_2-(\text{CH}_2)_4-\text{P}\Phi_2=\text{N}-\text{C}_3\text{N}_3(\Phi)-\text{N}_3=\text{P}\Phi_3$

PART NO 990088

TGA: RUN NO 212 DATE 7 JAN 75
 OPERATOR F3
 SAMPLE TDA (O.P.)
 5-7-81.4
 ATM RIC
 FLOW RATE 67 ml/min

T-AXIS
 SCALE °C/in 50
 PROG RATE °C/min 5
 HEAT COOL ISO
 SHIFT in 0

OTA DSC
 SCALE °C/in
 (mcu/scr./in)
 WEIGHT mg
 REFERENCE

TGA
 SCALE mg/in 10
 SUPPRESSION mg 9.19
 WEIGHT mg 9.26
 TIME CONST sec 10
 dY (mg/min)/in 0.2

TMA
 SCALE mils/in
 MODE
 SAMPLE SIZE
 LOAD g
 dY (10X) (mils/min)/in

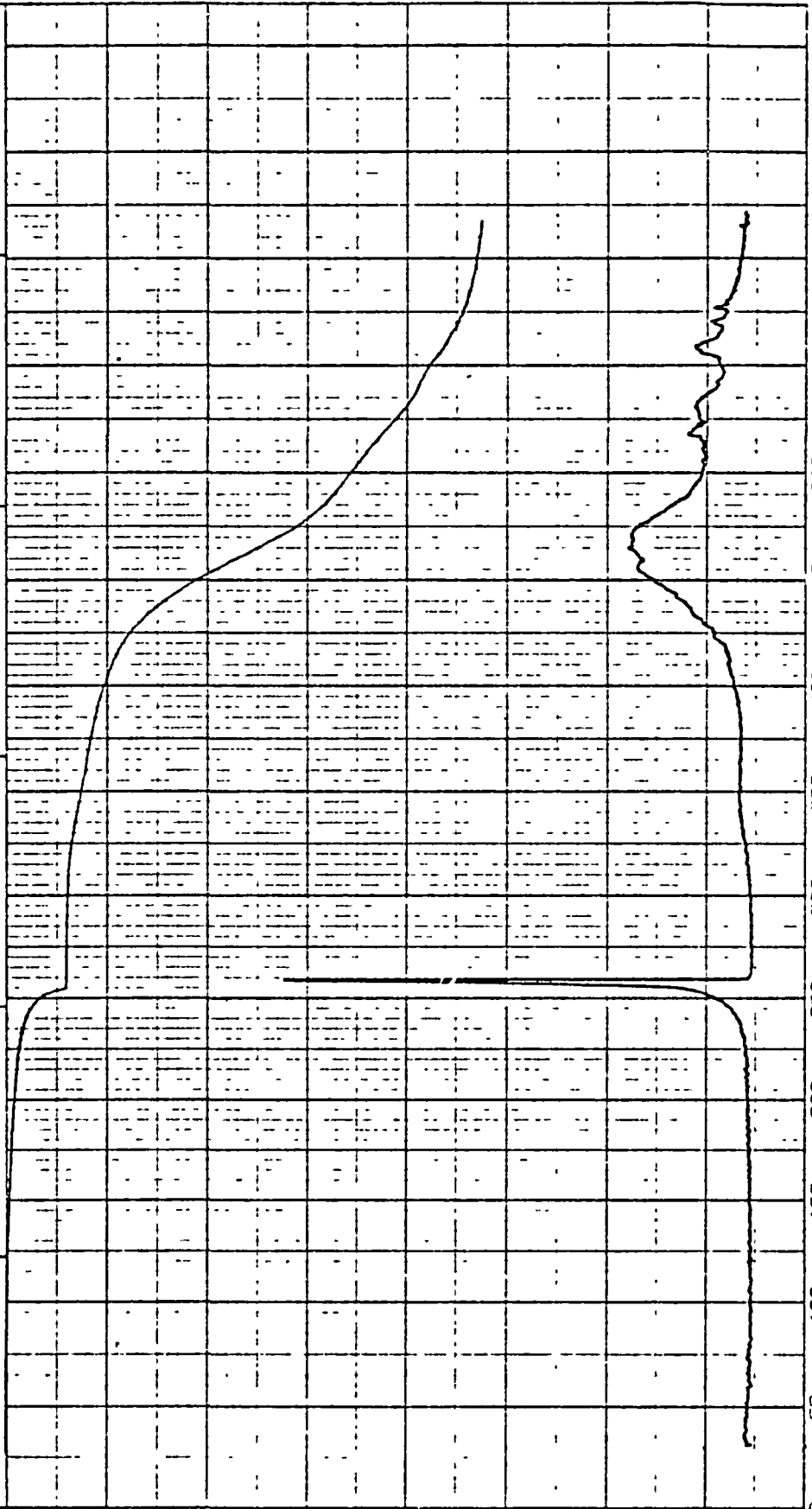


Figure 6: TGA of N₃-C₃N₃(φ)-N=Pφ₂-φ-φ-Pφ₂=N-C₃N₃(φ)-N₃

PART NO 990088

DTA
 RUN NO. 97 DATE 30 Jun 75
 OPERATOR F.S.
 ANALYST TDA (R.P.P.)
 3-77-84-1
 ATTA - N₂
 FLOW RATE 50 ml/min

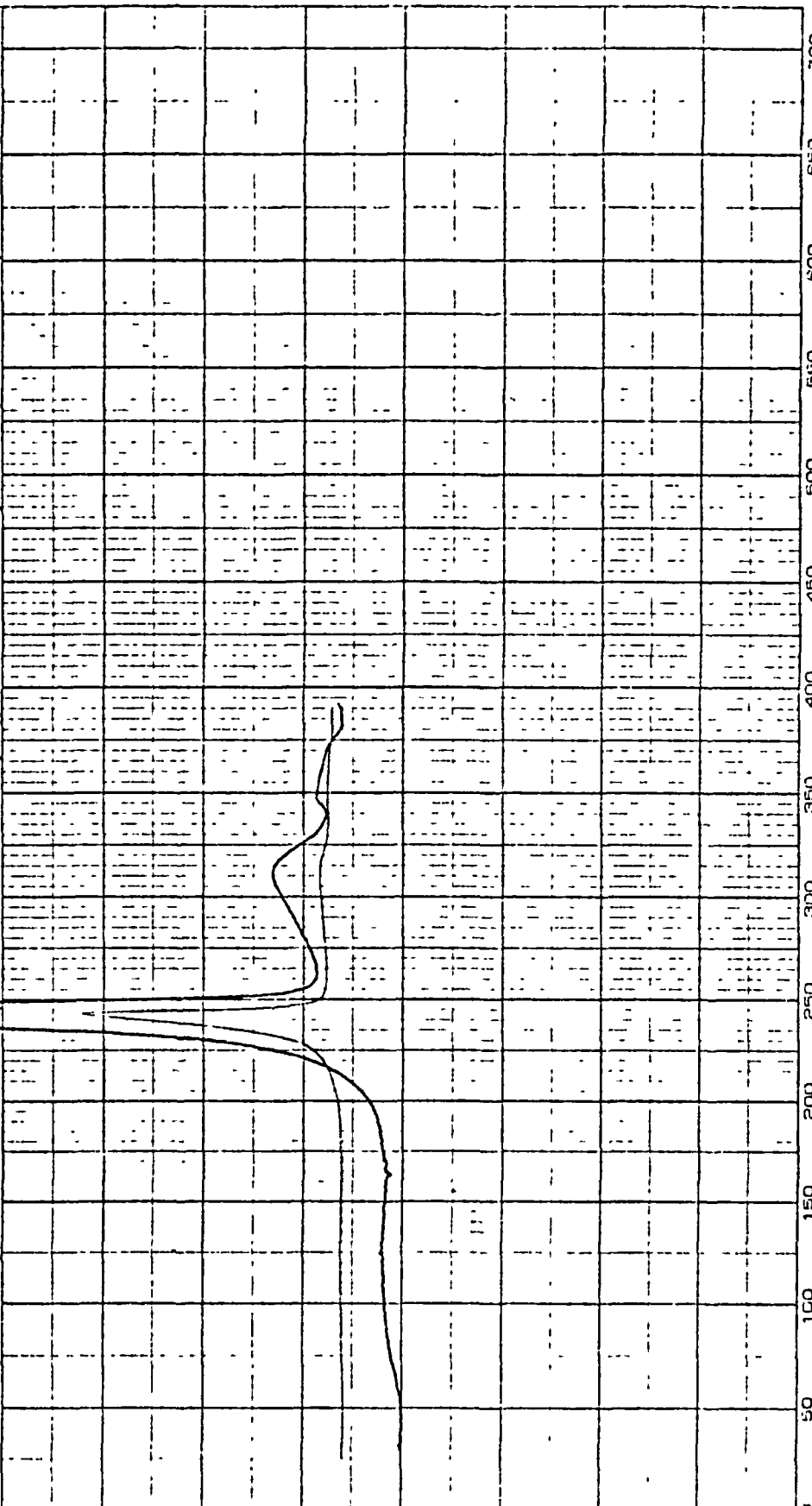
T-AXIS
 SCALE °C/in 50
 PROC RATE °C/min 5
 HEAT COOL 150
 SHIFT in 0

DTA DSC
 SCALE °C/in (mcal/sec)/in
 WEIGHT mg
 REFERENCE Red
 0.2 °C/in Green

TGA
 SCALE mg/in
 SUPPRESSION mg
 WEIGHT mg
 TIME CONST sec
 dY (mg/min)/in

TMA
 SCALE mils/in
 MODE
 SAMPLE SIZE
 LOAD g
 dY (10X) (mils/min)/in

Baseline 930
 Thermocouple F
 Pyro-Nachbaur 174



TEMPERATURE °C (CHROMEL / ALUMEL)

Figure 7: DTA of N₃-C₃N₃ (6) - N = P₆ - P₆ = N-C₃N₃ (7) - N₃ in nitrogen

PART NO 990088

DTA
 RUN NO 118 DATE 15 APR 1975
 OFF. HATOR FS
 SAMPLE $\Phi_3 P-N-C_3 N_3$
 3-11-15-3 441 dead
 47-001-001-001-001
 DTA N₂
 FLOW RATE 50 ml/min

T-AXIS
 SCALE °C/in 50
 PROG RATE °C/min 5
 HEAT COOL 150
 SHIFT in 0

DTA-DSC
 SCALE °C/in
 (mcal/heat)/in
 WEIGHT mg
 REFERENCE Al_2O_3
 Red 1.0 °C/in
 Green 0.2 °C/in

TGA
 SCALE mg/in
 SUPPRESSION mg
 WEIGHT mg
 TIME CONST min
 μY (mg/min)/in

TMA
 SCALE mils/in
 MODE
 SAMPLE SIZE
 LOAD g
 μY (10X) (mils/min)/in

Thermoscope C
 Sample 544
 page 124. NBS books 309

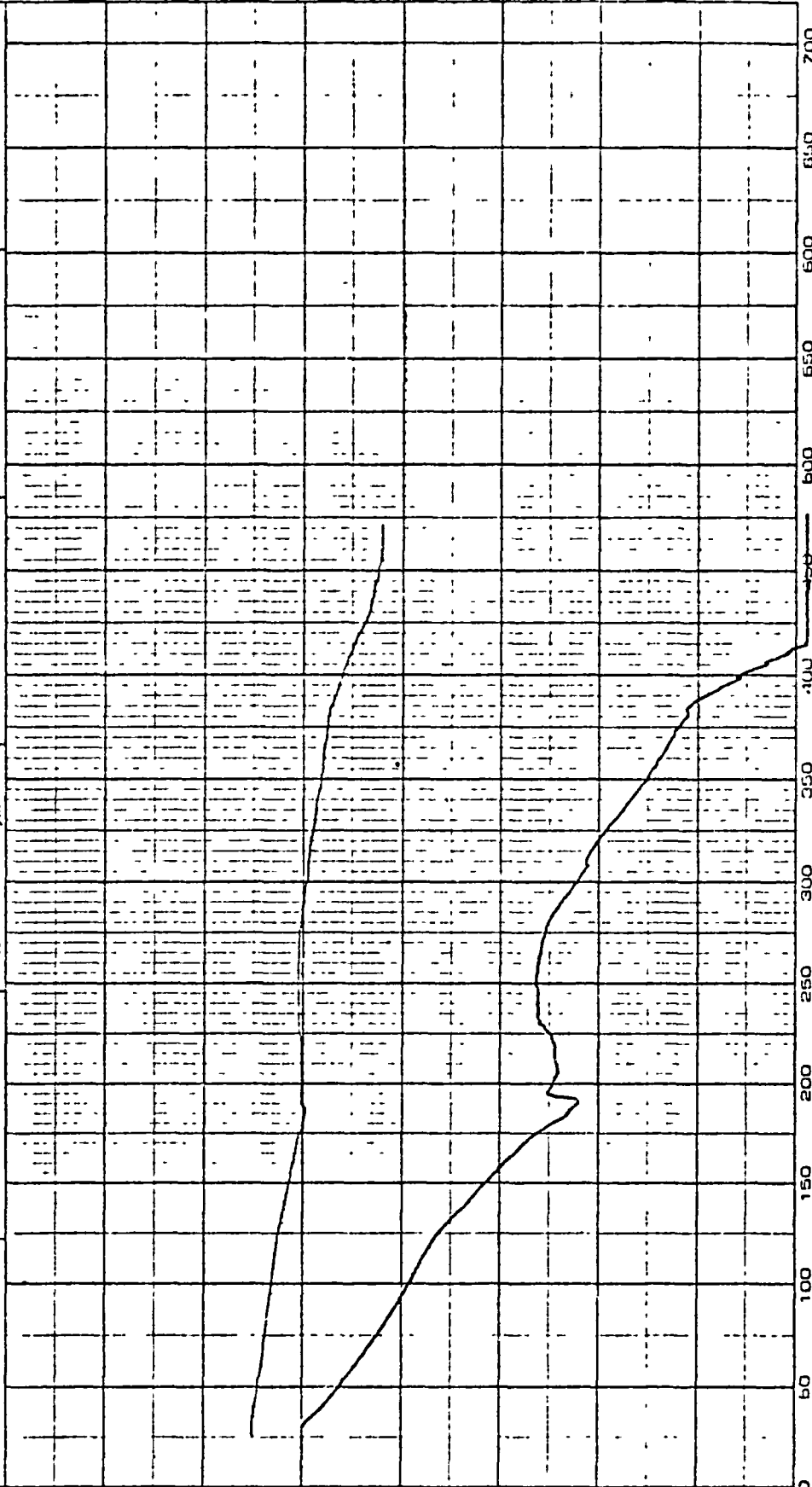
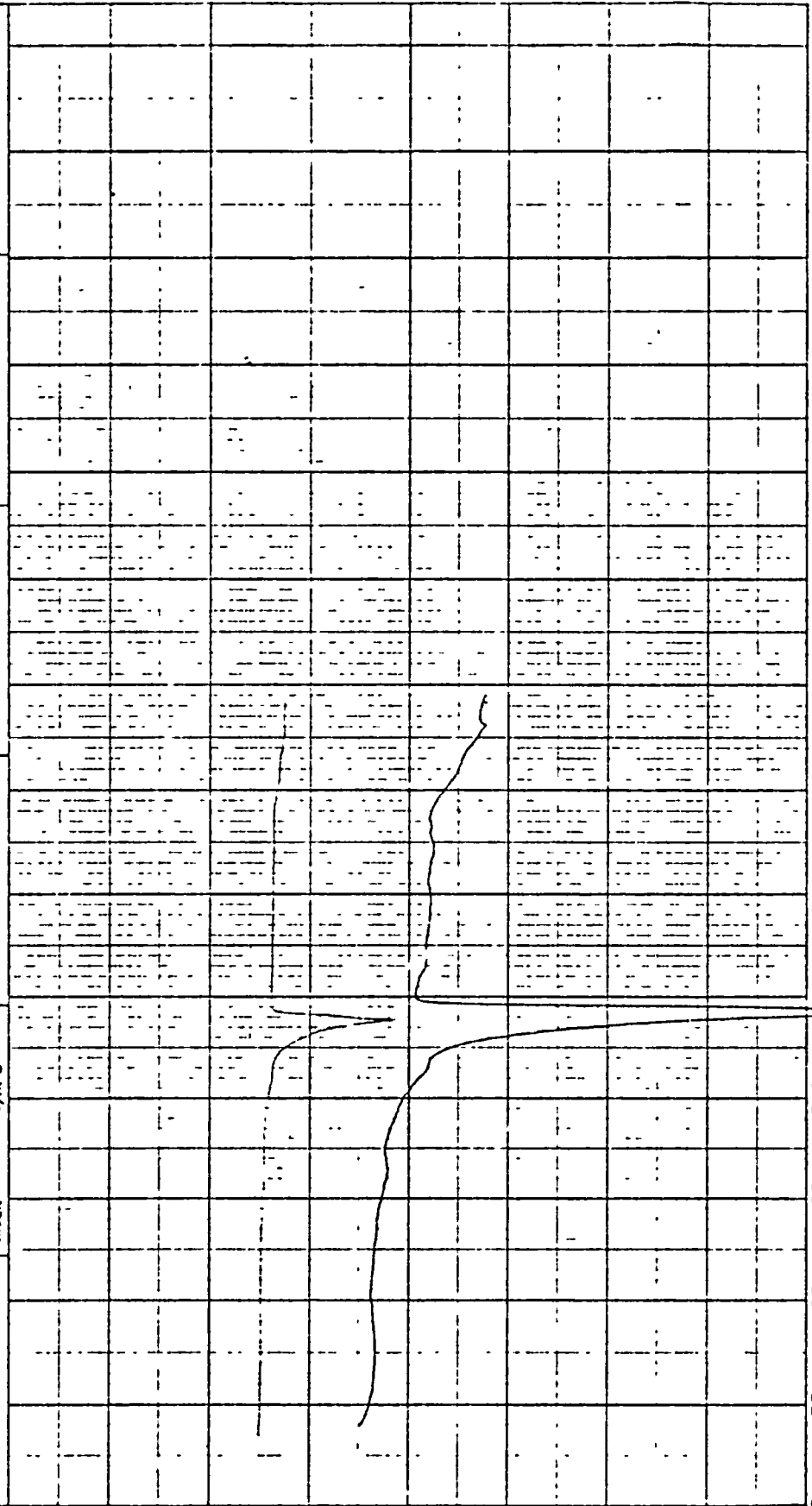


Figure 8: DTA in nitrogen of $\Phi_3 P-N-C_3 N_3$ (Φ)-N= $P\Phi_2$ - Φ - Φ - $P\Phi_2$ =N-C₃N₃(Φ)-N= $P\Phi_3$

PART NO 990088

DTA
 DATE 16 June 75
 OPERATOR F.S.
 SAMPLE Model IC₁
 (M=Ph₂O₇)
 3-15-75
 ATM N₂
 FLOW RATE 50 ml/min
 SCALE °C/in 50
 PRG RATE °C/min 5
 HEAT COOL ISO
 SHIFT in 0
 Bed 1.9 °C/in
 Green 0.2 °C/in
DTA-DSC
 SCALE °C/in
 (mlal/usc)/in
 WEIGHT mg
 REFERENCE NiO₃
ICA
 SCALE mg/in
 SUPPRESSION mg
 WEIGHT mg
 TIME CONST 000
 dy (mj/min)/in
TMA
 SCALE mil/in
 MODE
 SAMPLE SIZE
 LOAD g
 dy (10X) (mils/min)/in
 Baseline 145
 Thermocouple H



TEMPERATURE °C (CHROMEL / ALUMEL)

Figure 9: DTA in nitrogen of model compound, $\Phi N = \Phi_2 - \Phi - \Phi - P\Phi_2 = N\Phi$.

PART NO 990088

TGA RUN NO. <u>269</u> DATE <u>11 Dec 75</u> OPERATOR <u>FS</u> SAMPLE Model <u>TC</u> <u>CON-PO-07</u> <u>1-15-75</u> ATM. Bic. <u>0</u> FLOW RATE <u>67 ml/min</u>		T-AXIS SCALE °C/in. <u>50</u> PROG RATE °C/min <u>5</u> HEAT <input checked="" type="checkbox"/> COOL <input type="checkbox"/> ISO <input type="checkbox"/> SHIFT in. <u>0</u>		DTA-DSC SCALE °C/in. _____ (mcal/sec)/in. _____ WEIGHT mg _____ REFERENCE _____		TGA SCALE mg/in. <u>1.0</u> SUPPRESSION mg. 0(50) _____ WEIGHT mg <u>11.36</u> TIME CONST sec. <u>1</u> dY (mg/min)/in. <u>0.2</u>		TMA SCALE mils/in. _____ MODE _____ SAMPLE SIZE _____ LOAD 0 _____ dY (10X) (mils/min)/in. _____	
--	--	---	--	--	--	--	--	--	--

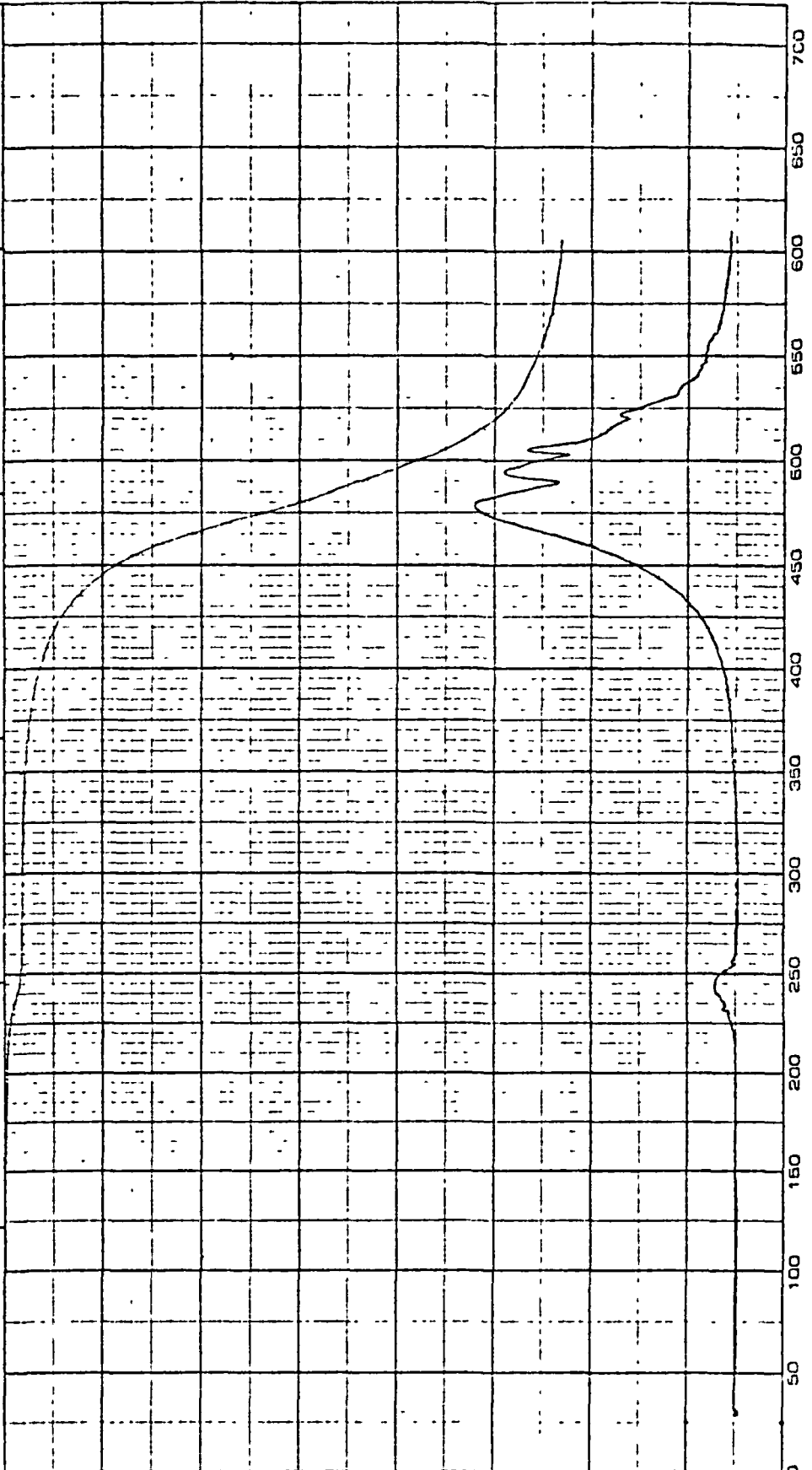


Figure 10. TGA in air of model compound, $\Phi N = P\Phi_2 - \Phi - \Phi - P\Phi_2 = N\Phi$.

PART NO 990088

DTA
 DATE 17 Sept 75
 OPERATOR FS
 SAMPLE $\phi_3\text{P-N-CH}_2\phi_2\text{-NH}_2$
 8-25-75-4
 ATM N₂
 FLOW RATE 50 ml/min

T-AXIS
 SCALE °C/in. 50
 PROG RATE °C/min 5
 HEAT. COOL ISO
 SHIFT in 0

DTA OSC
 SCALE °C/in. (mcal/sec)/in.
 WEIGHT mg
 REFERENCE Al₂O₃
 Red 10 °C/in
 Green 02 °C/in

TGA
 SCALE mg/in.
 SUPPRESSION mg
 WEIGHT mg
 TIME CONST sec
 dy (10X) (mlb/min)/in

TMA
 SCALE mils/in
 MODE
 SAMPLE SIZE
 LOAD g
 dy (10X) (mlb/min)/in

Thermostat's J
 Base line 368

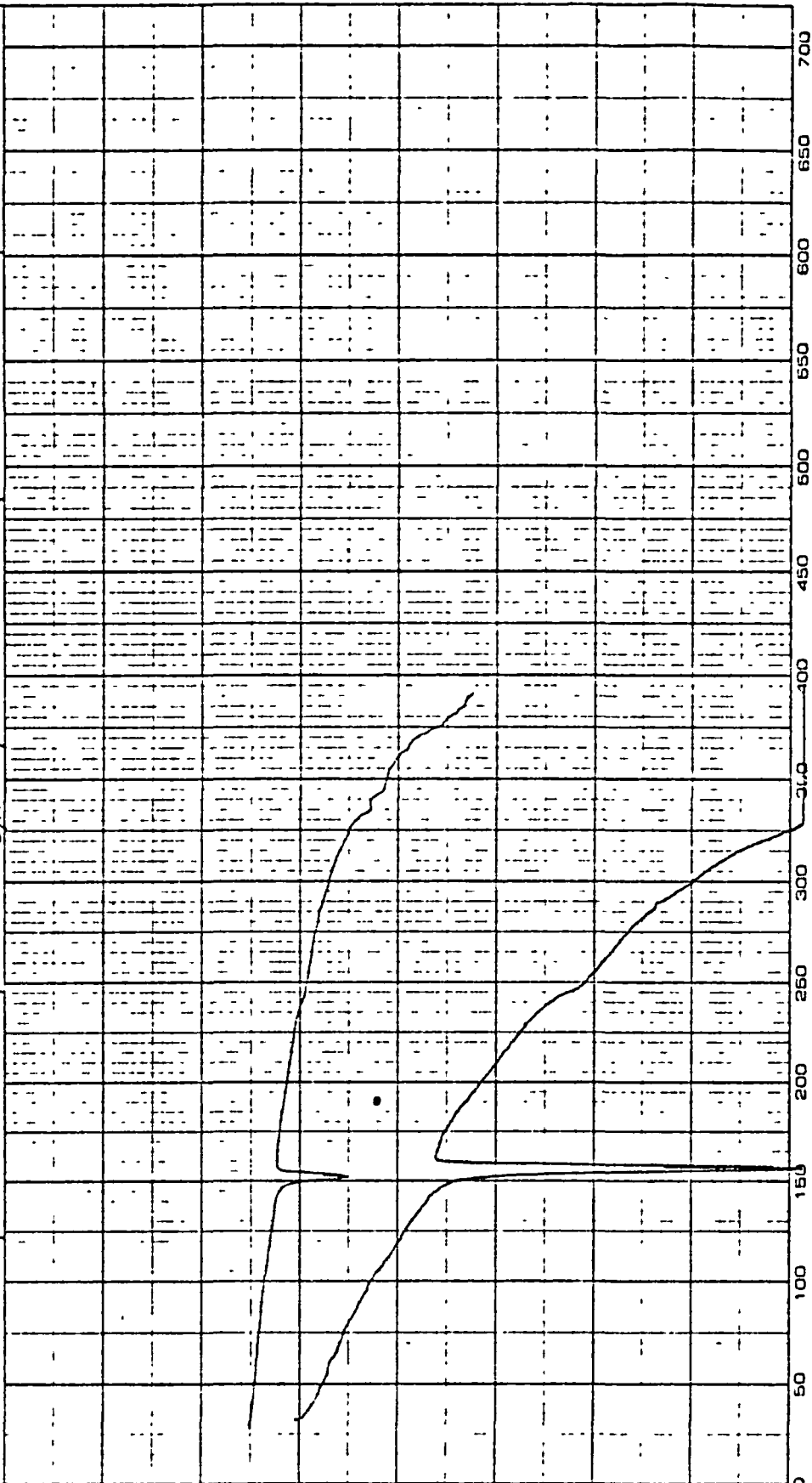


Figure 11: DTA in nitrogen of phosphazene, $\phi_3\text{P-N-CH}_2\phi_2\text{-NH}_2$

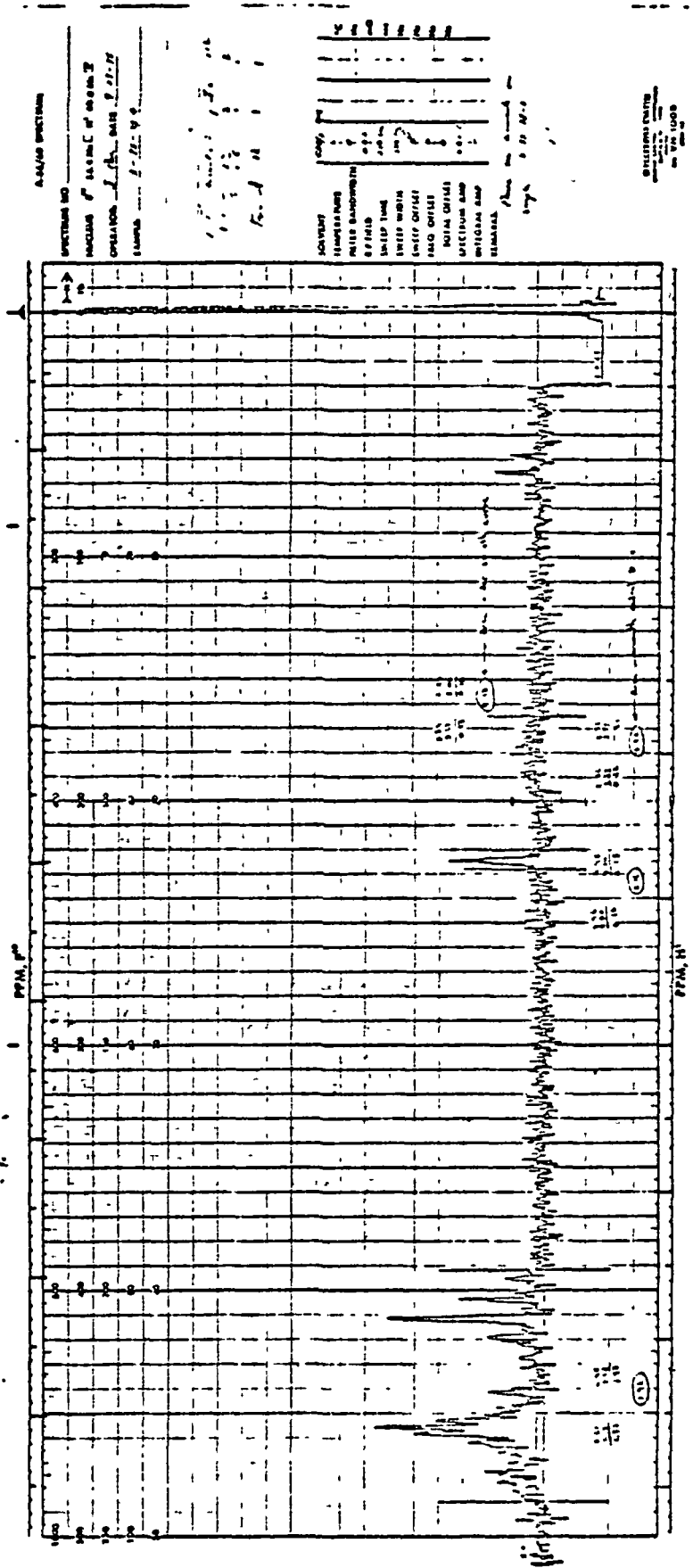


Figure 12: NMR spectrum of $\Phi_3\text{P}=\text{N}-\Phi\text{CH}_2\Phi-\text{NH}_2$

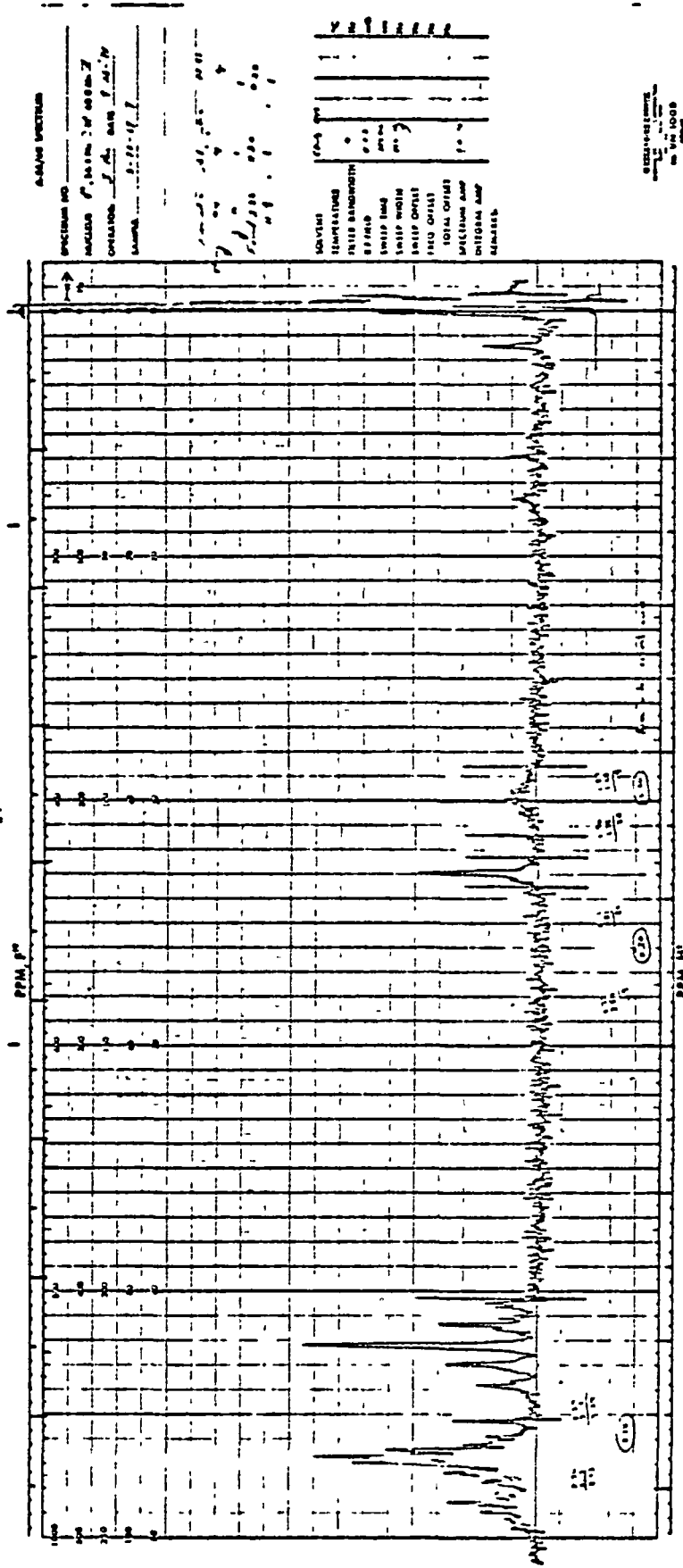


Figure 13: NMR spectrum of $H_2N-CH_2-CH_2-NH_2$ in CH_2Cl_2 solution. The spectrum shows a complex multiplet between 1 and 2 ppm and a sharp singlet at approximately 3.1 ppm.

PART NO 990088

DATE 1/10/66
 OPERATOR J. S. W. M.
 SAMPLE 3-74-6-3
 5 mg (4) + 0.1 P (1) DPP
 0.2 CH₂ CN
 FLOW RATE 67 ml/min

T-AXIS
 SCALE °C/in. 50
 PROG RATE °C/min 5
 HEAT COOL ISO
 SHIFT in. 0

DTA/DSC
 SCALE °C/in. (mc-41/mc-1)/in.
 WEIGHT mg
 REFERENCE

TGA
 SCALE mg/in. 10
 PURIFICATION mg 0 (20)
 WEIGHT mg 11.47
 TIME CONST sec 1
 DIV (10X) (mlb/min)/in. 2

TMA
 SCALE mlb/in.
 MODE
 SAMPLE SIZE
 LOAD g
 DIV (10X) (mlb/min)/in.

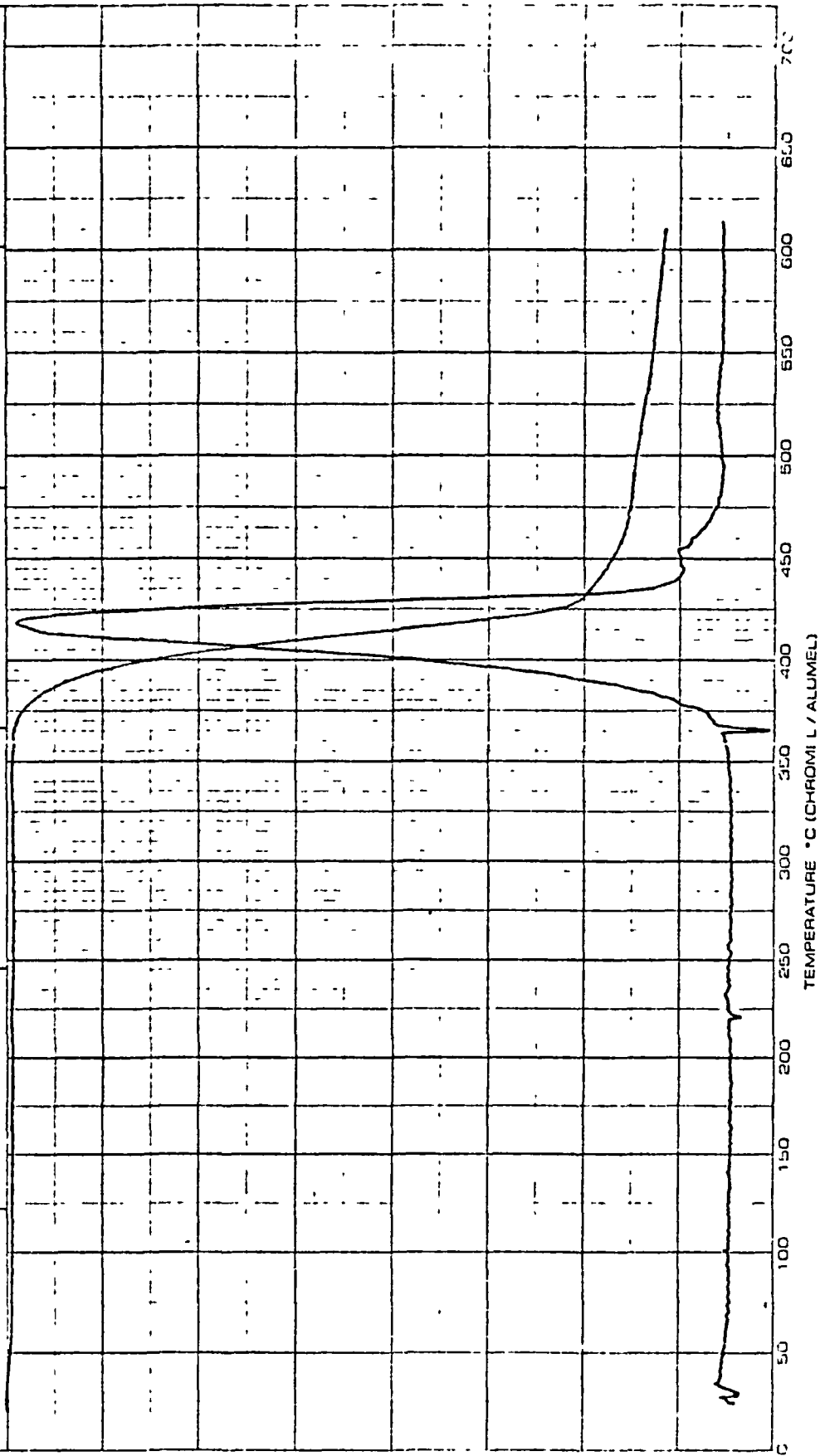


Figure 14: TGA in air of TDA-DPPB prepared in acetonitrile

P/21 P/O 920048

TGA-173

19A0674
37-19-4
66.873 + 65.55 (M)
AIR
67ml/min

TAXIS
SCALE °C/min 50
PROG RATE °C/min 5
HEAT CO ISO
PURGE m 0

DTA DSC
SCALE C/in
WEIGHT mg
REFERENCE

TGA
SCALE mg/min 10
SUBSTITUTION mg 0 (20)
WEIGHT mg 10.56
TIME (CONST) min 1
DT (mg/min) / min 0.2

TMA
SCALE mils/min
MODE
SAMPLE SIZE
LOAD g
DTY (DUX) (mils/min)/in

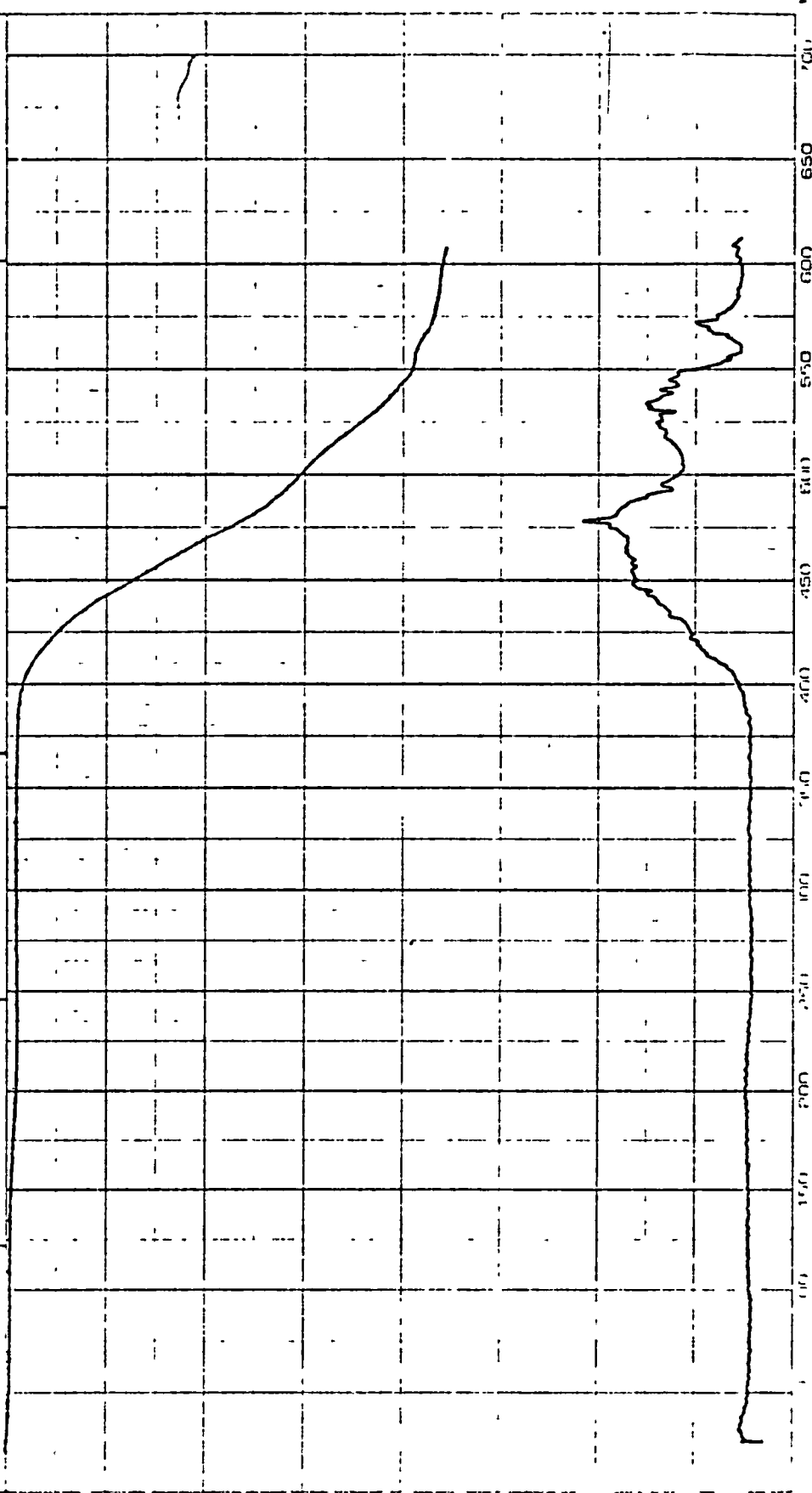


Figure 15: TGA in air of benzene soluble product from the reaction of TDA with BDBI

PART NO 990088

TGA 190 DATE 250674
 OPERATOR FS
 SAMPLE TGA (91)φ
 Inertable
 5 TA 50-1
 ATM Air 3
 FLOW RATE 67 ml/min

T AXIS
 SCALE °C/min 50
 PROG RATE °C/min 5
 HEAT COOL ISO
 SHIFT in 0

DTA DSC
 SCALE C/in
 (mcal/sec)/in
 WEIGHT mg
 REFERENCE

TGA
 SCALE mg/min 1.0
 SUPPRESSION mg 9 (50)
 WEIGHT mg 9.15
 FILM CONST sec 1
 dy (mg/min)/in. 9.2

TMA
 SCALE mils/in
 MODE
 SAMPLE SIZE
 LOAD g
 dy (10X) (mils/min)/in.

X

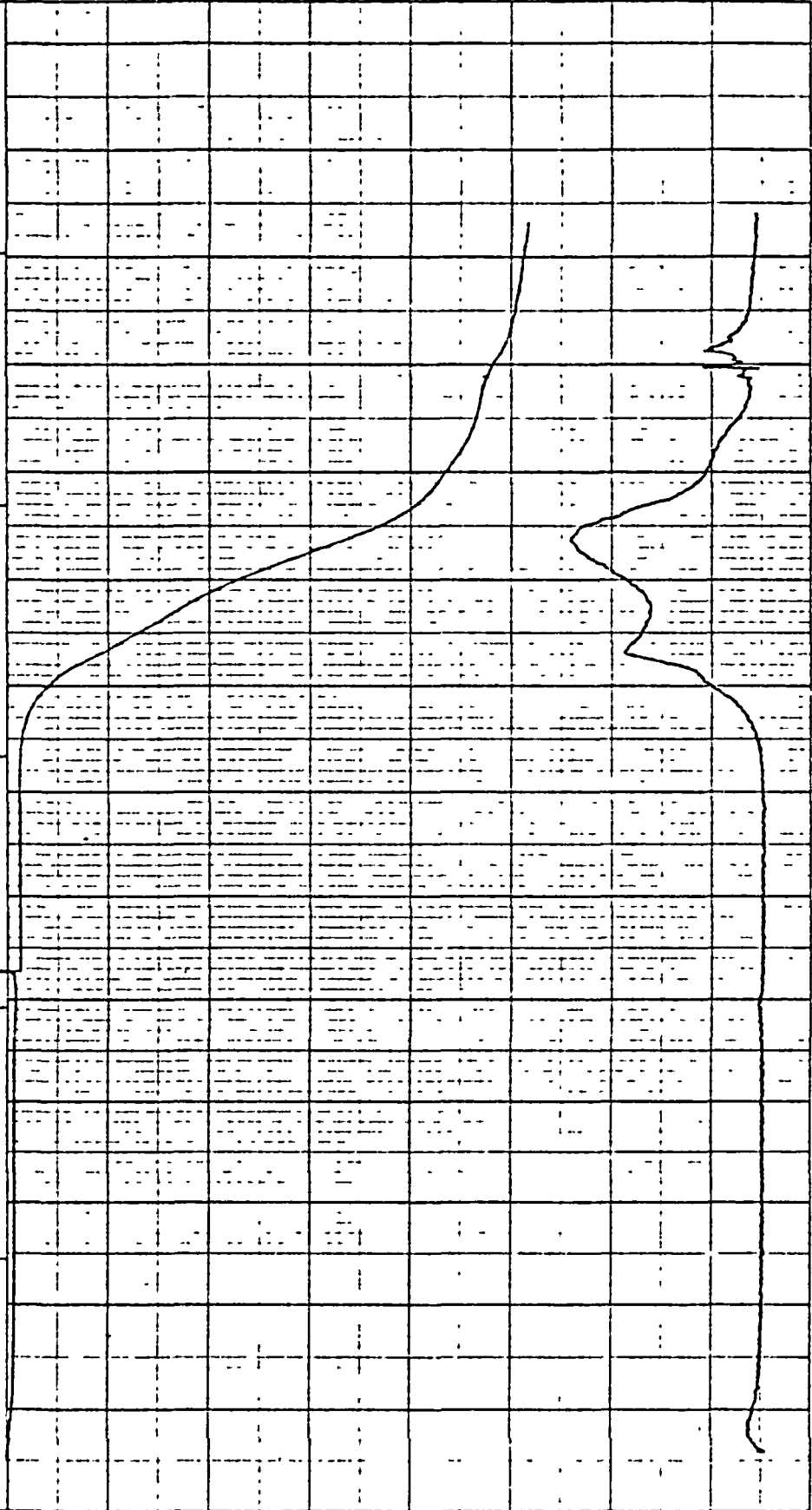


Figure 16: TGA in air of product from the reaction of PDPB with a stoichiometric amount of TDA
 (benzene insoluble fraction)

PART NO 990088

DSC

RUN NO 78 DATE 15 Jan 78
OPERATOR F.S.
SAMPLE TMA DPE TPA
WGT 11 molar ratio
TMA N₂ 3-7-78-1
FLOW RATE 50cc/min

T-AXIS

SCALE °C/in 50
PROG RATE °C/min 5
HEAT COOL ISO
SHIFT in 0

DTA-DSC

SCALE °C/in
(mcal/sec)/in
WEIGHT mg
REFERENCE
Red 1.0 (cal/sec)/in
Green 0.2 (cal/sec)/in

TGA

SCALE mg/in
SUPPRESSION mg
WEIGHT mg
TIME CONST 600
μV (mg/min)/in

TMA

SCALE mil/in
MODE
SAMPLE SIZE
LOAD g
μV (10X) (mil/min)/in

*

Baseline 505
Sample 3-7-78

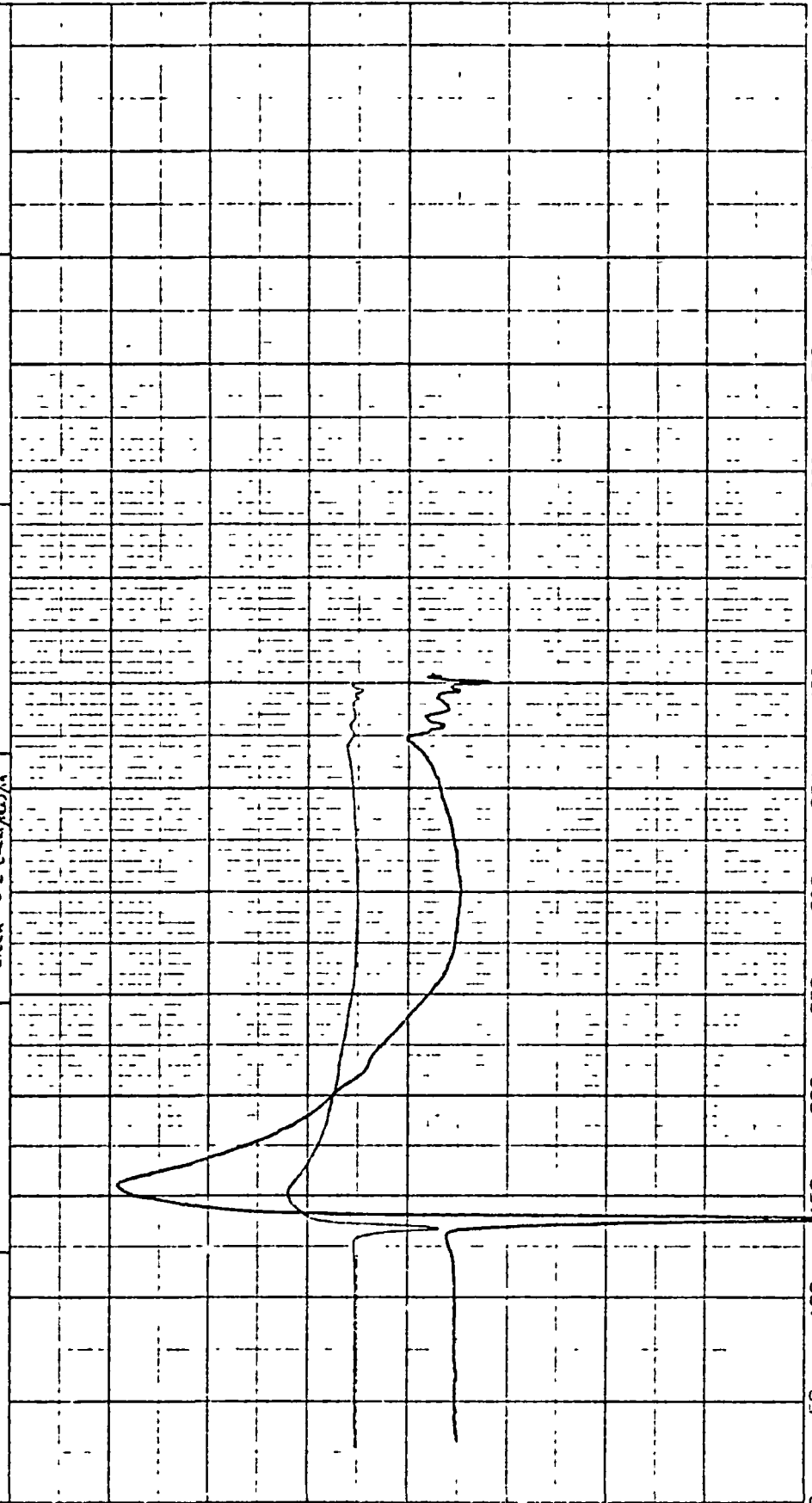


Figure 17: DSC of N₃-C₃N₃ (P)₂-N=N=P₂-(CH₂)₄-P₂ = N-C₃N₃(P)₂-N₃ + P₂-(CH₂)₄-P₂

PART NO 990088

TGA
 DATE 19 Dec 74
 OPERATOR F.S.
 SAMPLE 9-74-53-4
 5.7M No 1 insoluble
 treated w H₂O
 ATM Air
 FLOW RATE 52 ml/min

T-AXIS

SCALE °C/in 50
 PROG RATE °C/min 5
 HEAT COOL ISO
 SHIFT in 0

DTA-OSC

SCALE °C/in
 (mcal/sect/in)
 WEIGHT mg
 REFERENCE

TGA

SCALE mg/in 1.0
 SUPPRESSION mg 0.0(50)
 WEIGHT mg 372
 TIME CONST sec 1.0
 dY (mg/min)/in 0.2

TMA

SCALE
 MOD
 SAMPLE SIZE
 LOAD
 dY (10⁻³X) (mils/min)/in

Note, black particles
 on bottom of tube
 Possible boil-off
 from sample in boat
 causing sharp decreases
 in weight

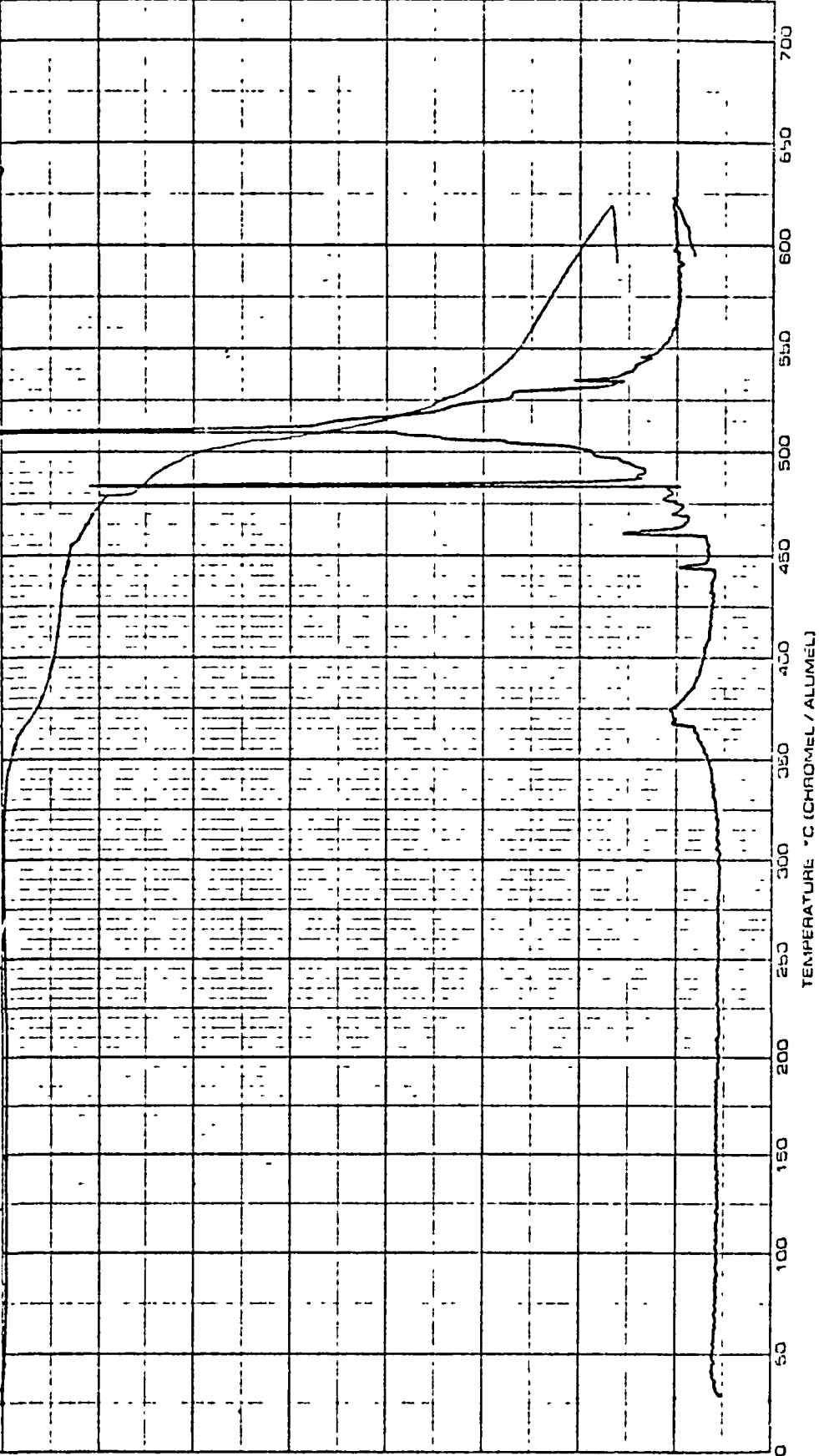


Figure 18: TGA in air of material from the reaction of MDA and D31-bis-dichlorophosphorane in benzene in the presence of triethylamine, originally heated neat.

PART NO 990088

TGA 24 April 75
 OPERATOR FS
 SAMPLE (C12P007) + 84.1M
 + MDA
 Insoluble, treated w H₂O
 ATM - Air
 FLOW RATE - 67.0 ml/min

T-AXIS
 SCALE °C/in 50
 PROG RATE °C/min 5
 HEAT or COOL ISO
 SHIFT in 0

DTA DSC
 SCALE °C/in
 (mcal/gac)/in
 WEIGHT mg
 REFERENCE

TGA
 SCALE mg/min 1.0
 SUPPRESSION mg - 0.00
 WEIGHT mg 11.16
 TIME CONST sec 1
 DY (mg/min)/in 0.2

TMA
 SCALE mils/in
 MODE
 SAMPLE SIZE
 LOAD g
 DY (TOX) (mils/min)/in

Prog 10: 10/10/75
 Note: sudden weight loss at 450°C may have been a result of spattering large chunk of material was observed at bottom of tube

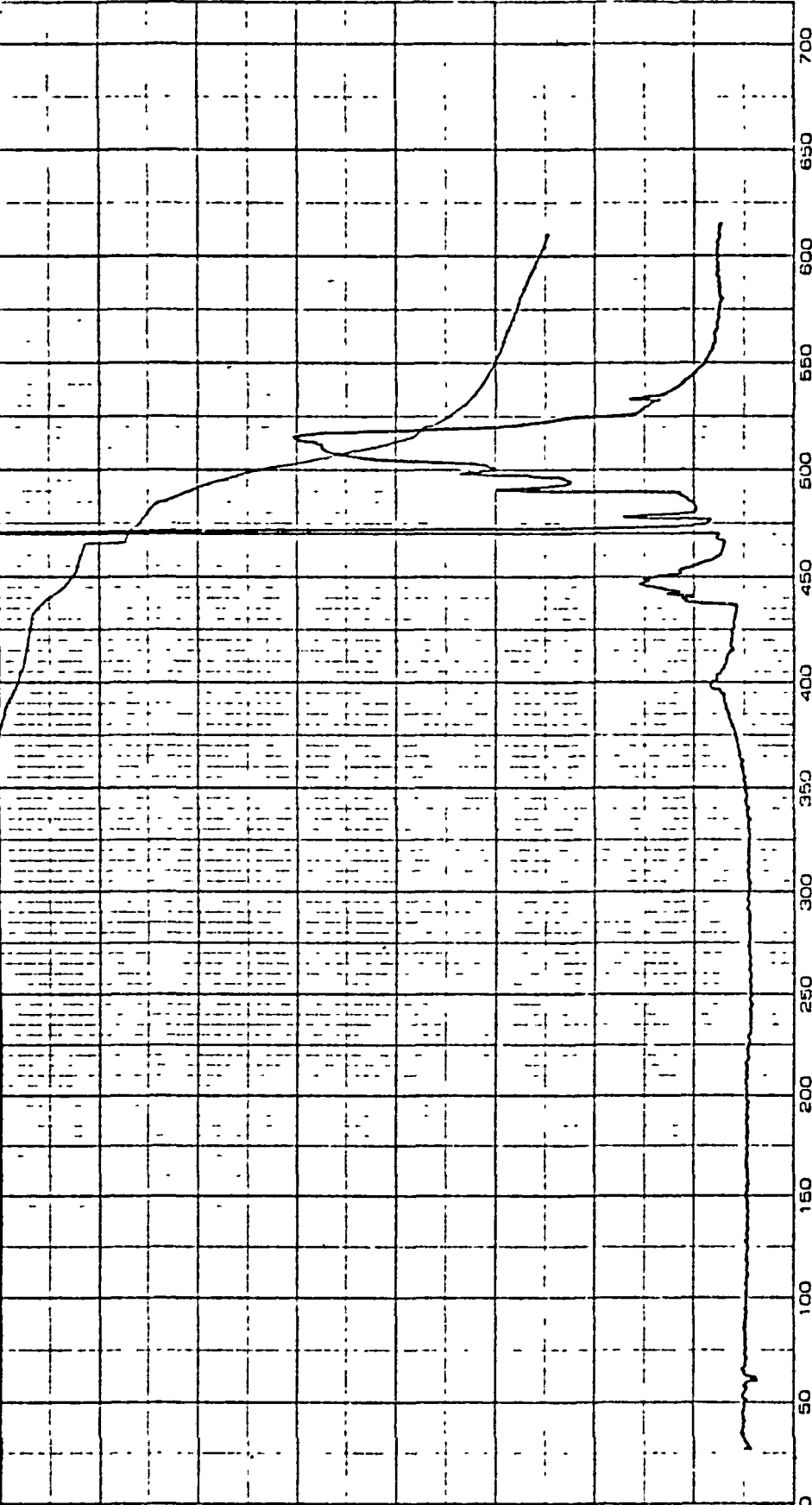


Figure 19: TGA in air of insoluble material from the reaction of MDA and 3DBI-bis-dichloro-phosphorane in acetonitrile in the presence of triethylamine.

PART NO 990088

TGA
 RUN NO: 217 DATE: 2/19/79
 OPERATOR: FS
 SAMPLE: 3-77-133-4
 MDA (0.100 g) + 0.5%
 W. II Inert. (0.300 g) H₂O
 ATM: Air
 FLOW RATE: 6.7 ml/min

T-AXIS
 SCALE °C/in: 50
 PROG RATE °C/min: 5
 HEAT COOL: ISO
 SHIFT in: 0

DTA-DSC
 SCALE °C/in: (mcal/sec)/in
 WEIGHT mg
 REFERENCE

TGA
 SCALE mg/in: 1.0
 SUPPRESSION mg: 0 (2x)
 WEIGHT mg: 12.26
 TIME CONST sec: 1
 dy (mg/min) / in: 0.3

TMA
 SCALE mils/in
 MODE
 SAMPLE SIZE
 LOAD 0
 dy (10X) (mils/min)/in

Pyrex 2.6 tube I.D.

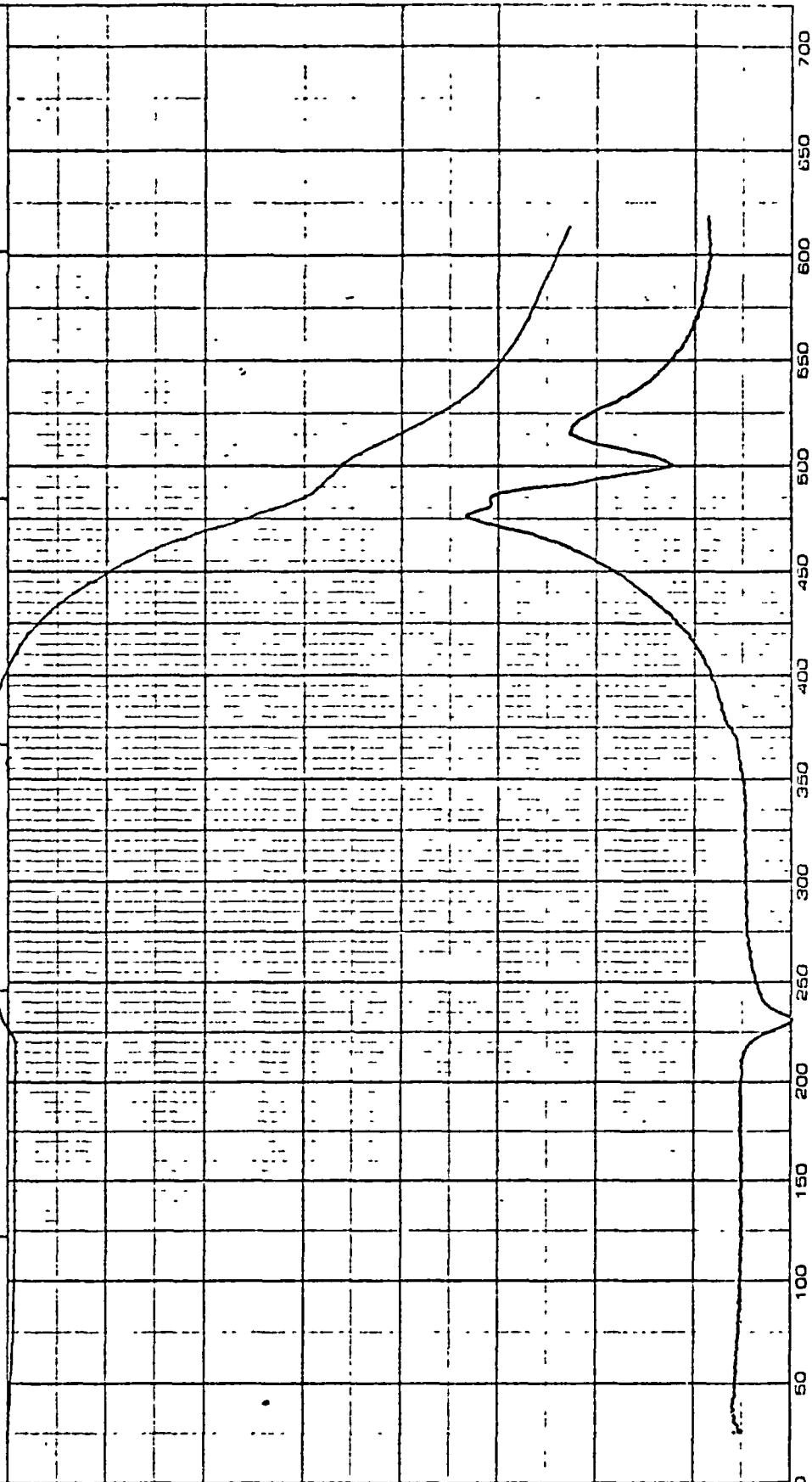


Figure 20: TGA in air of insoluble material from the reaction of MDA with 8DBI-bis-dichlorophosphorane in benzene/acetonitrile in the presence of excess triethylamine, inverse addition.

PART NO 990088

TGA
 RUN NO 258 DATE 2 June 75
 OPERATOR FS
 SAMPLE Insoluble mol'l
 Wt. 0.25 g, 0.0001 g
 3-14-75 100°C
 ATM. Air
 FLOW RATE 67 ml/min

T-AXIS
 SCALE °C/in. 50
 PROG RATE °C/min 5
 HEAT COOL ISO
 SHIFT in. 0

DTA-DSC
 SCALE °C/in. (mcal/gcc)/in.
 WEIGHT mg
 REFERENCE

TGA
 SCALE mg/in. 10
 SUPPRESSION mg 0.50
 WEIGHT mg 11.50
 TIME CONST sec 1
 dy (mg/min)/in 0.3

TMA
 SCALE mils/in.
 MODE
 SAMPLE SIZE
 LOAD g
 DY (TOX) (mils/min)/in.

Observed small particles
 on bottom of furnace tube
 after run completed - this
 may account for "spikes"
 in derivative trace

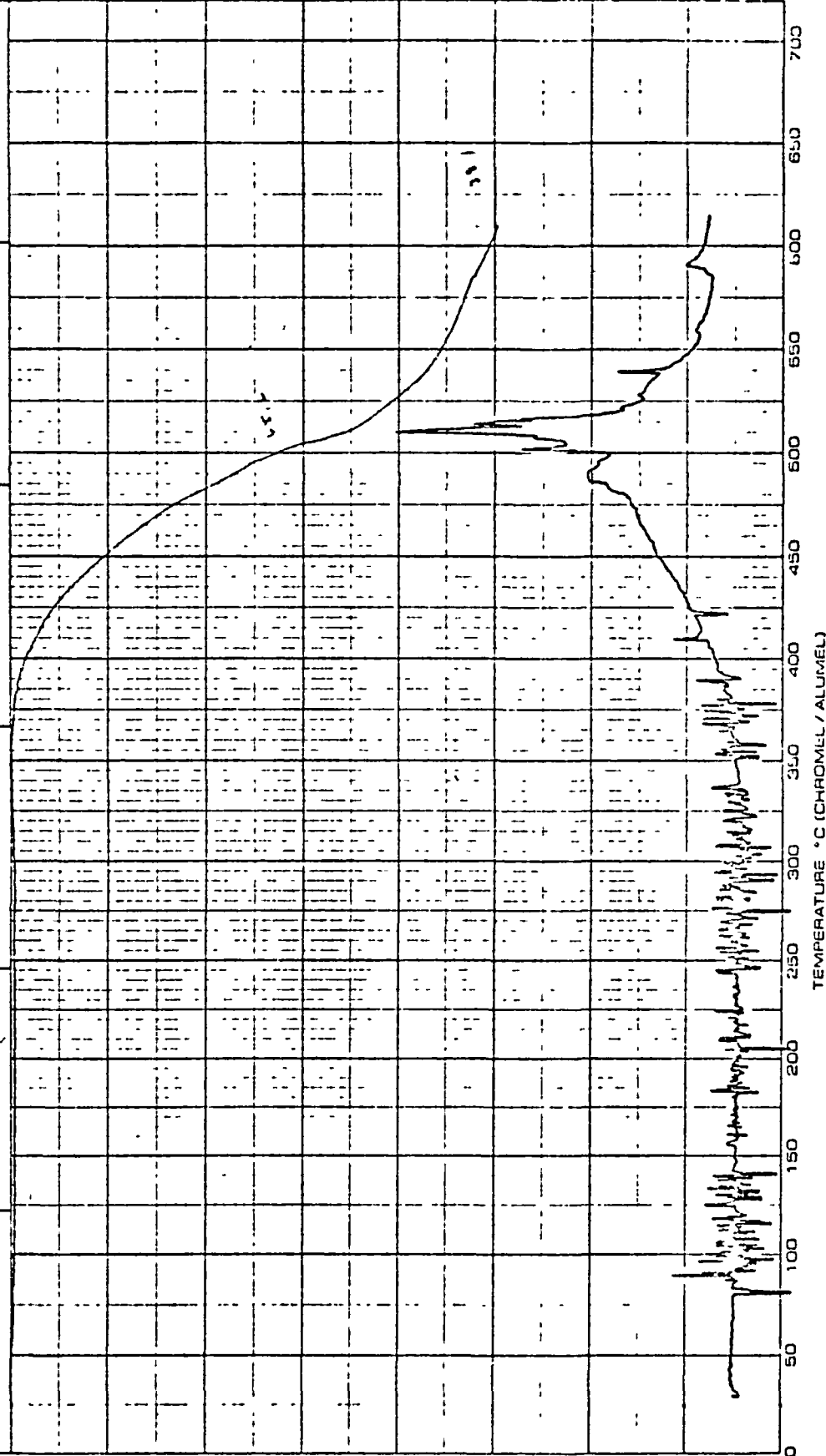


Figure 21: TGA in air of insoluble material prepared from PPDA and BDBI-bis-dichlorophosphorane in acetonitrile in the presence of triethylamine.

PART NO 990088

TGA
 RUN NO 253 DATE 8 May 75
 OPERATOR FS
 SAMPLE $C_{12}H_{10}O_2$ Re
 Inert 461 H_2O
 3-2-104-3
 ATM. R/P 4
 FLOW RATE 5 ml/min

T AXIS
 SCALE °C/in 50
 PROG RATE °C/min 5
 HEAT COOL ISO
 SHIFT in 0

DTA-DSC
 SCALE °C/in
 (mcal/sec)/in
 WEIGHT mg
 REFERENCE

TGA
 SCALE mg/in 1.0
 SUPPRESSION mg A (1.0)
 WLIGHT mg 142
 TIME CONST sec 1
 dY (mg/min)/in 0.3

TMA
 SCALE mils/in
 MODE
 SAMPLE SIZE
 LOAD 0
 dY (10X) (mils/min)/in

Page 192 Unbalanced
 3:21

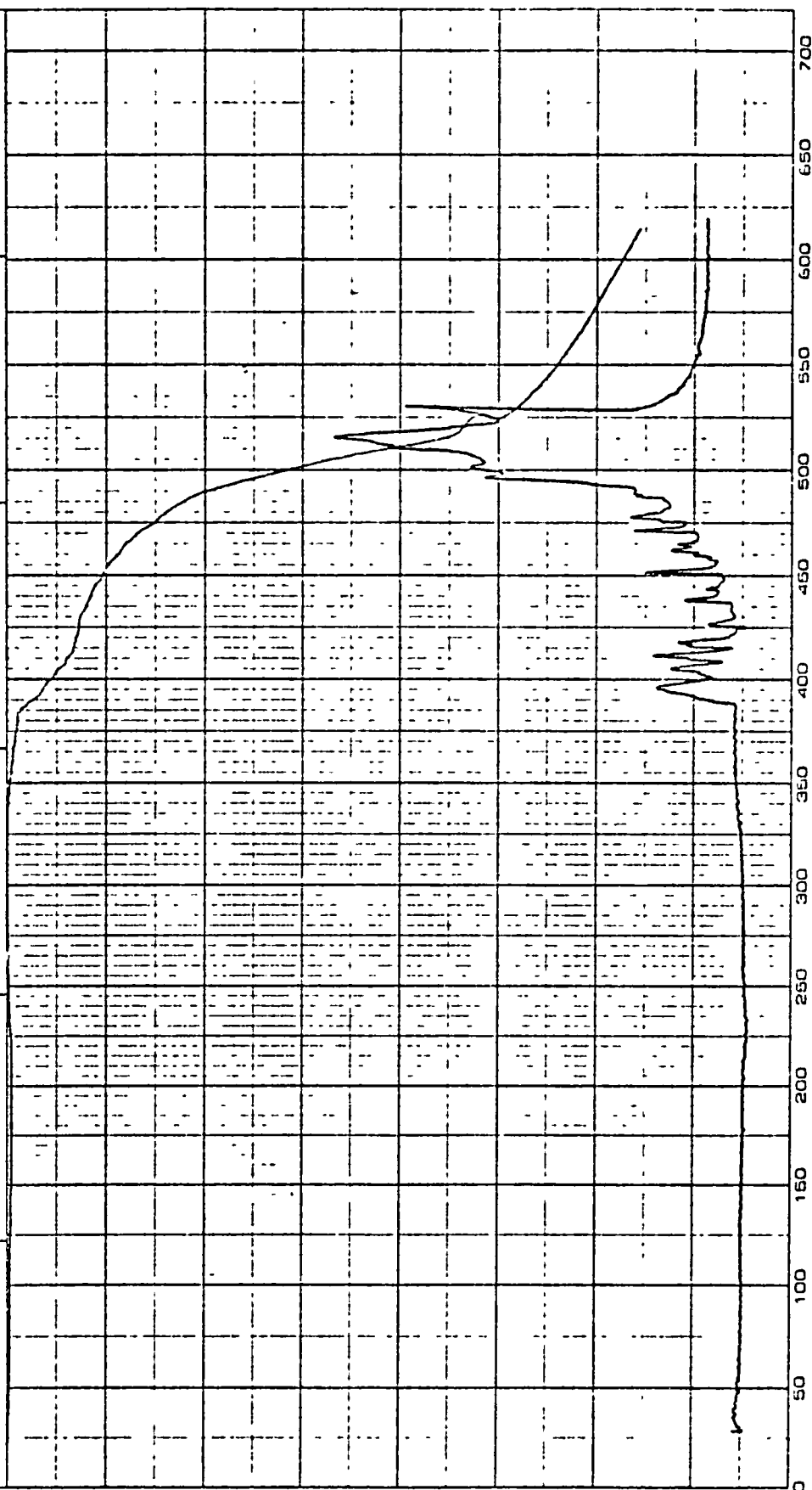


Figure 22: TGA in air of insoluble material from the reaction of MDA with PDPB-bis-dichlorophosphorane in acetonitrile in the presence of triethylamine.

PART NO 99088

TGA DATE 13 Mar 15
 OPERATOR FS
 SAMPLE 2-27-90-3
 (pyrolysis with ppt)

ATM Air
 FLOW RATE 41 ml/min

T-AXIS
 SCALE °C/min 50
 PROG RATE °C/min 5
 HEAT COOL ISO
 SHIFT in 0

DTA DSC
 SCALE °C/in
 (mV/dt/sec)/in
 WEIGHT mg
 REFERENCE

TGA
 SCALE mg/in 1.0
 SUPPRESSION mg 0.0(1.0)
 WEIGHT mg 11.50
 TIME CONST sec 1
 dY (mg/min)/in 0.2

TMA
 SCALE mil/in
 MODE
 SAMPLE SIZE
 LOAD g
 dY (10X) (mil/min)/in

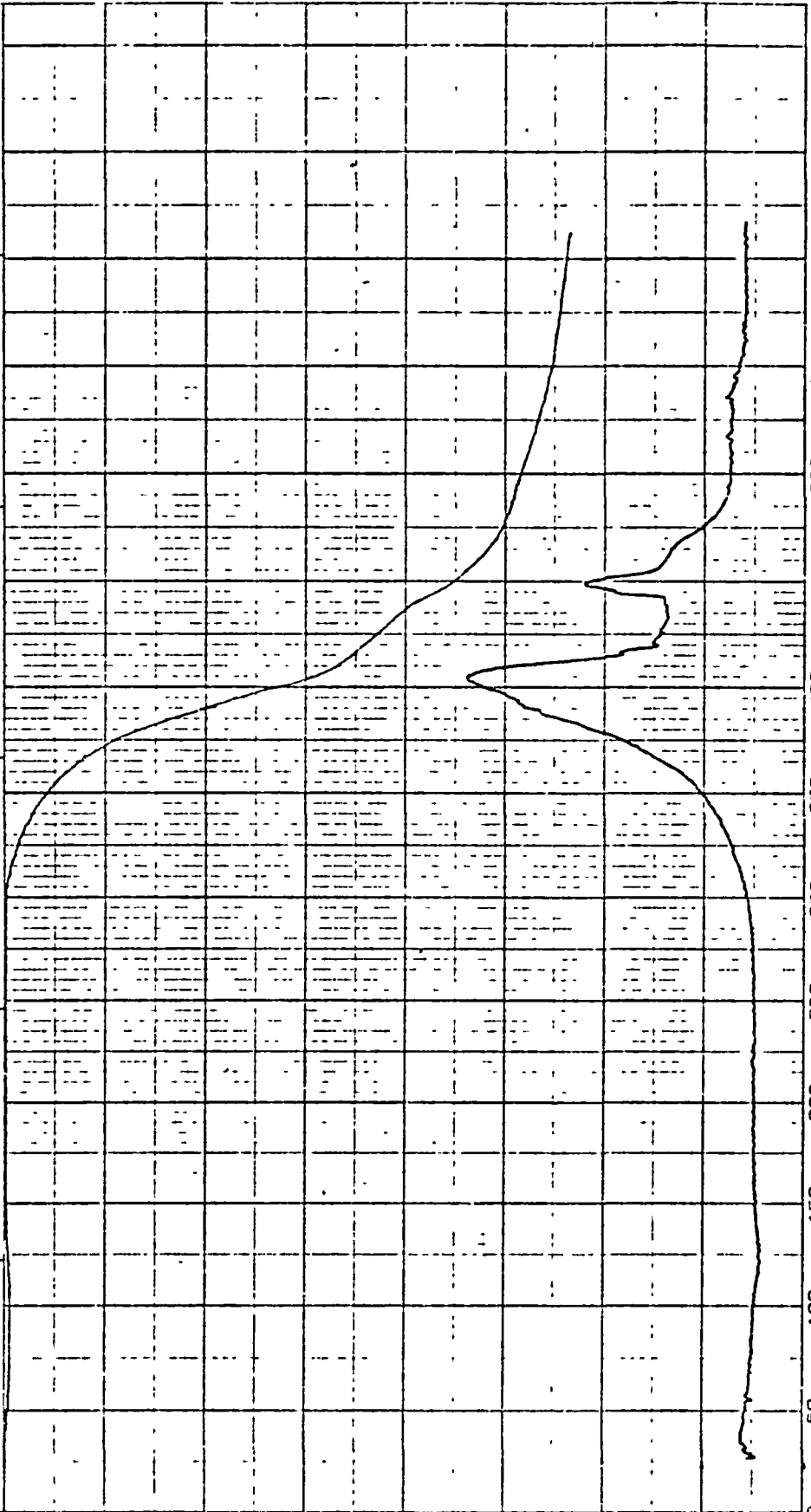


Figure 23: TGA in air of purified residue from pyrolysis of $N_3-C_3N_3(\phi)-N=P\phi_2-(CH_2)_4-P\phi_2=N-C_3N_3(\phi)-N_3$

P/ST NO 970608

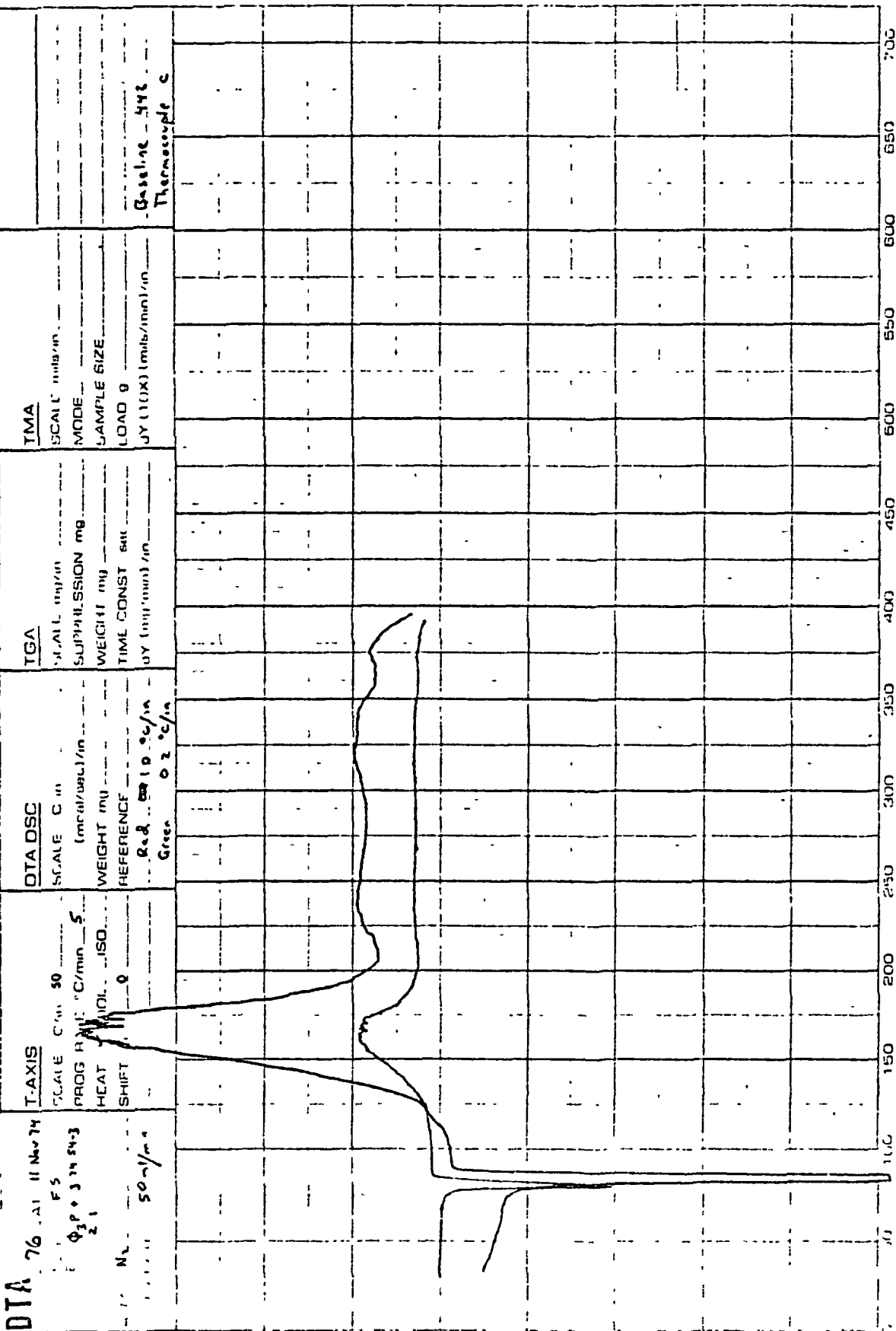


Figure 24: DTA of ϕ_3P and $N_3-C_3N_3(\phi)-N=P\phi_2-(CH_2)_4-P\phi_2=N-(\phi)C_3N_3-N_3$ mixture

PART NO 990088

DSC

DATE 15 Oct 74
 OPERATOR FS
 SAMPLE C₁₂H₁₀P₂
 IR # 4020 Read
 ATTA N₂
 FLOW RATE 50 ml/min

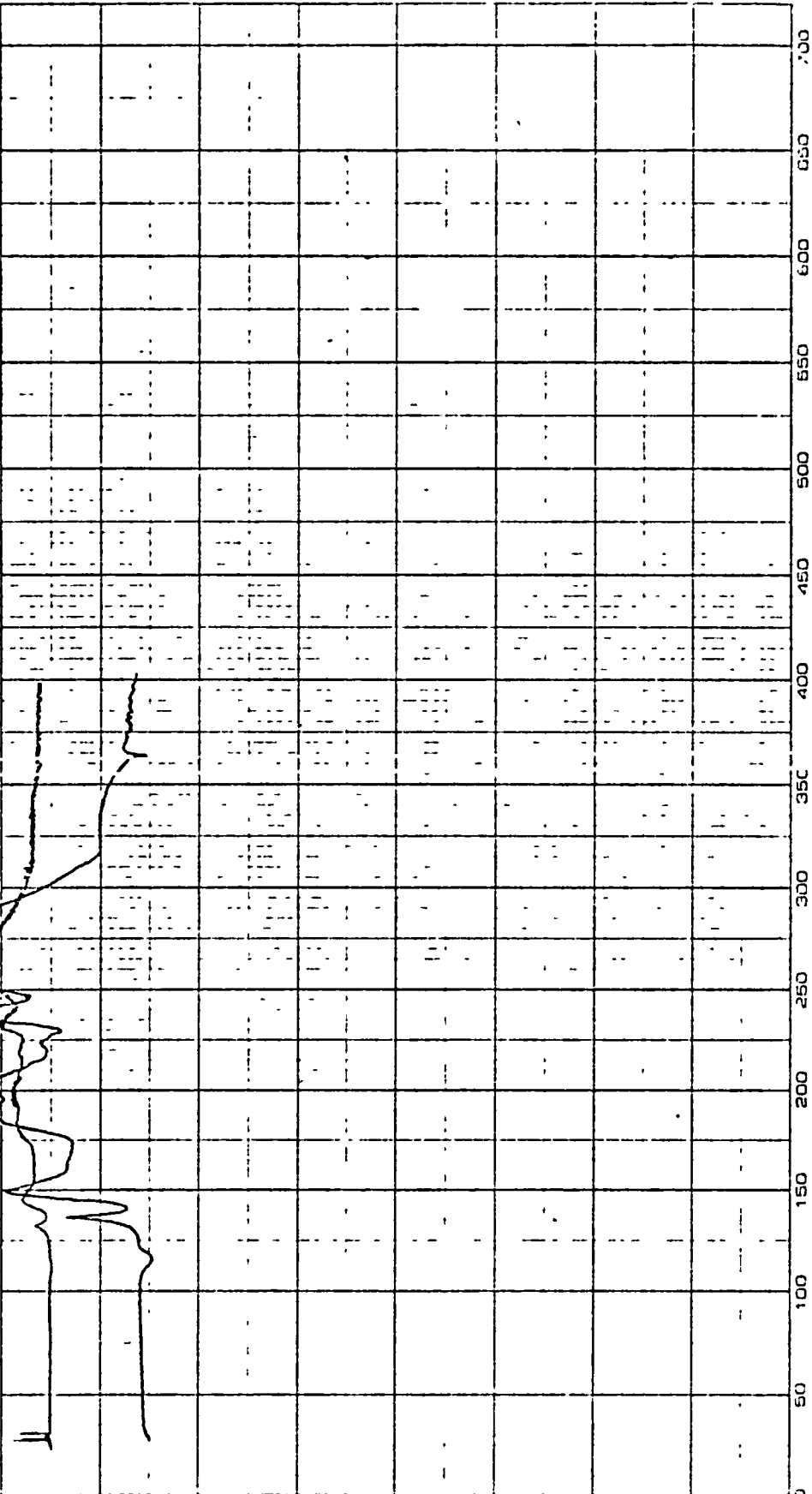
T-AXIS
 SCALE °C/min 50
 HEAT FLOW RATE °C/min 5
 HEAT FLOW COOL ISO
 SHIFT in 0

DSC
 SCALE °C/in
 WEIGHT mg
 FLOW RATE 10 (red/sec)/in
 O₂ (red/sec)/in

TGA
 SCALE mg/in
 SUPPRESSION mg
 WEIGHT mg
 TIME CONST sec
 RATE (mg/min)/in

TMA
 SCALE mils/in
 MODE
 SAMPLE SIZE
 LOAD g
 RATE (mils/min)/in

Baseline 505



TEMPERATURE °C (CHROMIUM / ALUMEL)

Figure 25: DSC of BDBI-bis-dichlorophosphorane

PART NO 990088

DSC
 RUN NO 54 DATE 2/18/74
 OPERATOR JN
 4.4' Methylenediamine
 21.2 g 16.9165
 T-14
 FLOW RATE: 50 ml/min

T-AXIS
 SCALE °C/in. 50
 PROG RATE °C/min 5
 HEAT COOL ISO
 SHIFT in 0

DTA DSC
 SCALE °C/in. _____
 (mgul/μcc)/in _____
 WLIGHT mU _____
 REFERENCE _____

TGA
 SCALE mg/in. _____
 SUPPRESSION mg _____
 WEIGHT mg _____
 TIME CONST sec. _____
 dY (mg/min)/in _____

TMA
 SCALE mil/in. _____
 MODE _____
 SAMPLE SIZE _____
 LOAD g _____
 dY (10X) (mil/min)/in _____

Page 26 PA 11-03-74

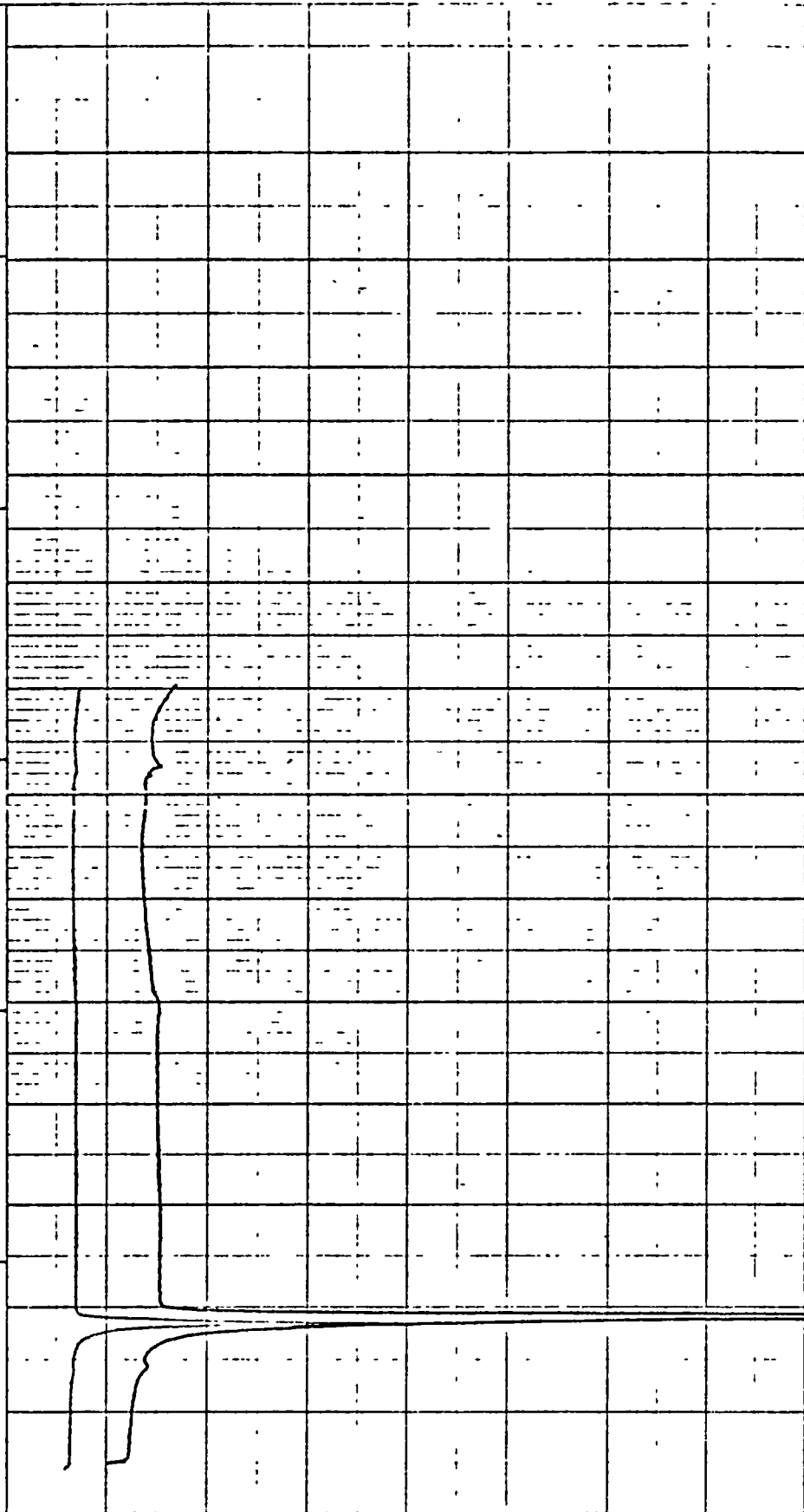


Figure 26: DSC of MDA

PART NO 990088

DSC 71

DATE: 11/11/83
OPERATOR: F.S.
SAMPLE NAME: (M.D.)
3-74-4-1
T. N₂
FLO. RATE 50 ml/min

T-AXIS

SCALE °C/in. 50
PROG RATE °C/min 5
HEAT COOL ISO
SHIFT in. 0

DTA/DSC

SCALE °C/in. (mcal/sec)/in.
WEIGHT mg
FILTRANCE
Red 1.0 (mcal/sec)/in.
Green 0.2 (mcal/sec)/in.

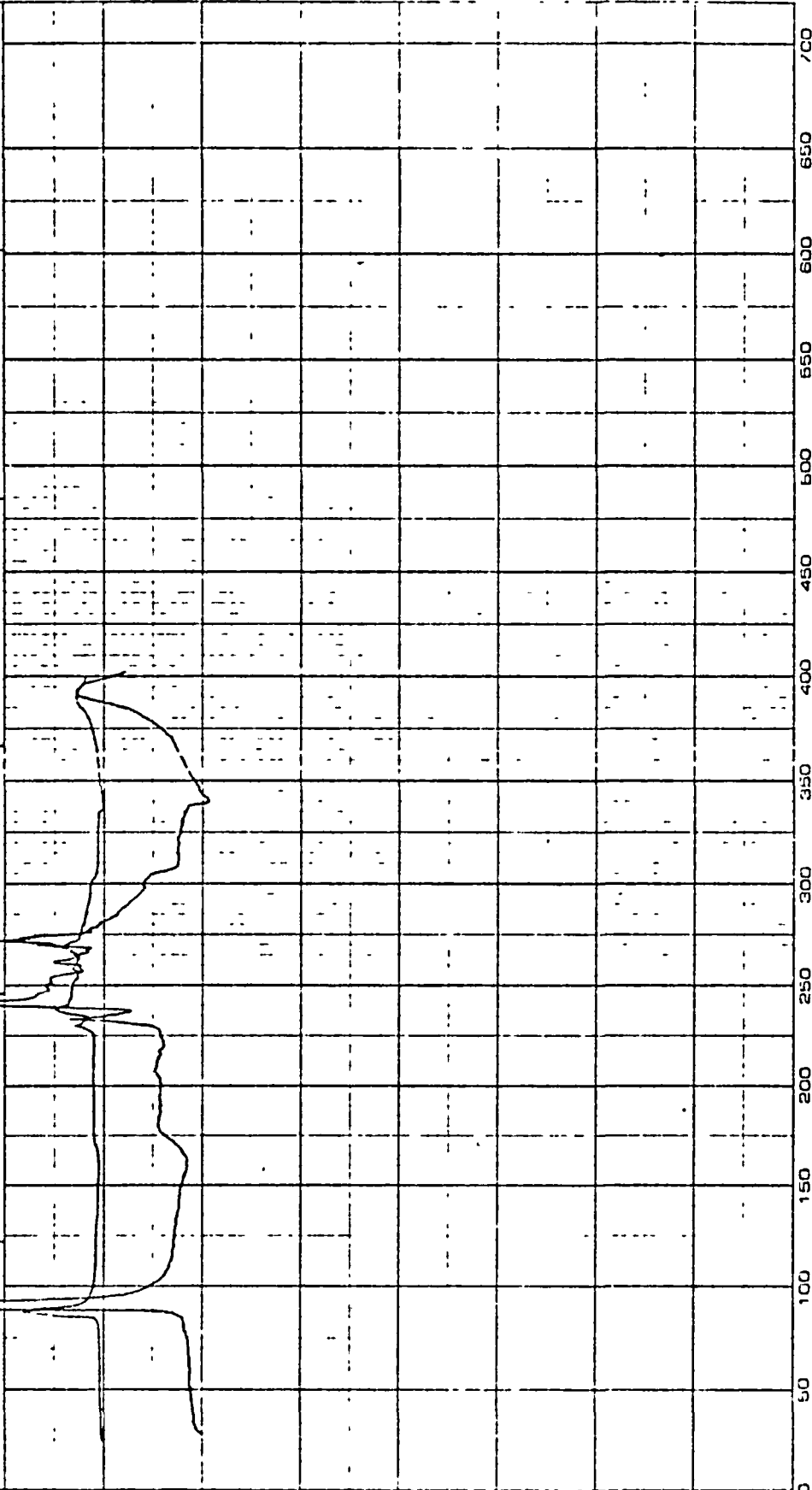
IGA

SCALE mg/in.
SUPPRESSION mg
WEIGHT mg
THERM CONST. mg.

TMA

SCALE mils/in.
MODE
SAMPLE SIZE
LOAD V
dY (10X) (mils/min)/in.

Residuals: 505



TEMPERATURE °C (CHROMIUM / ALUMEL)

Figure 27: DSC of a mixture of BDBI-bis-dichlorophosphorane and MDA

PART NO 990088

DSC
 DATE: 23 Oct 74
 OPERATOR: F S
 SAMPLE: Mixture of
 (MIP) and CCl₄ at 100°C
 AT: NL
 FLOW RATE: 50 ml/min

T AXIS
 SCALE °C/min: 50
 HEAT RATE °C/min: 5
 HEAT COOL: 150
 SHIFT in: 0

DTA-DSC
 SCALE °C/in: (mcal/wg)/in
 WEIGHT mg: Red 1.0 (mcal/sec), Green 0.2 (mcal/sec)
 REFERENCE

TGA
 SCALE mg/in
 SUPPRESSION mg
 WEIGHT mg
 TIME CONST sec
 dY (mg/min)/in

TMA
 SCALE mils/in
 MODE
 SAMPLE SIZE
 LOAD g
 dY (10x) (mils/min)/in

Baseline: 595

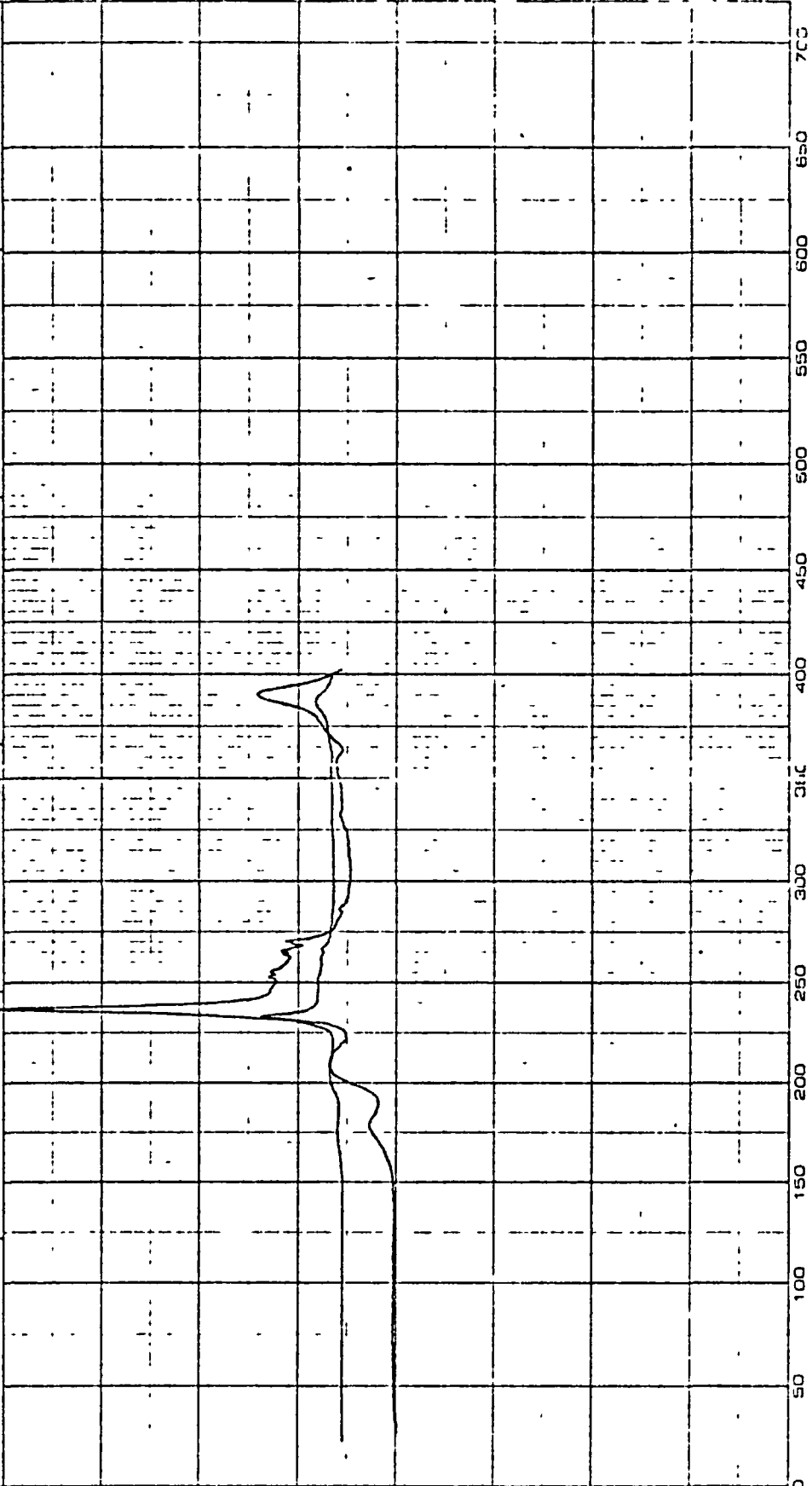
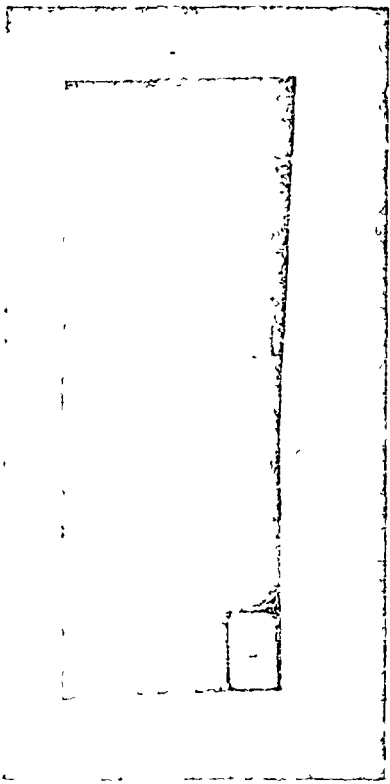
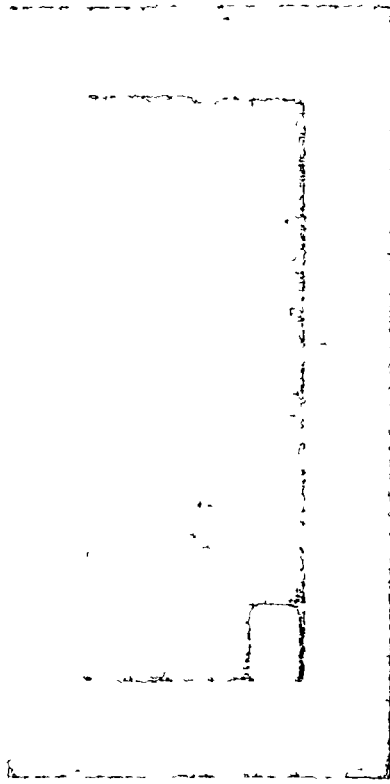


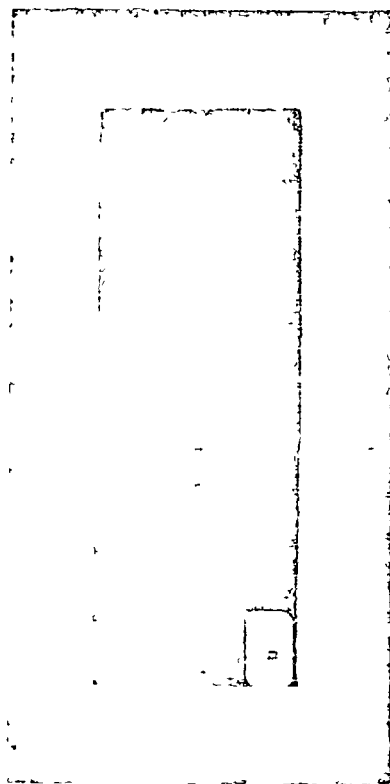
Figure 28: DSC of the reaction mixture MDA and BDBI-bis-dichlorophosphorane after heating at 110°C



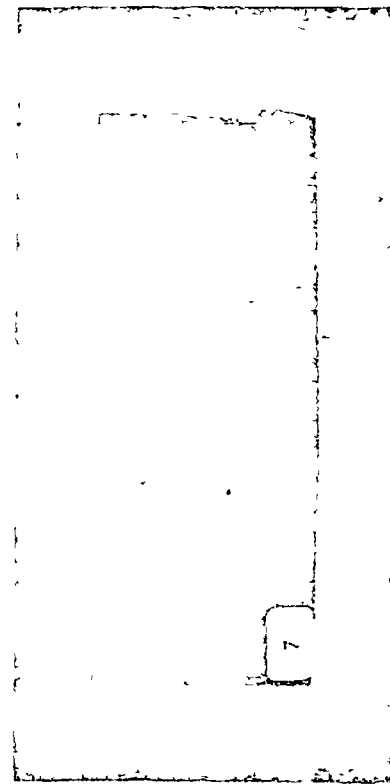
Laminate No. 1, unmodified
Burn-through time 76 sec
Sample warped



Laminate No. 2, unmodified
Burn-through time 83 sec
No warping



Laminate No. 6, phosphazene modified
After exposure to flame for 15 min
Sample warped slightly



Laminate No. 7, phosphazene modified
After exposure to flame for 15 min
No warping

Figure 29: Burn-through specimens. Sample identification given in Table VI.
Thickness of all samples 0.7 mm (0.028 inch).

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