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NEW HIGH TEMPERATURE CROSS LINKING MONOMERS

by

Daniel A. Scola

December 20, 1978

UNITED TECHNOLOGIES RESEARCH CENTER

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16. Abstract This report describes the results of a one-year program designed to synthesize new, nonvolatile crosslinking monomers and to prove their feasibility in the development of lower temperature curing PMR-polyimide resins with high temperature capability. The objective of this program is to develop PMR-polyimide resins capable of being processed at a maximum temperature of 232^{o}C to 288^{o}C (450^{o}F to 500^{o}F) without sacrifice of the high temperature 316^{o}C (600^{o}F) capability of the state-of-the-art PMR-15 polyimide resin. Four novel monomethyl esters were synthesized and characterized for use in the crosslinking studies. It was found that all four crosslinkers were capable of entering into a crosslinking reaction to produce polymer specimens which were strong, dense and free of voids. The infrared and DSC studies of each crosslinker with monomers 4,4'-methylenedianiline (MDA) and the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE) comprising the resin systems, crosslinker/MDA/BTDE suggested that curing could be accomplished at 288^{o}C (550^{o}F). However, fabrication of dense, void free polymer specimens required a temperature of 316^{o}C (600^{o}F) and a pressure of 0.69 MPa (100 psi). The crosslinkers, monomethyl ester of 2,5-bicyclo[2.2.1]heptadiene-2,3-dicarboxylic acid (NDE) and monomethyl ester of maleic acid (MAE) were selected for evaluation in Celion 6000/PMR polyimide composites. These composites were characterized at RT, 288^{o}C (550^{o}F) and 316^{o}C (600^{o}F) initially and after isothermal aging at 288^{o}C (550^{o}F) and 316^{o}C (600^{o}F) for several hundred hours. The results of the isothermal aging studies suggested that both PMR systems NDE-MDA-BTDE and MAE-MDA-BTDE are promising candidates as matrices for addition type polyimide composites. These studies demonstrated that alternate crosslinkers to NE/MDA/BTDE are feasible, but mechanisms to lower the crosslinking temperature must be developed to provide lower temperature processing PMR-type polyimides.

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New High Temperature Crosslinking Monomers

SUMMARY

This report describes the results of a one-year program designed to synthesize new, nonvolatile crosslinking monomers and to prove their feasibility in the development of lower temperature curing PMR-polyimide resins with high temperature capability. The objective of this program is to develop PMR-polyimide resins capable of being processed at a maximum temperature of 232°C to 288°C (450°F to 500°F) without sacrifice of the high temperature 316°C (600°F) capability of the state-of-the-art PMR-15 polyimide resin.

Four novel monomethyl esters were synthesized and characterized for use in the crosslinking studies. It was found that all four crosslinkers were capable of entering into a crosslinking reaction to produce polymer specimens which were strong, dense and free of voids. The infrared and DSC studies of each crosslinker with monomers 4,4'-methylenedianiline (MDA) and the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE) comprising the resin systems, crosslinker/MDA/BTDE suggested that curing could be accomplished at 288°C (550°F). However, fabrication of dense, void free polymer specimens required a temperature of 316°C (600°F) and a pressure of 0.69 MPa (100 psi).

The crosslinkers, monomethyl ester of 2,5-bicyclo[2.2.1]heptadiene-2,3-dicarboxylic acid (NDE) and monomethyl ester of maleic acid (MAE) were selected for evaluation in Celion 6000/PMR polyimide composites. These composites were characterized at RT, 288°C (550°F) and 316°C (600°F) initially and after isothermal aging at 288°C (550°F) and 316°C (600°F) for several hundred hours.

The results of the isothermal aging studies suggested that both PMR systems NDE-MDA-BTDE and MAE-MDA-BTDE are promising candidates as matrices for addition type polyimide composites. These studies demonstrated that alternate crosslinkers to NE/MDA/BTDE are feasible, but mechanisms to lower the crosslinking temperature must be developed to provide lower temperature processing PMR-type polyimides.

1.0 INTRODUCTION

This document constitutes the final report on the development of new high temperature crosslinking monomers initiated on June 6, 1977 and describes the work performed between that date and August 6, 1978. The major objectives are to synthesize new, nonvolatile crosslinking monomers and to prove their feasibility in the development of lower temperature curing (232 to 288°C), PMR-polyimide resins, without sacrifice of the high temperature (316°C) capability of the state-of-the-art PMR-15 polyimide resin.

The work performed under this contract was accomplished in four tasks as described below:

Task I - Monomer Synthesis

Four novel monomethyl esters were synthesized and characterized, and attempts were made to synthesize two other monomethyl esters. The monomers synthesized were the monomethyl ester of itaconic acid, the monomethyl ester of 2,5-bicylo-[2.2.1]heptadiene-2,3-dicarboxylic acid, monomethyl ester of 2,5-bicylo[2.2.2]-octadiene-2,3-dicarboxylic acid, and the monomethyl ester of maleic acid. The monomethyl ester of 3-vinyl-4-cyclohexene-1,2-dicarboxylic acid and 4-vinylphthalic acid were also attempted. A series of precursors leading to the above mentioned compounds were also synthesized and characterized.

Task II - Curing Studies

The reaction conditions to achieve curing of each PMR polyimide neat resin system in the temperature range from 93°C to 316°C were determined. Three crosslinking monomers were selected for polymerization studies. These were the monomethyl ester of itaconic acid (ITE), monomethyl ester of 2,5-bicylo[2.2.1]heptadiene-1,2-dicarboxylic acid (NDE) and the monomethyl ester of maleic acid (MAE).

Task III - Composite Studies

Two monomers, the monomethyl ester of 2,5-bicyclo[2.2.1]heptadiene-1,2-dicarboxylic acid (NDE), and the monomethyl ester of maleic acid (MAE) were used as crosslinking in PMR resins for evaluation in composites. The PMR systems, NDE/BTDE/MDA and MAE/BTDE/MDA were evaluated in composites reinforced with Celion 6000 graphite fiber. The shear and flexural properties of these composite systems at room temperature and 316°C in the as-fabricated condition and after isothermal aging at 316°C in flowing air (100 cc/min) for time periods up to 2000 hours were determined.

Task IV - Reporting Requirements

Monthly technical and financial reports and a final technical report were submitted to NASA to fulfill the requirements of this task of the program.

This document is divided into a Results and Discussion section and an Experimental section, each covering the key activity areas:

1. Monomer Synthesis
2. Curing Studies
3. Processing Studies
4. Characterization Studies

The significant conclusions reached and a summary of the results are given followed by recommendations for activities that warrant further investigation.

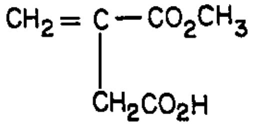
2.0 RESULTS AND DISCUSSION

2.1 Task I - Monomer Synthesis

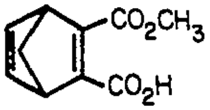
The objective of Task I was to select, synthesize and characterize monomers for evaluation as crosslinkers in PMR polyimide resin systems.

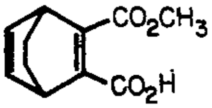
2.2 Monomer Selection

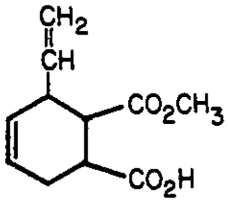
The monomers selected for synthesis in this program are listed as follows:

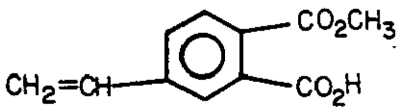


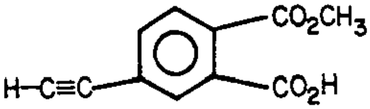
$CH_2{=}C(CH_2CO_2H){-}CO_2CH_3$







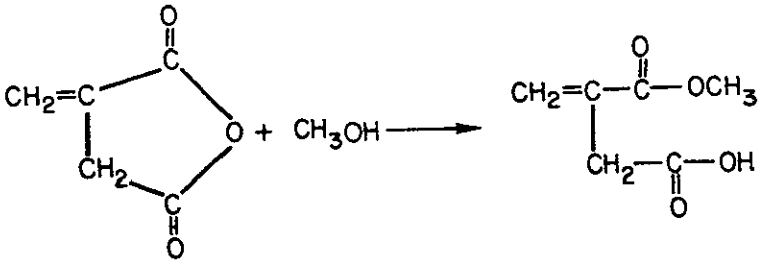




The synthesis of these monomers is discussed below.

2.2.1 Monomethyl Ester of Itaconic Acid

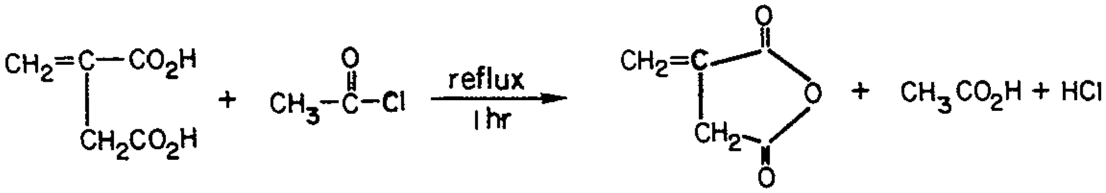
The monomethyl ester of itaconic acid was prepared from itaconic anhydride by reaction with a slight molar excess of anhydrous methanol at reflux temperature for one-half hour following the procedure of Baker, et al (Ref. 1).



Refluxing (4 hrs) equal molar ratios of the diacid and methanol in toluene, using p-toluene sulfonic acid as a catalyst gave only trace quantities of monoester and diester mixed in with unreacted diacid. Excess methanol (mole ratio methanol to acid, 5/1) with no catalyst under reflux conditions (4 hrs) was also unsuccessful. Refluxing a twenty-fold molar excess of methanol with the diacid using p-toluene sulfonic acid as a catalyst yielded mostly diester and anhydride by distillation at 90°C/25 mm Hg. Attempts to prepare this compound by hydrolysis of the dimethyl ester with calcium hydroxide were also unsuccessful. A sealed tube reaction at a mole ratio of methanol to anhydride 1.2/1.0 at 100°C for 3 hrs gave the monomethyl ester in a yield of 12%.

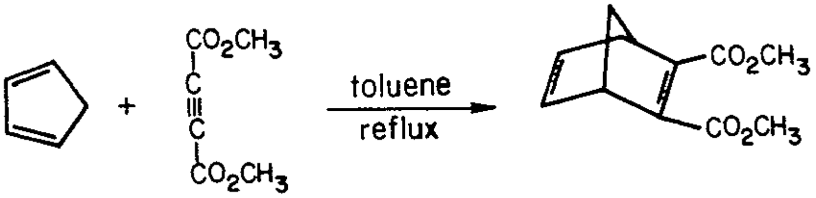
The best procedure was the method described above by heating the anhydride with a slight molar excess of methanol for 30 min under reflux conditions. The infrared (Fig. 1) and proton nuclear magnetic resonance (NMR) spectra (Fig. 2) are consistent for the monomethyl ester of itaconic acid.

2.2.2 Itaconic Anhydride



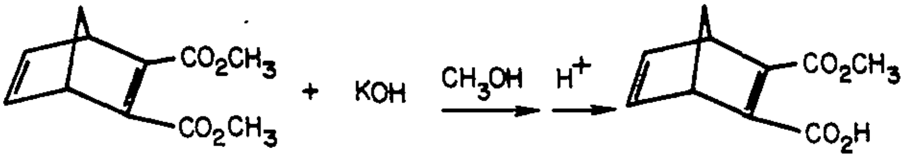
Commercial itaconic anhydride contained significant quantities of itaconic acid impurities which contaminated the monomethyl ester. Therefore, the anhydride was prepared in this program. Attempts to dehydrate itaconic acid in excess acetic anhydride under refluxing conditions (105-110°C) yielded only traces of anhydride. Treatment of itaconic acid with excess acetyl chloride (Ref. 2) at reflux temperature until the acid dissolved followed by removal of excess acid chloride and acetic acid by distillation, followed by purification of the syrupy residue by trituration in cold ether provided a white crystalline product in an 80% yield. The infrared spectrum (Fig. 3) is consistent for the anhydride and contains no impurities of itaconic acid. The NRM spectrum (Fig. 4) is further proof of identification.

2.2.3 Dimethyl Ester of 2,5-bicyclo[2.2.1]heptadiene-2,3-dicarboxylic Acid



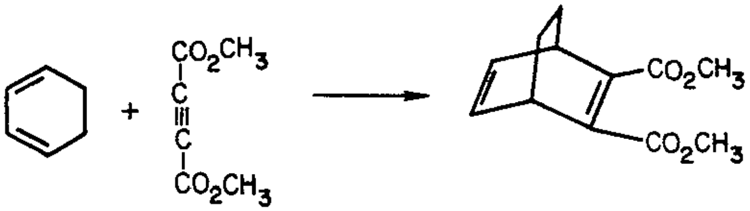
This novel compound was prepared by refluxing a solution of freshly distilled cyclopentadiene and dimethyl acetylenedicarboxylate in toluene for 2 hrs. Diels and Alder (Ref. 3) report the synthesis of this compound by adding a molar quantity of diester to freshly distilled cyclopentadiene, while cooling. The authors report a boiling point, but do not identify the ester by any other method. It was transformed to the dimethyl ester of 2-bicyclo[2.2.1]-heptene-2,3-dicarboxylic acid by reduction of the diene to the monoalkene, and to the dicarboxylic acid by hydrolysis of the diester monoalkene. In our synthesis, the diester was added dropwise to a solution of cyclopentadiene in toluene. An exotherm was not observed, therefore, the reaction mixture was heated to reflux. It was isolated by vacuum distillation (bp 121-128°C/1 mm Hg) in 89% yield. The infrared spectrum (Fig. 5), NMR spectrum (Fig. 6) and elemental analysis confirmed the structure. The reported (Ref. 3) boiling range was 134-135°C/10-11 mm Hg.

2.2.4 Monomethyl Ester of 2,5-bicyclo[2.2.1]heptadiene-2,3-dicarboxylic Acid

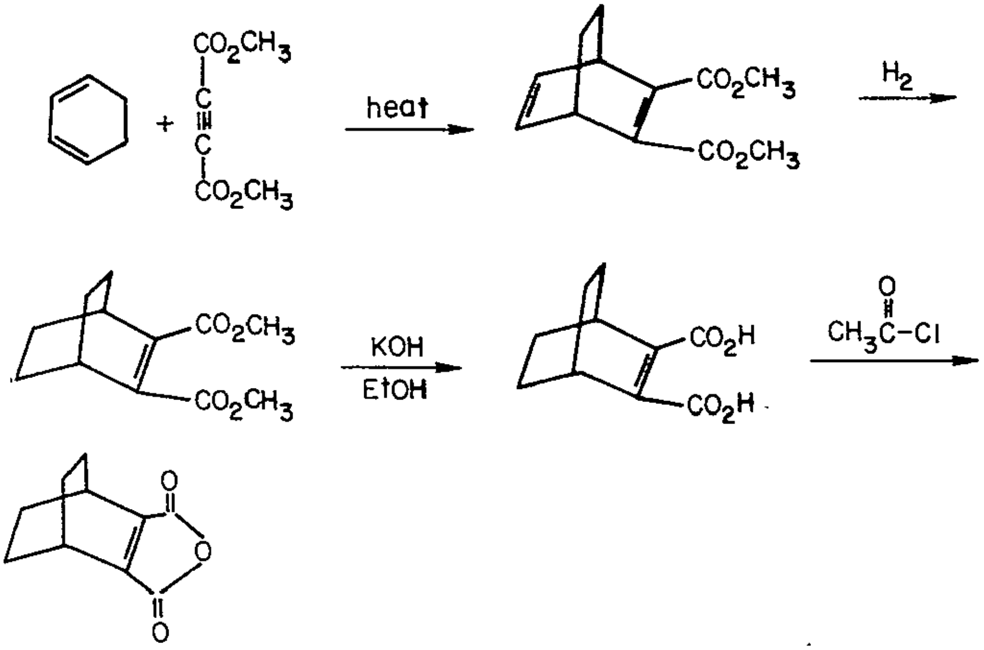


The monomethyl ester of 2,5-bicyclo[2.2.1]heptadiene-2,3-dicarboxylic acid (2,5-norbornadiene-2,3-dicarboxylic), NDE, was prepared by modifying a procedure of Zahorsky and Musso (Ref. 4) for the synthesis of the diethyl ester of 1,1, 2,2 -ethane tetracarboxylic acid. The produce was isolated by removal of the solvent, followed by extraction of the residue with ether to remove unreacted diester. The potassium salt of the monoester was liberated by acidification with 1N HCl. In some cases, the acid separated as an oil, in other cases it separated as a crystalline solid. When a solid was recovered, it was washed in cold water, air dried to yield white product, mp 103.5-105.5°C (64% yield). When the product separated as an oil, it was extracted with ether and the ether solution was dried and concentrated to yield an off-white solid. This was purified by washing in cold ether, yielding product mp 104-107.5°C. The infrared spectrum (Fig. 7) and NMR spectrum (Fig. 8) as well as elemental analysis confirmed the structure of this compound.

2.2.5 Dimethyl Ester of 2,5-bicyclo[2.2.2]octadiene-2,3-dicarboxylic Acid



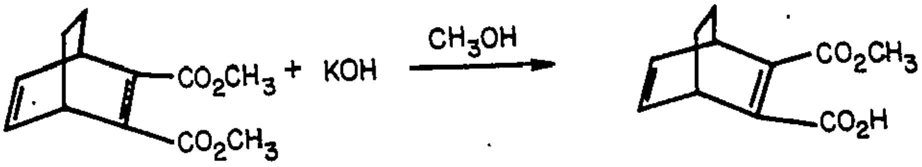
This was prepared by the method of Diels and Alder (Ref. 3) except that the reaction was carried out in toluene at reflux temperature. Diels and Alder refluxed the reactants in the absence of solvent for 1 hr, and make no attempt to isolate the addition product. Instead it was identified by reduction of the diene to the bicyclomonoalkene, followed by hydrolysis to the acid and then dehydration to 2-bicyclo[2.2.2]octene-2,3-dicarboxylic acid anhydride.



In the present work, refluxing in toluene appeared to yield product, but vacuum distillation caused decomposition to dimethyl phthalate as follows:

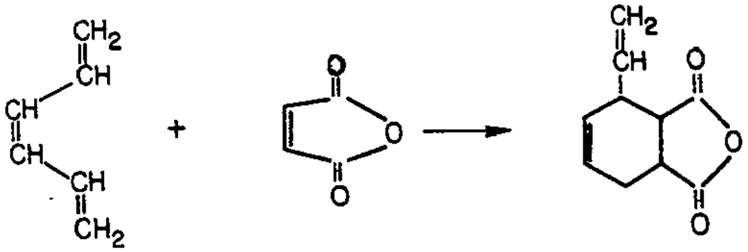
This was established by infrared studies, mass spectroscopy and elemental analysis. Refluxing the reactants at a lower temperature, in tetrahydrofuran, yielded an oil which by infrared spectroscopy appeared to contain to octadiene diester. However, elemental analysis indicated that this also contained impurity components. It was purified by extraction of the basic solution (from the KOH/CH_3OH hydrolysis reaction to obtain monoester) with ether and concentration of this extract to an oil. The infrared (Fig. 9), NMR (Fig. 10) and elemental analysis were all consistent for the dimethyl ester of 2,5-bicyclo[2.2.2]octadiene-2,3-dicarboxylic acid.

2.2.6 Monomethyl Ester of 2,5-Bicyclo[2.2.2]Octadiene-2,3-Dicarboxylic Acid



The monomethyl ester of 2,5-bicyclo[2.2.2]octadiene-2,3-dicarboxylic acid was prepared by modifying a procedure of Zahorsky and Musso (Ref. 4) for the synthesis of the diethyl ester of 1,1,2,2 -ethane tetracarboxylic acid. Unreacted diester was removed by extraction with ether. This afforded a way of purification of the diester, leading to its identification and characterization, as described above. The monoester was liberated from the potassium salt by acidification with 1N HCl, followed by extraction of the aqueous solution with ether. The monoester was isolated from the dried ether extracts by concentration to a solid. The elemental analysis was not consistent for this compound, but infrared (Fig. 11) and NMR spectroscopy (Fig. 12) studies suggested that the compound was mostly the desired monoester.

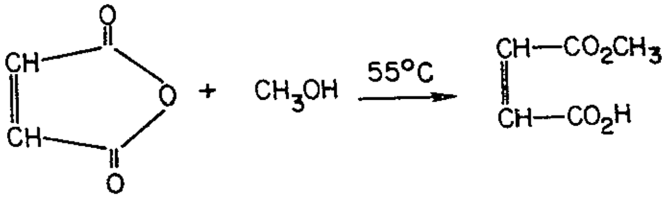
2.2.7 3-Vinyl-4-cyclohexene-1,2-dicarboxylic Acid Anhydride



This compound was prepared in only very small quantities (2.5g), by reaction of 1,3,5-hexatriene with maleic anhydride in tetrahydrofuran at reflux temperature. The oily residue which remained after concentration of the THF solution was vacuum distilled, yielding two fractions. The first fraction was identified as unreacted maleic anhydride, bp ∿ 140°C/1 mm Hg, mp 51-53.5°C. The second fraction, a yellow oil, bp 153-160°C/1 mm Hg, was identified as the correct product by elemental analysis, infrared spectroscopy (Fig. 13) and proton nuclear magnetic resonance (Fig. 14). Farmer and Warren (Ref. 5) report a boiling point of 148°C/6 mm Hg, a melting point of 51.5°C, and a water hydrolyzed product melting at 164-166°C. The melting point and boiling point were consistent for unreacted maleic anhydride, but the hydrolyzed product melting point was not. Kharasch and Sternfeld (Ref. 6) report a mp 45°C for the 3-vinylcyclohexene-1,2-dicarboxylic acid anhydride, and further attempted to prove the structure by reduction of the diacid (mp 160°C) to vinyltetrahydrophthalic acid (H_2 absorbed, 45.64 cc, calc 47.93 cc), mp 117°C. However, the melting point of succinic acid is 188°C, and its anhydride melts at 119°C. It is questionable whether both workers succeeded in isolating the desired compound. The elemental analysis and IR and proton NMR spectra of the compound isolated in our work were consistent for 3-vinyl-4-cyclohexene-1,2-dicarboxylic acid anhydride.

Attempts to prepare the monomethyl ester of 3-vinyl-4-cyclohexene-1,2-dicarboxylic acid by reaction of the triene with monomethyl ester of maleic acid in THF at reflux yielded only trace quantities of product, and mostly unreacted starting materials. Additional attempts to prepare this compound were curtailed due to the cost of the starting triene and time constraints.

2.2.8 Monomethyl Ester of Maleic Acid



The monomethyl ester was prepared using the procedure of Spatz and Stone (Ref. 7), with the exception that the reaction product was treated in vacuum at room temperature to remove excess methanol until a constant value for the refractive index was obtained. The product is obtained in quantitative yield as a colorless liquid, n_D^{20} 1.4580, Spatz & Stone (Ref. 7) report n_D^{20} 1.4634, Ushakov, et al (Ref. 8) report n_D^{20} 1.4640. The infrared spectrum (Fig. 15), proton NMR (Fig. 16) and elemental analysis were all consistent for the monomethyl ester of maleic acid.

2.2.9 Monomethyl Ester of 4-Vinylphthalic Acid

This is a multi-step synthesis which was initiated in this program but which was terminated due to time constraints. The approach was to start with relatively inexpensive trimellitic acid anhydride, convert this to 4-chloroformylphthalic acid anhydride, followed by Rosenmund reduction of the acid chloride to 4-formylphthalic acid anhydride. This latter compound was prepared in 32% yield using the procedure of Winslow and Laferriere (Ref. 9) without isolation of the acid chloride. One attempt to convert the aldehyde to a 4-vinylphthalic acid anhydride by reaction with triphenylmethylphosphonium bromide was unsuccessful.

Triphenylphosphonium bromide used in the above synthesis was prepared in a stoppered bottle at 0°C by reaction of 1.05 mole of methylbromide with 0.62 mole of triphenylphosphine in dry toluene. This yielded a white crystalline product, mp 229-231°C, in 69% yield. Some product was lost due to excessive pressure buildup, which caused the rubber stopper seal to break and release product.

2.2.10 PMR-Polyimide Monomers

The dimethylester of benzophenone-3,3',4,4'-tetracarboxylic acid (BTDE) used in preparing the PMR-15 polyimides was prepared by a method reported previously (Ref. 10). The 4,4'-methylenedianiline (MDA) used in preparing the PMR-15 polyimides was purchased from commercial sources in its highest purity available.

2.3 Cure Studies of PMR Polyimide Compositions

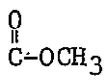
Because the objective of this program was to develop a low temperature curing PMR addition-type polyimide, a detailed study of the changes in the infrared spectrum of the PMR systems was investigated over the temperature range of 93 to 316°C with and without catalyst systems, to determine if cure takes place at a lower temperature than the 316°C cure temperature of PMR-15.

The curing studies of PMR-15 containing the monomers NE/MDA/BTDE were also included in this study for comparison with the novel systems investigated in this program. Amine catalysts were investigated in the temperature range 93 to 316°C to determine their effectiveness in lowering the imidization temperature. Studies by Kreuz, et al (Ref. 11) indicate that tertiary amines increase the rate of imidization by a factor of 10 over the free acid. Peroxide initiators were investigated in the temperature region 135 to 200°C to determine their effectiveness in initiating a crosslinking reaction. The amines studied in this program were triethyl amine, tri-n-butylamine and trimethyldodecylamine. The peroxide catalysts studied were t-butylhydroperoxide (t½, 1 hr, 200°C), cumenehydroperoxide (t½, 1 hr, 190°C), and dicumylperoxide (t½, 1 hr, 135°C). These were selected based on the temperature at which free radicals are generated.

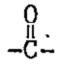
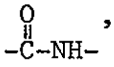
Three monomers were selected for polymerization studies. These were the monomethyl ester of itaconic acid (ITE), monomethyl ester of 2,5-bicyclo[2.2.1] heptadiene-1,2-dicarboxylic acid (NDE) and the monomethyl ester of maleic acid (MAE). The monomethyl ester of 2,5-bicyclo[2.2.2]octadiene-1,2-dicarboxylic was prepared, but because of the instability of this bicyclo-ring system, it was not selected for further investigation in a PMR polyimide resin system. The monomethyl ester of maleic acid was selected because in studies of the PMR-15 system containing what was supposed to be the monomethyl ester of 3-vinyl-4-cyclohexene-1,2-dicarboxylic acid, it was discovered that the monomer was really the monomethyl ester of maleic acid. However, infrared studies showed that the PMR system containing this monomer underwent a cure reaction similar to the NE/MDA/BTDE system. Therefore, this monomer was selected for further studies.

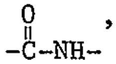
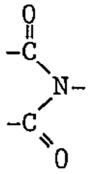
2.3.1 Infrared Studies of PMR-15 Cure Reactions

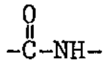
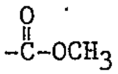
A study of the sequence of reactions involved in the processing of PMR-15 monomeric systems to a highly crosslinked polymeric material was made. This was accomplished by following the infrared changes as a function of temperature for a given time period for resin films deposited on sodium chloride salt discs. The infrared spectra for PMR-15 (Figs. 17-19) are shown for comparison with spectra of the novel PMR systems developed in this program. At room temperature, (Fig. 17a), there is absorption at 1720-1730 cm^{-1} due methyl ester carbonyl-



$\overset{\displaystyle O}{\overset{\|}{C}}\text{-}OCH_3$, a doublet at

3360 and 3420 cm^{-1} due to $-NH_2$ amine groups, and absorption at 1615 cm^{-1} probably due to carboxyl groups, $-CO_2H$, an abosrption at 1665 cm^{-1} most likely due to diarylketone  $\overset{O}{\overset{\|}{-C-}}$ and carboxyl groups, an absorption at 1580 and 1330 cm^{-1} assigned to the carboxyl ion $-CO_2-$, an absorption at 1435 cm^{-1} due to C-O stretch, and finally, an absorption at 2900 and 2950 cm^{-1} due to aliphatic C-H groups. The resin is mostly in the monomeric state at this stage. There is no evidence to suggest that a reaction to produce amide,  $\overset{O}{\overset{\|}{-C}}-NH-$, had occurred.

Treatment of the monomeric resin film at 93°C for 1 hr caused some changes in the PMR material, as shown in the spectrum (Fig. 17b). First of all, absorption due to NH_2 groups diminished considerably, with a simultaneous shift of the 1725-1730 cm^{-1} peak to 1730-1700 cm^{-1} (actually a doublet at 1705 and 1725 partly due to ester groups), a disappearance of the 1665 cm^{-1} peak originally assigned to carboxyl groups and diarylketone absorption, a disappearance of the peaks originally at 1615 and 1580 cm^{-1}, assigned to carboxyl groups, $-CO_2H$, appearance of absorptions due to amide  $\overset{O}{\overset{\|}{-C}}-NH-$, at 1600 cm^{-1} and 1565 cm^{-1}, the appearance of weak absorption due to imide functionality  appears as a shoulder at 1770 cm^{-1} and as a small peak at 720 cm^{-1}.

The specimens were heated at 121°C for an additional hour. This caused the appearance of a peak at 1850 cm^{-1} due to formation of anhydride and a shift of the 3360 peak to 3320 cm^{-1}, due to amide functionality  $\overset{O}{\overset{\|}{-C}}-NH-$ (Fig. 17c). Absorption bands at 1410 and 1185 cm^{-1} also appeared. Absorption due to imide groups at 1770 and 720 cm^{-1} became a little stronger. The sample was again heated consecutively for 1 hr at 149, 163, 177, and 204°C, with spectra taken after each treatment. During this treatment, shown by Figs. 17d and 18a, b, c, absorption due to imide functionality continually increased to yield strong peaks at 1775 cm^{-1} and 720 cm^{-1} and at 1730-1705 doublet; absorption due to carboxyl groups $-CO_2H$ persisted through very weak (1335 cm^{-1}); absorption due to amine disappeared (3360 cm^{-1} and 3420 cm^{-1}) and a broad band near 3470 cm^{-1} due to amide -N-H appeared. Absorption in the doublet region 1730-1705, after the 204°C treatment (Fig. 18c) was most likely partly due to traces of ester groups,  $\overset{O}{\overset{\|}{-C}}-OCH_3$. The peak (Fig. 18c) at 1850 cm^{-1} due to anhydride groups remains strong while that at 1600 broadens and shifts to 1615 cm^{-1}, indicating the weakening of abosrption due to amide groups. It is clear at this stage of the cure process that a considerable fraction of the amide and imide forming reactions are complete. It is also clear, however, that the imidization process is incomplete, since absorptions due to amide at 3470 cm^{-1} and 3320 cm^{-1} and anhydride bands at 1850 cm^{-1} still persist.

The spectrum for continued heating at 232°C for 1 hr is shown in Fig. 18a. There is a slight increase in the imide peak at 720 cm^{-1} due to the 232°C heat treatment, relative to the 204°C treatment, as can be seen by comparing Fig. 18c with Fig. 19a. The 232°C treatment removed the last traces of acide, since absorption due to carboxyl ion $-CO_2H-$ at 1330 cm^{-1} was absent, while the absorption due to anhydride group at 1850 cm^{-1} still persisted. The peak at 1705 to 1730 cm^{-1} is still broad indicating that ester may still be present. This is further evidence that although most of the imidization occurs in the temperature range 149 to 204°C, unreacted, anhydride, amide and ester are present at 232°C. The last traces of these are removed by treatment at 316°C for 1 hr shown by Fig. 19b. This causes a broadening of most peaks present after the 204°C and 232°C heat treatments, and an emergence of a peak at 1665 cm^{-1} which may be due to diarylketone groups. There is no evidence for absorption due to amide, ester or carboxyl groups. The heat treatment at 316°C for 1 hr completes the imidization reaction, removes anhydride and causes the crosslinking reaction to occur, and increases the molecular weight of the polyimide. This also causes a decrease in absorption due to imide functionality at 1775 and 1720 cm^{-1}. Postcure of the sample at 316°C for 16 hrs also shows this decrease and a strengthening of the 1660 cm^{-1} peak which emerged after the 1 hr treatment at 316°C.

From this infrared study one can conclude that in the temperature range from 149 to 204°C, imidization is essentially complete. However, there is still a small concentration of unreacted amide and ester present at this stage of the reaction. Apparently, for 100% conversion to imide groups, temperatures above 232°C are required. This is also suggested from dielectrometric studies reported by Gluyas (Ref. 12).

The point of this discussion is to trace the events of this reaction in the temperature range from room temperature to 316°C and to show at which temperature range most of the nonreactive volatile materials are produced. This study showed that any crosslinking monomer, substituted for NE in PMR must have a reactivity temperature profile in the range 204 to 232°C. If a reaction occurs below this temperature, it will coincide with the amidization-imidization reactions which are the nonreactive gas producing steps. This would lead to a high concentration of voids, due to the lack of resin flow on the consolidation stages of composite fabrication.

Therefore, crosslinking monomers must have a reactivity lower than the amide acids or amide esters which yield imide functionality, but higher in reactivity than the norbornenyl groups, for decreasing the crosslinking temperature.

2.3.2 Curing Studies with ITE as the Crosslinker in the ITE-PMR-14 System

Polymerization studies using the monomethyl ester of itaconic acid (ITE) as an end-cap in the PMR-14 system were investigated at a mole ratio of ITE/MDA/BTDE of 1.00/1.54/1.04. This mole ratio of monomer reactants generated a PMR formula molecular weight of 1400. When using NE instead of ITE, this identical molar ratio generates a PMR formula molecular weight of 1500, hence the name PMR-15. The monomers were deposited on a sodium chloride disc from a methanol solution, and the monomer film was freed of solvent by evacuation.

The infrared spectra of the uncatalyzed partially cured ITE-PMR-14 to the 260°C cured ITE-PMR-14 are shown in Figs. 20 through 26. For comparison, the infrared spectra of PMR-15 films cured at 149 and 204°C are shown in Figs. 27 and 28. The dimethyldodecylamine partially cured ITE-PMR-14 to the 316°C cured ITE-PMR-14 and the cumene hydroperoxide cured ITE-PMR-14 to the 316°C cured ITE-PMR-14 are shown in Figs. 29-36 and 37-42, respectively. The t-butyl hydroperoxide cured ITE-PMR-14 film is shown in Fig. 43. Heating the films at 93°C for 1/2 hr initiates formation of the imide group, which on further heating at 149, 177 and 204°C for 1/2 hr each causes almost complete imidization. For the amine catalyzed reaction, the 204°C treatment causes elimination of the amine catalyst as indicated by the absence of strong aliphatic absorption in the regions between 2850 and 2920 cm^{-1}. Continued heating to 316°C does not appear to change the imide absorption. Comparison of the uncatalyzed cure at 204°C (Fig. 26) with the amine catalyzed imidization at 204°C (Fig. 33) and peroxide catalyzed reaction (Fig. 38) shows that all three contain imide absorption at 720 cm^{-1} of about equal intensity, and in addition all other peaks appear to be the same relative intensity. This suggests that there is no difference in the uncatalyzed, amine catalyzed and peroxide cured ITE-PMR-14 systems.

Comparison of the infrared spectra of PMR-15 cured at 149°C (Fig. 20) or 204°C (Fig. 21) and above with the spectra of ITE-PMR-14 uncatalyzed (Fig. 24), amine catalyzed (Fig. 31 or 33), or peroxide initiated cure (Fig. 38) suggests that the ITE end-capped PMR-14 system is not undergoing imidization at a lower temperature than PMR-15.

The infrared spectra of ITE-PMR-14 cured in the presence of either t-butylhydroperoxide or dicumylperoxide were identical to that spectra of the ITE system cured in the presence of cumene hydroperoxide. This is illustrated by t-butylhydroperoxide cured ITE-PMR-14 (Fig. 43). The infrared studies sugfest that the peroxide cured ITE-PMR-14 system imidizes over the same temperature range (93 to 204°C) as PMR-15, but give no evidence of a crosslinking reaction over the temperature range 204 to 316°C.

2.3.3 Cure Studies with NDE as the Crosslinker in the NDE-PMR-15 Polyimide System

The monomethyl ester of 2,5-bicyclo[2.2.1]heptadiene-2,3-dicarboxylic acid (NDE) was combined with MDA and BTDE in the mole ratio of 1.00/1.54/1.034 (NDE/MDA/BTDE) yielding a PMR formula molecular weight of 1500, hence NDE-PMR-15. The NDE-PMR-15 system was studied in the uncatalyzed state, and in the presence of dicumylperoxide, t-butylhydroperoxide dimethyldodecylamine and tri-n-butylamine as catalysts, over a temperature range 93 to 316°C.

Uncatalyzed partially cured NDE-PMR-15 to uncatalyzed NDE-PMR-15 cured to 260°C, and dimethyldodecylamine (DMDA) catalyzed partially cured NDE-PMR-15 to DMDA catalyzed NDE-PMR-15 cured to 304°C are shown in Figs. 44-50 and 51-59, respectively. Comparison of these spectra of the two NDE-PMR-15 films with the spectra of NE-PMR-15 (Figs. 17-19) shows that these systems cure similarly and that the amine catalyzed system does not appear to lower the imidization temperature relative to NE-PMR-15 or uncatalyzed NDE-PMR-15.

The infrared spectra of the dicumylperoxide catalyzed partially cured NDE-PMR-15 and the 316°C cured NDE-PMR-15 are shown in Figs. 60-67. These spectra are distinctly similar to the uncatalyzed and amine catalyzed NDE systems. The infrared spectra of these peroxide treated films do not reveal whether or not crosslinking is occurring and if so, whether it occurs at a lower temperature than thermal crosslinking of the NDE or NE-PMR-15 polyimide systems.

A significant difference in the infrared spectra of the uncatalyzed and catalyzed NDE-PMR-15 systems and the uncatalyzed NE-PMR-15 systems is the fact that the NDE systems do not show an anhydride band at 1850 cm^{-1} in the temperature range between 204 and 316°C, as does the NE-PMR-15 resin. The amine catalyzed NDE system shows strong absorptions at 3210, 3320 and 3420 cm^{-1} due to dimethyldodecylamine and at 2850 and 2915 cm^{-1} due to CH_3- and -CH_2- groups of the amine which finally disappear after the 316°C treatment.

A comparison of the spectra of the uncatalyzed, dimethyldodecylamine dicumylperoxide and t-butylhydroperoxide NDE-PMR-15 systems cured at 204°C (Figs. 68-71) with the spectrum of PMR-15 cured at 204°C (Fig. 28) reveals that the NDE systems and the NE system respond similarly to form imide band of about equal concentration. The triethylamine catalyzed NDE-PMR-15 cured at 93 and 149°C for 1/2 hr each (Fig. 72) is similar to uncatalyzed NDE-PMR-15 and NE-PMR-15 cured under the same conditions, providing additional evidence that the amine does not offer any advantage for a low temperature imidization.

2.3.4 Cure Studies with MAE as the Crosslinker in the MAE-PMR-14 Polyimide System

The monomethyl ester of maleic acid (MAE) was combined with MDA and BTDE at a mole ratio of MAE/MDA/BTDE (1.00/1.535/1.025) to form a PMR system having a formula molecular weight 1400, hence MAE-PMR-14. Infrared spectroscopic studies were carried out on films deposited on sodium chloride salt plates from a 45 wt% solution in anhydrous methanol. This system was only studied in the uncatalyzed state because of the negative results generated from the catalized ITE- and NDE-PMR systems. The infrared spectra of partially cured MAE-PMR-14 to 288°C cured MAE-PMR-14 are shown in Figs. 73-80. The imidization reaction commences at 93°C and become prominent at 149°C (Fig. 75). At this temperature, an anhydride band appears at 1850 cm^{-1} similar to the NE-PMR-15 system. The imide band appears to reach its maximum absorption at 204°C, as is illustrated by the imide peak at 720 cm^{-1}; continued thermal treatment to 288°C (Fig. 80) does not alter the absorption at 720 cm^{-1}. After the 288°C treatment, absorption at 1850 cm^{-1} due to anhydride is still present, as it is in the NE-PMR-15 system.

2.3.5 Conclusion of the Infrared Spectroscopic Studies

The infrared spectroscopic studies of the curing reactions of the three PMR systems reveal that imidization occurs in these systems similar to the NE-PMR-15 system. The infrared studies, however, do not indicate whether or not cross-linking of these novel end-capped polyimides occur. This was accomplished by fabrication of resin samples of each PMR system, and characterization of these materials.

2.4 Process Studies of the PMR Systems

Each PMR system was subjected to a series of process studies to produce solid resin discs of each material, and to establish conditions for use in fabrication of Celion 6000/PMR composites. The procedure used was to prepare a 45 wt% solution of the PMR resin monomers at a mole ratio of end cap/MDA/BTDE of 1/1.54/1.04 as described for the infrared spectroscopic studies. The solutions were divided into several parts for study, amine catalyst or peroxide was added to some of the portions. The solutions were concentrated to powders for study by thermal analysis and for conversion to solid resin discs (2.51 cm diameter x 0.835 cm thick), over a temperature range 93 to 316°C at low pressures, 0.34 to 1.38 MPa (50 to 200 psi).

2.4.1 Thermal Analysis of PMR Uncured Powders

PMR-15, ITE-PMR-14, NDE-PMR-15 and MAE-PMR-14 methanol solutions were concentrated to powders at room temperature. The powders were evacuated to remove traces of methanol and then subjected to differential thermal analysis. Powders were also "B" staged at temperatures as determined by DSC analysis of uncured powders. These "B" staged powders were also subjected to DSC to determine the temperature of which polymer discs could be fabricated. The results of thermal analyses are described below.

2.4.1.1 Differential Scanning Calorimetry (DCS) of PMR-15 Powder

The DSC Thermogram uncured PMR-15 powder (Fig. 81) on first observation may appear to be considerably different than the thermograms of the other PMR systems shown in Figs. 82-84. Essentially this thermogram shows only one endotherm peak at 140°C followed by a gradual rise after approximately 250°C. However, the DSC's of the ITE- NDE- and MAE-PMR powders show a series of endotherms in the temperature region near 140°C and then exothermic peaks at the higher temperatures. The multiple peaks at the lower temperature may be due to catalytic activity, and not necessarily be related to the behavior of the PMR monomers.

2.4.1.2 Differential Scanning Calorimetry (DSC) of ITE-PMR-14 Powder

DSC thermogram of uncatalyzed ITE-PMR-14 (Fig. 82) shows a series of endotherms starting initially at room temperature, and peaking at 100, 183 and 320°C. The peaks at 100 and 183°C may be due to the condensation reactions, while the peak at 320°C is most likely due to the crosslinking reaction. The DSC thermogram of ITE-PMR-14 containing t-butylhydroperoxide (Fig. 83) also shows a series of endotherms similar to the uncatalyzed system, but at different temperatures. The thermal behavior of the two powders suggests that imidization is occurring at 180°C, and crosslinking near 300°C.

2.4.1.3 Differential Scanning Calorimetry of the NDE-PMR-15 Powders

DCS's of NDE-PMR-15 catalyzed with dicumylperoxide and t-butylhydroperoxide were also run. For the two peroxides, no differences in thermal behavior were noted. The DSC of the dicumylperoxide catalyzed material (Fig. 84) showed sharp endotherms at 143°C and at 188°C, followed by exotherm above 260°C. Some softening or melting occurred at 45°C and 53°C. The DSC of the t-butylhydroperoxide catalyzed material (Fig. 85) gave endotherms at 45, 115, 125, 160, 165, 170 and 175°C, followed by an exotherm above 260°C. The endotherms at 125°C and 175°C are the significant ones, and suggested that processing of the powder to a solid should be carried out at 175°C. DSC thermogram of "B" staged (200°C NDE-PMR-15, Fig. 86) shows an endotherm near 75°C, followed by an exotherm initiating at 200°C and continuing to 400°C. The DSC thermogram of the 130°C "B" staged NDE-PMR-15 (Fig. 87) shows a broad endotherm in the region of 100°C, followed by an exotherm near 150°C. The thermal behavior of the 200°C "B" staged powder suggests that a reaction is occurring above 200°C, while the thermogram of the 130°C "B" staged material indicates that the reaction is occurring near 150°C. It is difficult to define processing conditions from the thermograms.

2.4.1.4 Differential Scanning Calorimetry (DSC) of the MAE-PMR-14 Powder

DSC studies of the t-butylperoxide, dicumylperoxide, dimethyldecylamine catalyzed resin powders prepared by evaporation of the solvent from the MAE-PMR-14 solutions were done. The DSC (Fig. 88) of the t-butylhydroperoxide catalyzed powders showed an endotherm at 60°C, and a series of sharp endotherms between 125 and 180°C. The DSC of dimethyldodecyamine catalyzed powder (Fig. 89) gave sharp endotherms at 140 and 150°C. At 230°C, both materials developed endotherm peaks followed by exotherms above 250°C, at which point the DSC's were discontinued. The thermograms suggest that imidization occurs at 180°C for the peroxide catalyzed material, and 150°C for the amine catalyzed material. Above 250°C, a reaction occurs which may be attributed to crosslinking of the maleimide groups. The thermal behavior of this powder suggested that fabrication of resin specimens would require a temperature above 250°C.

2.4.2 Process Studies to Fabricate Solid Polymer Discs

2.4.2.1 ITE-PMR-14

The results of the process studies of the ITE-PMR-14 system are listed in Table I. It became obvious from the fabrication of the first two discs that a processing temperature of 300°C was required to produce strong, hard dense resin discs. This was true even in the presence of dicumylperoxide, which produces free radicals at 200°C. The peroxide radical sources were added to the resin system to lower the crosslinking temperature. However, the presence of free radicals did not appear to influence the processing conditions, as is indicated by identical 300°C conditions required to produce uncatalyzed, peroxide or amine containing PMR discs.

2.4.2.2 NDE-PMR-15

The conditions required to produce dense resin discs of this NDE-PMR-15 polyimide system are listed in Table II. The final process conditions required to produce strong, dense resin discs were 250°C/1 hr at 0.69 MPa. An intermediate temperature of 180°C or 200°C is required for imidization similar to NE-PMR-15. However, even though moderate conditions produced solid, dense discs, these discs required additional processing at 300°C for further crosslinking and thermal stabilization to occur.

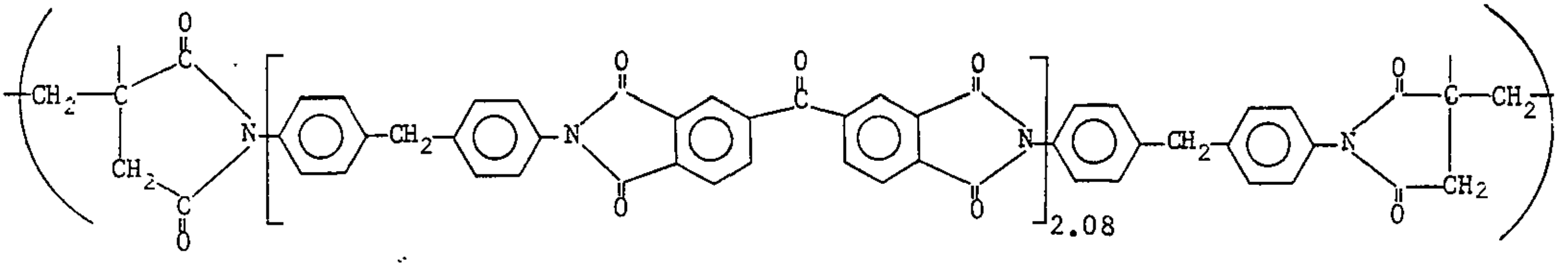
2.4.2.3 MAE-PMR-14

Process studies to produce meat polymer discs of MAE-PMR-14 polyimide are listed in Table III. As with the ITE- and NDE-PMR systems, final process conditions required to produce strong, dense discs are 300°C/1 hr at 0.69 MPa (100 psi).

2.5 Characterization of the Novel PMR Polyimide Resin Discs

2.5.1 Elemental Analysis - ITE-PMR-14

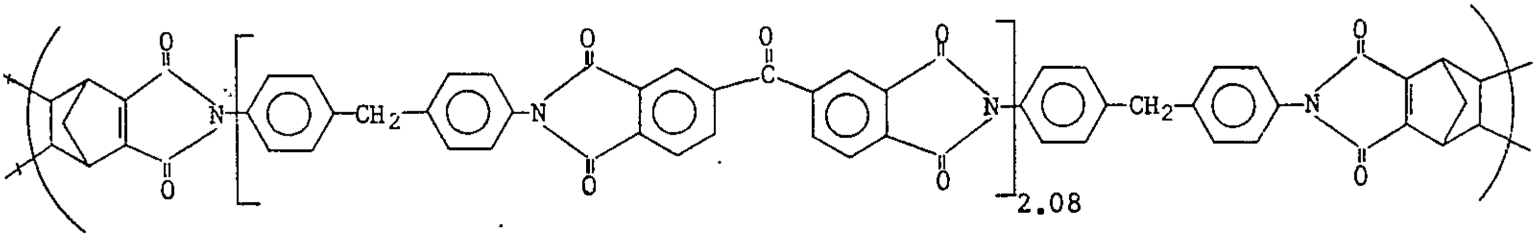
Results of elemental analysis of several discs are listed in Table IV. The calculated values for carbon, hydrogen and nitrogen are based on the theoretical molecular structure shown below.



The analysis for carbon, hydrogen and nitrogen for the three samples are in good agreement with the calculated values derived from the theoretical molecular strucure. This is evidence that the structure as drawn approximates closely the structure of the actual molecule.

2.5.1.1 NDE-PMR-15

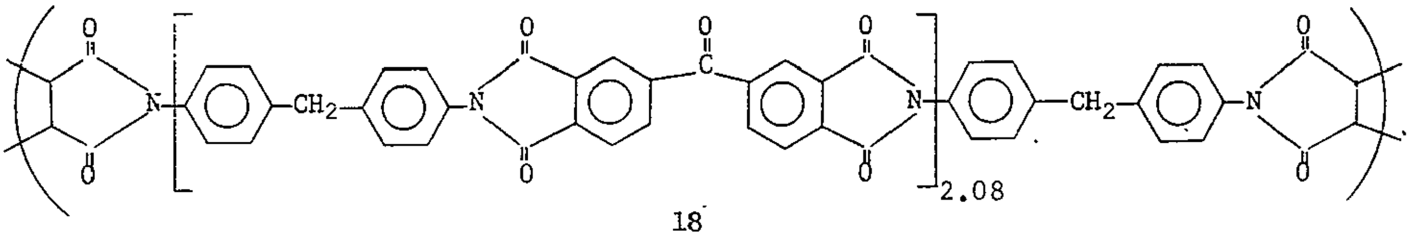
The results of the elemental analyses of several discs of this PMR system are listed in TableIV. The calculated values for carbon, hydrogen and nitrogen are based on the theoretical molecular structure shown below.



Here, as with the ITE-PMR system, the analyses for carbon, hydrogen, and nitrogen for the four samples discs are in good agreement with the calculated values derived from the theoretical molecular structure. This is evidence that the structure as drawn approximates closely the structure of the actual molecule.

2.5.1.2 MAE-PMR-14

Results of the elemental analyses of two MAE-PMR-14 discs are also listed in Table IV. The calculated carbon, hydrogen and nitrogen values are based on the theoretical molecular structure shown below.



Comparison of the calculated values for carbon, hydrogen and nitrogen with the found values, particularly disc MAE-PMR-14-II-5, shows good agreement in the carbon and nitrogen values, but only fair agreement in the hydrogen value. This is reasonable evidence that the structure as drawn approximates closely the structure of the actual molecule.

2.5.2 Thermomechanical Analysis

Samples of resin discs were subjected to thermomechanical analyses to determine the glass transition temperature (Tg) of each resin. The results of these tests are listed in Table V. The data show that the glass transition temperatures of these PMR systems are lower than the glass transition temperature of PMR-15, suggesting that the degree of crosslinking in these resin discs as cured, is lower than that of PMR-15. The Tg of PMR-15 is 315°C. NDE-PRM-III-2 and III-4 discs were reprocessed by heat treatment of the discs at 300°C/hr, 1.38 MPa. The treatment caused considerable improvement in the glass transition temperature of each disc (Table V). This is further evidence that the initial process conditions produced a polymer disc with a low degree of crosslinking. The additional cure raises the Tg to about 300°C.

2.5.3 Thermal Analysis of Cured PMR Resins

DSC thermograms of cured PMR resin systems are shown in Figs. 90-93. Except for ITE-PMR-14 the thermal behavior patterns are similar to PMR-15. The DSC thermogram of PMR-15 (Fig. 90) shows very little change over the temperature range 50 to 250°C. At 250°C the sample starts to exotherm and becomes more exothermic as it approaches 350°C. The DSC thermogram of NDE-PMR-15-III-4 (Fig. 91) and MAE-PMR-14-II-5 (Fig. 92) shows essentially the same behavior as PMR-15. However, the thermogram of MAE-PMR-14-II-5 reveals a slight endotherm at about 260°C, then the sample goes into exothermic behavior about 300°C. For the ITE-PMR-14-II resin system, the DSC thermogram (Fig. 93) shows a slight endotherm at 25 to 75°C, then a plateau region up to 200°C where essentially no change takes place, and finally a strong exothermic reaction starting at 225°C and continuing to 400°C.

2.6 Characterization of the Novel PMR Polyimides In Celion 6000/PMR Composites

As a result of the infrared and processing studies, two monomers, NDE and MAE were selected for further evaluation in composites.

Celion 6000/PMR composites, fabricated as described in Section 3.4, were subjected to isothermal aging studies in flowing air (100 cc/min) at 288°C and 316°C for time periods ranging from zero to 2000 hours.

2.6.1 Physical Properties

Some properties and composition of each composite are listed in table VI. It is clear from the data in Table VI that the fiber volume in most composites is low, and more important, that the void volume is high. The glass transition temperature (Tg) of the NDE composites falls in the region of about 320°C, while the Tg of the MAE composite is in the region of 270°C.

2.6.2 Mechanical Properties

The results of the shear and flexural properties at room temperature 288°C and 316°C are listed in Tables VII through XVI. Interlaminar shear strengths of NDE-PMR-15 composites are listed in Tables VII, VIII, and IX. The room temperature shear strength of NDE-PMR-15-3 composite is low initially (∿ 55.1 MPa) relative to what is expected for Celion 6000/PMR-15 (∿ 82.7 MPa). However, after 1020 hours aging at 288°C, the composite retains about 60 percent if its initial room temperature strength and about 70 percent of its initial 316°C strength.

The shear strengths of NDE-PMR-15-4 composite are poor after aging 192 hrs at 288°C, but are relatively good after aging 192 hrs at 316°C. This suggests that the resin system is becoming stabilized at the higher temperature. This stabilization may be caused by increased crosslinking of the resin system.

The shear properties of NDE-PMR-15-5 composites are considerably better than the 15-3 and 15-4 composites, and began to approach the values for a Celion 6000/PMR-15 (82.7 MPa, RT; 41.4 MPa, 316°C). Here again, the shear strength after isothermal aging at 316°C are much better than those after isothermal aging at 288°C. After 508 hours at 316°C, shear average strength values of 55.8, 38.6 and 31.7 MPa at room temperature, 288 and 316°C, respectively, are obtained. It is clear that the quality of the composite has considerable influence on the initial and isothermally aged composites, as can be seen from the difference in shear strength for the three composites containing the same resin. The flexural strengths and moduli of the three composites NDE-PMR-15-3, -4 and -5 are listed in Tables X, XI, and XII, respectively. NDE-PMR-15-5 exhibited the highest flexural strengths and moduli of the three composites. The flexural strengths after isothermal aging at 316°C for 192 hours at RT, 288°C and 316°C average 899 MPa, 524 MPa, and 346 MPa, while the moduli are 87.5 GPa, 55.8 GPa and 38.6 GPa. The modulus value at room temperature reflects the low fiber content of this composite, and also explains why the strengths are lower than expected.

The shear strengths of the Celion 6000/MAE-PMR-14 composite systems are listed in Tables XIII and XIV. For example composite Celion 6000/MAE-PMR-14-1 exhibited superior shear strength initially and after isothermal aging at 288°C and 316°C than the other Celion 6000/MAE-PMR-14 composite. Initial RT, 288 and 316°C shear strengths for postcured composites are 71.3, 42.2 and 40.7 MPa at 316°C respectively, and after isothermal aging at 288°C for 1028 hours these values fall to approximately average strengths of 38.6 MPa, 34.4 PMa and 24.1 MPa. After aging 808 hours at 316°C, this composite exhibited shear strengths of 62.6 at RT, 51.2 at 288°C and 49.3 MPa at 3.16°C, which, are at least equivalent or better than the postcured values. The improvement in strength on isothermal aging at 316°C indicates that additional thermal stabilization and crosslinking may be occurring.

The flexural properties of Celion 6000/MAE-PMR-14-5 and -7 composites are listed in Tables XV-XVI. Composite 14-5 exhibits superior properties to the other MAE composite. The flexural strength of 1135 MPa at RT for the postcured MAE-PMR-14-5 composite decreased to approximately 517 MPa after aging at 288°C for 192 hours. The initial modulus for this system was 91 GPa at room temperature, falling to 63 MPa after aging at 288°C for 192 hours. The low modulus value suggests a low fiber content, which is borne out by the data in Table VI. After isothermal aging at 316°C for 808 hours, the RT strength value was maintained, but the 288 and 316°C strength values showed considerable decline.

In general, the MAE composites exhibited superior shear strengths to the NDE composites. However, the flexural properties of the NDE composites are superior to the MAE composites. This suggests that the quality of the composites within each resin system vary widely and show considerable range in properties, as is demonstrated by the shear and flexural strength data for each composite containing the same resin system.

The results of the mechanical tests show clearly that the novel PMR resins require additional process studies to fabricate composites which approach the properties of the state-of-the-art Celion 6000/PMR-15 resin systems.

3.0 EXPERIMENTAL RESULTS

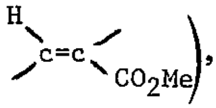
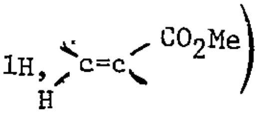
3.1 Monomer Synthesis

The synthesis or attempted synthesis of each monomer is described in this section.

3.1.1 Monomethyl Ester of Itaconic Acid

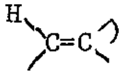
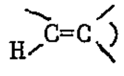
One hundred grams (0.89 mole) of itaconic anhydride was placed in a round bottom flask fitted with a reflux condenser. To this was added 28.5g (6.89 mole) of anhydrous methanol. The mixture was heated to reflux for 30 minutes, then allowed to cool to room temperatures. To this was added 30 ml of cold absolute ether, causing precipitation of a white solid. This was filtered, and air dried to yield 69.5g of crude off white solid, mp 61-67°C (54 percent yield). The infrared spectrum (Fig. 1) and proton NMR spectrum (Fig. 2) are consistent with the desired product. A recrystallized portion melted at 65-68.5°C.

NMR ($CDCl_3$): δ 3.37 (m, 2H, $-CH_2-$), 3.68 (m, 3H, $-OCH_3$),

5.83 (m, 1H ), 6.43 (m, 1H, ) 10.43 (s,1H, $-\overset{O}{\overset{\|}{C}}-OH$)

3.1.2 Itaconic Anhydride

Itaconic acid (500g, 3.84 mole) was placed in a 3-liter 3 neck round bottom flask equipped with a reflux condenser and thermometer. To this was added 1 liter (1105g, 10.4 mole) of acetyl chloride. The reaction mixture was refluxed until the acid dissolved (1.25 hrs). The reaction mixture was refluxed an additional 15 minutes. The reaction mixture was distilled under reduced pressure (∿ 17 mmHg) with a nitrogen ebulator, collecting material boiling between 39 to 50°C. When distillation slowed down, 600 ml of toluene was added, and distillation continued, collecting material boiling 28 to 52°C. Toluene (600 ml) was added a second time, and distillation resumed, collecting material boiling 32 to 50°C, until distillation stopped. Upon cooling, a crystalline material separated. This was broken-up, slurried in 200 ml of cold ether, then filtered to yield 465 g of crude product. The crude solid was slurried in 150 ml cold ether, filtered, and air dried to yield a white crystalline solid (378g) m.p. 67-69°C (88 percent yield). The infrared spectrum (Fig. 3) and proton NMR spectrum (Fig. 4) are consistent with the desired product.

NMR ($CDCl_3$): δ 3.63 (m, 2H, $C-CH_2-\overset{O}{\overset{\|}{C}}$), 5.98 (t, 1H, ), 6.55(t, 1H, )

3.1.3 Cyclopentadiene from Pyrolysis of Dicyclopentadiene

A 3 neck flask was equipped with a thermometer, distillation column and an addition funnel containing 300 ml of dicyclopentadiene. An oil bath was placed under the flask and heated to a temperature of 250°C, while slowly adding the dicyclopentadiene. An internal flask temperature of 200°C, causes cracking of this dicyclopentadiene to cyclopentadiene. The cracking was continued, collecting vapors boiling at 43°C, until 200 ml of cyclopentadiene was collected.

3.1.4 Dimethyl Ester of 2,5-Bicyclo[2.2.1]heptadiene-1,2-dicarboxylic Acid

To a 3 neck flask equipped with stirrer, reflux condenser, thermometer and addition funnel was added 60 g (0.42 mole) of dimethylacetylene dicarboxylic acid in 50 ml of toluene. To this was added 28.8g (0.445 mole) of freshly prepared cyclopentadiene in 10 ml of toluene, over a period of 15 minutes while stirring. After the addition, the solution was refluxed for 2 hours. The toluene was distilled under reduced pressure (water aspirator). The residue was vacuum distilled, collecting 77.9g (88 percent yield) of product at bp 121-129°C/1 mmHg, reported b.p. 134-135/10-11 (Ref. 3). The infrared spectrum (Fig. 5) and proton NMR spectrum (Fig. 6) are consistent for the desired product. Mass spectroscopic analysis of this liquid gave a parent peak at m/e = 208, consistent with a molecular weight of 208 for this compound.

Elemental Analysis:
Calc for $C_{11}H_{12}O_4$: C, 63.5; H, 5.76

found: C, 63.6; H, 5.85

NMR ($CDCl_3$): δ 2.23 (s, 2H, CH_2), 3.81 (s, 3H, OCH_3),
3.96 (s, 2H, Bridgehead H), 6.96 (s, 2H, $\mathrm{{}^{H}\!\!>C=C<{}^{H}}$)

3.1.5 Monomethyl Ester of 2,5-Bicyclo[2.2.1]heptadiene-2,3-dicarboxylic Acid

This compound was prepared by a modification of the procedure of Zahorsky and Musso (Ref. 4) for the synthesis of the diethylester of 1,1,2,2-ethanetetracarboxylic acid.

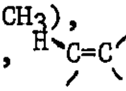
To a 3-neck 500 ml round bottom flask equipped with a stirrer, reflux condenser, addition funnel and nitrogen inlet was added 39g (0.187 mole) of dimethylester of bicyclo (2.2.1) heptadiene 1,2-dicarboxyclic acid in 50 ml of anhydrous methanol. To this was added over an 8 hour period, 12.35g (0.187 mole) of potassium hydroxide in 200 ml of methanol at room temperature. The reaction mixture was concentrated to an amber oil containing some solid. This mixture was dissolved in 100 ml of water, and extracted with ether (4x30 ml). The combined ether extracts were washed with 2x25 ml of distilled water. The ether extract was dried over anhydrous sodium sulfate, decanted and then concentrated to an oil (18.0g). The water solution containing the potassium salt of the acid, was acidified with 1N HCI to a pH $\approx$ 2.0, causing a precipitate to form. This solid was filtered, carefully washed with cold water and air dried, to yield 23.5g of white product, mp 103.5-105.5°C. The oil recovered from the ether extract was found to be unreacted diester. After correction for recovered starting material was made, the product yield quantitative. The yield with no correction for recovered diester was 64 percent.

The infrared spectrum (Fig. 7) and proton NMR spectrum (Fig. 8) of the compound are consistent for the monomethylester of the dicarboxylic acid.

Elemental Analysis:

Cal. for $C_{10}H_{10}O_4$: C, 62.30; H, 5.15

Found: C, 62.17; H, 5.16

NMR ($CDCl_3$): δ 2.22 (s, 2H, Bridge H), 3.95 (s, 3H, $O-CH_3$), 4.22 (m, 2H, Bridgehead H), 6.90 (s, 2H, 
$\text{H}\diagdown C{=}C\diagup\text{H}$), 12.57 (bs, 1H, CO_2H).

3.1.6 Dimethyl Ester of 2,5-Bicyclo[2.2.2]octadiene-2,3-dicarboxylic Acid

This compound was prepared by the method of Diels and Alder (Ref. 3) except that the reaction was done in toluene at reflux temperature. To a 250 ml 3-neck round bottom flask equipped with stirrer, reflux condenser, addition funnel and thermometer was added a solution of 30g (0.211 mole) of dimethylacetylene dicarboxylate in 50 ml of tetrahydrofuran. While cooling to 5°C, a solution of 17.0g (0.213 mole) of 1,3-cyclohexadiene in 10 ml of tetrahydrofuran was added over a 15 minute period. No exotherm was observed. The solution was heated to reflux for 2 hours, cooled to room temperature and concentrated to an oil using the rotary evaporator. Then it was treated at 40°C in vacuum for 4 hours. Solid impurities were removed by dissolving the oil in ether, filtering and then concentrating to an oil. The oil was again treated at room temperature in vacuum for 6 hours. The infrared spectrum of this oil was consistent for the dimethylester of 2,5-biyclo (2.2.2) octadiene 1,2-dicarboxylic acid, showing strong ester absorption at 1720 cm^{-1}, strong absorption at 1640 cm^{-1} due to alkene, and strong absorption at 1430 cm^{-1} due to CH_2 and CH_3 groups. There was no evidence for aromatic absorption at 770 cm^{-1}, expected for dimethylphthalate. The NMR spectrum (Fig. 10) also supported the structure of the desired product.

Elemental Analysis of this oil was performed

Calc for $C_{12}H_{14}O_4$: C, 64.8; H, 6.3

Found: C, 60.1; H, 5.79

Calc for dimethyphthalate: C, 61.8; H, 5.15

NMR ($CDCl_3$): δ 1.42 (s, 4H, CH_2-CH_2), 3.75 (s, 6H, CO_2CH_3), 4.00 (bs, 2H, CH-CH), 6.37 (t, 2H, CH=CH).

The elemental analysis is not consistent for the structure of the desired compound and in fact is closer for dimethylphthalate. However, the mass spectrogram showed a peak at m/e = 222, consistent for the molecular weight of a compound with the desired structure. This indicates that impurities are present in the product.

The compound was also prepared on a 0.105 mole scale as described above but with two exceptions: (1) it was refluxed in toluene for 2 hours and (2) isolation involved vacuum distillation to yield a colorless viscous liquid, bp 138-141°/ 5mm Hg (74.2g, 79.5 percent yield). The infrared spectrum of this compound gave a broad absorption, due to the ester group (1730 cm^{-1}) and absorptions at 1595, 1575 and 1490 cm^{-1}, characteristic of an aromatic compound while mass spectroscopic analysis gave m/e peaks at 194 corresponding to dimethylphthalate and 28.5 corresponding to ethylene, but no parent peak at 222 corresponding to the bicyclic dimethyl ester. Elemental analysis of product prepared in the manner gave the following results.

Elemental Analysis:
Calc for $C_{12}H_{14}O_4$: C, 64.8; H, 6.3
Found: C, 60.1; H, 4.75

Calc for dimethylphthalate: C, 61.8; H, 5.15

The elemental analysis suggests that the compound isolated from the distillation is dimethylphthalate. Therefore, it is apparent that either the reflux condition in toluene or distillation causes decomposition of the bicyclooctadiene derivative to dimethylphthalate. This observation led to preparation of the compound in tetahydrofuran, as described above, with no attempt to purify it by distillation. As shown above this leads to an impure product. A sample of the pure product was isolated as described below for the synthesis of the monomethylester of 2,5-bicyclo [2.2.2] octadiene-2,3-dicarboxylic acid.

3.1.7 Monomethyl Ester of 2,5-Bicyclo[2.2.2]octadiene-2,3-dicarboxylic Acid

This compound was prepared by a modification of the method of Zahorsky and Musco (Ref. 4) for the synthesis of the diethylester of 1,1,2,2-ethanetetracarboxylic acid. To a 3-neck 250 ml round bottom flask equipped with stirrer, reflux condenser, addition funnel and nitrogen inlet was added 14.0g (0.063 mole) of the impure diethylester of 2,5-bicyclo [2.2.2] octadiene-2,3-dicarboxylic acid and 50 ml of absolute methanol. To this was added in an atmosphere of nitrogen over an eight hour period at room temperature a solution of 4.56g (0.069 mole) of potassium hydroxide in 25 ml of anhydrous methanol. The reaction mixture was concentrated to an amber oil to remove methanol. This amber oil was dissolved in 25 ml of water and then extracted with five 25 ml portions of ether. The ether extracts were combined, washed with water, and then dried over anhydrous magnesium sulfate. The dried ether extract was concentrated to an amber oil. This oil was analyzed for carbon and hydrogen.

Elemental Analysis:

Cal for $C_{12}H_{14}O_4$: C, 64.8; H, 6.35

Found: C, 65.0; H, 6.38

The elemental analysis and infrared spectrum (Fig. 9) and proton NMR spectrum (Fig. 10) are strong evidence for this compound, the dimethylester of 2,5-bicyclo [2.2.2] octadiene-2,3-dicarboxylic acid.

NMR ($CDCl_3$): δ 1.35 (bs, 4H, bridge H), 3.70 (s, 6H, $-OCH_3$)

4.00 (m, 2H, bridgehead H), 6.37 (m, 2H, $^{H}_{H}{>}C{=}C{<}$),

The water solution from the above extraction was acidified with 1N HCI. The oily material isolated was extracted with ether (5x25ml). The combined ether extracts were dried over anhydrous magnesium sulfate, then concentrated to a oily material which crystallized to 7.1g of an oily tan solid (80.6 percent after corrections for unreacted diester is made). A capillary melting point could not be determined for this material. DSC showed a sharp endotherm at 50°C, and two endotherms at 180 and 225°C. The endotherm at 50°C is most likely the melting point of the monomethyl ester. The endotherms at 180 and 225°C could be associated with decomposition of the bicyclo ester to phthalate ester. The infrared spectrum (Fig. 11) and proton NMR spectrum (Fig. 12) of this material are reasonable for acid ester. Elemental analysis gave the following results:

Calc for $C_{11}H_{12}O_4$: C, 63.5; H, 5.75

Found: C, 61.4; H, 5.95

NMR ($CDCl_3$): δ 1.43 (s, 4H, bridge H), 3.57 (s, 3H, $-OCH_3$), 4.30 (m, 2H, Bridgehead),

6.37 (m, 2H, $^{H}_{H}{>}C{=}C{<}$), 9.50 (s, 1H $-CO_2H$).

The analysis shows that the monomethyl ester contained impurities. Mass spectroscopy of this compound gave small peaks at m/e = 209, 208 and 207, consistent for a compound with a molecular weight of 208. The elemental analysis suggests that an impurity of dimethylacetylene dicarboxylic acid is present.

3.1.8 4-Formylphtalic Acid Anhydride

To a three-liter three-neck round bottom flask equipped with a stirrer, condenser, drying tube (calcium chloride), addition funnel, thermometer and nitrogen inlet was added 900 ml of sodium dried toluene and 315g (1.65 mole) of trimelletic anhydride. This was heated to 80°C while 300 g (2.52 mole) of thionyl chloride was added dropwise over a 2 hour period. A clear orange solution resulted. Excess thionyl chloride was removed by distillation. This was continued until a negative silver nitrate test was obtained. Xylene was then added to maintain the same volume as before distillation. To this was added 36g of freshly prepared palladium on barium sulfate catalyst. While stirring vigorously, hydrogen was bubbled through the solution and allowed to vent into distilled water.

This was continued until no more hydrogen chloride evolved, as determined by a negative reaction with blue litmus paper. The reaction mixture was cooled to 50°C, 10g of activated charcoal was added and the material was heated and stirred. Finally it was filtered, using Celite ^{R} to remove the charcoal. The filtrate was cooled and an equal volume of petroleum ether was added. This solution was cooled. The yellow solid which precipitated was filtered, and dried at 45°C in the vacuum oven, to yield 92.9g (32 percent yield) mp 108-118°C. The filtrate was diluted with an equal volume of petroleum ether and cooled in the freezer. An additional quantity of solid (13.1g) was recovered mp 88-165°C. A sublimed sample melted at 122-123°C (reported, sublimed sample, mp 127-129°C) (Ref. 9). The infrared spectrum is consistent for the desired product.

3.1.9 Attempted Synthesis of 4-Vinylphthalic Acid Anhydride (Ref. 9)

To a 250 ml flask equipped with a stirrer, thermometer, and reflux condenser was added a slurry of 3.57g (0.0085 mole) of triphenylmethyl phosphonium bromide in 50 ml of sodium dried toluene. To this was added 2.8g of sodium methoxide while stirring. After stirring for 1 hour, 5.0g of 4-formylphthalic acid anhydride was added over a period of 3 hours while stirring was continued. The reaction mixture was vacuum filtered to remove solid. The filtrate was concentrated to yield an oil and solid. The solid melted at 115-126°C, and appeared to be unreacted 4-formylphthalic acid anhydride. The solid and filtrate were recombined, placed in the reaction flask and diluted with 50 ml of toluene. To this was added 6.52g of triphenylmethylphosphonium bromide and 1.0g of sodium methoxide, and the reaction mixture was stirred for 2 hours at room temperature, then filtered, to remove the solid. The toluene filtrate was concentrated to another solid. The infrared spectrum of both solids was taken. The infrared spectrum of the toluene insoluble material showed no absorption due to anhydride group and very weak absorption at 3045 cm^{-1} due to C=C-H stretch. This was not considered to be 4-vinyl phthalic acid anhydride, but contained absorption due to the aromatic ring. It was not further identified. The infrared spectrum of the toluene soluble material also showed no absorption due to anhydride, but showed absorption at 3045 cm^{-1} due to C=C-H stretch, broad absorption at 1700-1725 cm^{-1} probably due to carboxyl group or aldehyde group, absorption due to aromatic at 1580-1480 cm^{-1}, and aromatic substitution patterns at 885 cm^{-1} (lone H on aromatic ring), at 700 and 740 cm^{-1}. This was not considered to be the product and was not further identified.

3.1.10 3-Vinyl-4-cyclohexene-1,2-dicarboxylic Acid Anhydride

1,3,5-hexatriene (5.0g, 0.0625 mole) in 25 ml of tetrahydrofuran was added to a solution of 6.0g (0.0615 mole) of maleic anhydride in 25 ml of tetrahydrofuran in an atmosphere of nitrogen while cooling in an ice bath. After the initial reaction, the reaction mixture was refluxed for 2 hours. After cooling to room temperature, the solution was concentrated to a mixture of crystalline material and yellow oil. The infrared of this oily material appeared to be consistent for the desired compound. Vacuum distillation yielded 0.35g of white solid, by 140°C/1 mmHg, m.p. 51-53.5°C, and 2.5g of yellow oil, b.p. 153-160°C/1 mmHg (reported for the compound, b.p. 148°C/6 mmHg, m.p. 51.5°C, (Ref. 5). The infrared spectrum of the solid was consistent with the structure of a compound containing a double bond and anhydride, and was found to be maleic anhydride, (m.p. 51-53.5°C). The infrared spectrum of the solid and the elemental analysis confirmed this.

Calc for $C_4H_2O_3$: C, 48.9; H, 2.04

Found: C, 49.7; H, 2.4

The infrared spectrum (Fig. 13) of the oil showed strong aliphatic absorptions at 2860, 2920 cm^{-1} and 1450 cm^{-1} in addition to the C=C-H stretch at 3020 and 3080 cm^{-1}, C=C stretch at 1640 cm^{-1} (nonconjugated); $C=CH_2$ out-of-plane deformation at 910 cm^{-1}, and cyclic anhydride absorption at 1775 and 1845 cm^{-1}. The proton NMR spectrum (Fig. 14) was also consistent for this compound.

NMR ($CDCl_3$): δ 2.50 (bm, 2H, $C-CH_2-C$), 3.42 (bm, 3H, $\overset{O}{\overset{\|}{C}}-CH-CH-\overset{O}{\overset{\|}{C}}$, C=C-CH-C=C),

5.08 (bm, 1H, $^{H}\!\!\searrow C=C\langle$), 5.33 (d, 2H, HC=CH),

5.98 (bm, 2H, $CH_2=C$)

Calc for $C_{10}H_{10}O_3$: C, 67.40; H, 5.6

Found: C, 67.18; H, 5.68

The spectroscopic and elemental analysis are consistent for the structure of 3 vinyl-4-cyclohexene-1,2-dicarboxylic acid anhydride.

3.1.11 Attempted Preparation of the Monomethyl Ester of 3-Vinyl-4-cyclohexene-1,2-dicarboxylic Acid

In an atmosphere of nitrogen, 1,3,5-hexatriene (4.0g, 0.05 mole) in 50 ml tetahydrofuran was added to a solution of monomethylester of maleic acid (6.36g, 0.05 mole) in 25 ml tetrahydrofuran, while stirring, at room temperature. No exotherm was observed. The reaction mixture was refluxed for two hours and this concentrated to a yellow oil at room temperature. The infrared spectrum was compared with the infrared spectrum of the starting material, monomethylester of maleic anhydride, and both are almost identical. The mass spectrogram showed peaks at m/e = 239, 208, 194 and 131, indicating the presence of traces of the monomethylester of 3-vinyl-4-cyclohexene-1,2-dicarboxylic acid and starting monomethylester of maleic acid (m/e = 130), and a high molecular weight material. Elemental analysis of the oil gave the following results:

Calc for $C_{11}H_{14}O_4$: C, 62.85; H, 6.66

Found: C, 43.94; H, 5.36

Calc for Monomethylester of Maleic Acid: C, 46.15; H, 4.60

It is clear from the elemental analysis and the infrared spectrum that the oil consisted mostly of starting material and perhaps a small quantity of product as an impurity. This oil was used to prepare a PMR-14 solution for application to a sodium chloride salt plate to study in the infrared as a film. The PRM-14 solution was defined as monomethylester of maleic acid/dimethylester of benzophenonetetracarboxylic acid/4,4-methylenedianiline (MAE/BTDE/MDA).

3.1.12 Monomethyl Ester of Maleic Acid

The procedure of Spatz and Stone (Ref. 7) was used.

To a three-neck round bottom flask equipped with a condenser, stirrer and reflux condenser was added 110g (1.12 mole) of maleic anhydride and 5.7g (0.006 mole) of anhydrous methanol. The mixture was heated to 55°C to dissolve the anhydride, after which an additional quantity of anhydrous methanol 38.4g, (1.12 mole) was added. The temperature was maintained at 55°C for 2 hours while stirring. The reaction mixture was cooled to room temperature and treated in vacuum for 3 hours, to yield 140g (96 percent yield) or colorless liquid, n_D^{20} 1.4588 (reported n_D^{20} 1.4634, n_D^{20} 1.4640). The infrared spectrum (Fig. 15) and proton NMR spectrum (Fig. 16) are consistent with the desired product.

Calc for $C_5H_6O_4$: C, 46.18; H, 4.64

Found: C, 46.44; H, 4.75

NMR ($CDCl_3$): δ 3.83 (s, 3H, $-OCH_3$), 6.37 (m, 2H, $\overset{H}{\diagdown}C{=}C\overset{H}{\diagup}$), 8.18 $\left(\text{s, 1H, } -\overset{\overset{O}{\|}}{C}-OH\right)$

3.1.13 Triphenylmethylphosphonium Bromide

This compound was prepared by reacting triphenylphosphine (0.62 mole, 199g) in 160 ml dry toluene at $0^{o}C$ with methylbromide (1.05 mole, 100g) in a stoppered bottle. The pressure developing on warming to room temperature exceeded the strength of the stopper seal, and therefore a stream of reaction produce shot onto the ceiling of the hood. The remaining material in the bottle was slurried in hot toluene and filtered. The white solid which was collected was dried in a vacuum oven at $100^{o}C$ for 2 hrs. A white product, mp $229-231^{o}C$, weighing 179.4g (69 percent yield) was obtained.

3.1.14 Dimethyl Ester of Benzophenone-3,3',4,4'-tetracarboxylic Acid

This compound was prepared by refluxing a solution of 322.2g (1.0 moles) of benzophenone-3,3',4,4'-tetracarboxylic acid anhydride (BTDA) in 310g (10 moles) of absolute alcohol for 3 1/2 hrs. Excess methanol was distilled off and the viscous residue was treated in vacuum (0.1 mmHg) at $70^{o}C$ for 3 hrs to yield 380.4g (99 percent yield) of an amber-glassy solid. The infrared was consistent for the desired compound.

3.2 Polymerization Studies - Evaluation of Monomers in PMR - Polyimide Systems

Monomers synthesized as described in 3.1 were subjected to curing studies by combining them with 4,4'-methylenedianiline and the dimethylester of 3,3',4,4'-benzophenonetetracarboxylic acid to prepare PMR addition type polymides. The procedure for performing the infrared studies of these PMR's and the preparation of polymers discs from powders of these PMR systems are described below.

3.2.1 PMR-14 With Itaconic Acid Ester End Cap (ITE-PMR-14)

A solution of monomethylester of itaconic acid ITE (5g, 0.0347 mole), dimethylester of benzophenonetetracarboxylic acid (BTDE), (13.9g, 0.036 mole) and 4,4'-methylenedianiline (MDA), (10.6g, 0.0535 mole) was prepared by dissolving ITE and BTDE in anhydrous methanol (36.0g), followed by addition of MDA, to yield a solution with the molar ratio BTDE/MDA/ITE of 1.04/1.54/1.00. A solution with this composition was used to study the uncatalyzed, peroxide catalyzed, and amine catalyzed PMR polymerization reaction. A film of each material, containing the peroxide or amine catalyst was prepared by placing a small portion of the solution on a sodium chloride salt plate, and allowing the solvent to volatilize. The thin film was evacuated at room temperature for 1/2 hr, and then the infrared spectrum after each temperature treatment was taken.

The uncatalyzed and the catalyzed polymerization reactions were studied by subjecting the PMR films to the following temperature cycles:

Heat Treatment, °C	Time
RT	-
93	1/2 hr
177	1/2 hr
201	1/2 hr
232	1/2 hr
260	1/2 hr
288	1/2 hr
316	1/2 hr

3.2.1.1 Results

Uncatalyzed - this PMR system forms an amber colored PMR-polyimide film, similar to PMR-15, with the imidization reaction slowly occurring from 93 °C to 232°C; the imide bands appearing over this temperature range of 1775 and 1720 cm^{-1}, which become broad bands on treatment up to 316°C. After the 316°C cure the peak at 3060 cm^{-1} still persists indicating that crosslinking is incomplete. Cure does take place, but appears to be incomplete over this temperature range, for the 1/2 hr time period exposure.

Peroxide-induced cure of ITE-PMR-14
cumene hydroperoxide (0.92 mole-% based on vinyl groups)
cumene hydroperoxide-dicumylperoxide (1.4 mole-% based on vinyl groups)
t-butyl hydroperoxide (1.6 mole-% based on vinyl groups)

The uncured films deposited on the sodium chloride salt plate was subjected to the following heat treatments:

Heat Treatment, °C	Time, hr
RT	-
204	1.0
232	1.0
260	0.5
316	1.0

The uncured films in all three cases showed infrared absorptions similar to uncured PMR-15 containing NE as end caps. Heat treatment for 1 hr at 204°C caused considerable change in the absorption spectra. The spectra showed sharp imide bands at 1775 cm^{-1} and 1720 cm^{-1}, similar to NE-PMR-15, and continued heating up to 316°C strengthened these bands, but did not cause broadening in the time period involved (1 hr). The absorption spectra differed from the NE-PMR-15 spectrum in that a peak at 1665 cm^{-1} was not present, and the peak at 1600 cm^{-1} was broader in the ITE-PMR-15 spectra than in the NE-PMR-15 spectrum. The peroxide initiated samples appeared to have undergone complete cure. Furthermore, imidization appears to be complete at 260°C, while for the uncatalyzed and triethylamine catalyzed samples, heat treatment at 316°C caused broadening of the imide peaks, but did not appear to cause complete crosslinking of the vinyl group.

These results clearly show that the itaconic end-capped PMR-14 can be imidized and polymerized by free radical methods. Additional studies were made to verify these results and to produce ITE-PMR-14 polymer discs polymerized by free radical initiators. These results are discussed below.

A second preparation of ITE-PMR-14 solutions was made by dissolving itaconic acid monomethyl ester (ITE) 2.5g, (0.0174 mole), and dimethyl ester of benzophenone tetracarboxylic acid (BTDE), (5.3g, 0.0267 mole) in anhydrous methanol (18.0g), followed by the addition of 4,4'-methylenedianiline (MDA), (6.95g, 0.0180 mole) to the solution. A film was prepared on a sodium chloride salt plate to follow the cure process by infrared spectroscopy. To one-quarter of the solution was added 1.07g dimethyldodecylamine (10 mole percent of the acid content). A film of this on sodium chloride salt plate was prepared.

The uncatalyzed and dimethyldodecylamine catalyzed ITE-PMR films were heat treated as shown below, and the infrared spectrum of the film was taken after each treatment.

Heat Treatment, °C	Time, hr
93	0.5
149	"
177	"
204	"
232	"
260	"
288	"
316	"

The systems were labeled ITE-PMR-14-II. The infrared spectra of the uncatalyzed ITE-PMR-14-II material and NE-PMR-15 showed no sign of imidization after treatment at 93°C for 1/2 hr. However, the infrared spectrum of the amine catalyzed material showed a definite peak at 1775 cm^{-1} due to the imide bond. After treatment at 93°C and 149°C for 1/2 hr each, the imide peak of the amine catalyzed material becomes even more prominent, while the imide peaks of both the uncatalyzed

ITE-PMR-14 and uncatalyzed NE-PMR-15 are much less pronounced in size. After the 204°C treatment, no differences appeared in the sizes of the imide peaks of the three materials.

A significant difference in the infrared spectra of the ITE-PMR-15-II systems both catalyzed and amine catalyzed compared with the NE-PMR-15 systems is the absence of an anhydride peak at 204°C and above. This peak emerges at 204°C in the NE-PMR-15 system and becomes stronger as 316°C is approached. After heating at 316°C for 1 hour, the anhydride peak disappears. This suggests that NE in the NE-PMR-15 system has a greater tendency to convert to anhydride than the ITE in the ITE-PMR-14 system, or that the ITE is lost through volatilization.

The peroxide cured ITE-PMR-14 systems discussed above was similar to NE-PMR-15 except for the absence of anhydride peaks during the cure between 204°C to 316°C.

3.2.2 PMR-15 with Monomethyl Ester of 2,5-Bicyclo[2.2.1]heptadiene-2,3-dicarboxylic Acid (NDE) End Cap, (NDE-PMR-15)

The following solution was prepared:

NDE 3.44g (0.0174 mole)
MDA 5.30g (0.0268 mole)
BTDE 6.90g (0.0180 mole)
anhydrous methanol 19.50g

A small portion was removed to prepare uncatalyzed films. The remaining solution was divided into four portions and treated as follows:

Solution 1. NDE-PMR-15 0.0344g dicumylperoxide (1.45 mole % based on moles vinyl group)
2. NDE-PMR-15 0.0172g dicumylperoxide (2.63 mole % based on moles vinyl group)
3. NDE-PMR-15 0.0344g t-butylhydroperoxide (2.59 mole % based on moles vinyl group)
4. NDE-PMR-15 0.0172g t-butylhydroperoxide (1.29 mole % based on moles vinyl group)

A series of films were prepared and subjected to the single treatment shown below, and the infrared spectrum of each was taken after each treatment.

Heat Treatment, $^{\circ}$C	Time, hr
177	1
204	1
218	1
232	1
288	1

Another NDE-PMR-15 solution having the same composition as shown above was prepared. One-fifth of the sample was removed for studies in the uncatalyzed condition. To the remaining solution (28.0g) dicumylperoxide (0.025g) was added. Four films were prepared by depositing a solution on sodium chloride salt plate, and then allowing the solution to evaporate at room temperature. The films were subjected to the following heat cycles and then the infrared spectrum was taken after each treatment.

Heat Treatment, °C

93, 149, 177, 204, 232, 260, 288 - 1/2 hr at each temp
149, 204 - 1/2 hr at each temp
163, 232 - 1/2 hr at each temp
204, 232 - 1/2 hr at each temp

Another NDE-PMR-15 solution with the same composition as described above was prepared except that the quantities were doubled. Half of the solution was used to prepare powder and film for uncatalyzed studies. The other film was divided into two portions - to one portion was added dimethyldodecylamine (5.38g to 17.59g of solution). To the other portion (17.59g) was added 2.48g tri-n-butylamine. Films of each solution, uncatalyzed, dimethyldodecylamine catalyzed and tri-n-butylamine catalyzed were prepared for infrared studies.

The films were subjected to the following heat treatments:

(a) 93, 149, 177, 204, 232, 260°C - 1/2 hr each temp
(b) 177, 204°C - 1/2 hr each temp
(c) 163, 232°C - 1/2 hr each temp
(d) 204, 232°C - 1/2 hr each temp

The infrared spectrum was taken after each heat treatment. A detailed study of the infrared spectra of the series was made and is discussed in Section 2.2.1.

3.2.3 PMR-14 with Maleic Acid Monomethyl Ester End-Cap (MAE-PMR-14)

As discussed above, analysis indicated that the reaction between 1,3,5-hexatriene and monomethyl ester of maleic acid yielded only starting monomethyl ester of maleic acid. The PMR solution was prepared before this fact was known. Therefore, instead of 4-vinylcyclohexene-1,2-dicarboxylic acid monomethyl ester as endcap, the PMR solution contained MAE as the endcap. The following solution was prepared: MAE, 1.0g; MDA, 1.44g; BTDE, 1.90g; anhydrous methanol, 6.62cc. The solution was divided into four equal portions. To one portion was added 0.30g triethylamine. To the second was added 0.173g dimethyldodecylamine.

To the third was added 0.00486g dicumylperoxide. To the fourth was added 0.00486g of t-butylhydroperoxide. Films of each were prepared on sodium chloride salt crystals. Each film was treated as follows, and the infrared spectrum was taken after each treatment.

Treatment

RT, vacuum 1/2 hr
93°C, 1/2 hr
149°C, "
177°C, "
204°C, "
232°C, "
260°C, "
288°C, "
316°C, "

The solutions remaining after preparation of the polymer films were concentrated to the powder for DSC studies. The infrared, and DSC studies are discussed in Sections 2.2.1 and 2.3.1, repsectively.

3.3 Process Studies on PMR Powders to Prepare Polymer Discs

PMR solutions of the monomers, ITE, NDE and MAE each with BTDE and MDA were prepared and concentrated to powder for a study of the process conditions required to prepare void free-polymer specimens. The results of these studies are described below.

3.3.1 Process Studies on ITE-PMR-14 Polyimide Resin System

The following ITE-PMR-14 solutions were prepared for process studies.

	wt, in grams			
	I	II	III	IV
itaconic acid monomethyl ester (ITE)	5.0	5.0	5.0	5.0
4,4'-methylenedianiline (MDA)	10.3	10.6	10.6	10.6
3,3',4,4'-benzophenone tetracarboxylic acid dimethyl ester (BTDE)	15.2	13.9	13.9	13.9
anhydrous methanol	36.0	36.0	36.0	36.0

The BTDE was dissolved in methanol, followed by addition of ITE, then MDA. All four solutions were a deep red color. The solution of ITE-PMR-14-I was divided into five equal portions and treated as follows.

Solution 1. Added 0.187g dicumyl peroxide and 0.066g t-butyl hydroperoxide, concentrated to a solid.
2. Added 0.11g t-butyl hydroperoxide, concentrated to a solid.
3. Added 0.105g cumene hydroperoxide, concentrated to a powder.
4. Added 0.23g dimethyldodecylamine, and 0.105g cumene hydroperoxide, concentrated to a solid.
5. No catalyst.

Solution ITE-PMR-14-II was divided into three equal portions and treated as follows.

Solution 1. Added 0.105g t-butyl hydroperoxide, concentrated to a powder.
2. Added 0.105g dicumyl peroxide and 0.105g cumene hydroperoxide, concentrated to a powder.
3. No catalyst, concentrated to a powder.

Solution ITE-PMR-14-III was divided into two equal portions and treated as follows.

Solution 1. No catalyst, concentrated to a powder.
2. Added 0.23g dimethyldodecylamine, concentrated to a solid.

Solution ITE-PMR-14-IV was divided into five equal parts and treated as follows.

Solution 1. No catalyst, concentrated to a solid.
2. Added 0.019g t-butyl hydroperoxide, concentrated to a solid.
3. Added 0.23g dimethyl dodecylamine, concentrated to a solid.
Solutions 4 and 5 were kept for reserve.

The process study data for ITE-PMR-14 polymer system are shown in Table I. Considerable difficulty was encountered in attempts to prepare a dense, void free, strong polymer disc. Most of the discs prepared were very brittle, and weak. Peroxide catalysts or dimethyldodecylamine did not decrease the processingg temperature and did not generate a disc with improved quality over the uncatalyzed material. In order to produce a dense polymer disc, a process temperature of 300°C for at least 1 hr at 0.51 MPa (75 psi) was required.

3.3.2 Process Studies on NDE-PMR-15 Polyimide Resin System

The following NDE-PMR-15 solutions were prepared for process studies.

	wt, in grams		
	II	III	IV
2,5-norbornadiene-2,3-dicarboxylic acid monomethyl ester (NDE)	4.60	4.60	4.60
4,4'-methylenedianiline (MDA)	7.22	7.20	7.20
3,3'-4,4'-benzophenonetetracarboxylic acid dimethyl ester (BTDE)	9.42	9.42	9.42
anhydrous methanol	37.0	37.0	37.0

The BTDE was dissolved methanol, followed by the addition of NDE, and finally MDA. Each solution had a reddish-brown color.

A solution was prepared as described for NDE-PMR-15-II. It was divided into five equal portions and treated as follows:

Solution 1. Added 0.0172g t-butyl hydroperoxide, concentrated to a powder at 140°C, 1 hr, then added 0.108g dicumyl peroxide.
2. Added 0.034g t-butyl hydroperoxide concentrated to a powder at 140°C, 1 hr, then added 0.36g dicumyl peroxide
3. Added 0.034g dicumyl peroxide, concentrated to a powder at 140°C, 1 hr, then added .30g t-butyl hydroperoxide.
4. Added 0.0172g dicumyl peroxide, concentrated to a powder at 140°C, 1 hr.

The powders and resultant discs were labeled NDE-PMR-15-II-1, II-2A, II-3A and II-5.

The solution NDE-PMR-III was dissolved into four equal parts and treated as follows:

Solution 1. Added 0.148g dimethyldodecylamine, concentrated to a powder, then added 0.130g cumene hydroperoxide, mixed thoroughly.
2. Added 0.189g dicumyl peroxide, concentrated to a powder.
3. Added 0.189g dicumyl peroxide, then 0.63 t-butyl hydroperoxide, concentrated to a powder.
4. No catalyst, concentrated to a powder.

The powders and resultant discs were labeled NDE-PMR-15-III-1 through IV.

A similar solution NDE-PMR-15-IV was prepared as described above and concentrated to a powder. Discs prepared from this powder were labeled NDE-PMR-IV-1 through 3.

The results of the process studies on the NDE-PMR-15 system are listed in Table II. Processing at 130°C in the presence of dicumyl peroxide, followed by processing with t-butyl hydroperoxide at 180°C or 200°C did not appear to reduce the temperature required to obtain complete cure of the material. Complete cure of this system is in the temperature range 275-300°C. Discs prepared below this temperature under pressure 0.69 MPa (100 psi) expanded considerably when subjected to a temperature of 300°C for 1 hr. This suggested that the neat resin discs were incompletely cured at 250°C. The presence of gaseous products due to decomposition of peroxide may also have caused the expansion of the discs at the elevated temperatures. It is apparent that consolidation to a dense, void free material can be obtained at 250°C, but the material requires further heating for complete cure. Composites prepared with this material were cured at 300°C for 1 hr.

3.3.3 Process Studies on MAE-PMR-14 Polyimide Resin System

The following MAE-PMR-14 polyimide solutions were prepared for process studies.

	wt, in grams	
	I	II
maleic acid monomethylester	7.5	3.75
4,4'-methylenedianiline	10.92	8.75
3,3',4,4'-benzophenone tetracarboxylic acid dimethyl ester	14.48	11.40
anhydrous methanol	59.0	43.0

The solution was divided into five equal parts and treated as follows.

Solution 1. Added 0.26g dimethyl dodecylamine, concentrated to a powder.
2. Added 0.115g t-butyl hydroperoxide, concentrated to a powder.
3. Added 0.175g cumene hydroperoxide, concentrated to a powder.
4. Added 0.31g dicumyl peroxide, concentrated to a powder.
5. No catalyst, concentrated to a powder.

The process study data for the MAE-PMR-14 polymer system are shown in Table III. After several runs with peroxide catalyst, it became clear that catalysts did not decrease the processing temperature or improve the processing characteristics, over the uncatalyzed material.

3.4 Evaluation of Novel PMR Polyimide Resins in Composites

Two PMR polymer systems were selected for further evaluation in composites consisting of Celion 6000 graphite fibers with the novel PMR polyimide resin. The two monomers selected for cross-linkers in PMR-15 addition type polymers were the monomethyl ester of 2,5-bicyclo [2.2.1] heptadiene-2,3-dicarboxylic acid (NDE) and the monomethyl ester of maleic acid (MAE). The novel PMR polyimide systems consist of NDE/MDA/BTDE and MAE/MDA/BTDE. Dense, solid, void free polymer discs were prepared from each system. However, processing with each system was studied over the temperature range from 180°C to 300°C, at a pressure of about 1.38 MPa.

3.4.1 Prepreg Processing with NDE/MDA/BTDE

A Celion 6000 (polyimide sized) graphite fiber/PMR-15 polyimide prepreg was prepared by passing Celion 6000 (PI sized) graphite fiber yarn through a solution of 45 w/o of NDE/MDA/BTDE in anhydrous methanol and then wound onto a 43.2 cm diameter drum to yield a prepreg tape 8.89 cm wide x 132 cm long. Small sections of the tape were evaluated for processing characteristics to provide process information for fabrication of 8.89 cm x 20.3 x 0.254 cm composites. These studies showed that the NDE-PMR-15 tape should be processed at 150°C for 30 min to affect almost complete imidization. The mole ratio of NDE/MDA/BTDE used was 100:1.54:1.04.

3.4.2 Prepreg Processing with MAE/MDA/BTDE

A Celion 6000 (PI sized) graphite fiber/PMR-14 polyimide prepreg was prepared as described for the NDE-PMR-15 system. The mole ratio of MAE/MDA/BTDE used was 1.00:1.54:1.04. Process studies on the tape were made to determine conditions for composite fabrication. These studies revealed that tape processing at 100°C for 1 hr provided material that contained a partially imidized system capable of being processed into a dense composite.

3.4.3 Composite Fabrication

3.4.3.1 Celion 6000/NDE-PMR-15 Composites

Several compoistes were fabricated by stacking 7 to 8 plies of the preprocessed tape into a 3.8 x 20.3 cm mold or 8.89 x 20.3 cm mold. The mold was placed into a preheated press (260°C) and allowed to reach the press temperature, during which time outgassing occurs. When the mold temperature reached 225°C, pressure (1.38 MPa) was applied to consolidate the plies. The temperature of the press was set to 316°C. The mold and press temperature increased to 316°C during a period of 10 min, while maintaining a pressure of 0.86 MPa. During this period, pressure was released several times to allow for outgassing of the composite.

The mold was held at 316°C, .89 MPa for a period of 80 min. It was allowed to cool to room temperature in the mold, and then postcured at 316°C for 16 hrs in the free state.

3.4.3.2 Celion 6000/MAE-PMR-14 Composites

Several of these composites were fabricated in the manner described for the NDE system, except that the mold was placed in a press preheated at 222°C. When the mold reached this temperature, the composite system was consolidated at 1.38 MPa, the press temperature was set for 316°C, and the mold was allowed to reach this temperature, during which time pressure was maintained at 1.38 MPa, except for pressure releases to allow for outgassing. The composites were allowed to cool in the press and then postcured at 316°C for 16 hrs in the free state. Composites of 3.8 x 20.3 x .254 cm and 8.89 x 20.3 x .254 cm wize were fabricated in this manner.

3.4.4 Composite Characterization

The composites were cut into shear specimens with a span-to-depth ratio of 4:1, and flexural specimens with a span-to-depth ratio of 20:1. These were tested for shear, flexural strengths and flexural moduli at room temperature, 288°C and 316°C. Some specimens were tested before postcuring. In addition, shear and flexural specimens were subjected to isothermal aging in flowing air (100 cc/min) for time periods of 200, 500, 800, 1000 and 2000 hrs at two temperatures, 288°C and 316°C. Selected specimens were monitored for weight changes at 100 hr intervals under these isothermal aging conditions. Fiber volume, resin volume and void volume of each composite were also determined, as well as the glass transition temperature (Tg) by thermal mechanical analysis (TMA). The results of these studies are discussed in Section 2.5.

3.4.5 Mechanical Properties of Composites

Shear and flexural properties of Celion 6000/PMR-type polyimide composite systems are listed in Tables VII through XVI. A discussion of the results of these tests can be found in Section 2.5.

4.0 SUMMARY OF RESULTS AND CONCLUSIONS

Four monomethyl esters were synthesized and characterized for use in crosslinking studies to produce PMR addition-type polyimides. The monomers are the monomethyl ester of itaconic acid (ITE), the monomethyl ester of 2,5-bicyclo [2.2.1]heptadiene-2,3-dicarboxylic acid (NDE), the monomethyl ester of 2,5-bicyclo [2.2.2]octadiene-2,3-dicarboxylic acid (ODE), and the monomethyl ester of maleic acid (MAE). These crosslinkers with the exception of the ODE were capable of entering into a crosslinking reaction to produce polymer specimens which were strong, dense and free of voids. However, none of the crosslinkers affected a crosslinking at a lower temperature than the state-of-the-art PMR-15 polyimide derived from the monomethyl ester of 5-bicyclo[2.2.1]heptene-2,3-dicarboxylic acid (NE), 4,4'-methylenedianiline (MDA), and the dimethyl ester of 3,3', 4-4'-benzophenonetetracarboxylic acid (BTDE).

Two of the crosslinkers, monomethyl ester of 2,5-bicyclo[2.2.1]heptadiene-2,3-dicarboxylic acid (NDE) and the monomethyl ester of maleic acid (MAE) were combined with MDA and BTDE to form the PMR systems NDE-MDA-BTDE (NDE-PMR-15) and MAE-MDA-BTDE (MAE-PMR-14) and were evaluated in Celion 6000/PMR polyimide composites.

The results of the flexural and shear strengths after isothermal aging at 550°F and 600°F for up to 2000 hours suggest that both PMR systems are promising candidates as matrices for addition type polyimide components.

5.0 RECOMMENDATIONS

Additional investigations to synthesize the two monomethyl esters, monomethyl ester of 3-vinyl-4-cyclohexene-1,2-dicarboxylic acid and the monomethyl ester of 4-vinylphthalic acid should be performed and the two monomers should be evaluated for their ability to lower the crosslinking temperature of PMR type polyimides. In addition, monomeric bis-imides with therminal olefinic groups, capable of crosslinking to dense polyimides, should be synthesized and evaluated as monomeric type polyimide materials.

Additional composite process studies should be performed in order to optimize the mechanical properties of the NOE-PMR-15 and MAE-PMR-14 graphite fiber composites

6.0 REFERENCES

1. Baker, B. R., R. E. Schaub and J. H. Williams: J. Org. Chem., 17, pp. 116-131, 1952.
2. Price, C. C. and A. J. Tomisek: J. Am. Chem. Soc., 65, p. 440, 1943.
3. Diels, O. and K. Alder: Annalen der Chemie, 490, pp. 236-242, 1931.
4. Zahorsky, U. I. and H. Musso: Annalen Der Chemie, 11, pp. 1777-1778, 1973.
5. Farmer, E. H. and F. L. Warren: J. Chem Soc., 1929, pp. 897-909.
6. Kharasch, M. S. and E. Sternfeld: J. Am. Chem. Soc., 61, p. 2318, 1939.
7. Spatz, S. M. and H. Stone: J. Org. Chem., 23, pp. 1559-1560, 1958.
8. Ushakov, S. N., A. F. Mikolaeva, A. M. Toroptseva and M. S. Thizna: Chem. Abstr., 53, p. 14935b, 1957.
9. Winslow, E. C. and A. Laferriere: J. Poly. Sci., 60, pp. 65-80, 1962.
10. Delvigs, P., T. T. Serafini and G. R. Lightsey: NASA Technical Note, NASA TND-6877, August 1972.
11. Kreuz, J. A., A. L. Endrey, F. P. Gay and C. E. Sroog: J. Polymer Sci. Part A-1, 4, pp. 2607-2616, 1966.
12. Gluyas, R. E.: Thermal Analyses of PMR-Polymide Resin, NASA TMS-73448, July 1976.

TABLE I

PROCESS STUDIES TO PREPARE NEAT POLYMER DISCS OF ITE-PMR-14 POLYIMIDE POWDER

Disc No.	Catalyst	Initial Process Temp °C/time	Inter-mediate Process Temp °C/time	Final Process Temp °C/time	Final Process Pressure MPa (psi)	Density of Polymer Disc g/cc Observation
ITE-PMR-14-I-1	DCP t-BHP	150/1 hr	200/1 hr	230/20 min 250/1 hr	0.069 (10)	weak, brittle
I-2	none	150/1 hr	200/1 hr	310/1 hr	0.069 (10)	weak, brittle
ITE-PMR-14-II-1	t-BHP	-	200/1 hr	300/1 hr	0.517 (75)	1.04 porous
II-2	DCP CHP	150/1 hr	200/1 hr	300/1 hr	0.517 (75)	1.32-porous, hard, strong
II-3	none	150/1 hr	200/1 hr	300/1 hr	0.517 (75)	1.31-hard, strong
ITE-PMR-14-III-1	none	-	200/1 hr	250/1 hr	0.517 (75)	1.19-porous, weak brittle
-III-2	DMDA	-	200/1 hr	310/1 hr	0.344 (50)	weak, brittle
ITE-PMR-14-IV-1	none	-	200/1 hr	300/1 hr	0.482 (70)	1.31-strong, brittle
IV-2	t-BHP	-	200/1 hr	300/1 hr	0.413 (60)	weak, brittle
IV-3	DMDA	-	200/1 hr	300/2 hrs	0.413 (60)	1.28-hard, strong

DCP = dicumyl peroxide
t-BHP = tertiary-butylhydroperoxide
DMDA = dimethyldodecylamine
CHP = cumene hydroperoxide

TABLE II

PROCESS STUDIES TO PREPARE NEAT POLYMER DISCS OF NDE-PMR-15 POLYIMIDE POWDER

Disc No.	Catalyst	Initial Process Temp °C/time	Inter-mediate Process Temp °C/time	Final Process Temp °C/time	Final Process Pressure MPa (psi)	Density of Polymer Disc g/cc Observations
DE-PMR-15-II-1	DCP t-BHP	130/1 hr	180/1 hr	150/1 hr	0.69 (100)	0.966 - hard, strong, porous
II-2A	DCP t-BHP	140/1 hr	200/1 hr	250/1 hr	0.69 (100)	1.25 - strong, hard, void free
II-3A	t-BHP DCP	130/1/2 hr	180/1 hr	250/1 hr	0.69 (100)	1.17 - hard, strong, void free
II-5	none	-	180/1 hr	250/1 hr	0.69 (100)	0.750 - hard, strong, porous
DE-PMR-15-III-1a	DMDA CHP	-	180/1 hr	250/1 hr	1.38 (200)	0.90 - hard, strong, porous
III-1b	DMDA CHP	-	180/1/2 hr 200/1/2 hr	230/10 min 250/1 hr	0.517 (75)	1.17 - strong, hard, void free
III-2	DCP	-	180/1 hr 200/1/2 hr	230/10 min 250/1 hr	0.69 (100)	1.23 - strong, hard void free
III-3a	DCP t-BHP	-	180/1 hr 200/1 hr	250/1 hr	0.69 (100)	1.08 - strong, hard, void free
III-3b	DCP t-BHP	-	180/1 hr	250/1 hr	0.69 (100)	0.78 - hard, strong, porous
III-4	none	-	180/1 hr 200/1/2 hr	250/1 hr	3.45 (500)	1.25 - strong, hard, void free
IV-1	none	-	180/1 hr 200/1/2 hr	250/1 hr	0.517 (75)	0.905 - strong, hard, void free
IV-2	none	-	180/1 hr 200/1/2 hr	250/1 hr	0.517 (75)	1.04 - strong, hard, void free
IV-3	none	-	180/1 hr 200/1/2 hr	250/1 hr	0.517 (75)	1.05 - strong, hard, void free

P = dicumyl peroxide
BHP = tertiary-butylhydroperoxide
DA = dimethylododecylamine
P = cumene hydroperoxide

TABLE III

PROCESS STUDIES TO PREPARE NEAT POLYMER DISCS OF MAE-PMR-14 POLYIMIDE POWDER

Disc No.	Catalyst	Initial Process Temp °C/time	Intermediate Process Temp °C/time	Final Process Temp °C/time	Final Process Pressure MPa (psi)	Density of Polymer Disc g/cc Observation
MAE-PMR-14-I-2	t-BHP	-	200/1 hr	300/1 hr	0.517 (75)	1.20-dense, har
I-4	DCP t-BHP	-	200/2 hrs	300/1 hr	1.38 (200)	no consolidatio
I-5	none	-	200/2 hrs	300/1 hr	0.69 (100)	~0.50-weak, po
MAE-PMR-14-II-5	none	-	200/2 hrs	300/1 hr	0.69 (100)	0.96-hard, stro void free

DCP = dicumyl peroxide
t-BHP = tertiary-butylhydroperoxide
DMDA = dimethyldodecylamine
CHP = cumene hydroperoxide

TABLE IV

ELEMENTAL ANALYSIS OF PMR POLYIMIDES

Sample No		Percent		
		C	H	N
ITE-PMR-14-	Calculated For $C_{83}H_{50}N_6O_{14}$	73.6	3.72	6.19
-II-3	Found	73.4	4.19	6.18
-IV-1	Found	73.3	4.37	6.07
-IV-3	Found	73.2	4.48	5.90
NDE-PMR-15-	Calculated For $C_{93}H_{59}N_6O_{14}$	75.50	3.62	5.62
-II-2a	Found	74.06	4.20	5.96
-III-2	Found	74.80	4.45	6.00
-III-4	Found	74.50	4.26	6.12
-IV-3	Found	74.27	4.52	6.04
MAE-PMR-14-	Calculated for $C_{81}H_{66}N_6O_{16}$	73.30	3.49	6.32
-I-2	Found	75.21	4.54	7.90
-II-5	Found	73.89	4.44	6.19

TABLE V

THERMOMECHANICAL DETERMINATION OF GLASS TRANSITION TEMPERATURE OF PMR RESINS

PMR Resin Sample	Tg, °C
PMR-15	315
ITE-PMR-14-IV-1	200
ITE-PMR-14-IV-3	215
NDE-PMR-15-III-2	225
NDE-PMR-15-III-4	215
Reprocessed NDE-PMR-15-III-2	315
Reprocessed NDE-PMR-15-III-4	295
MAE-PMR-14-II-5	225

TABLE VI

PHYSICAL PROPERTIES OF CELION-6000/PMR COMPOSITES

Composite No	Density g/cc	Vol/% Resin	Vol/% Fiber	Vol/% Void	Tg°C From TMA
NDE-PMR-15-3	1.34	49.6	41.8	8.6	~ 320
NDE-PMR-15-4	1.39	38.6	52.7	8.5	~ 325
NDE-PMR-15-4	1.39	39.7	51.3	9.0	
NDE-PMR-15-5	1.38	45.6	46.9	7.4	330
NDE-PMR-15-5	1.42	45.9	49.1	5.0	
MAE-PMR-14-1	1.37	54.5	40.2	5.3	255
MAE-PMR-14-1	1.33	55.2	36.9	7.9	
MAE-PMR-14-5	1.42	47.5	47.6	4.9	275
MAE-PMR-14-5	1.45	47.2	49.8	2.9	
MAE-PMR-14-7	1.36	35.8	56.4	7.8	--

TABLE VII

SHEAR STRENGTH[1] OF CELION-6000/NDE-PMR-15-3 COMPOSITE AFTER ISOTHERMAL AGING IN FLOWING AIR (100 CC/MIN)

Postcured					
		Strength			
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
53.7	7780	32.8	4760	30.0	4360
56.4	8180	46.8	6790	27.9	4040
51.8	7510	30.8	4470	30.4	4410

After 192 hrs @ 288°C					
		Strength			
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
48.8	7080	26.3	3820	14.6	2120
51.7	7500	29.1	4230	21.5	3120

After 1028 hrs @ 288°C					
		Strength			
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
30.7	4500	cracked on aging		24.0	3500
39.0	5700			18.4	2700

After 2098 hrs @ 288°C					
		Strength			
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
27.1	3940	7.70	1120	13.1	1900

---

[1] S/D = 4/1

TABLE VIII

SHEAR STRENGTH[1] OF CELION-6000/NDE-PMR-15-4 COMPOSITE AFTER ISOTHERMAL AGING IN FLOWING AIR (100 CC/MIN)

Postcured

Strength					
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
64.1	9290	36.4	5280	37.2	5400
--	--	31.9	4630	46.7	6780

After 192 hrs @ 288°C

Strength					
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
41.2	6000	20.4	2970	20.4	2970
40.2	5820	--	--	16.6	2410

After 928 hrs @ 288°C

Strength					
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
23.7	3440	19.7	2860	11.2	1620
25.8	3740	19.7	2860	--	--

After 1028 hrs @ 288°C

Strength					
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
22.3	3240	18.0	2610	18.3	2700
21.1	3100	29.9	4330	--	--

After 2098 hrs @ 288°C

Strength					
RT		288		316°C	
MPa	psi	MPa	psi	MPa	psi
15.4	2240	14.8	2140	7.70	1160

After 192 hrs @ 316°C

Strength					
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
41.0	5970	36.4	5300	58.2	844

After 573 hrs @ 316°C

Strength					
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
22.0	3180	14.3	2100	18.2	2640

After 808 hrs @ 316°C

Strength					
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
21.7	3150	24.8	3600	15.8	229

After 1114 hrs @ 316°C

Strength					
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
57.5	834	5.03	729	4.73	.682

---

1. S/D = 4/1

TABLE IX

SHEAR STRENGTH[1] CELION-6000/NDE-PMR-15-5 COMPOSITE ISOTHERMALLY AGED IN FLOWING AIR (100 CC/MIN)

Postcured

Strength					
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
72.8	10,600	46.0	6680	33.3	4830
51.2	7430	40.5	5870	37.0	5370

After 192 hrs @ 288°C

Strength					
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
51.7	7500	62.3	9040	50.4	7310

After 928 hrs @ 288°C

Strength					
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
27.7	4020	cracked on aging		27.3	4000

After 1028 hrs @ 288°C

Strength					
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
32.6	4720	--	--	24.6	3600

After 2098 hrs @ 288°C

Strength					
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
9.24	1340	8.93	1300	6.67	968
6.79	985				

After 192 hrs @ 316°C

Strength					
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
55.5	8050	22.1	3210	13.0	1890
66.9	9700	18.4	2670	17.1	2470

After 508 hrs @ 316°C

Strength					
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
62.3	9040	35.3	5120	31.4	4600
49.3	7150	42.1	6100	31.4	4600

After 808 hrs @ 316°C

Strength					
RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi
27.5	3980	29.5	4280	34.6	5020
28.9	4200	33.0	4790	22.2	3220

After 1114 hrs @ 316°C

Strength					
RT		288°C		316°C	
MPa	psi	MPa	psi		
16.1	2330	9.83	1430	14.3	2080
19.7	2850				

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[1] S/D = 4/1

TABLE X

FLEXURAL PROPERTIES[1] OF CELION-6000/NDE-PMR-15-3 COMPOSITE ISOTHERMALLY AGED IN FLOWING AIR (100 CC/MIN)

Postcured Strength						Postcured Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	GPa	10^6psi	GPa	10^6psi	GPa	10^6psi
984	143	543	78.8	532	77.2	88.0	12.8	72.9	10.9	61.2	8.88
1073	156	703	102.0	457	66.3	91.1	13.2	75.3	10.6	52.3	7.59
1004	146	660	96.5	--	--	83.8	12.1	71.6	10.4	--	--

After 1028 hrs @ 288°C

Strength						Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	GPa	10^6psi	GPa	10psi	GPa	10^6psi
--	--	250	36.2	330	47.9	--	--	56.0	8.13	53.2	7.71

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[1] Four point flexure, S/D = 20/1

TABLE XI

FLEXURAL PROPERTIES[1] OF CELION-6000/NDE-PMR-15-4 COMPOSITE AFTER ISOTHERMALLY AGED IN FLOWING AIR (100 CC/MIN)

Strength						Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	MPa	10^6psi	MPa	10^6psi	MPa	10^6psi
360	52.2	391	56.7	352	51.1	88.9	12.8	102.7	14.9	82.7	12.0
356	51.7	232	33.7	361	52.3	93.7	13.6	79.9	11.6	91.0	13.2

After 192 hrs @ 288°C

Strength						Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	GPa	10^6psi	GPa	10^6psi	GPa	10^6psi
318	46.1	504	73.1	345	50.0	79.0	11.5	61.8	8.97	71.3	10.3
449	65.1			284	41.2	92.4	13.4			64.3	9.37
552	75.6					86.0	12.5				

After 192 hrs @ 316°C

Strength						Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	GPa	10^6psi	GPa	10^6psi	GPa	10^6psi
519	75.3	337	48.8	291	42.2	83.6	12.1	81.6	11.8	64.3	9.33

After 523 hrs @ 316°C

Strength						Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	GPa	10^6psi	GPa	10^6psi	GPa	10^6psi
737	107	435	63.1	326	47.3	111	16.1	84.9	12.3	51.6	7.48

After 1114 hrs @ 316°C

Strength						Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	GPa	10^6psi	GPa	10^6psi	GPa	10^6psi
384	55.7	101	14.7	92.7	13.4	47.6	6.91	21.8	3.16	32.2	4.67
69.3	10 1	112	16.2	94.9	13.8	17.7	2.57	26.3	3.82	6.3	.92

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[1] Four point flexure, S/D = 20/1

TABLE XII

FLEXURAL PROPERTIES[1] OF CELION-6000/NDE-PMR-15-5 COMPOSITE ISOTHERMALLY AGED IN FLOWING AIR (100 CC/MIN)

Postcured

Strength						Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	GPa	10^6psi	GPa	10^6psi	GPa	10^6psi
703	102	566	82.1	290	42.0	100.1	14.6	198	28.7	58.7	8.51
588	88.2	235	34.1	--	--	73.1	10.6	98.8	14.3	--	--

After 192 hrs @ 288°C

Strength						Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	GPa	10^6psi	GPa	10^6psi	GPa	10^6psi
538	81.0	512	74.2	347	50.3	85.2	12.4	43.1	6.24	40.9	5.9

After 192 hrs @ 316°C

Strength						Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	GPa	10^6psi	GPa	10^6psi	GPa	10^6psi
1170	170	524	76.0	464	67.3	92.1	13.4	65.1	9.44	39.4	5.72
626	90.8	525	76.2	298	43.2	83.6	12.1	59.6	8.62	37.6	5.46

After 1114 hrs @ 316°C

Strength						Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPA	Ksi	MPa	ksi	GPa	10^6psi	GPa	10^6psi	GPa	10^6psi
228	33.1	161	23.4	237	34.3	36.3	5.26	2.92	.42	32.0	4.65
259	36.3	188	27.3	268	38.9	38.4	5.58	51.1	7.42	44.6	6.47

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[1] Four point flexure, S/D = 20/1

TABLE XIII

SHEAR STRENGTHS[1] OF CELION-6000/MAE-PMR-14-1 COMPOSITE ISOTHERMALLY AGED IN FLOWING AIR (100 CC/MIN)

"As Fabricated"						Postcured					
RT		288°C		316°C		RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi	MPa	psi	MPa	psi	MPa	psi
86.5	12,600	55.5	8050	30.6	--	71.3	10,300	42.2	6120	40.7	5900
80.5	11,700	--	--	30.2	4380	--	--	--	--	--	--

After 192 hrs @ 288°C						After 928 hrs @ 288°C					
RT		288°C		316°C		RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi	MPa	psi	MPa	psi	MPa	psi
72.4	11500	33.4	4850	22.5	3260	53.1	7700	31.4	4550	36.4	5280
79.8	11600	28.3	4110	22.5	3260	--	--	--	--	37.2	5400

After 1028 hrs @ 288°C						After 2098 hrs @ 288°C					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	MPa	psi	MPa	psi	MPa	psi
33.6	4900	29.3	4240	28.1	4100	31.8	4620	18.4	2670	16.6	2410
44.1	6400	40.2	5840	19.1	2800	33.7	4890	--	--	--	--

After 508 hrs @ 316°C						After 808 hrs @ 316°C					
RT		288°C		316°C		RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi	MPa	psi	MPa	psi	MPa	psi
50.6	7350	44.1	6000	30.3	4400	62.6	9080	51.2	7430	49.3	7150
--	--	--	--	--	--	--	--	--	--	--	--

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1. S/D = 4/1

TABLE XIV

SHEAR STRENGTH[1] OF CELION-6000/MAE-PMR-14-5 COMPOSITE ISOTHERMALLY AGED IN FLOWING AIR (100 CC/MIN)

As Fabricated						Postcured					
RT		288°C		316°C		RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi	MPa	psi	MPa	psi	MPa	psi
65.6	9500	18.9	2400	15.2	2220	49.5	7170	26.5	3840	15.4	2230
42.8	6200	16.6	2160	20.5	2980	81.4	11,810	22.8	3310	14.4	2020
60.3	8740	14.9	2220	13.5	1950						

After 192 hrs @ 288°C						After 808 hrs @ 316°C					
RT		288°C		316°C		RT		288°C		316°C	
MPa	psi	MPa	psi	MPa	psi	MPa	psi	MPa	psi	MPa	psi
76.0	11,000	13.5	1950	9.41	1371	27.5	3780	29.1	4.28	34.6	5020
74.6	10,800	20.1	2920	24.2	3510	28.9	4200	33.0	4.79	22.2	3222

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[1] S/D = 4/1

TABLE XV

FLEXURAL PROPERTIES[1] OF CELION-6000/MAE-PMR-14-5 COMPOSITE ISOTHERMALLY AGED IN FLOWING AIR (100 CC/MIN)

"As Fabricated"

Strength						Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	GPa	10^6psi	GPa	10^6psi	GPa	10^6psi
435	63.1	101	14.6	118	17.1	90.9	13.2	10.1	1.47	11.7	1.70
346	50.2	137	19.8	125	18.1	90.2	13.1	12.4	1.80	13.9	2.01
316	45.9	98.1	14.2	109	15.8	90.3	13.1	10.6	1.53	8.71	1.26

Postcured

Strength						Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	GPa	10^6psi	GPa	10^6psi	GPa	10^6psi
1141	166	454	65.8	233	33.8	91.5	13.3	58.2	8.44	23.2	3.36
1129	164	407	59.0	127	18.4	90.8	13.2	57.9	8.40	11.2	1.63

After 192 hr @ 288°C

Strength						Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	GPa	10^6psi	GPa	10^6psi	GPa	10^6psi
614	89.0	268	38.8	222	32.2	65.0	9.42	36.3	5.27	31.3	4.53
442	64.1	329	47.7	270	39.2	60.0	8.70	49.6	7.20	16.8	2.43

After 808 hr @ 316°C

Strength						Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	GPa	10^6psi	GPa	10^6psi	GPa	10^6psi
531	77.0	128	18.7	150	21.7	77.4	11.2	39.3	5.71	29.6	4.29
180	26.1	--	--	203	29.5	56.2	8.15	--	--	41.4	6.00

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1. Four point flexure, S/D = 20/1

TABLE XVI

FLEXURAL PROPERTIES[1] OF CELION-6000/MAE-PMR-14-7 COMPOSITE ISOTHERMALLY AGED IN FLOWING AIR (100 CC/MIN)

Postcured

Strength						Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	GPa	10^6psi	GPa	10^6psi	GPa	10^6psi
829	120	355	51.5	168	24.3	67.6	9.81	30.8	4.4	15.6	2.2
727	105	269	39.0	207	30.0	66.4	9.63	29.5	4.3	28.2	4.1

After 312 hrs @ 288°C

Strength						Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	GPa	10^6psi	GPa	10^6psi	GPa	10^6psi
558	80.9	405	58.7	372	54.0	72.2	10.5	63.4	9.2	42.9	6.2
590	85.6	597	86.6	419	60.7	53.3	7.7	43.7	6.3	45.1	6.5

After 528 hrs @ 288°C

Strength						Modulus					
RT		288°C		316°C		RT		288°C		316°C	
MPa	ksi	MPa	ksi	MPa	ksi	GPa	10^6psi	GPa	10^6psi	GPa	10^6psi
599	86.8	424	61.5	431	62.6	58.5	8.49	54.9	7.96	63.7	9.24
639	92.6	576	83.5	415	60.1	83.7	12.1	54.8	7.94	44.1	6.40

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[1] Four point flexure, S/D = 20/1

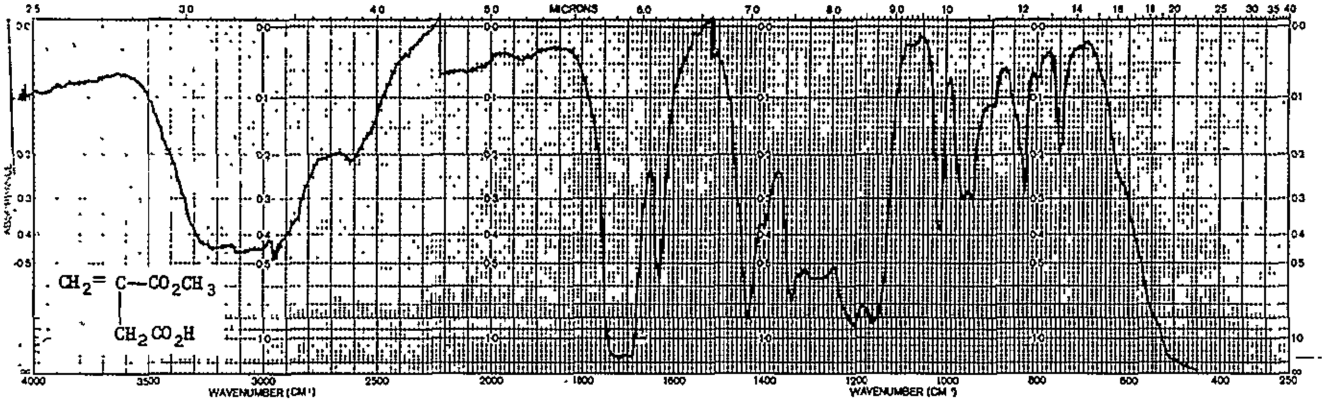


FIG. 1 INFRARED SPECTRUM OF MONOMETHYL ESTER OF ITACONIC ACID

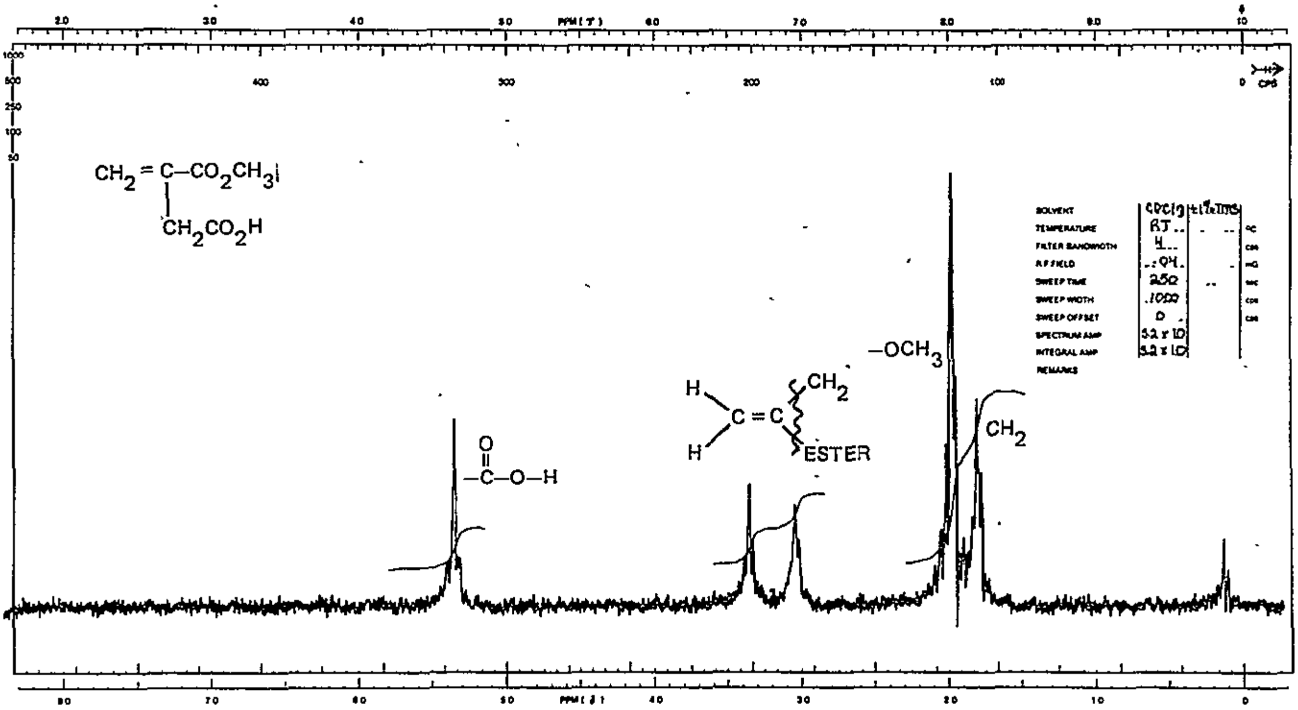


FIG. 2 PROTON NMR SPECTRUM OF MONOMETHYL ESTER OF ITACONIC ACID

79–06–157–1

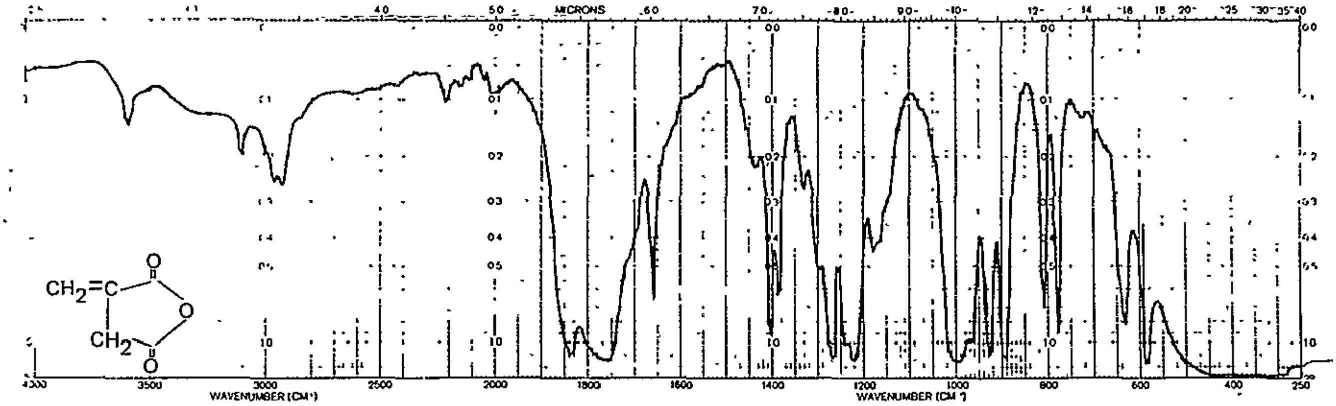


FIG. 3 INFARED SPECTRUM OF ITACONIC ANHYDRIDE

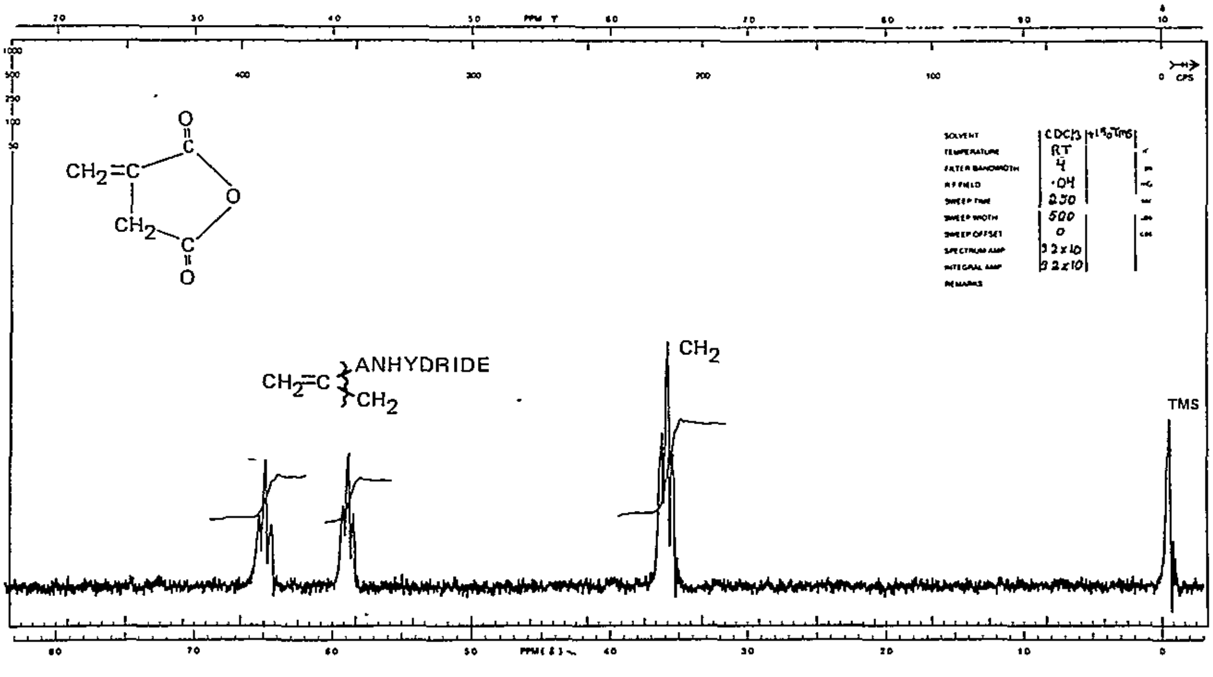


FIG. 4 PROTON NMR SPECTRUM OF ITACONIC ANHYDRIDE

79–06–157–2

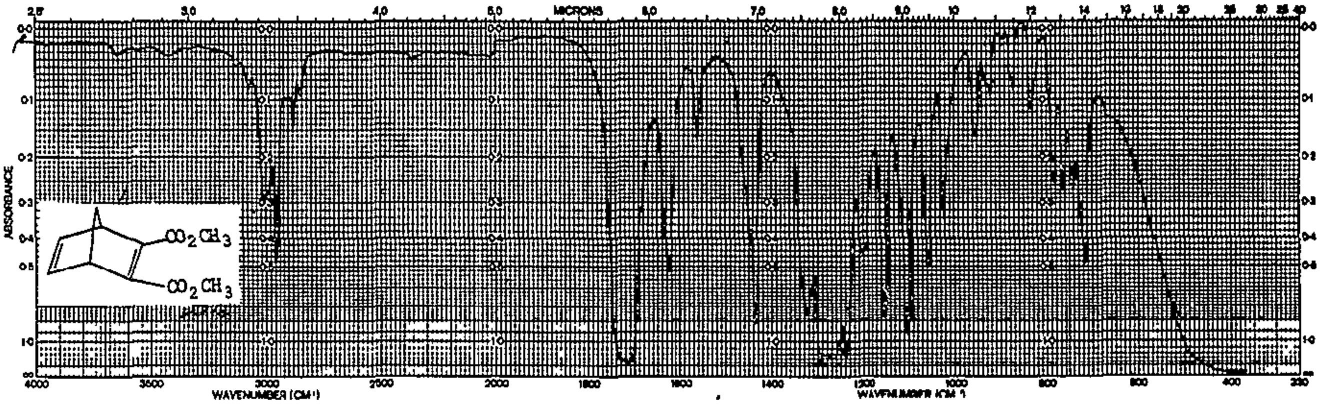


FIG. 5 INFRARED SPECTRUM OF DIMETHYL ESTER OF BICYCLO [2.2.1] HEPTADIENE–2, 3–DICARBOXYLIC ACID

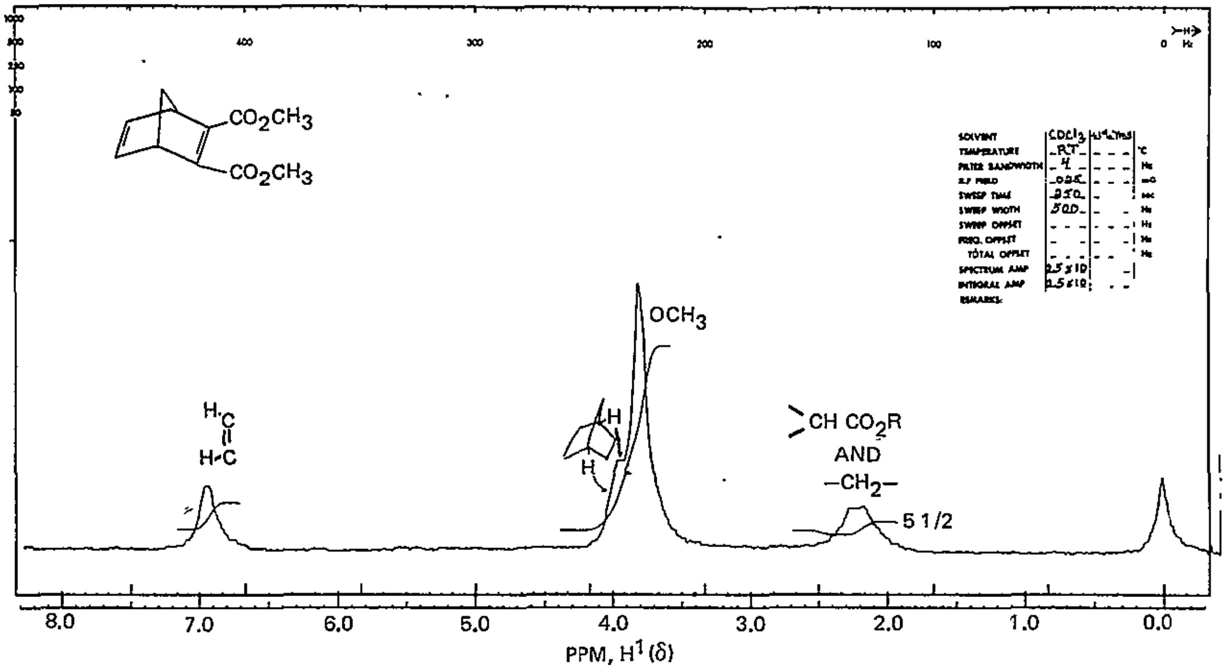


FIG. 6 PROTON NMR SPECTRUM OF DIMETHYL ESTER OF 2, 5–BICYCLO [2.2.1] HEPTADIENE–2, 3–DICARBOXYLIC ACID

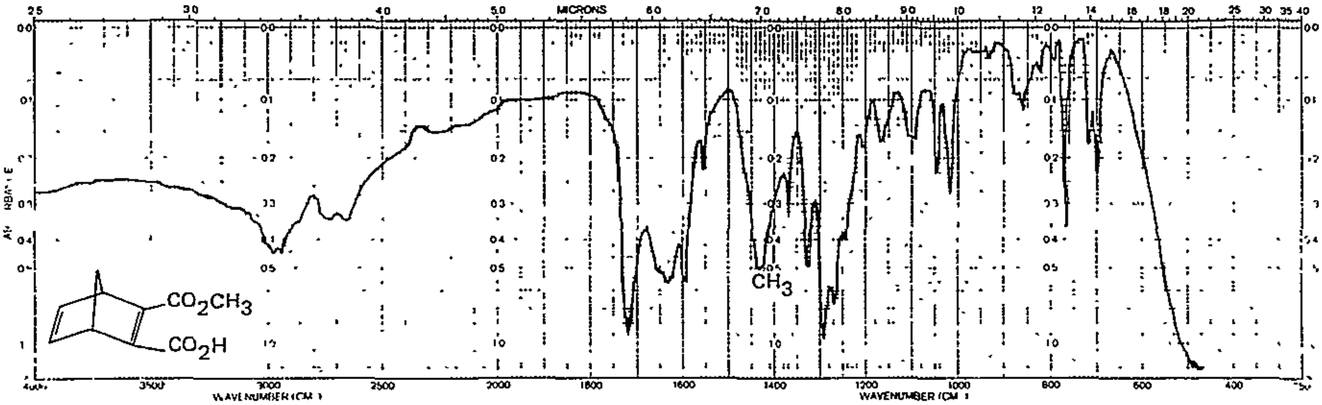


FIG. 7 INFARED SPECTRUM OF THE MONOMETHYL ESTER OF 2, 5–BICYCLO [2.2.1] HEPTADIENE–2,3–DICARBOXYLIC ACID

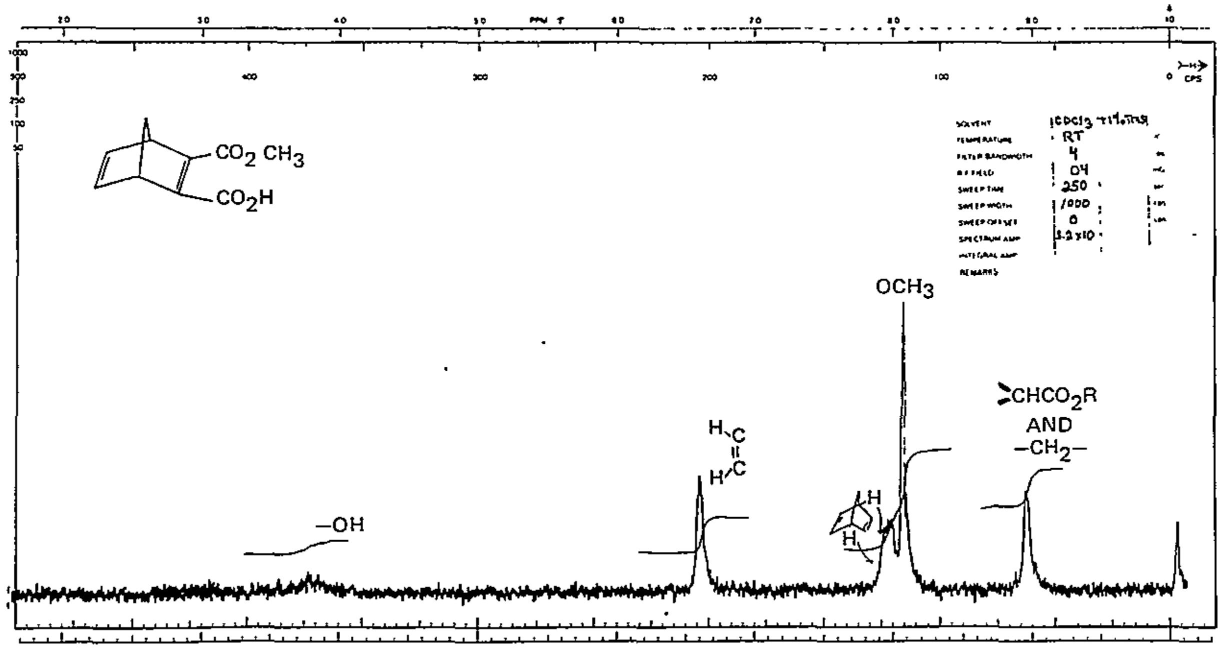


FIG. 8 PROTON NMR SPECTRUM OF THE MONOMETHYL ESTER OF 2, 5–BICYCLO [2.2.1] HEPTADIENE–2,3–DICARBOXYLIC ACID

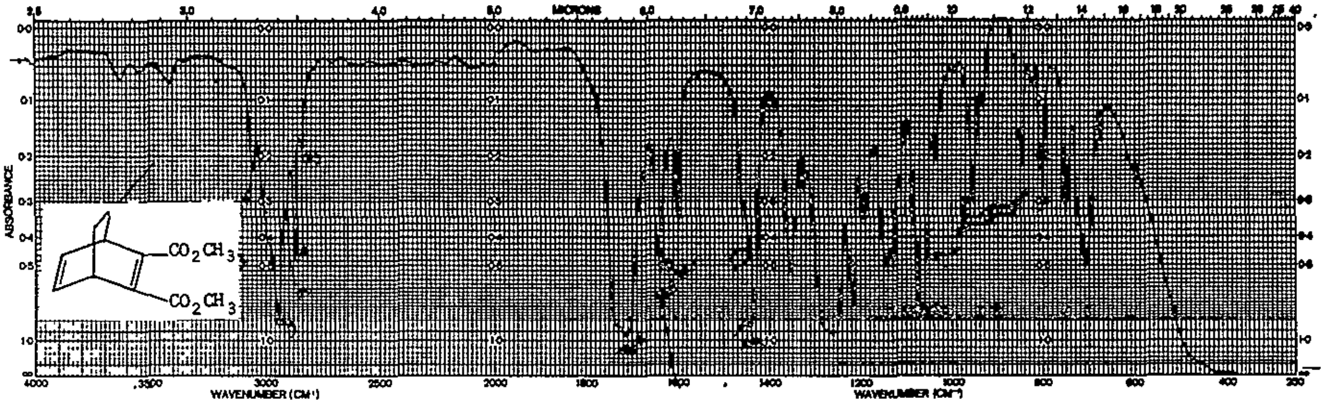
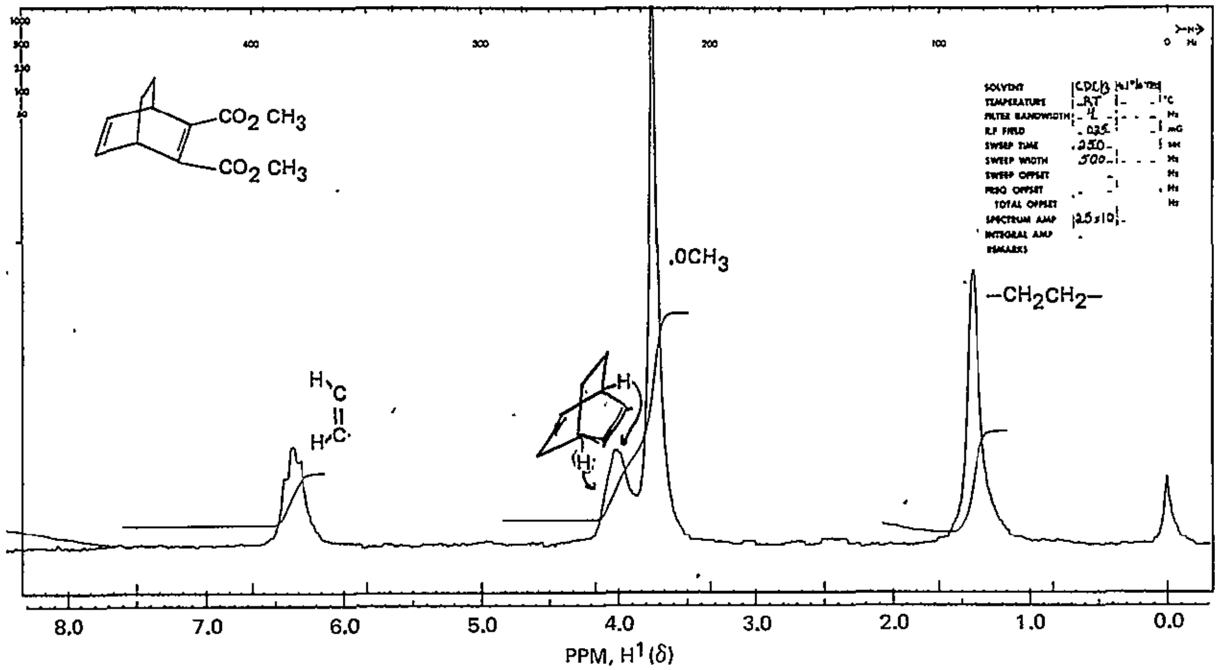


FIG. 9 INFRARED SPECTRUM OF THE DIMETHYL ESTER OF 2,5- -BICYCLO [2.2.2] OCTADIENE–2,3–DICARBOXYLIC ACID



SOLVENT CDCl3
TEMPERATURE RT °C
FILTER BANDWIDTH 4 Hz
R.F FIELD .035 mG
SWEEP TIME 250 sec
SWEEP WIDTH 500 Hz
SWEEP OFFSET Hz
FREQ OFFSET Hz
TOTAL OFFSET Hz
SPECTRUM AMP 2.5×10
INTEGRAL AMP
REMARKS

FIG. 10 PROTON NMR SPECTRUM OF THE DIMETHYL ESTER OF 2, 5- -BICYCLO [2.2.2] OCTADIENE–2,3–DICARBOXYLIC ACID

79–06–157–5

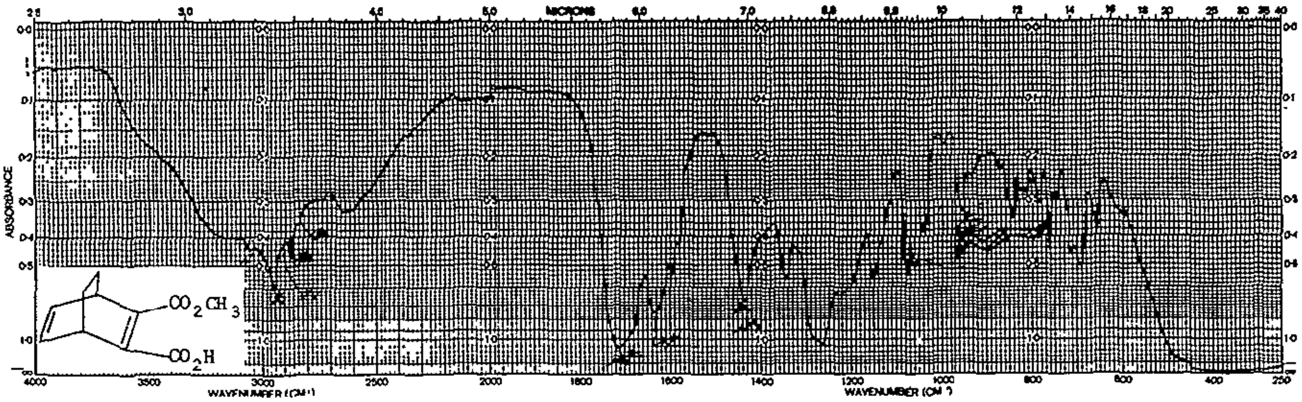


FIG 11 INFRARED SPECTRUM OF THE MONOMETHYL ESTER OF 2,5–BICYCLO [2.2.2] OCTADIENE–2,3–DICARBOXYLIC ACID

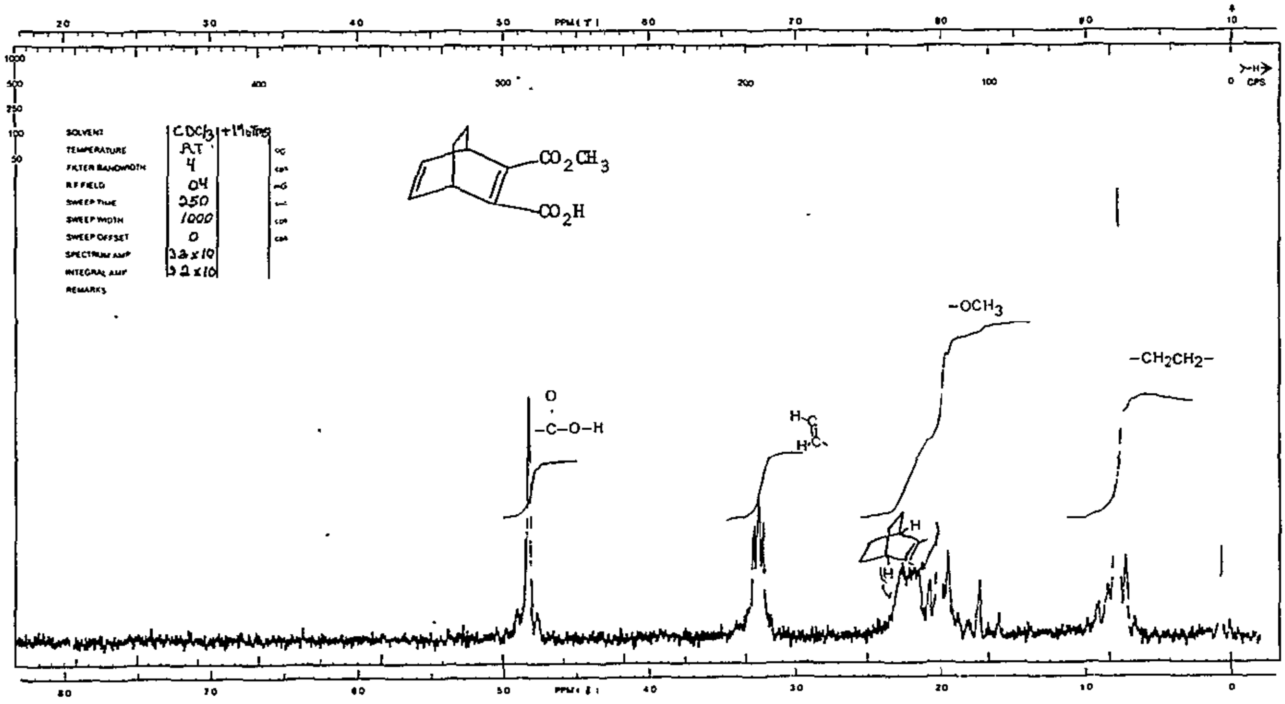


FIG 12 PROTON NMR SPECTRUM OF THE MONOMETHYL ESTER OF 2,5–BICYCLO [2.2.2] OCTADIENE–2,3–DICARBOXYLIC ACID

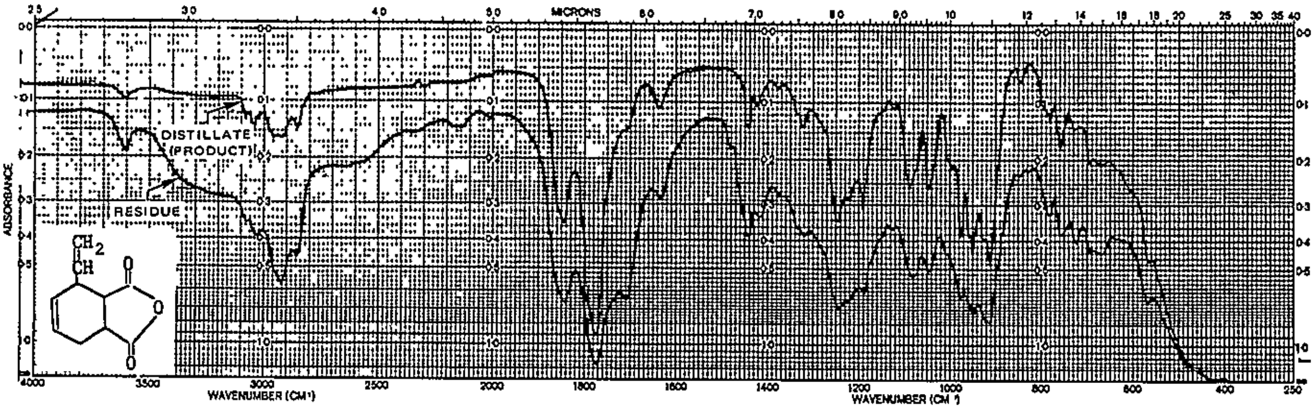


FIG. 13 INFRARED SPECTRUM OF 3–VINYL–4–CYCLOHEXENE–1,2–DICARBOXYLIC ACID ANHYDRIDE

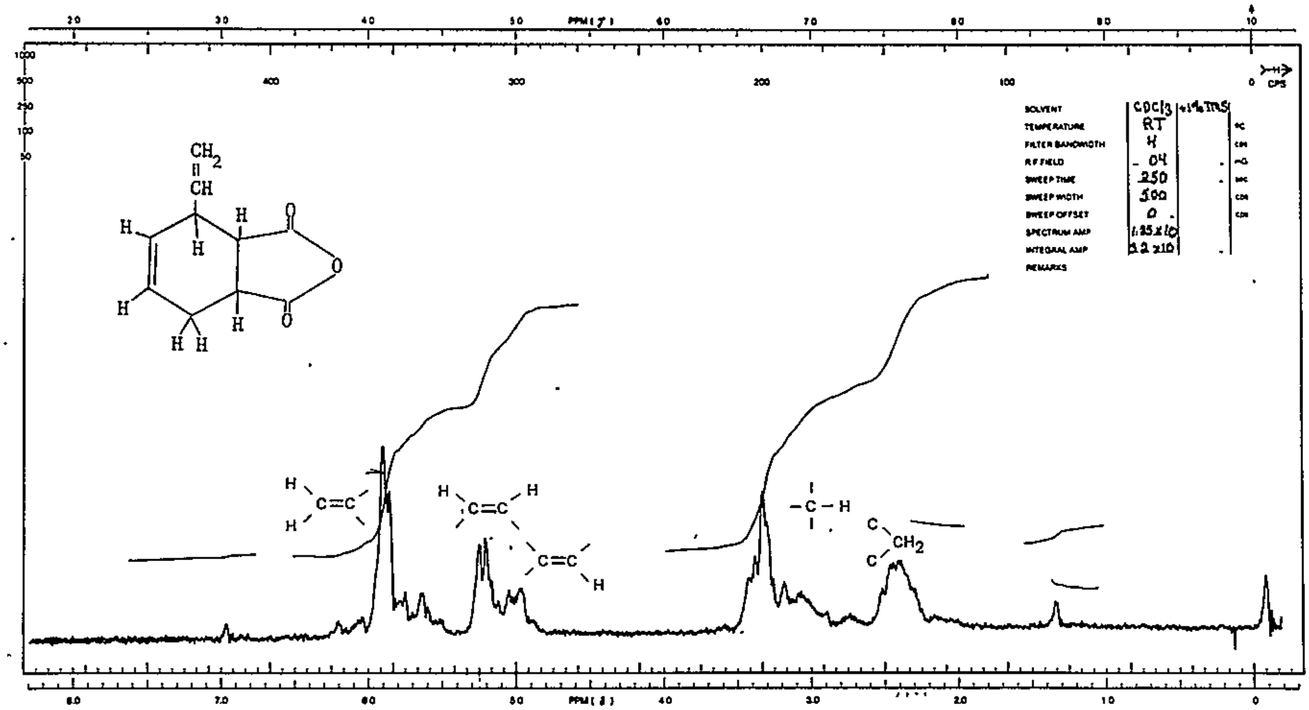


FIG. 14 PROTON NMR SPECTRUM OF 3–VINYL–4–CYCLOHEXENE–1,2–DICARBOXYLIC ACID ANHYDRIDE

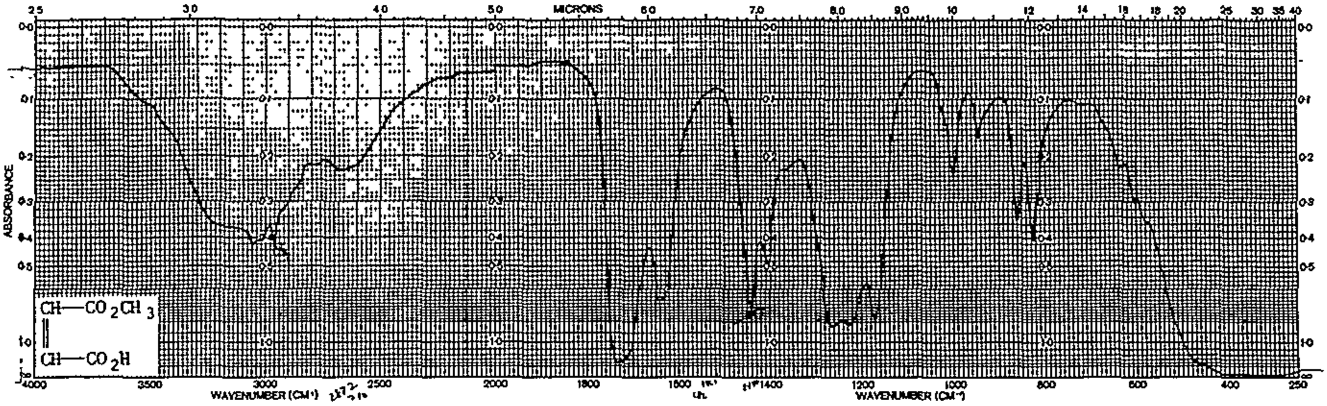


FIG. 15 INFRARED SPECTRUM OF THE MONOMETHYL ESTER OF MALEIC ACID

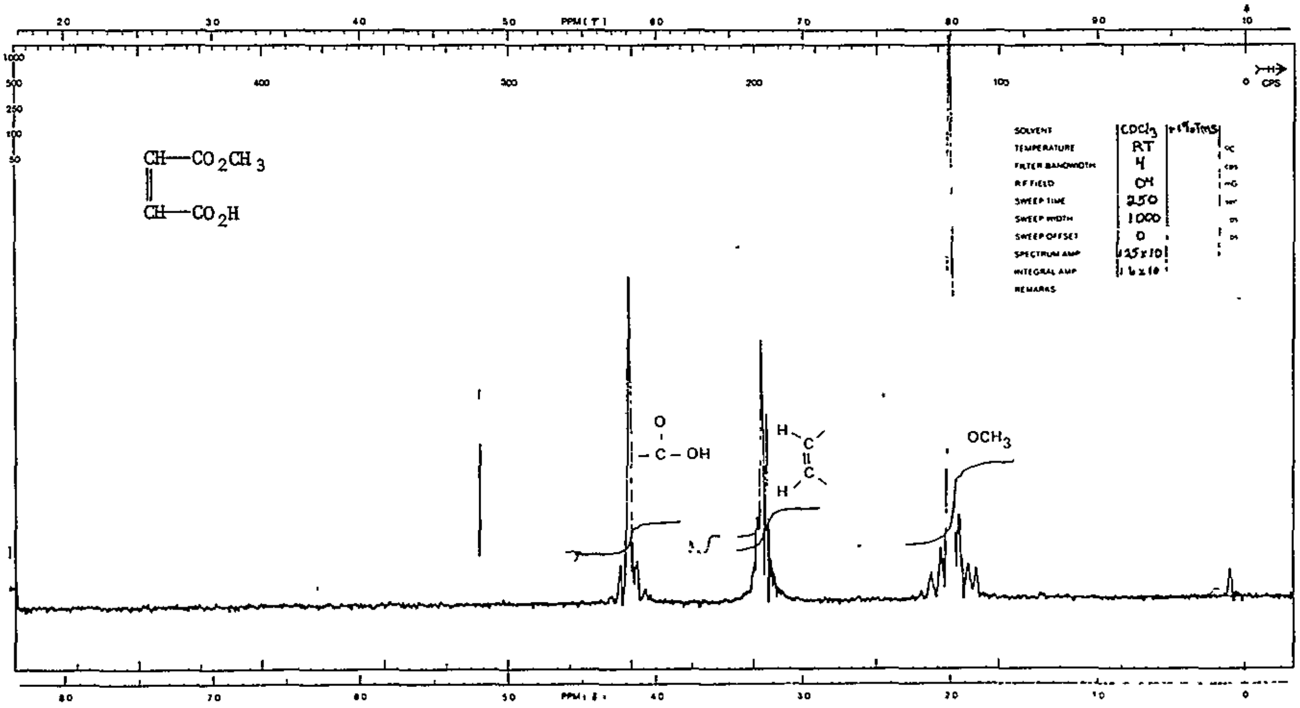


FIG. 16 PROTON NMR SPECTRUM OF THE MONOMETHYL ESTER OF MALEIC ACID

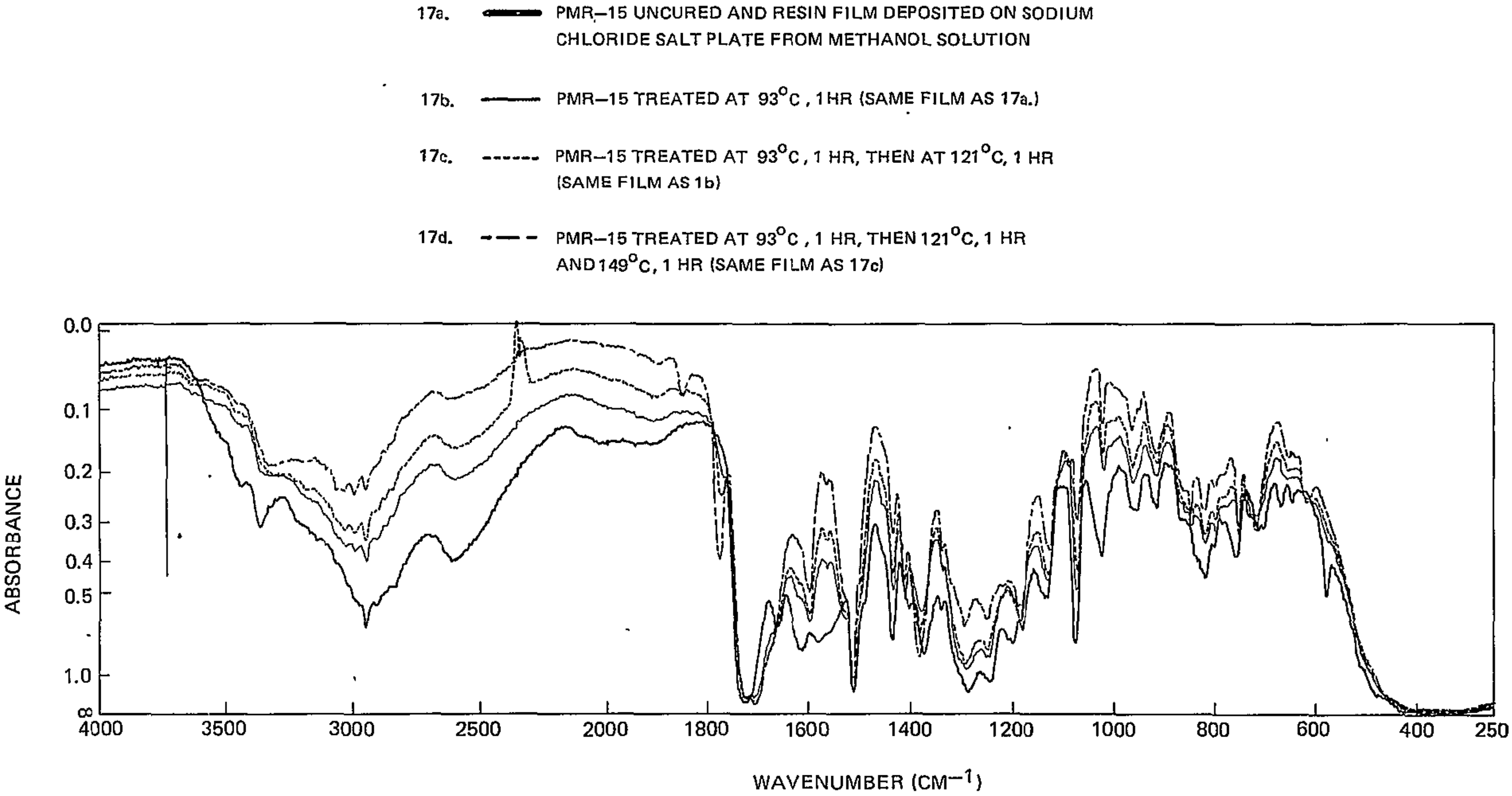


FIG. 17 INFRARED SPECTRA OF PMR–15 POLYIMIDE RESIN

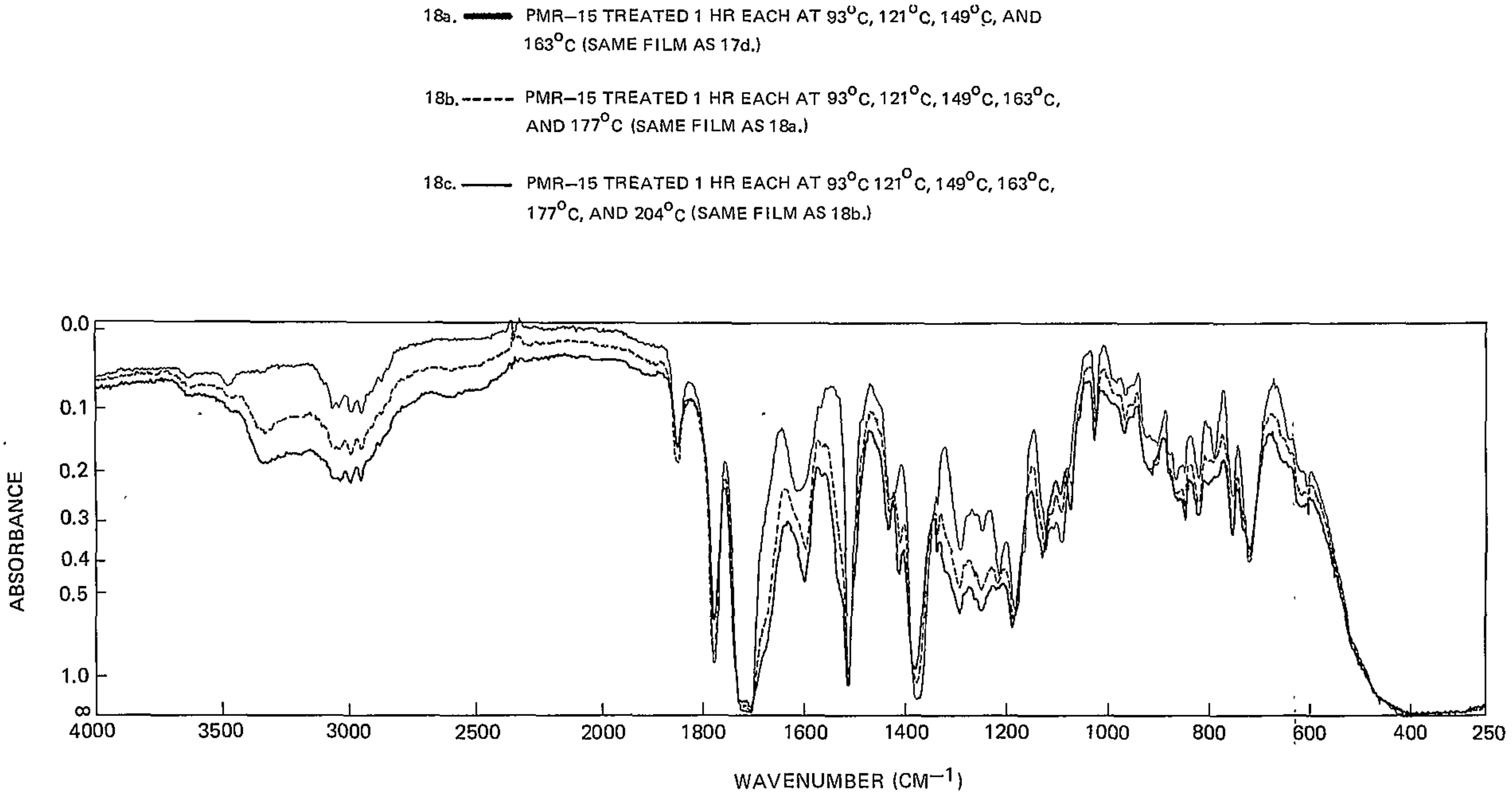


FIG. 18 INFRARED SPECTRA OF PMR–15 POLYIMIDE RESIN

19a. ——— PMR–15 TREATED 1 HR EACH AT 93°C, 121°C, 149°C, 163°C, 177°C, 204°C, AND 232°C, (SAME FILM AS 18c)

19b. - - - - - PMR–15 TREATED 1 HR EACH AT 93°C, 121°C, 149°C, 163°C, 177°C, 204°C, 232°C, AND 316°C (SAME FILM AS 19a)

19c. –·–·– PMR–15 TREATED 1 HR EACH AT 93°C, 121°C, 149°C, 163°C, 177°C, 204°C, 232°C, 316°C, AND FINALLY FOR 16 HRS AT 316°C (SAME FILM AS 19b)

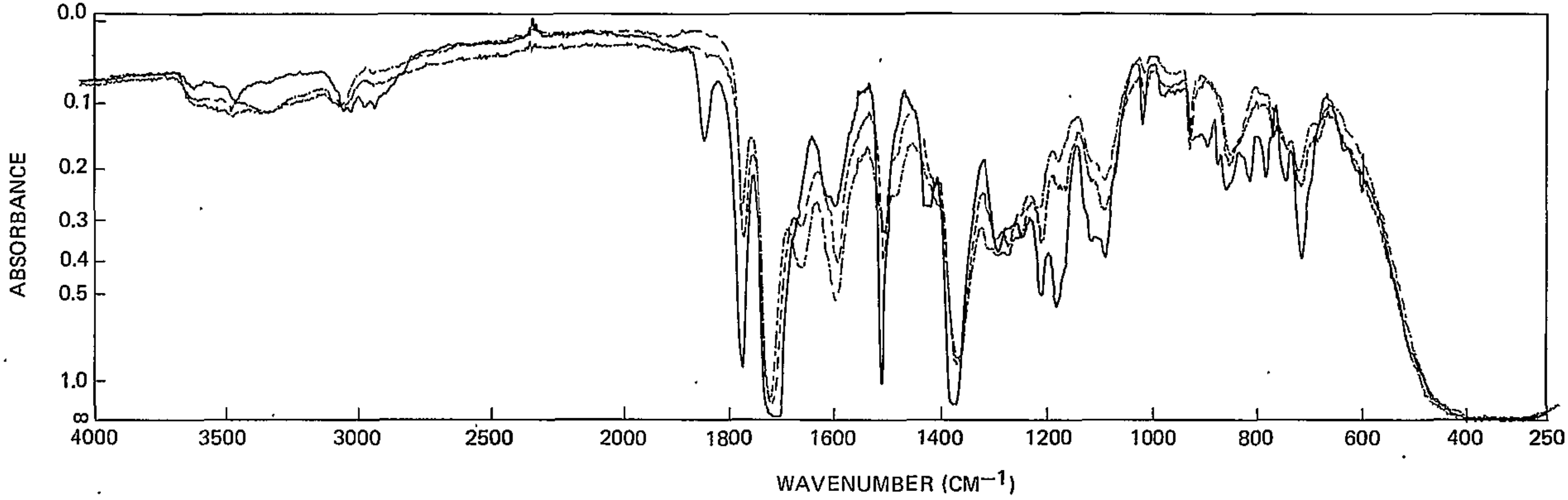


FIG. 19 INFRARED SPECTRA OF PMR–15 POLYIMIDE RESIN

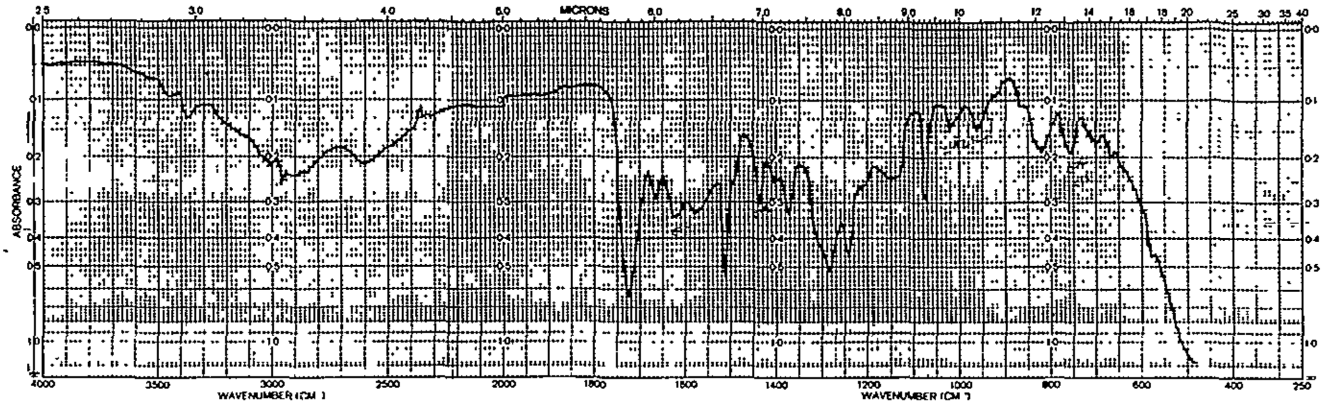


FIG. 20 INFRARED SPECTRUM OF UNCURED ITE–PMR–14 FILM

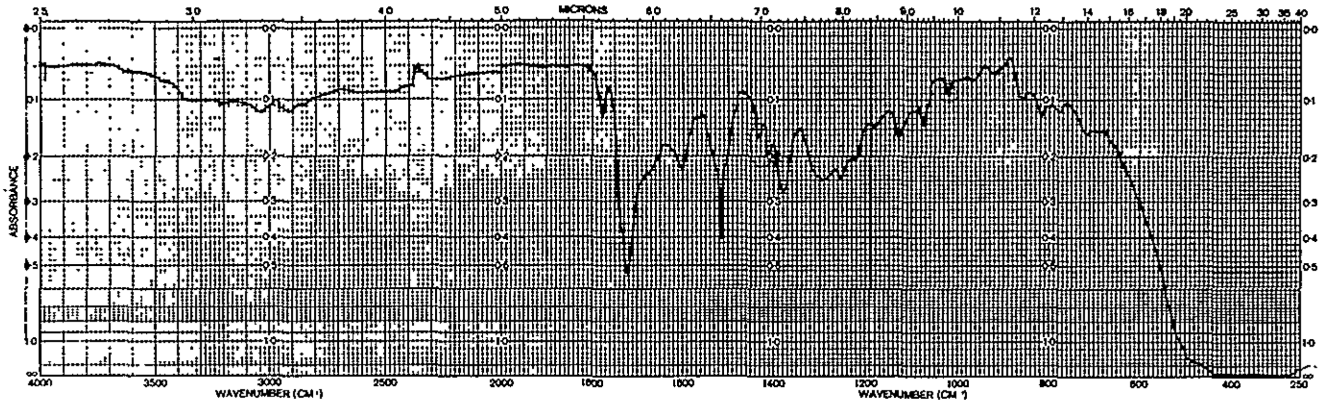


FIG. 21 INFRARED SPECTRUM OF ITE–PMR–14 FILM, HEAT AT 93°C FOR 1/2 HR.

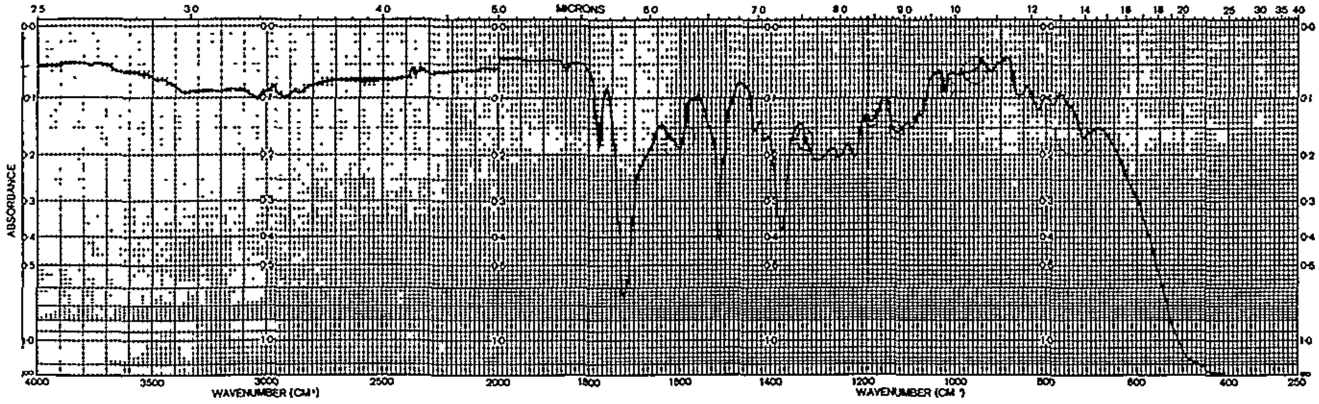


FIG. 22 INFRARED SPECTRUM OF ITE–PMR–14 FILM, 93°C, 144°C, 1/2 HR. EACH

79–06–157–10

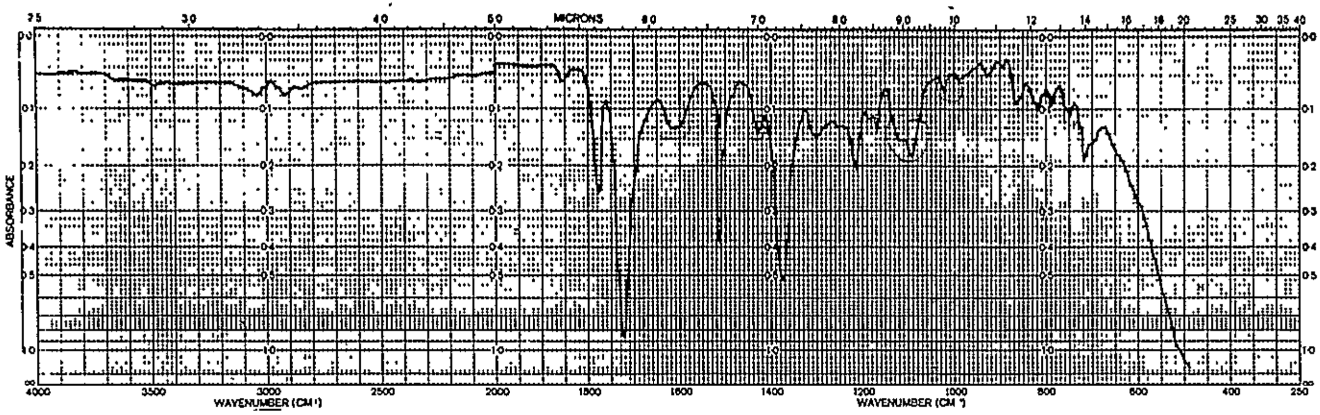


FIG. 23 INFRARED SPECTRUM OF ITE–PMR–14 FILM, HEATED AT 93, 149, 177°C, 1/2 HR. EACH

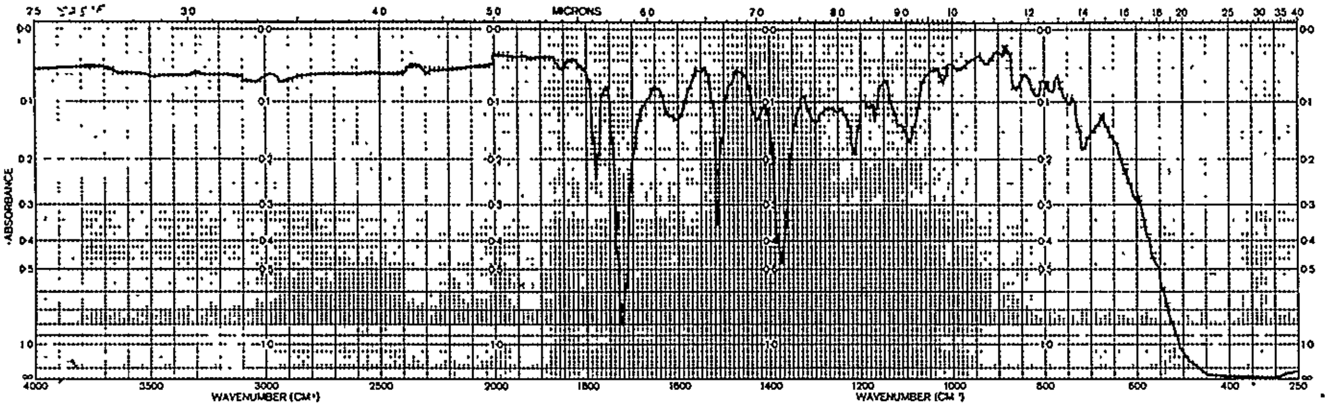


FIG. 24 INFRARED SPECTRUM OF ITE–PMR–14 FILM, HEATED AT 93, 149, 177, 204°C, 1/2 HR. EACH

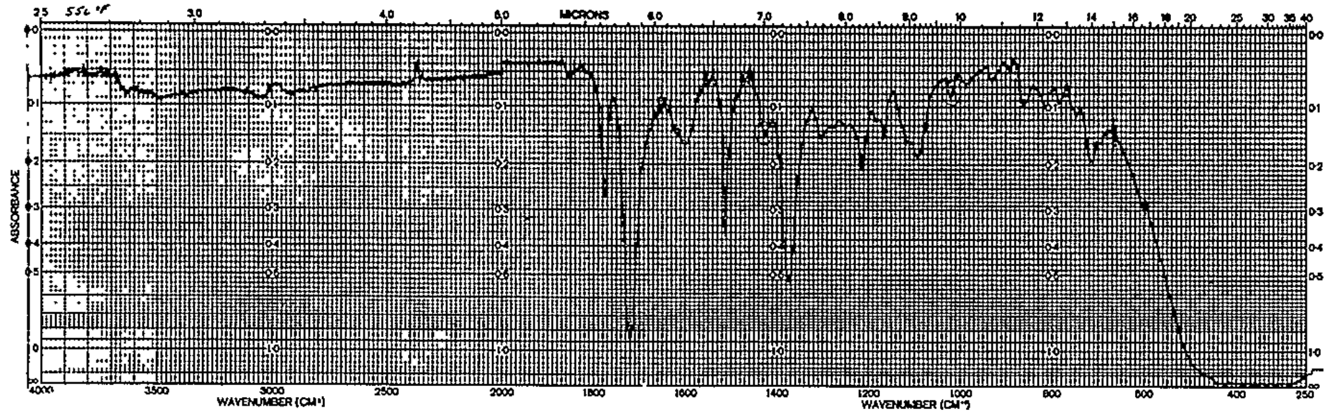


FIG. 25 INFRARED SPECTRUM OF ITE–PMR–14 FILM, HEATED AT 93, 149, 177, 204, 232°C, 1/2 HR. EACH

79–06–157–11

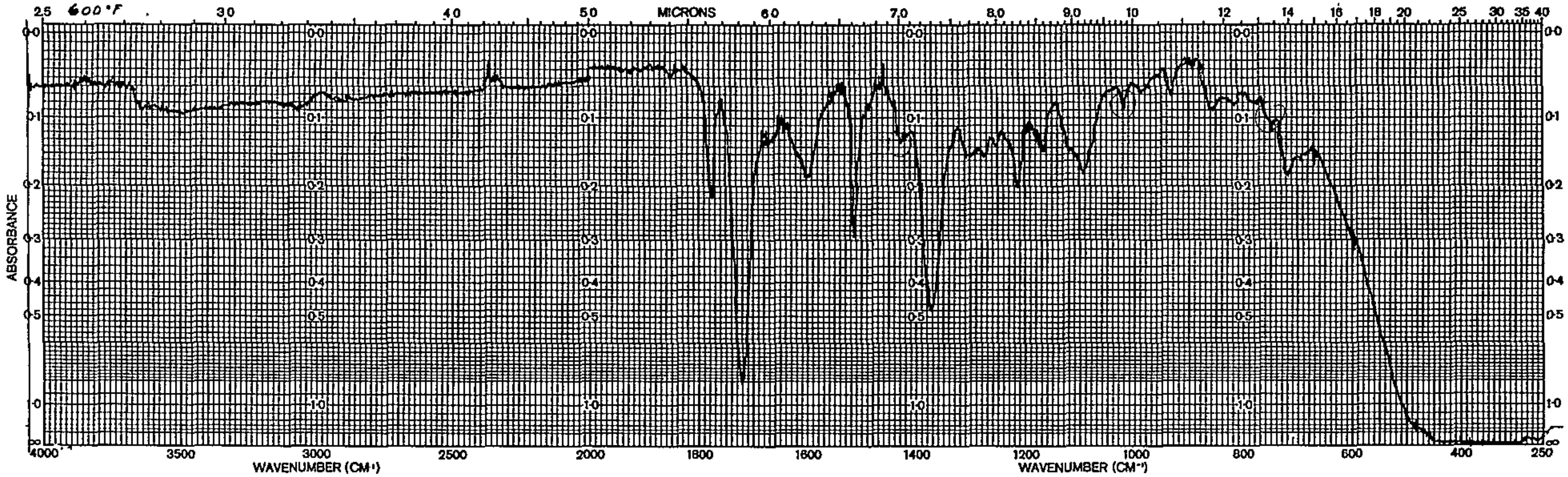


FIG. 26 INFRARED SPECTRUM OF ITE–PMR–14 FILM HEATED AT 93, 149, 177, 204, 232, 260°C, 1/2 HR. EACH

78–12–40–9

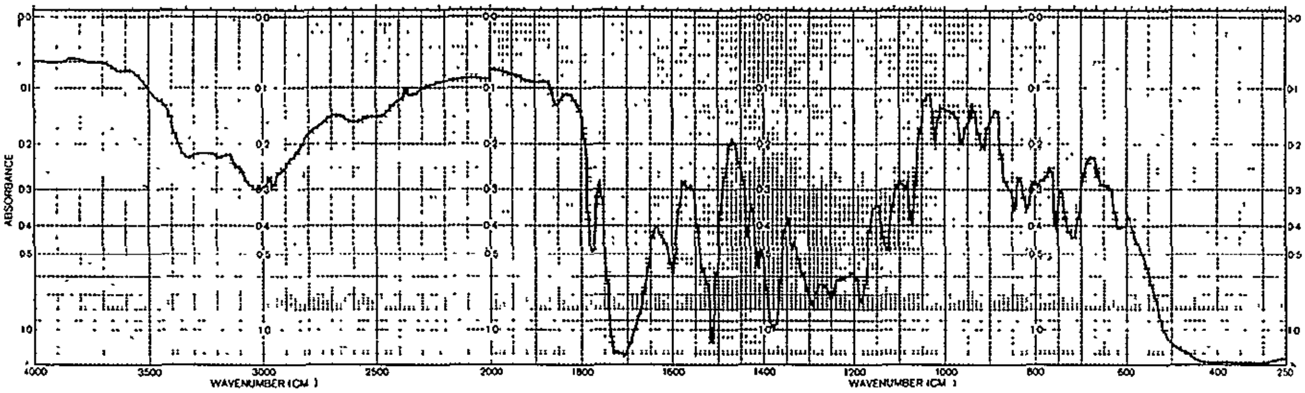


FIG. 27 INFRARED SPECTRUM OF PMR–15 FILM HEATED AT 93°C, 149°C, 1/2 HR. EACH

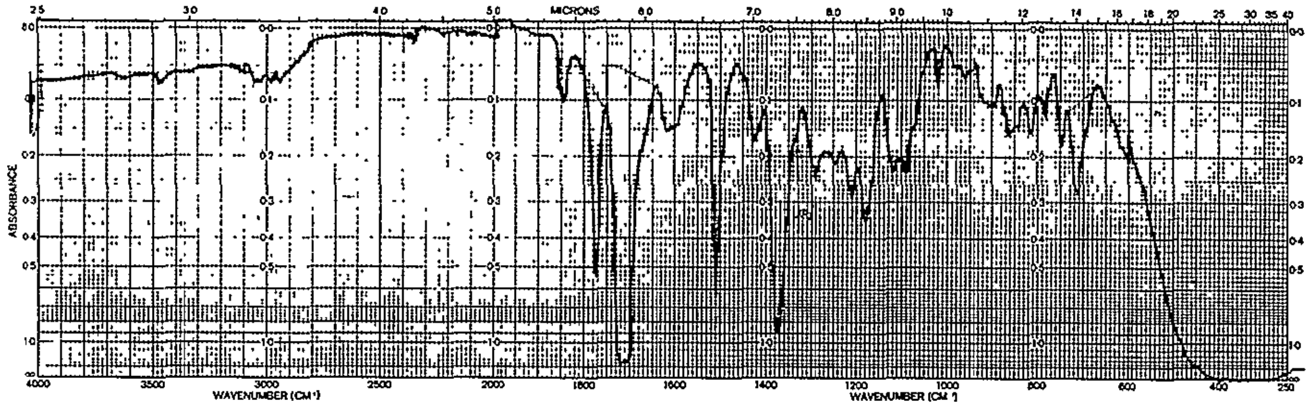


FIG. 28 INFRARED SPECTRUM OF PMR–15 FILM HEATED AT 204°C, 1 HR.

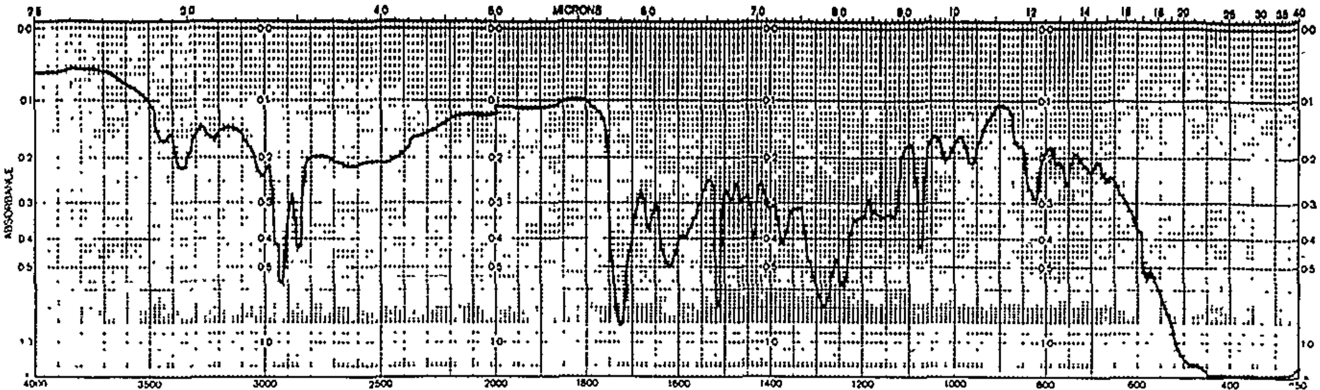


FIG. 29 INFRARED SPECTRUM OF UNCURED ITE–PMR–14 FILM CONTAINING DIMETHYLDODECYLAMINE (DMDA)

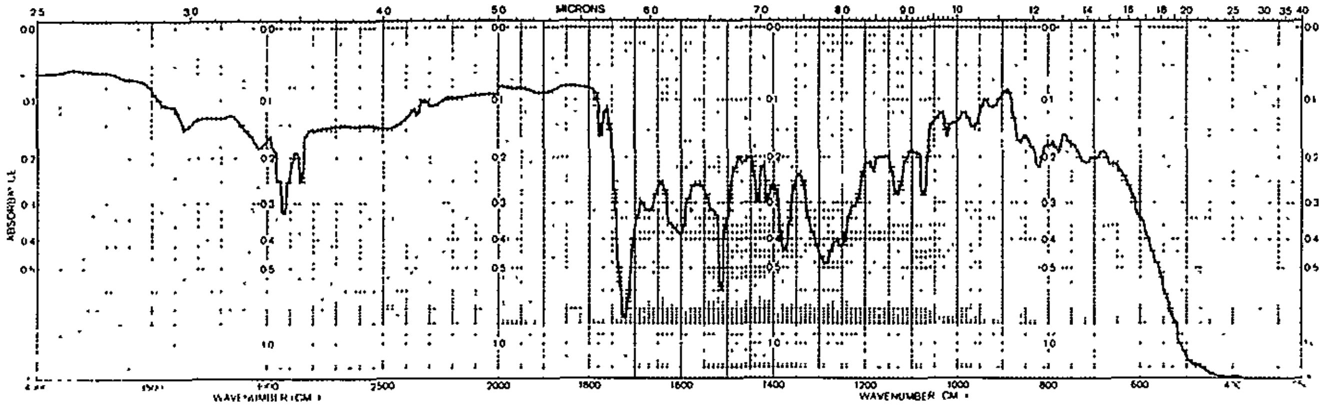


FIG. 30 INFRARED SPECTRUM OF ITE–PMR–14–DMDA FILM HEATED AT 93C° 1/2 HR.

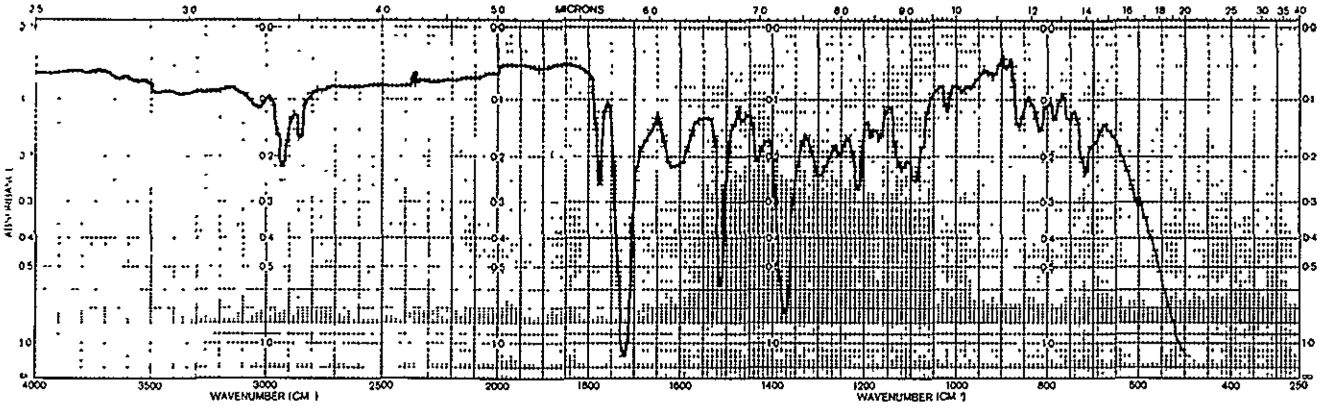


FIG. 31 INFRARED SPECTRUM OF ITE–PMR–14–DMDA FILM HEATED AT 93,149C°, 1/2 HR. EACH

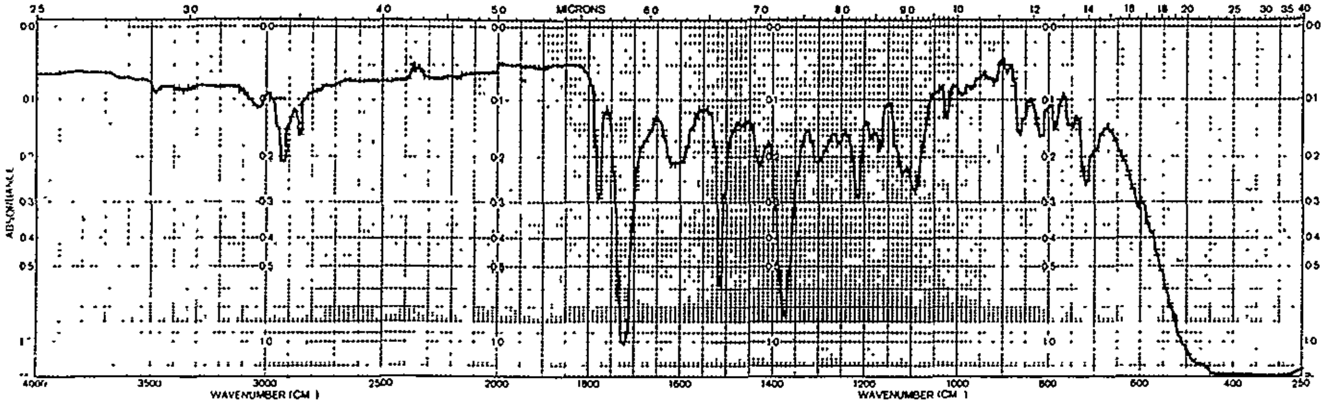


FIG. 32 INFRARED SPECTRUM OF ITE–PMR–14–DMDA FILM HEATED AT 93,149,177C°, 1/2 HR. EACH

79–06–157–12

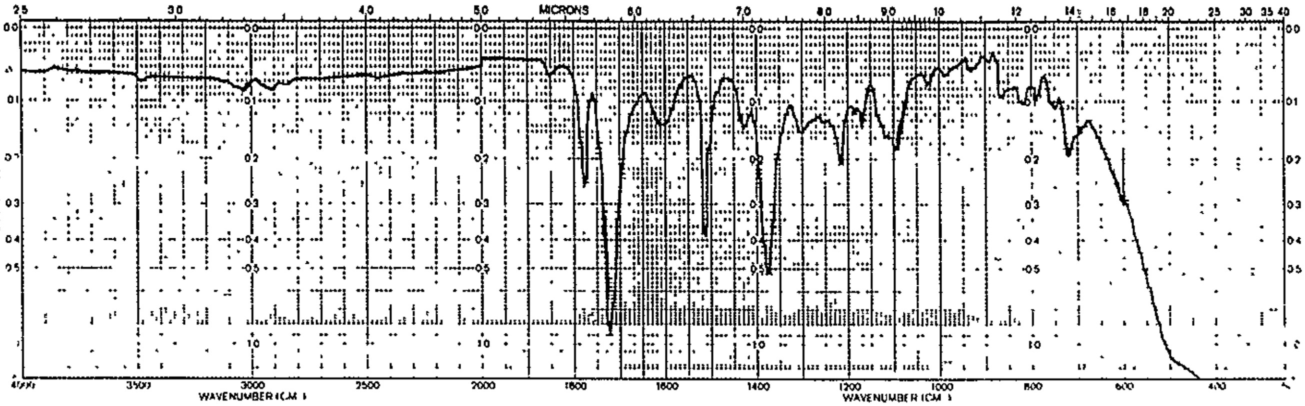


FIG. 33 INFRARED SPECTRUM OF ITE–PMR–14–DMDA FILM HEATED AT 93, 149, 177, 204°C, 1/2 HR. EACH

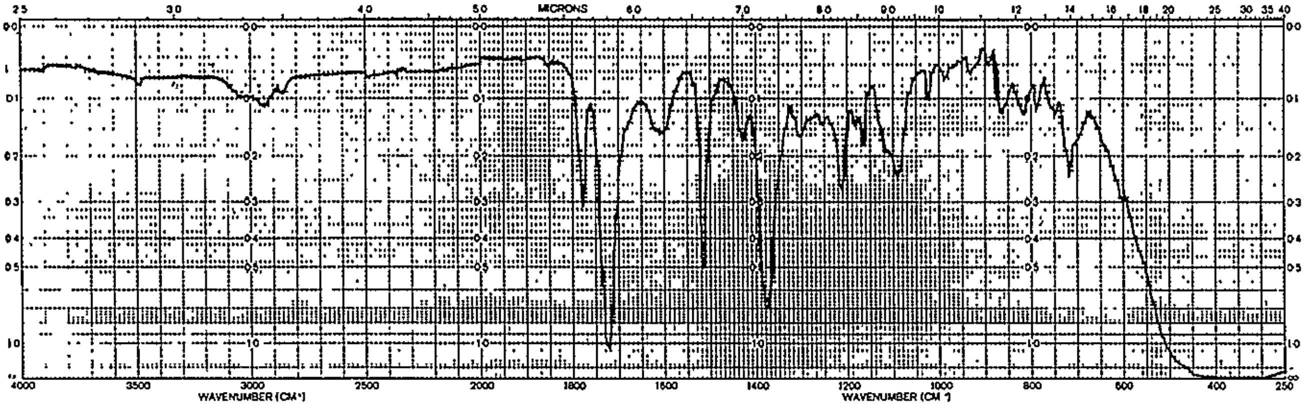


FIG. 34 INFRARED SPECTRUM OF ITE–PMR–14–DMDA FILM HEATED AT 93, 149, 177, 204, 273°C, 1/2 HR. EACH

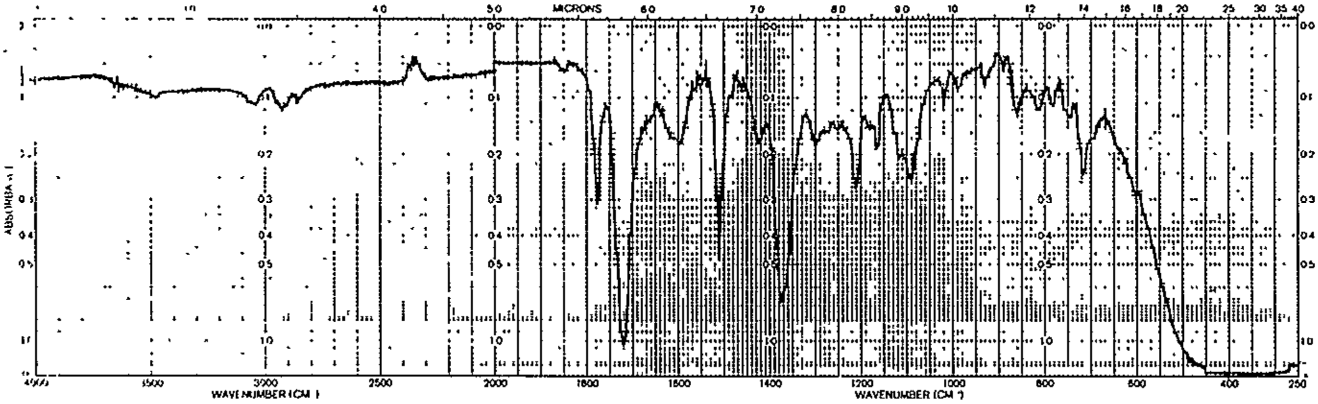


FIG. 35 INFRARED SPECTRUM OF ITE–PMR–14–DMDA FILM HEATED AT 93, 149, 177, 204, 273, 288°C, 1/2 HR. EACH

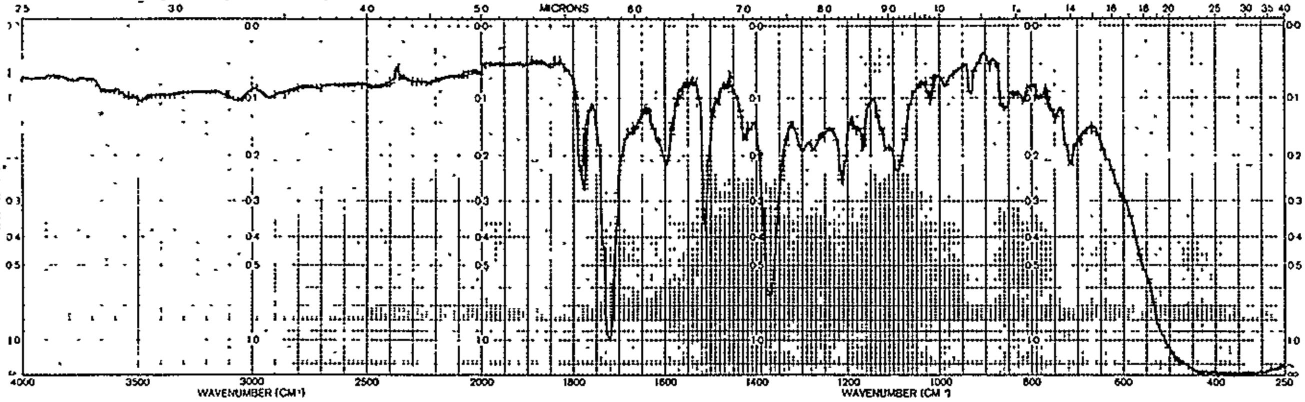


FIG. 36 INFRARED SPECTRUM OF ITE–PMR–14–DMDA FILM HEATED AT 93, 149, 177, 204, 273, 288, 316°C, 1/2 HR. EACH

79–06–157–13

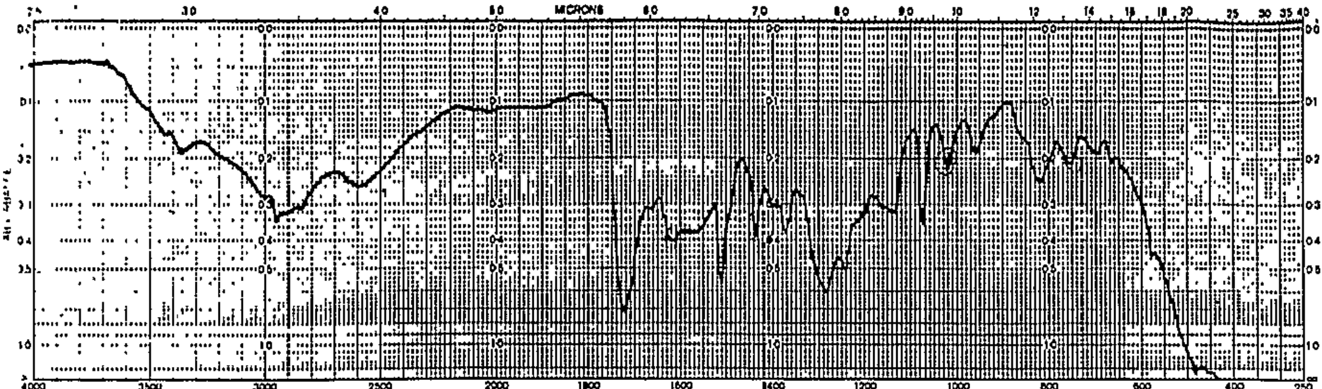


FIG. 37 INFRARED SPECTRUM OF UNCURED ITE–PMR–14 FILM CONTAINING CUMENE HYDROPEROXIDE (CHP)

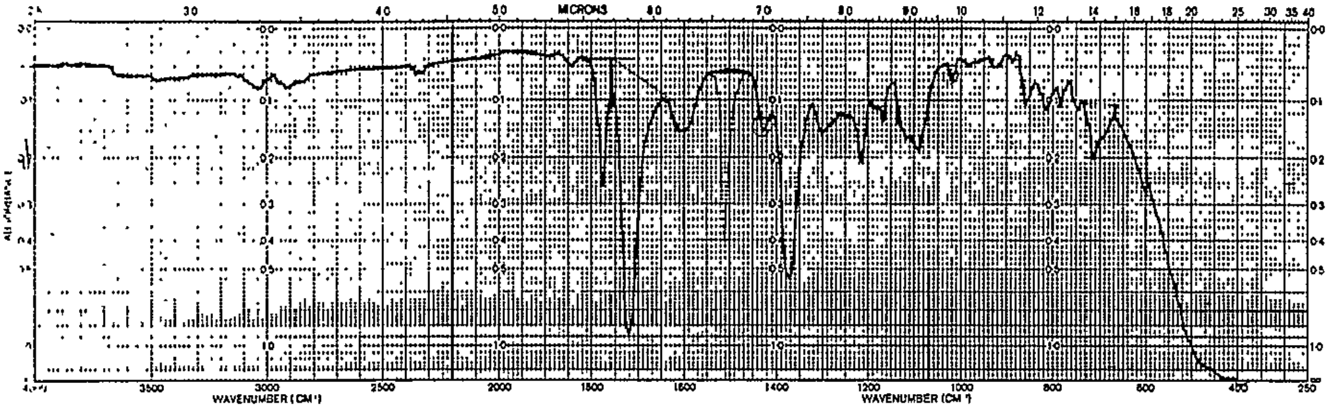


FIG. 38 INFRARED SPECTRUM OF ITE–PMR–14–CHP FILM HEATED AT 204°C, 1 HR.

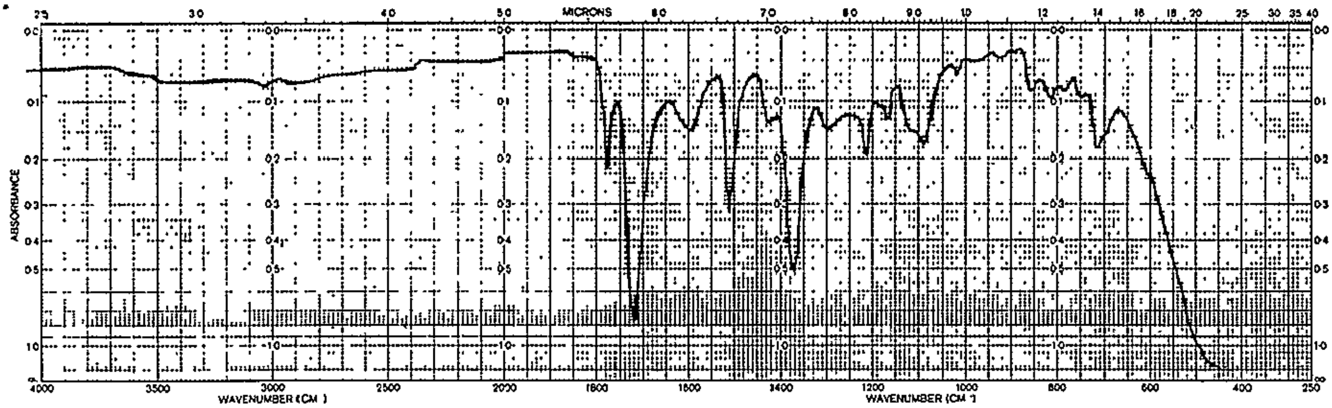


FIG. 39 INFRARED SPECTRUM OF ITE–PMR–14–CHP FILM HEATED AT 204, 232°C, 1 HR. EACH

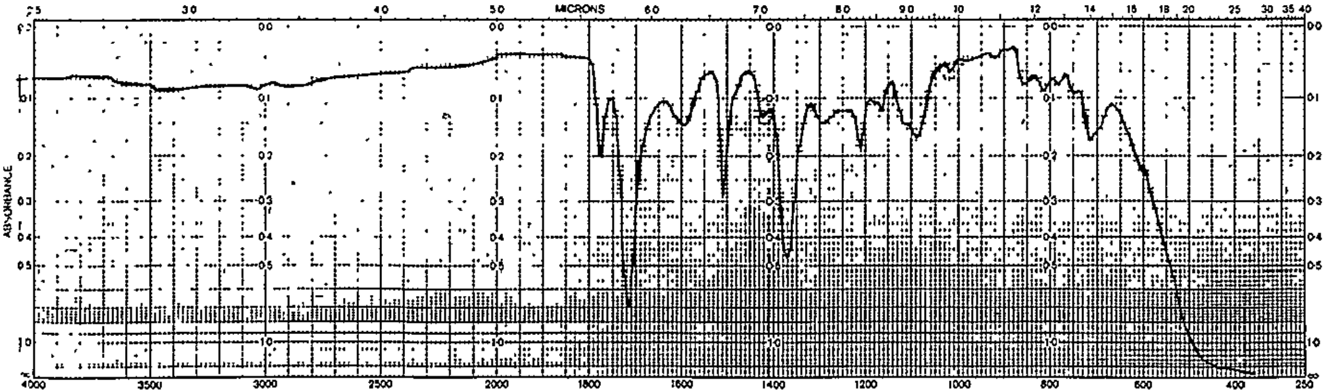


FIG. 40 INFRARED SPECTRUM OF ITE–PMR–14–CHP FILM HEATED AT 204(1 HR.), 232(1 HR.), 260°C, 1/2 HR.

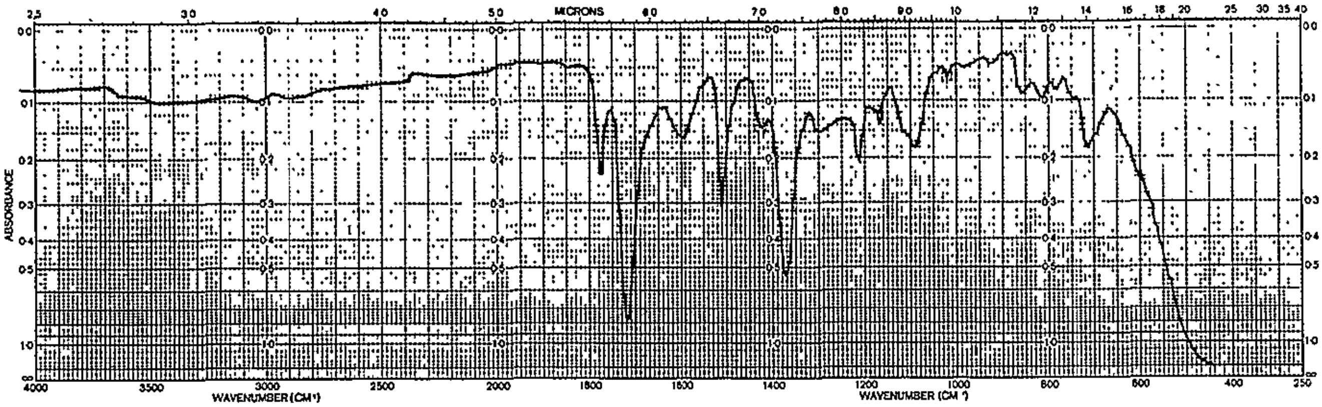


FIG. 41 INFRARED SPECTRUM OF ITE–PMR–14 CHP FILM HEATED AT 204(1 HR.),232(1 HR.), 260(1/2 HR.),316C°,(1/2 HR.)·

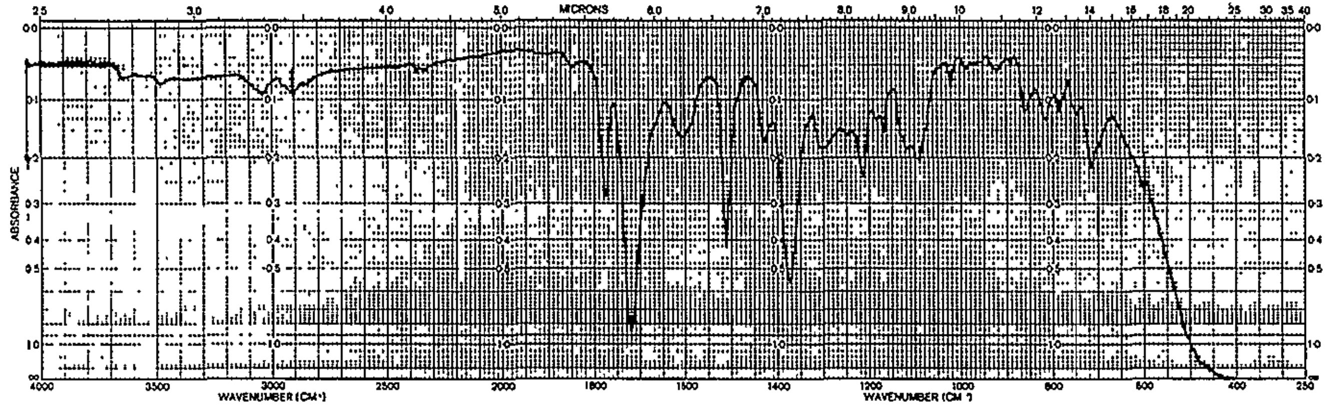


FIG. 42 INFRARED SPECTRUM OF ITE–PMR–14 CHP FILM HEATED AT 204(1 HR.),232 (1 HR.), 260 (1/2 HR.), 316C°(1 HR.)

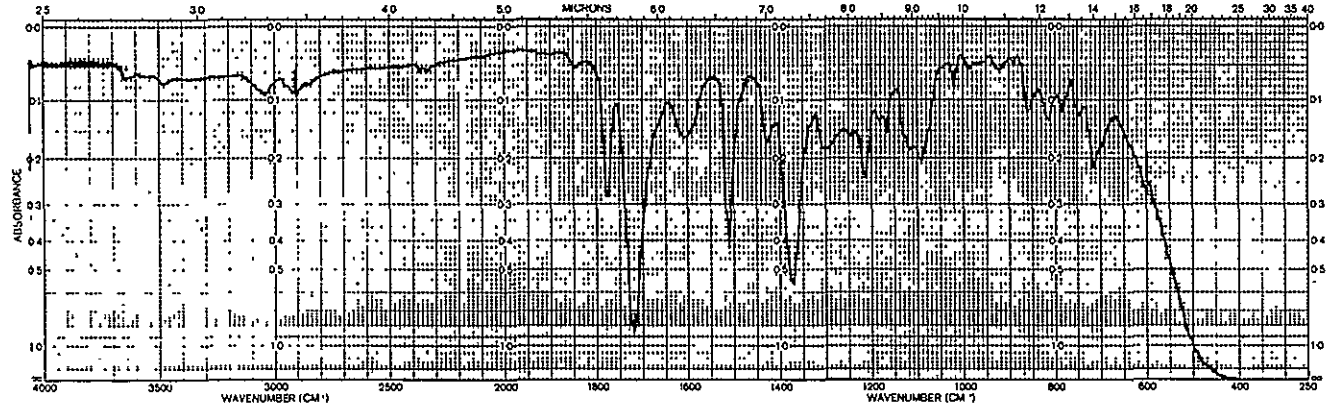


FIG. 43 INFRARED SPECTRUM OF ITE–PMR–14 t-BHP FILM HEATED AT 204C° FOR 1 HR.

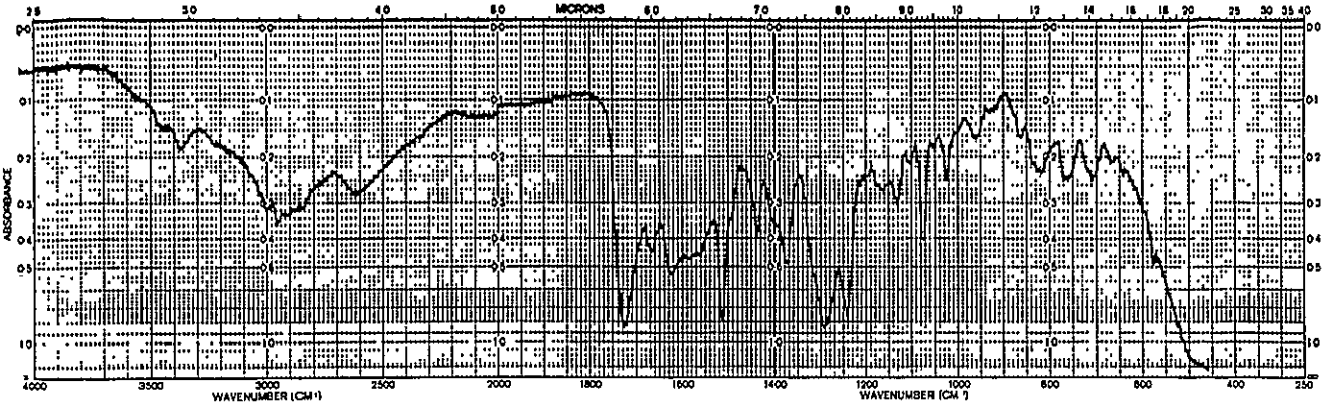


FIG. 44 INFRARED SPECTRUM OF UNCURED NDE–PMR–15 FILM

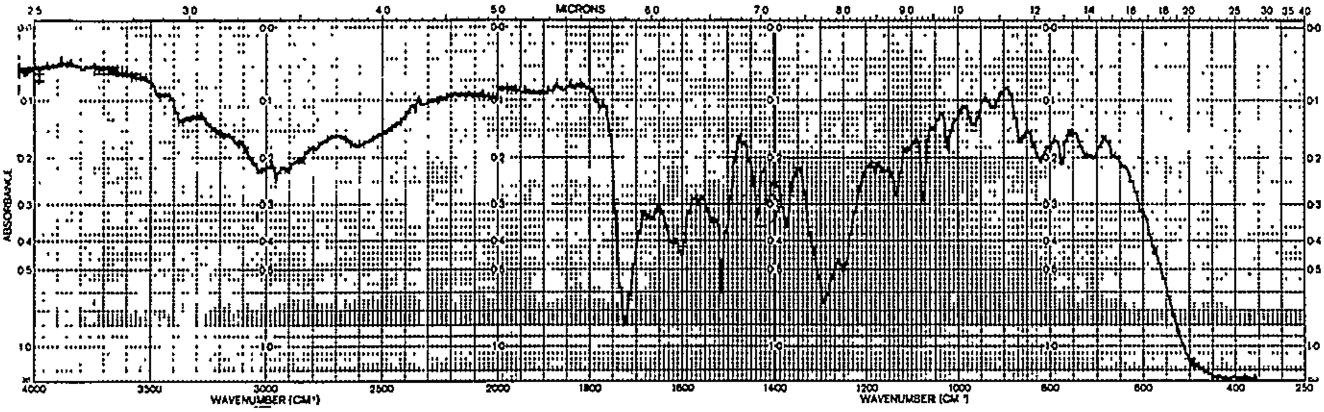


FIG. 45 INFRARED SPECTRUM OF NDE–PMR–15 FILM HEATED AT 93°C FOR 1/2 HR.

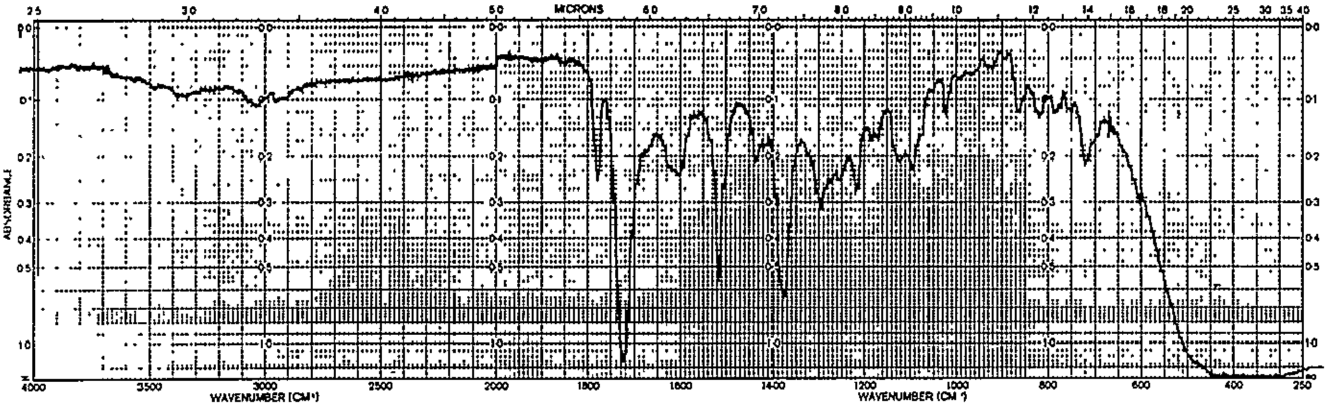


FIG. 46 INFRARED SPECTRUM OF NDE–PMR–15 FILM HEATED AT 93, 149°C, 1/2 HR. EACH

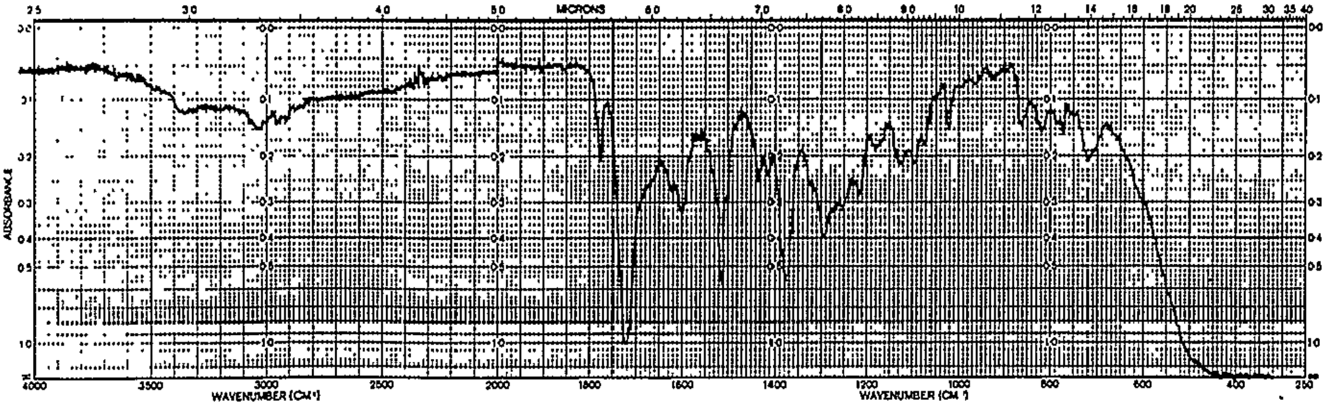


FIG. 47 INFRARED SPECTRUM OF NDE–PMR–15 FILM HEATED AT 93, 149, 177°C, 1/2 HR. EACH

79–06–167–16

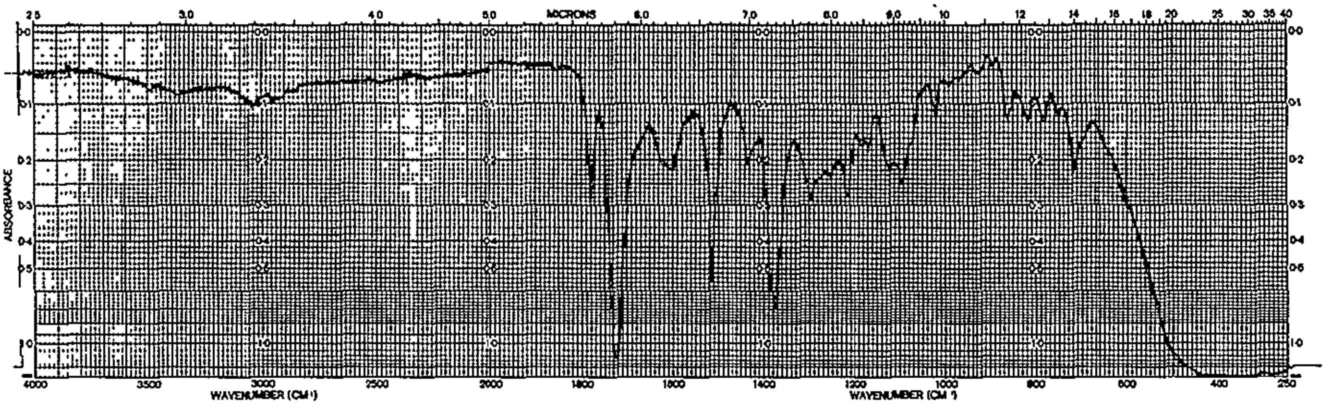


FIG. 48 INFRARED SPECTRUM OF NDE–PMR–15 FILM HEATED AT 93, 149, 177, 204°C, 1/2 HR. EACH

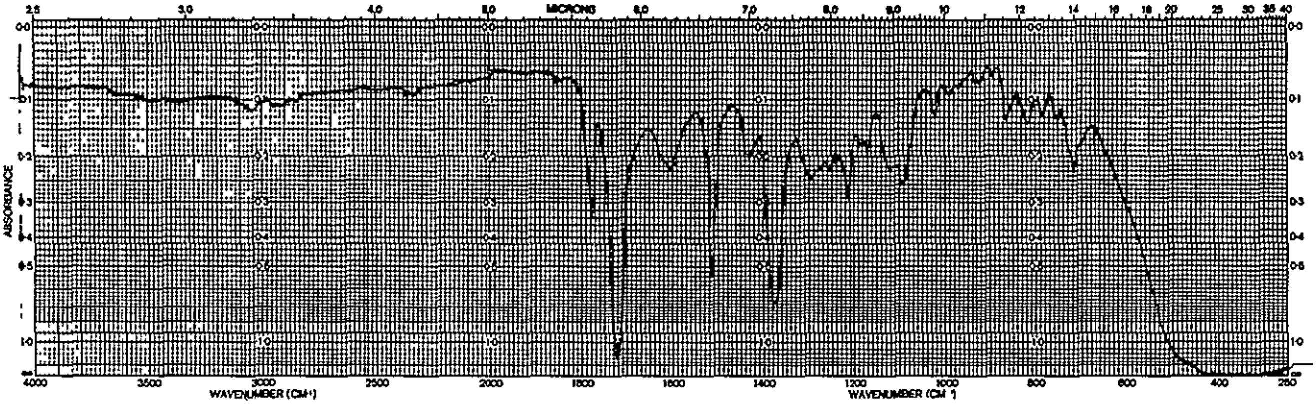


FIG. 49 INFRARED SPECTRUM OF NDE–PMR–15 FILM HEATED AT 93, 149, 177, 204, 232°C, 1/2 HR. EACH

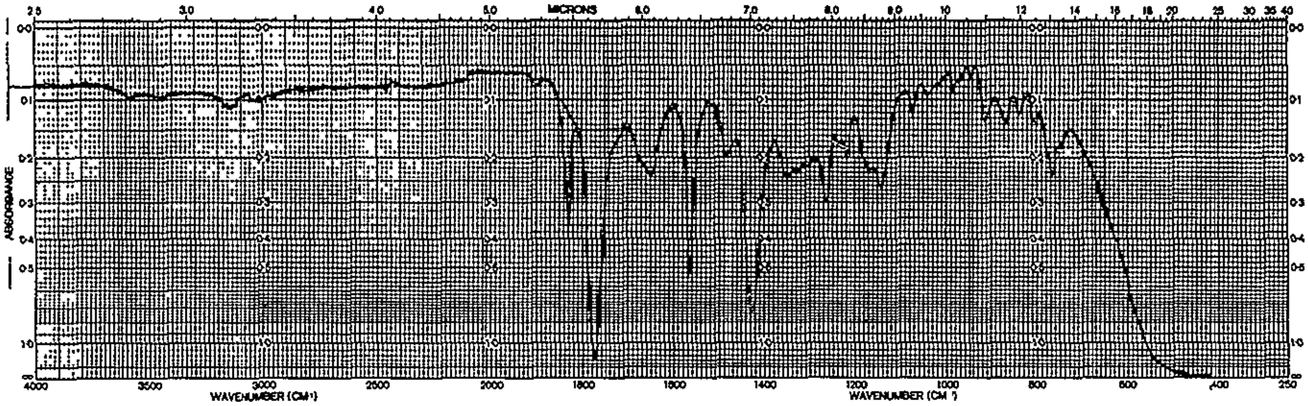


FIG. 50 INFRARED SPECTRUM OF NDE–PMR–15 FILM HEATED AT 93, 149, 177, 204, 232, 260°C, 1/2 HR. EACH

79–06–157–17

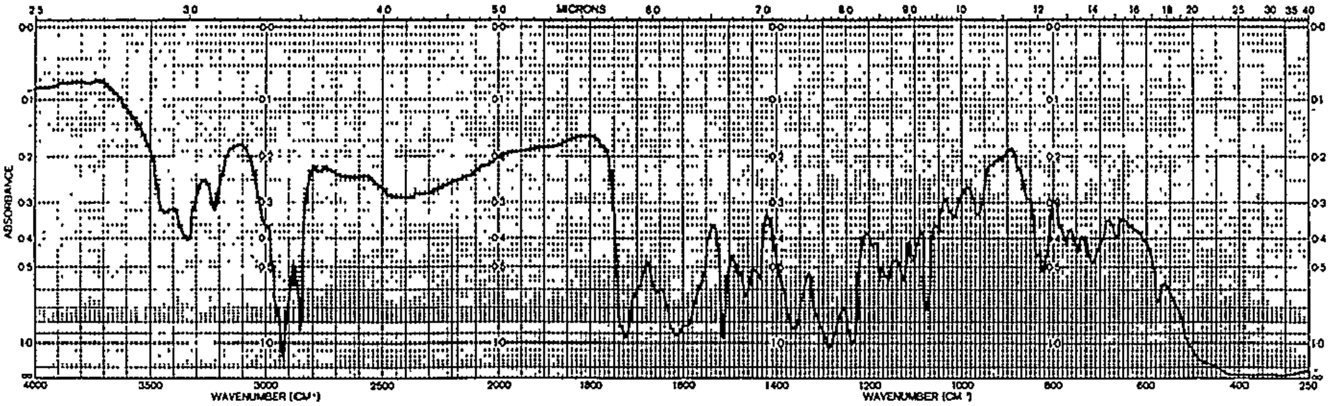


FIG. 51 INFRARED SPECTRUM OF UNCURED NDE–PMR–15 CONTAINING DIMETHYLDODECYLAMINE (DMDA)

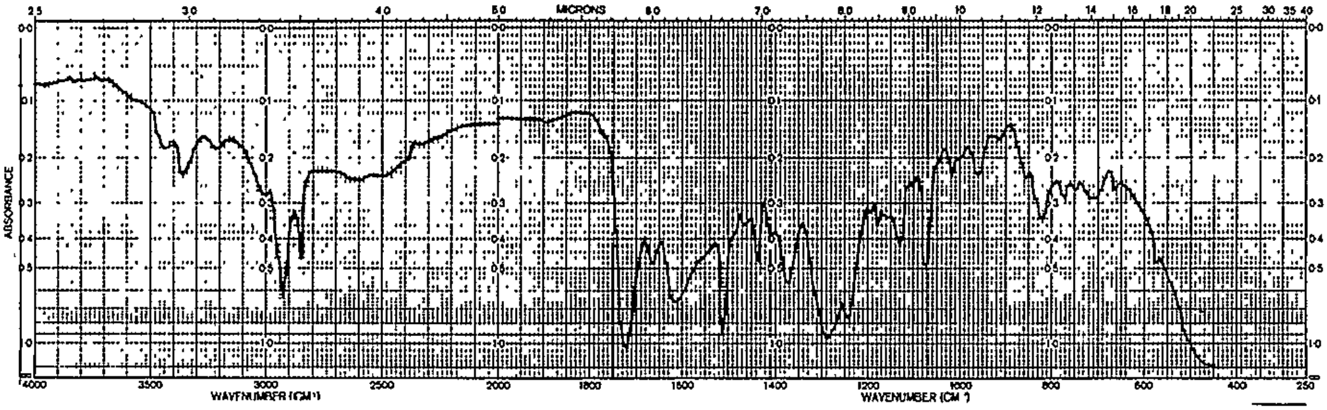


FIG. 52 INFRARED SPECTRUM OF NDE–PMR–15–DMDA FILM HEATED AT 93°C, 1/2 HR.

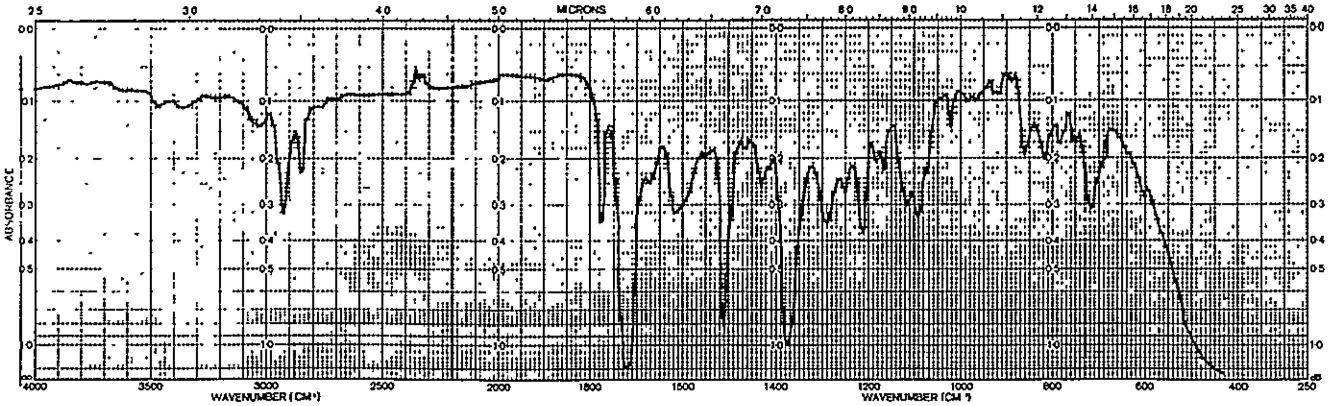


FIG. 53 INFRARED SPECTRUM OF NDE–PMR–15–DMDA FILM HEATED AT 93, 149°C, 1/2 HR. EACH

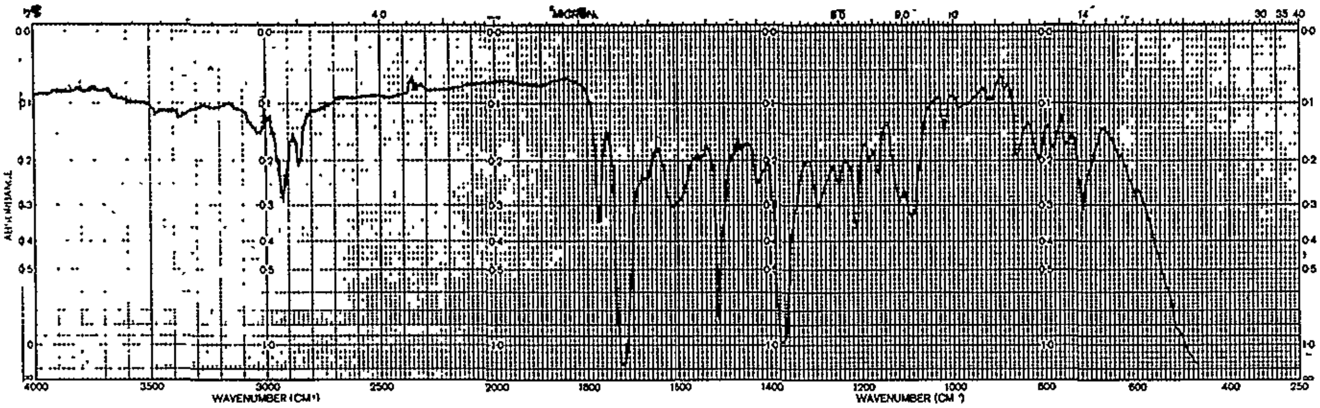


FIG. 54 INFRARED SPECTRUM OF NDE–PMR–15–DMDA FILM HEATED AT 93, 149, 177°C, 1/2 HR. EACH

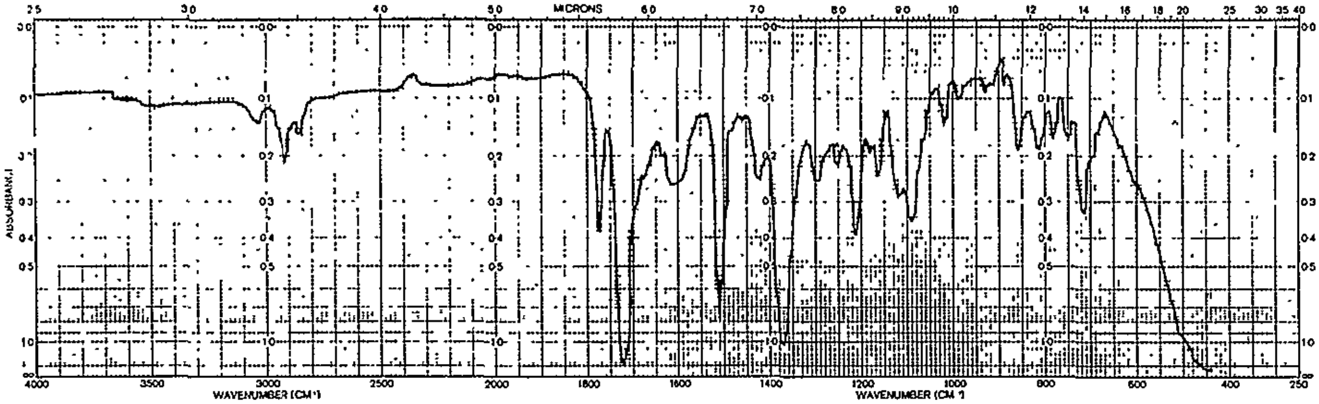


FIG. 55 INFRARED SPECTRUM OF NDE–PMR–15–DMDA FILM HEATED AT 93, 149, 177, 204°C, 1/2 HR. EACH

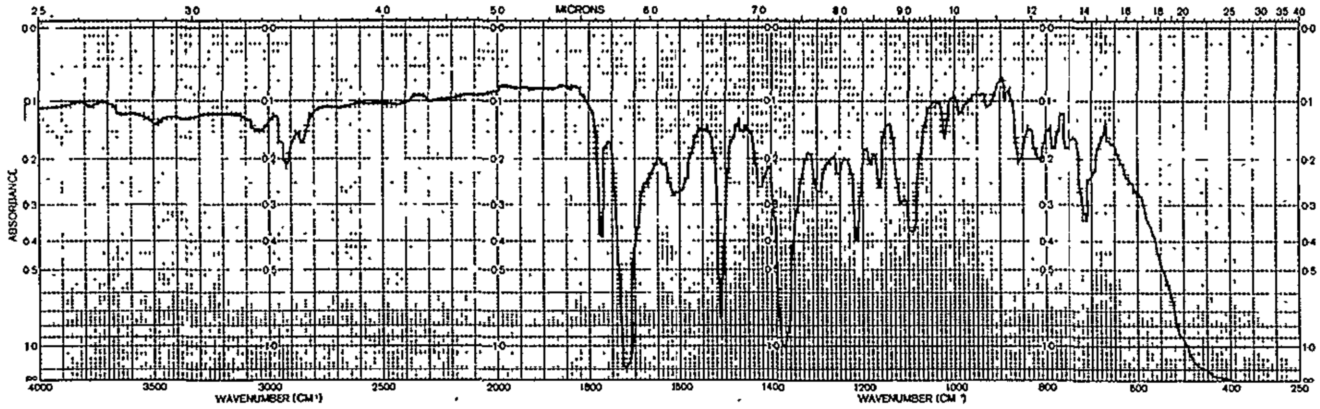


FIG. 56 INFRARED SPECTRUM OF NDE–PMR–15–DMDA FILM HEATED AT 93, 149, 177, 204, 232°C, 1/2 HR. EACH

79–06–167–19

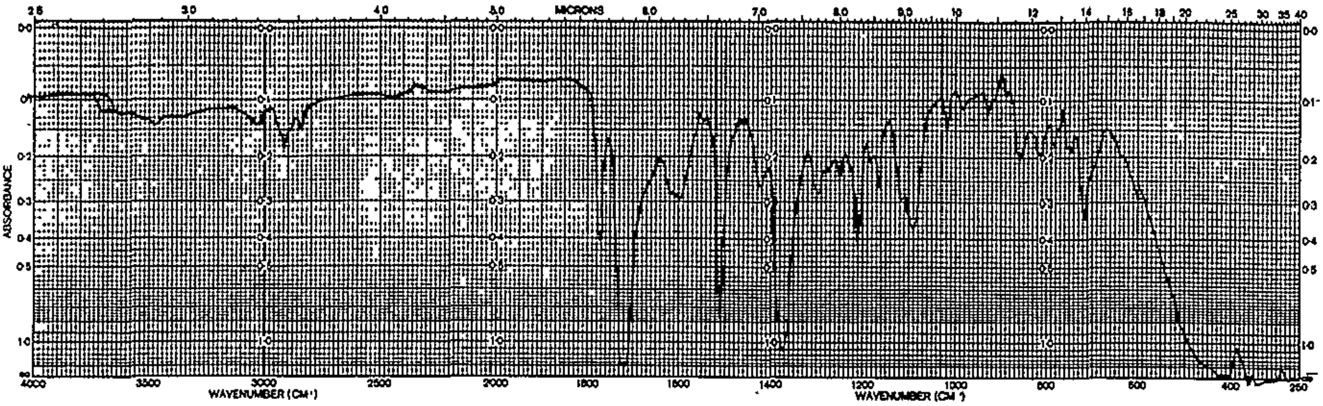


FIG. 57 INFRARED SPECTRUM OF NDE–PMR–15–DMDA FILM HEATED AT 93, 149, 177, 204, 232, 260°C, 1/2 HR. EACH

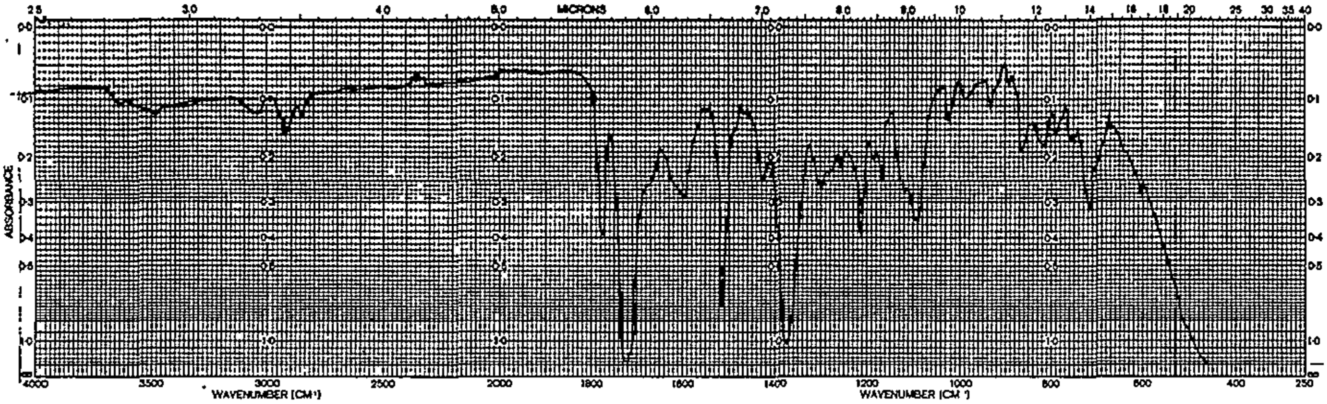


FIG. 58 INFRARED SPECTRUM OF NDE–PMR–15–DMDA FILM HEATED AT 93, 149, 177, 204, 232, 260, 288°C, 1/2 HR. EACH

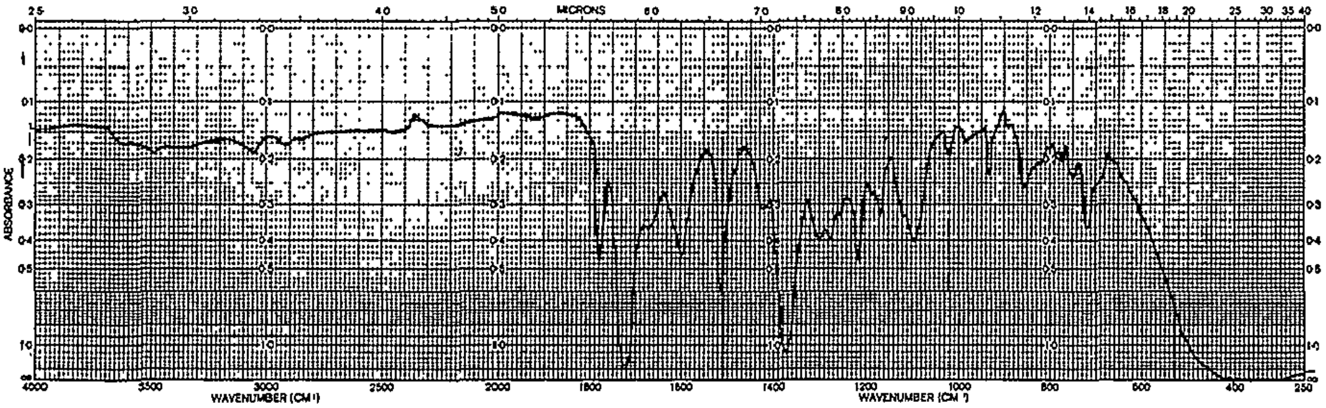


FIG. 59 INFRARED SPECTRUM OF NDE–PMR–15–DMDA FILM HEATED AT 93, 149, 177, 204, 232, 260, 288, 316°C, 1/2 HR. EACH

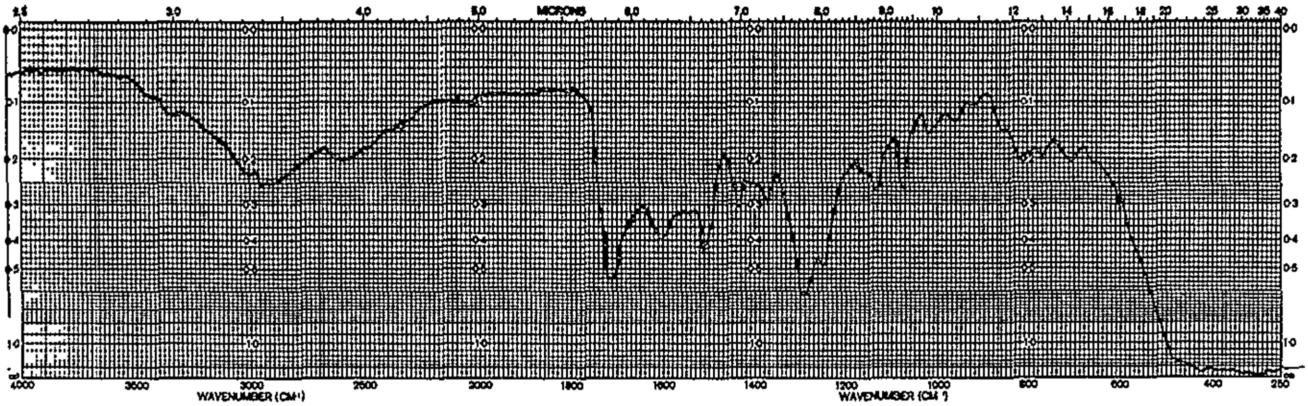


FIG. 60 INFRARED SPECTRUM OF NDE–PMR–15 FILM CONTAINING DICUMYLPEROXIDE (DCP)

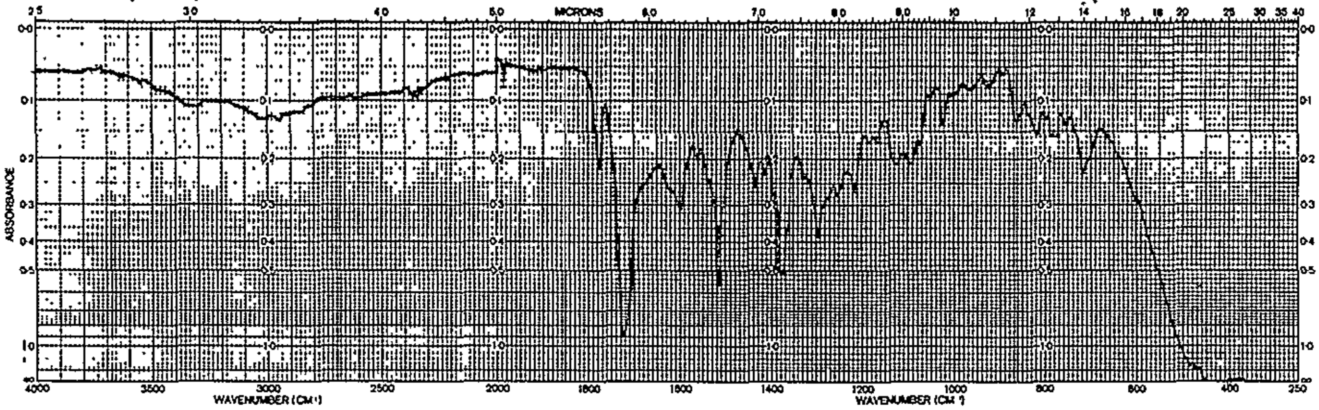


FIG. 61 INFRARED SPECTRUM OF NDE–PMR–15–DCP FILM HEATED AT 93, 149°C, 1/2 HR. EACH

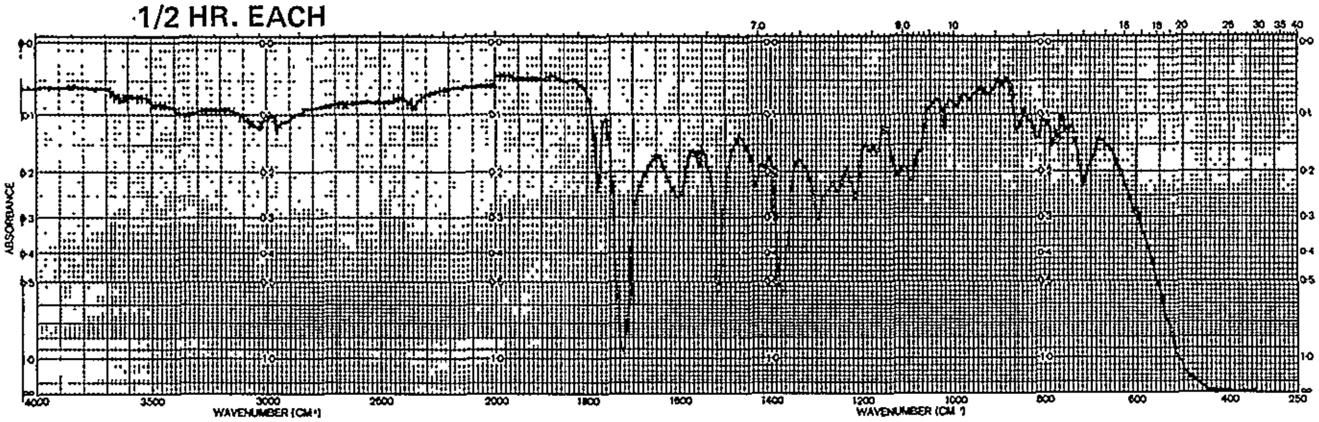


FIG. 62 INFRARED SPECTRUM OF NDE–PMR–15–DCP FILM HEATED AT 93, 149, 17.7°C, 1/2 HR. EACH

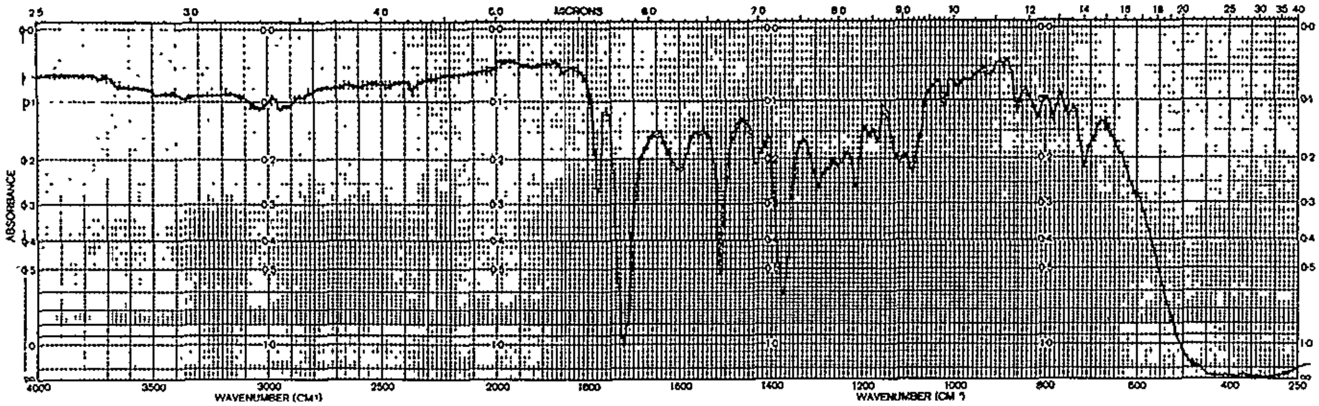


FIG. 63 INFRARED SPECTRUM OF NDE–PMR–15–DCP FILM HEATED AT 93, 149, 177, 204°C, 1/2 HR. EACH

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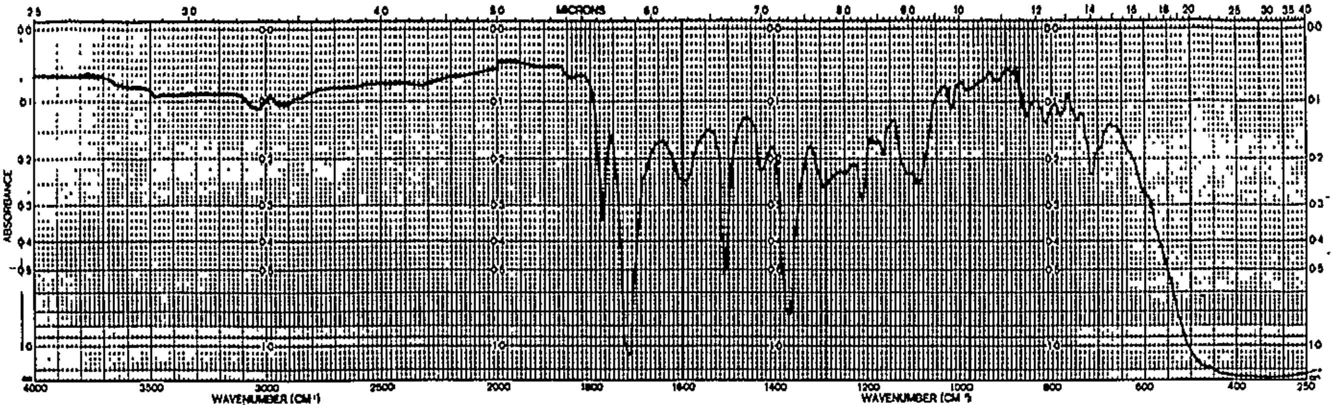

FIG. 64 INFRARED SPECTRUM OF NDE–PMR–15–DCP FILM HEATED AT 93, 149, 177, 204, 232°C, 1/2 HR. EACH

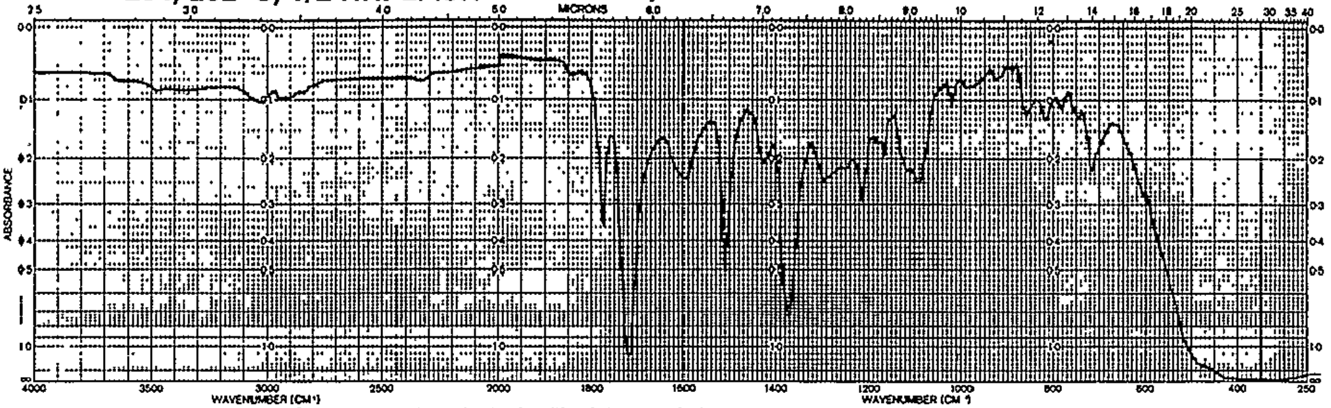

FIG. 65 INFRARED SPECTRUM OF NDE–PMR–15–DCP FILM HEATED AT 93, 149, 177, 204, 232, 260°C, 1/2 HR. EACH

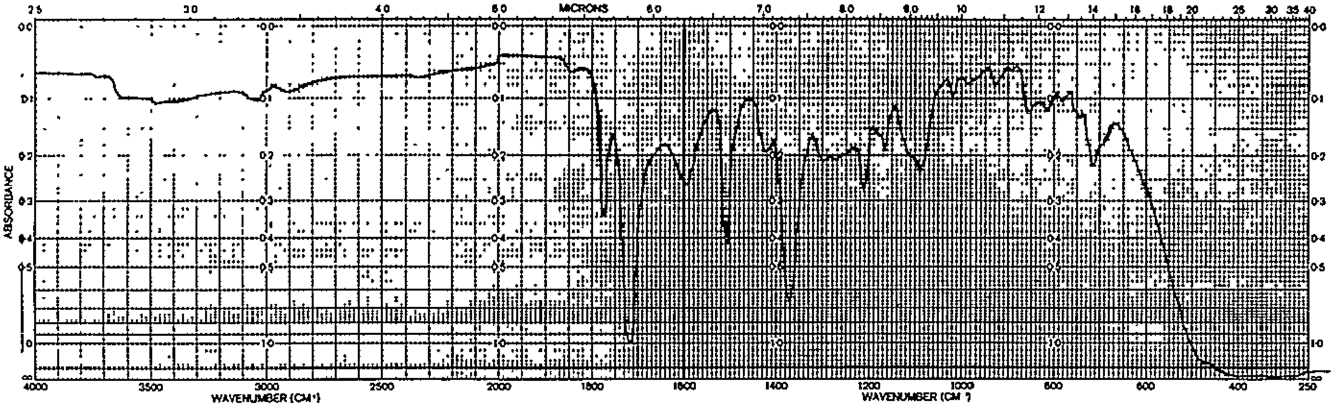

FIG. 66 INFRARED SPECTRUM OF NDE–PMR–15–DCP FILM HEATED AT 93, 149, 177, 204, 232, 260, 288°C, 1/2 HR. EACH

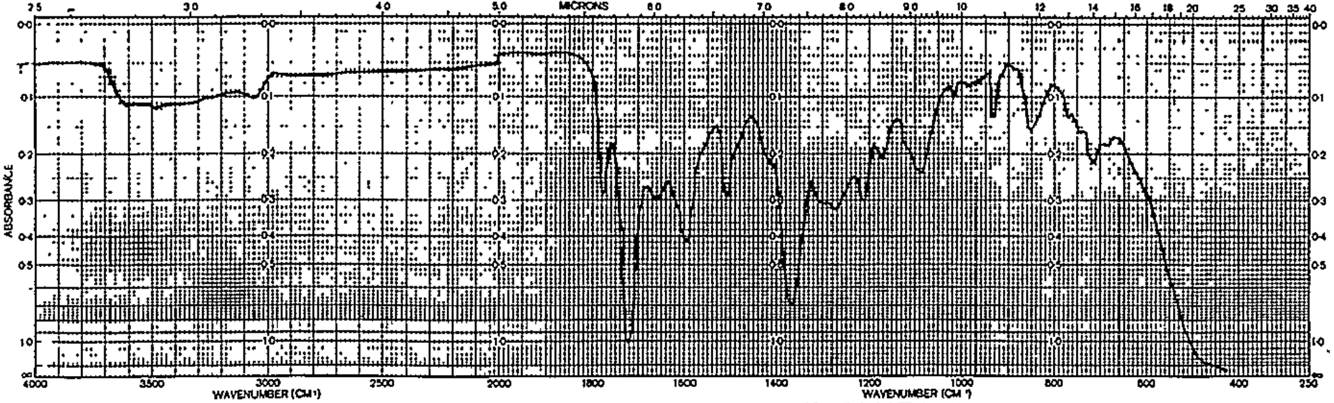

FIG. 67 INFRARED SPECTRUM OF NDE–PMR–15–DCP FILM HEATED AT 93, 149, 177, 204, 232, 260, 288, 316°C, 1/2 HR. EACH

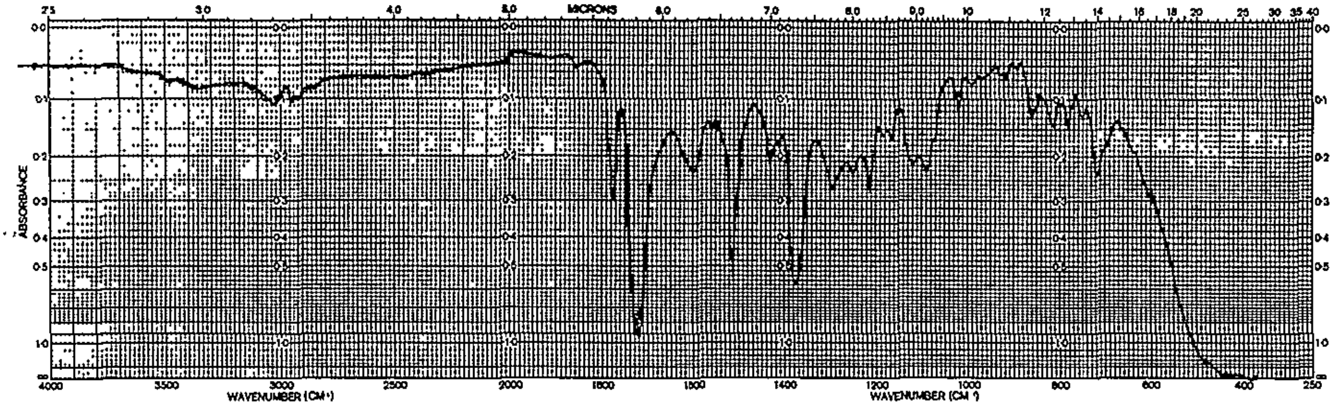

FIG. 68 INFRARED SPECTRUM OF UNCURED NDE–PMR–15 HEATED AT 204°C, 1/2 HR.

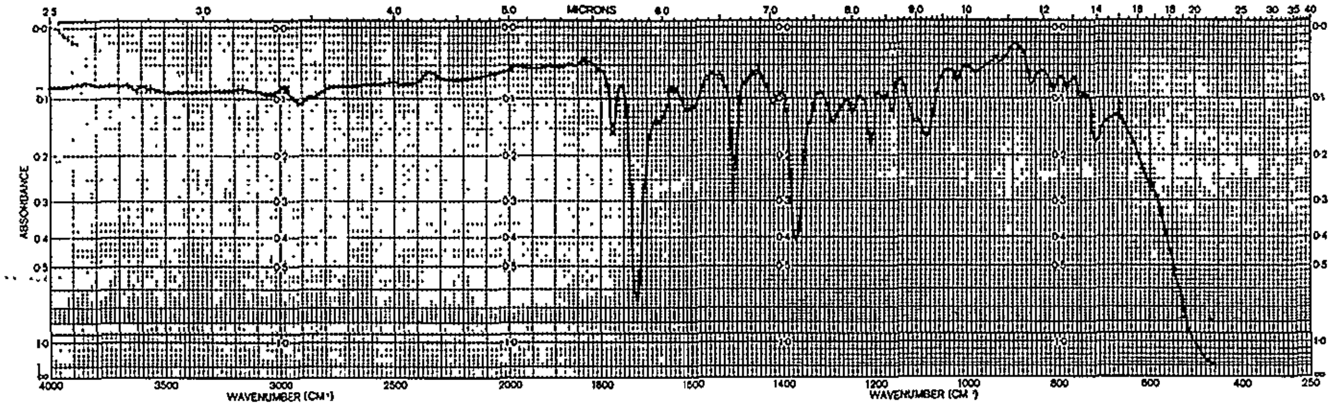

FIG. 69 INFRARED SPECTRUM OF NDE–PMR–15 FILM CONTAINING DMDA, HEATED AT 204°C, 1/2 HR.

C-2

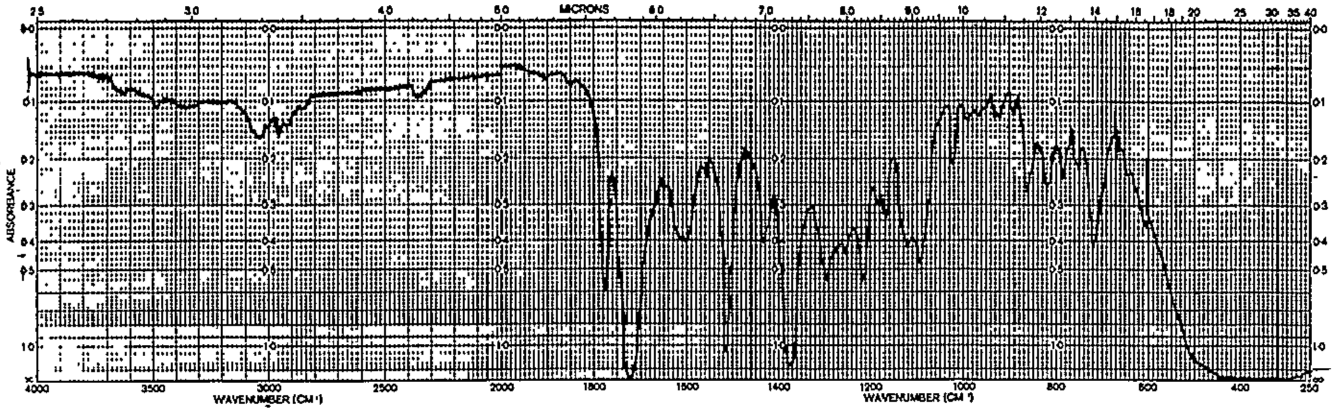

FIG. 70 INFRARED SPECTRUM OF NDE–PMR–15 FILM CONTAINING DCP HEATED AT 204°C, 1 HR.

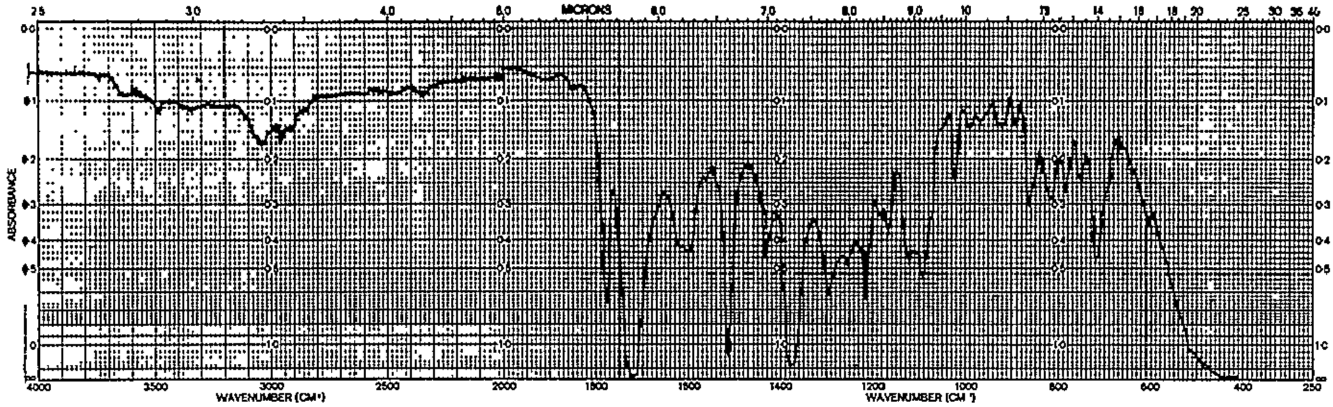

FIG. 71 INFRARED SPECTRUM OF NDE–PMR–15 FILM CONTAINING t–BHP HEATED AT 204°C, 1 HR.

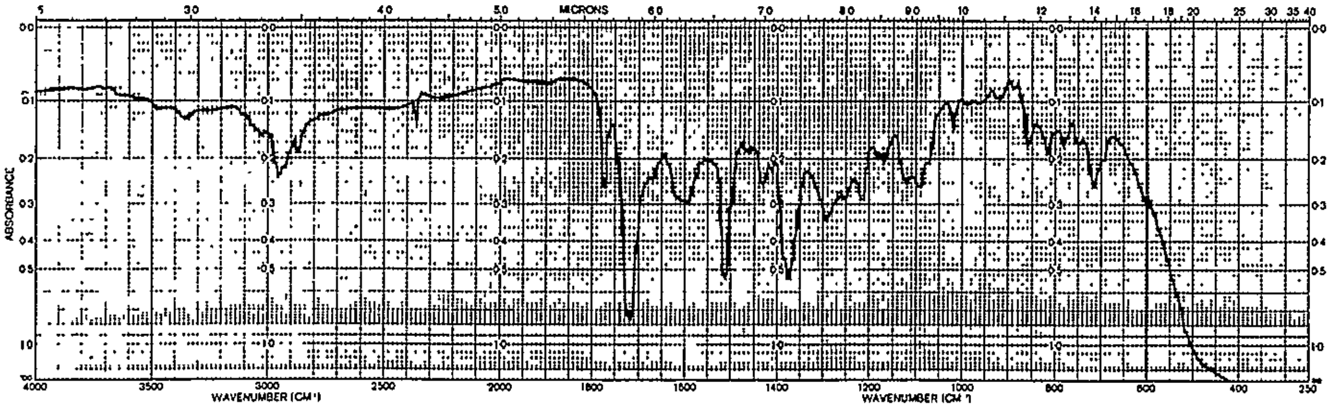

FIG. 72 INFRARED SPECTRUM OF NDE–PMR–15 FILM CONTAINING TRI–N–BUTYLAMINE HEATED AT 93, 149°C, 1/2 HR. EACH

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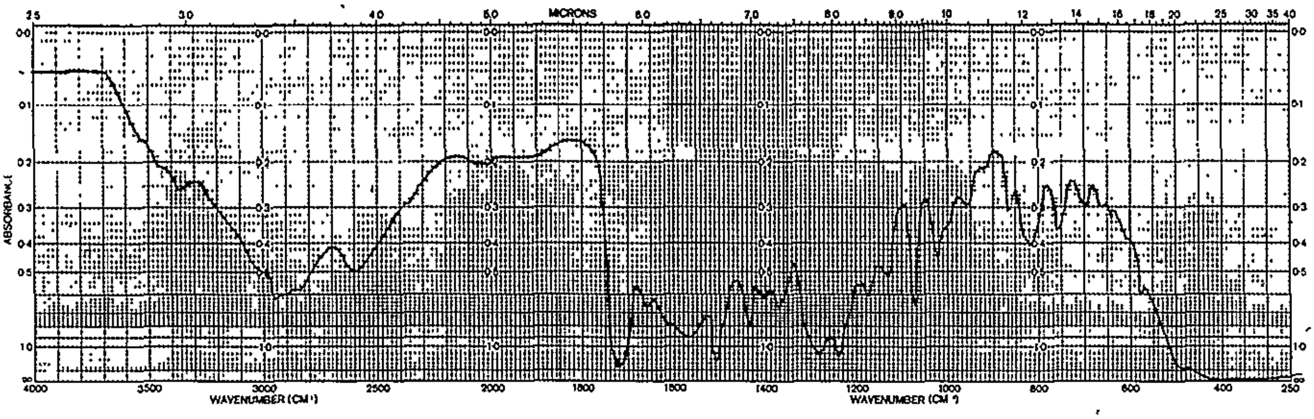

FIG. 73 INFRARED SPECTRUM OF UNCURED MAE–PMR–14 FILM

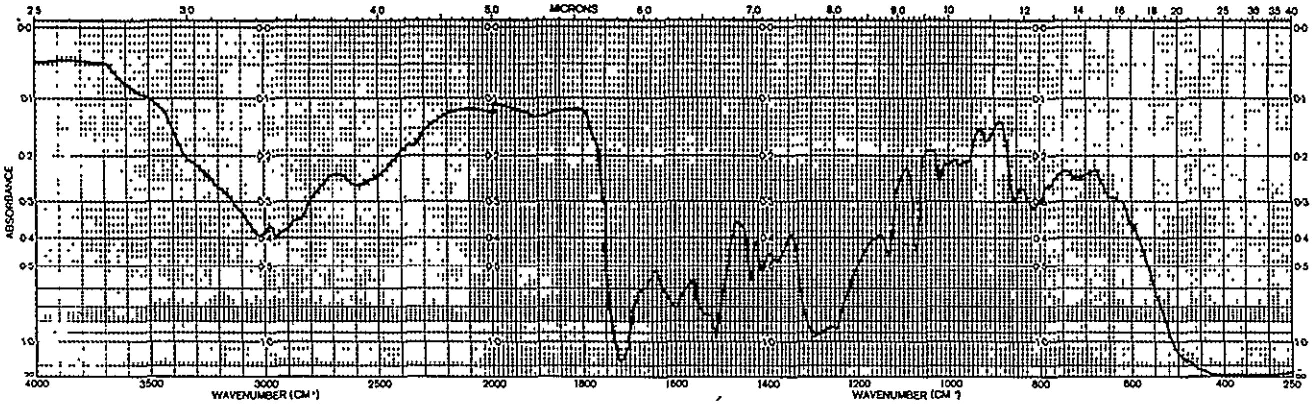

FIG. 74 INFRARED SPECTRUM OF MAE–PMR–14 FILM HEATED AT 93°C, 1/2 HR.

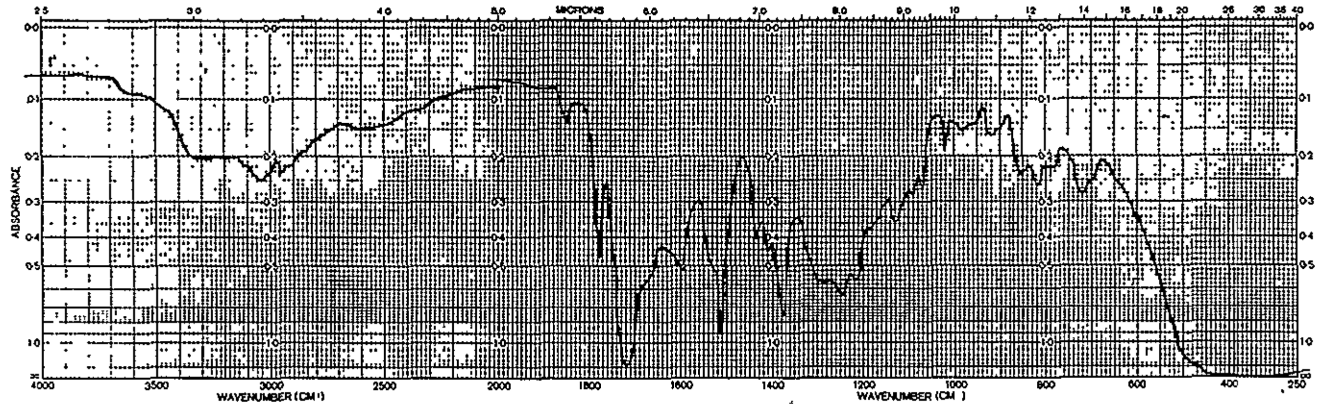

FIG. 75 INFRARED SPECTRUM OF MAE–PMR–14 FILM HEATED AT 93, 149°C, 1/2 HR. EACH

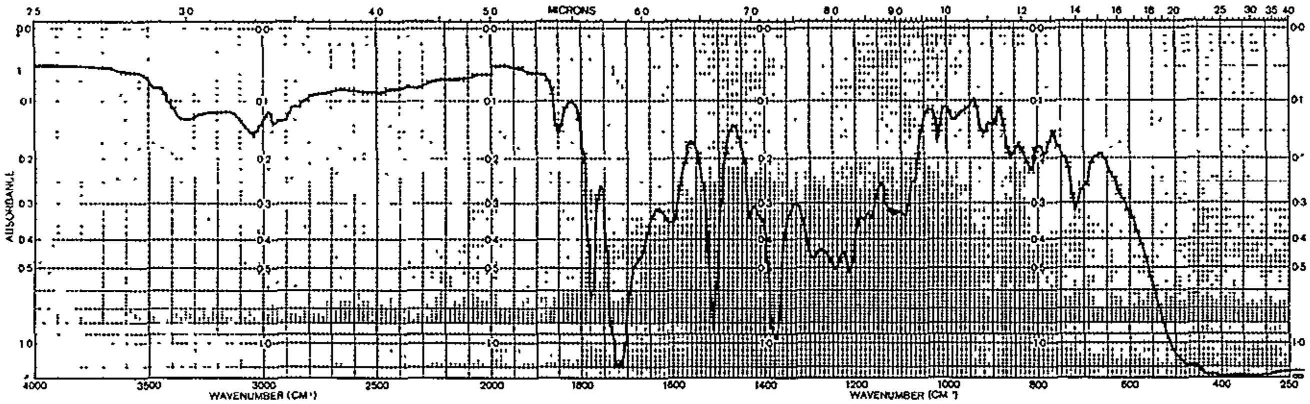

FIG. 76 INFRARED SPECTRUM OF MAE–PMR–14 FILM HEATED AT 93, 149, 177°C, 1/2 HR. EACH

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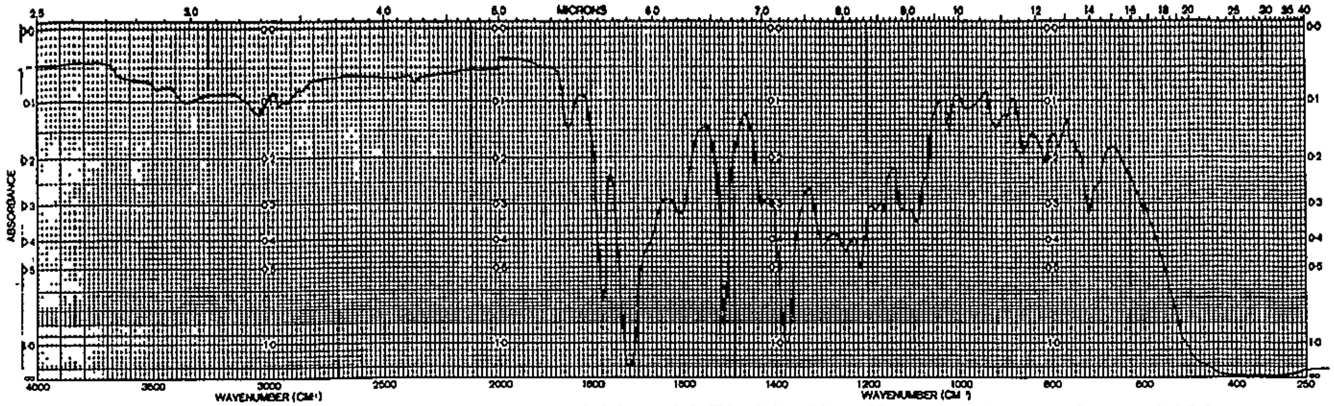


FIG. 77 INFRARED SPECTRUM OF MAE–PMR–14 FILM HEATED AT 93, 149,177, 204°C, 1/2 HR. EACH

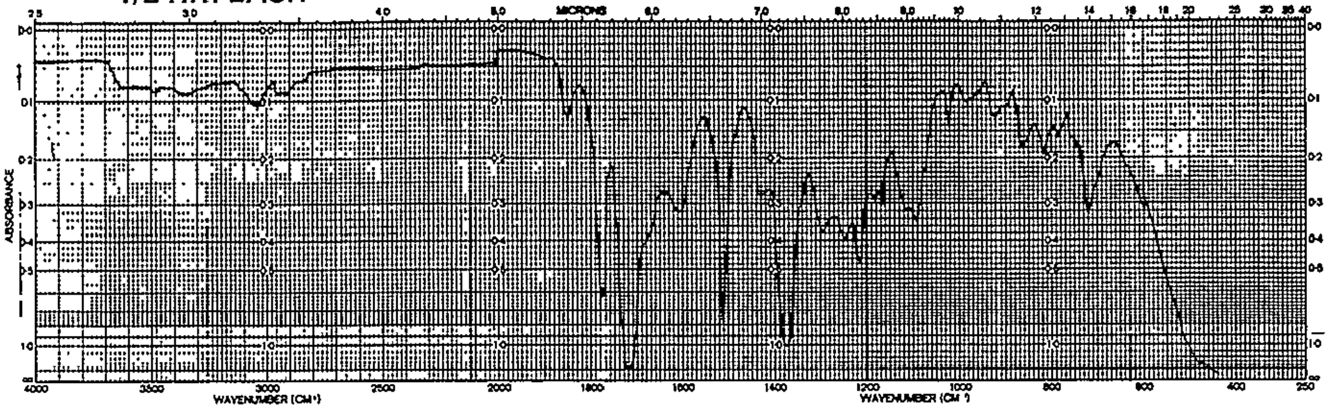


FIG. 78 INFRARED SPECTRUM OF MAE–PMR–14 FILM HEATED AT 93, 149, 177, 204, 232°C, 1/2 HR. EACH

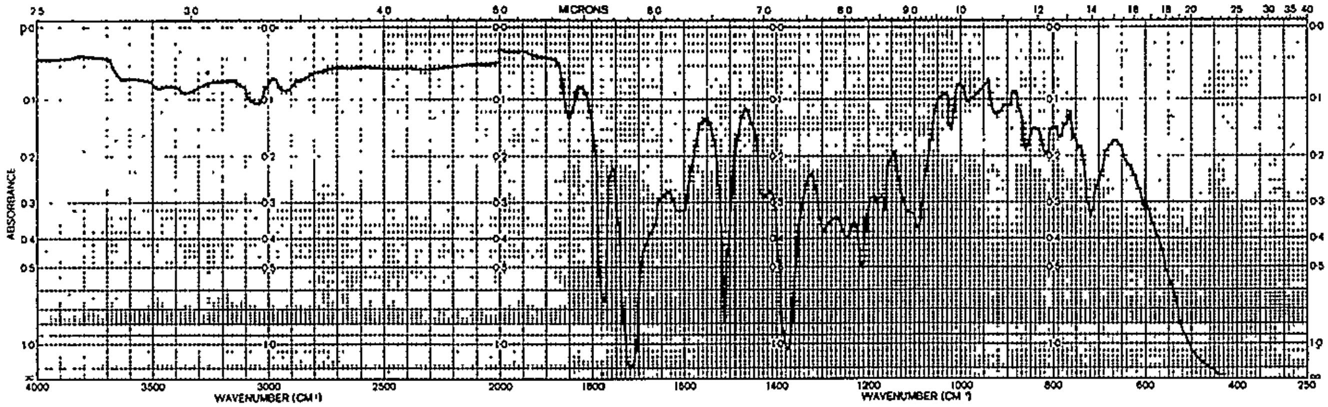


FIG. 79 INFRARED SPECTRUM OF MAE–PMR–14 FILM HEATED AT 93, 149, 177, 204, 232, 260°C, 1/2 HR. EACH

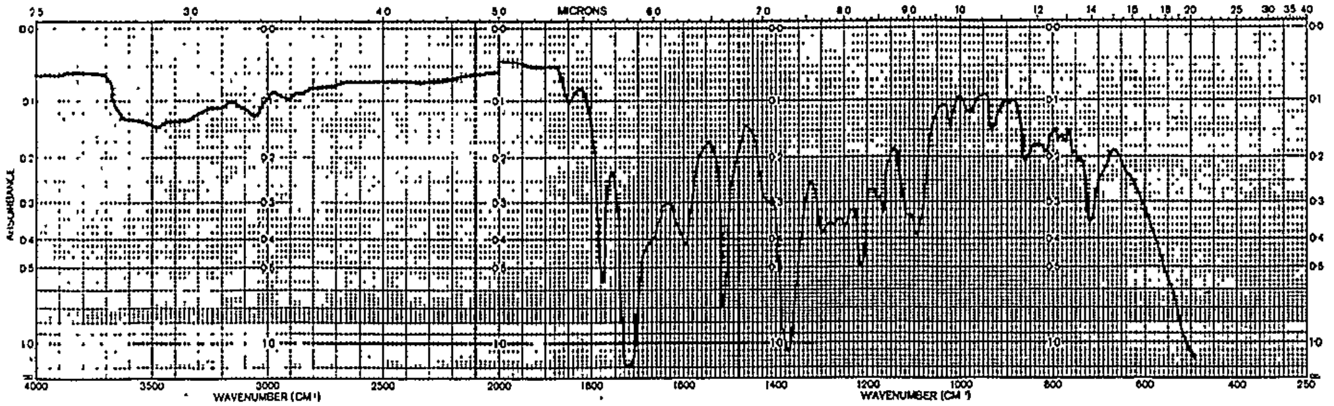
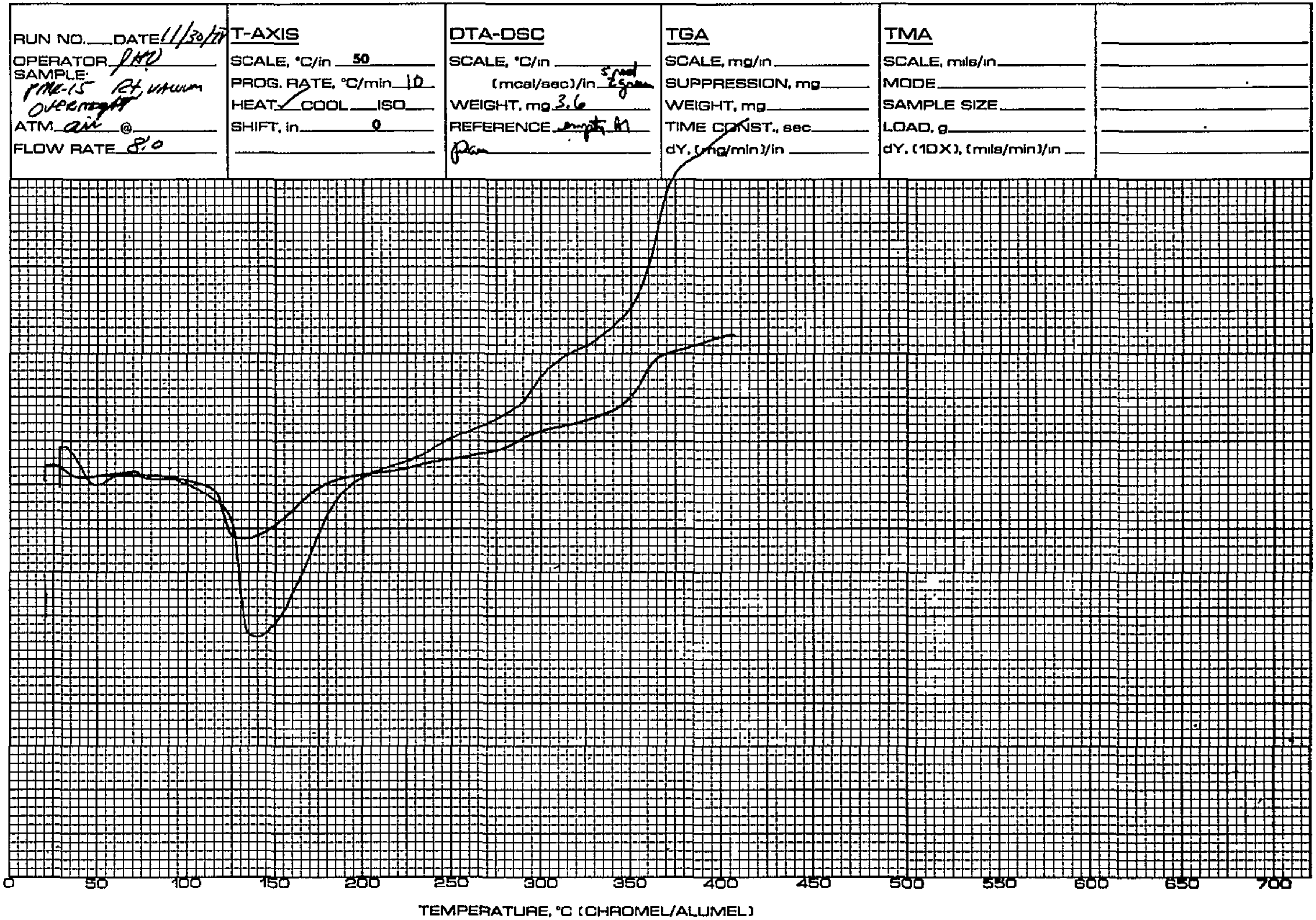


FIG. 80 INFRARED SPECTRUM OF MAE–PMR–14 FILM HEATED AT 93, 149, 177, 204, 232, 260, 288°C, 1/2 HR. EACH

79–06–157–26



RUN NO.____ DATE 11/30/77
OPERATOR JAW
SAMPLE: PMR-15 RT, vacuum overnight
ATM air @____
FLOW RATE 8.0

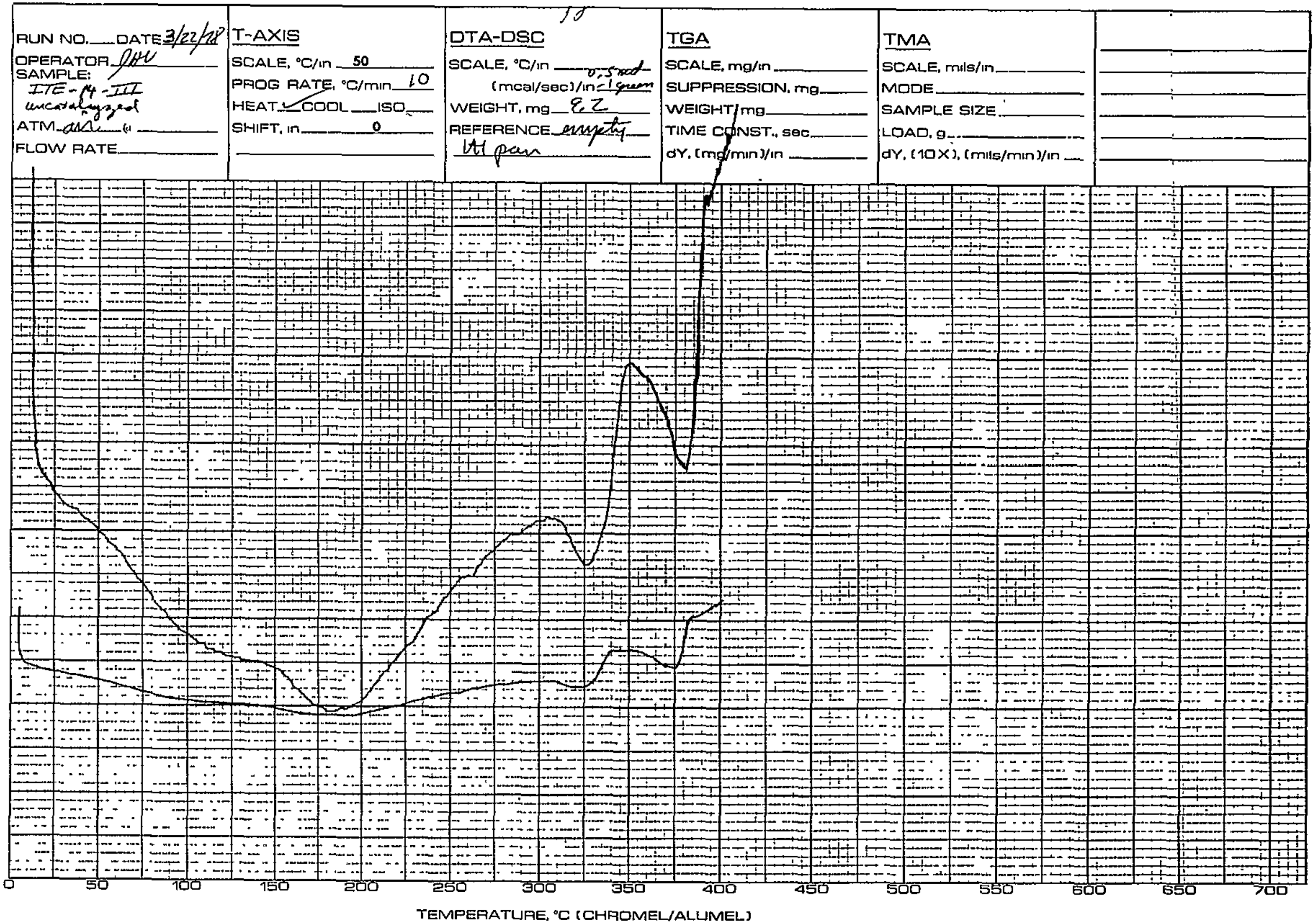
T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT ✓ COOL ____ ISO ____
SHIFT, in 0

DTA-DSC
SCALE, °C/in ____
(mcal/sec)/in 5 mcal [illegible]
WEIGHT, mg 3.6
REFERENCE empty Al pan

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 ____

FIG. 81 DSC THERMOGRAM OF UNCATALYZED PMR—15 POWDER



RUN NO.__ DATE 3/22/78
OPERATOR JHL
SAMPLE:
ITE-14-III
uncatalyzed
ATM air
FLOW RATE __

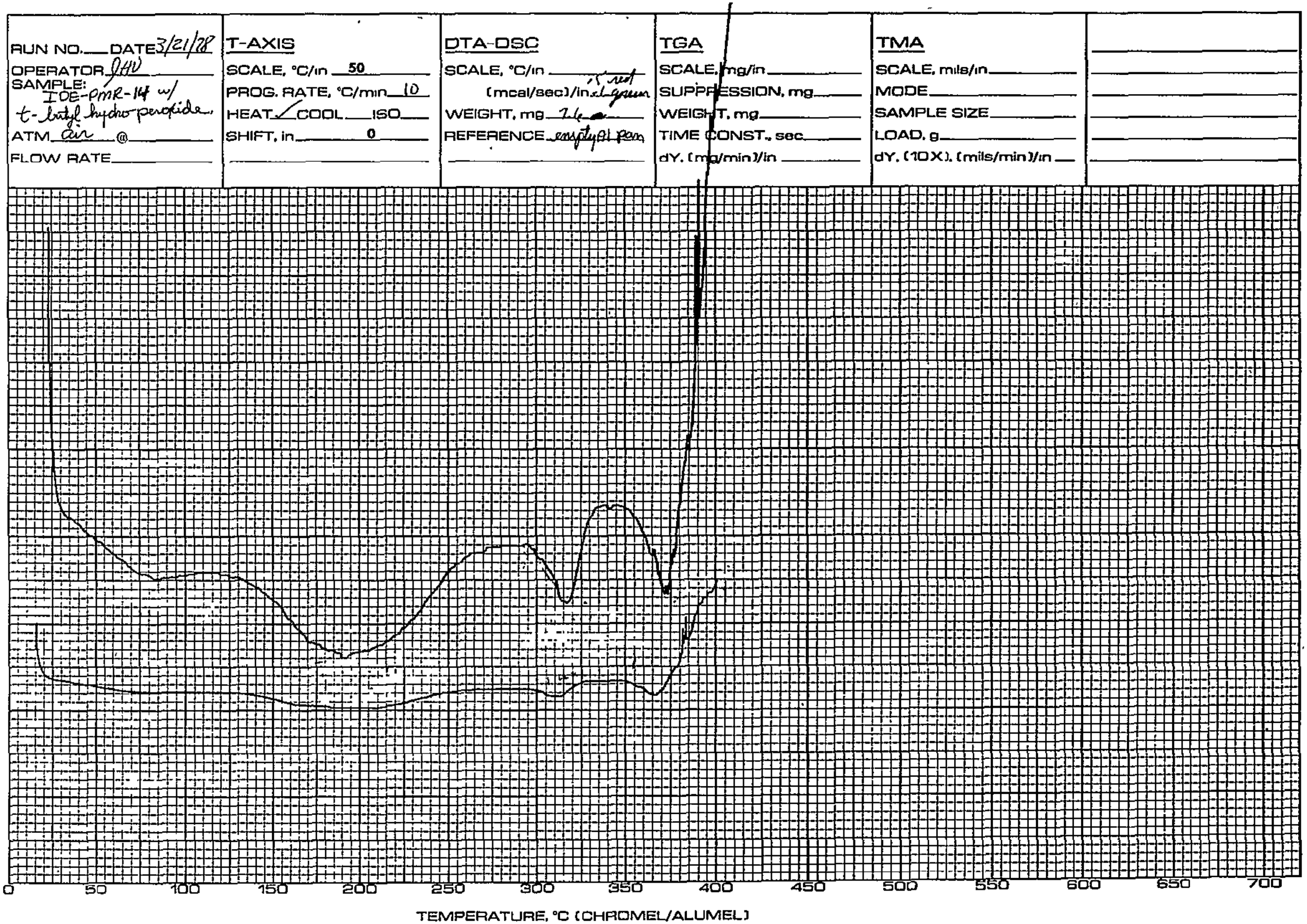
T-AXIS
SCALE, °C/in 50
PROG RATE, °C/min 10
HEAT ✓ COOL __ ISO __
SHIFT, in 0

DTA-DSC
SCALE, °C/in 0.5 mcal
(mcal/sec)/in 1 gram
WEIGHT, mg 8.2
REFERENCE empty Al pan

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 __

FIG. 82 DSC THERMOGROM OF UNCATALYZED ITE–PMR–14 POWDER



RUN NO.__ DATE 3/21/78
OPERATOR JHV
SAMPLE: ITE-PMR-14 w/ t-butyl hydroperoxide
ATM air @ __
FLOW RATE __

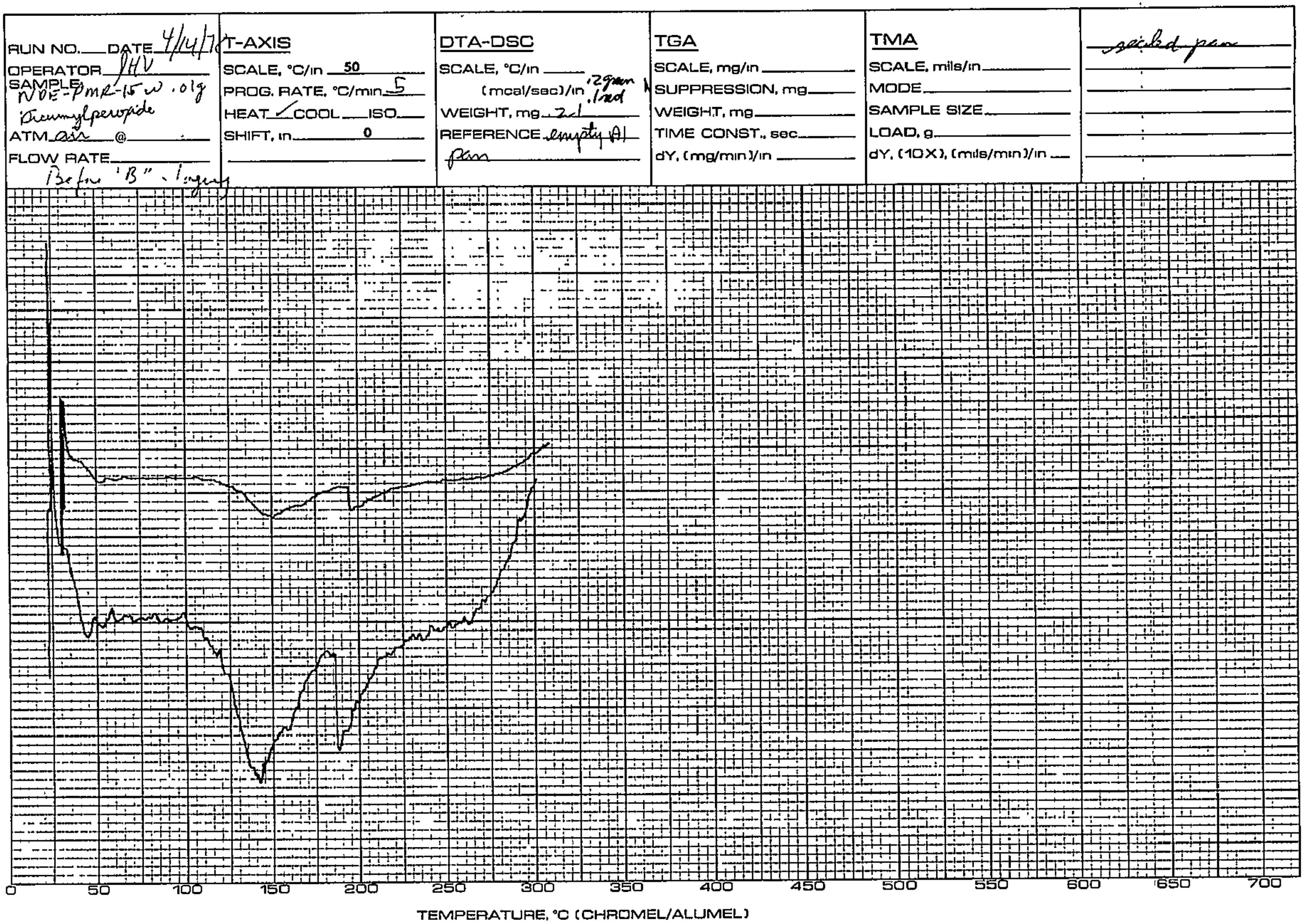
T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT ✓ COOL __ ISO __
SHIFT, in 0

DTA-DSC
SCALE, °C/in __
(mcal/sec)/in .5 red .1 green
WEIGHT, mg 2.6
REFERENCE empty Al pan

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 __

FIG. 83 DSC THERMOGRAM OF t–BUTYLHYDROPEROXIDE CATALYZED ITE–PMR–14 POWDER



RUN NO.____ DATE 4/14/78
OPERATOR JHV
SAMPLE NDE-PMR-15 w .01g Dicumylperoxide
ATM air @____
FLOW RATE____
Before "B" - Inquiry

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

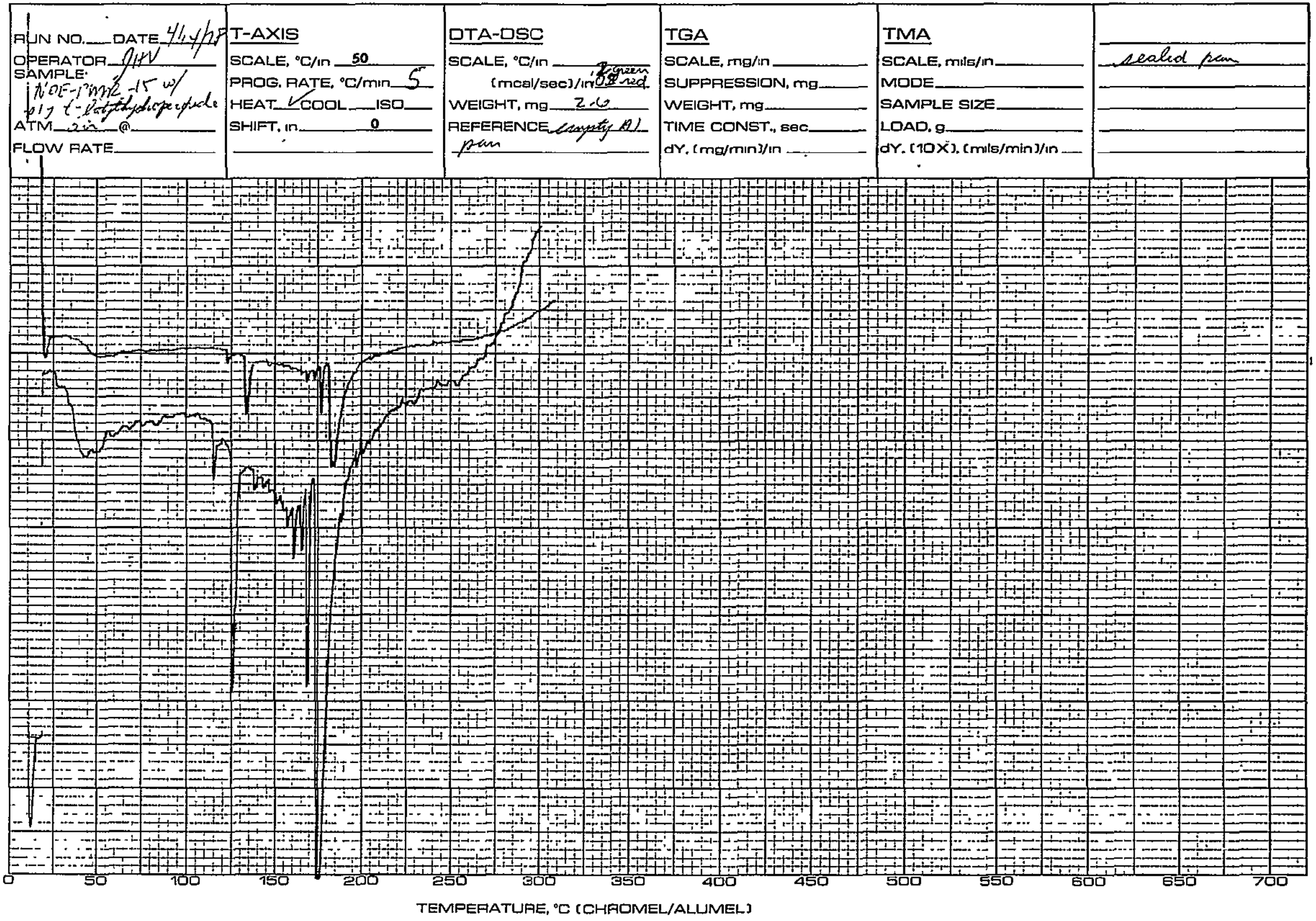
DTA-DSC
SCALE, °C/in ____
(mcal/sec)/in .2 mcal/in .1 mcal
WEIGHT, mg 2.1
REFERENCE empty Al pan

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 ____

sealed pan

FIG. 84 DSC THERMOGRAM OF DICUMYLPEROXIDE CATALYZED NDE–PMR–15 POWDER



RUN NO.___ DATE 4/4/78

OPERATOR JHV

SAMPLE: NDE-PMR-15 w/ 1% t-butylhydroperoxide

ATM air @

FLOW RATE

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 8 green 0.8 red

WEIGHT, mg 2.6

REFERENCE empty Al pan

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

sealed pan

FIG. 85 DSC THERMOGRAM OF t–BUTYLHYDROPEROXIDE CATALYZED NDE–PMR–15 POWDER

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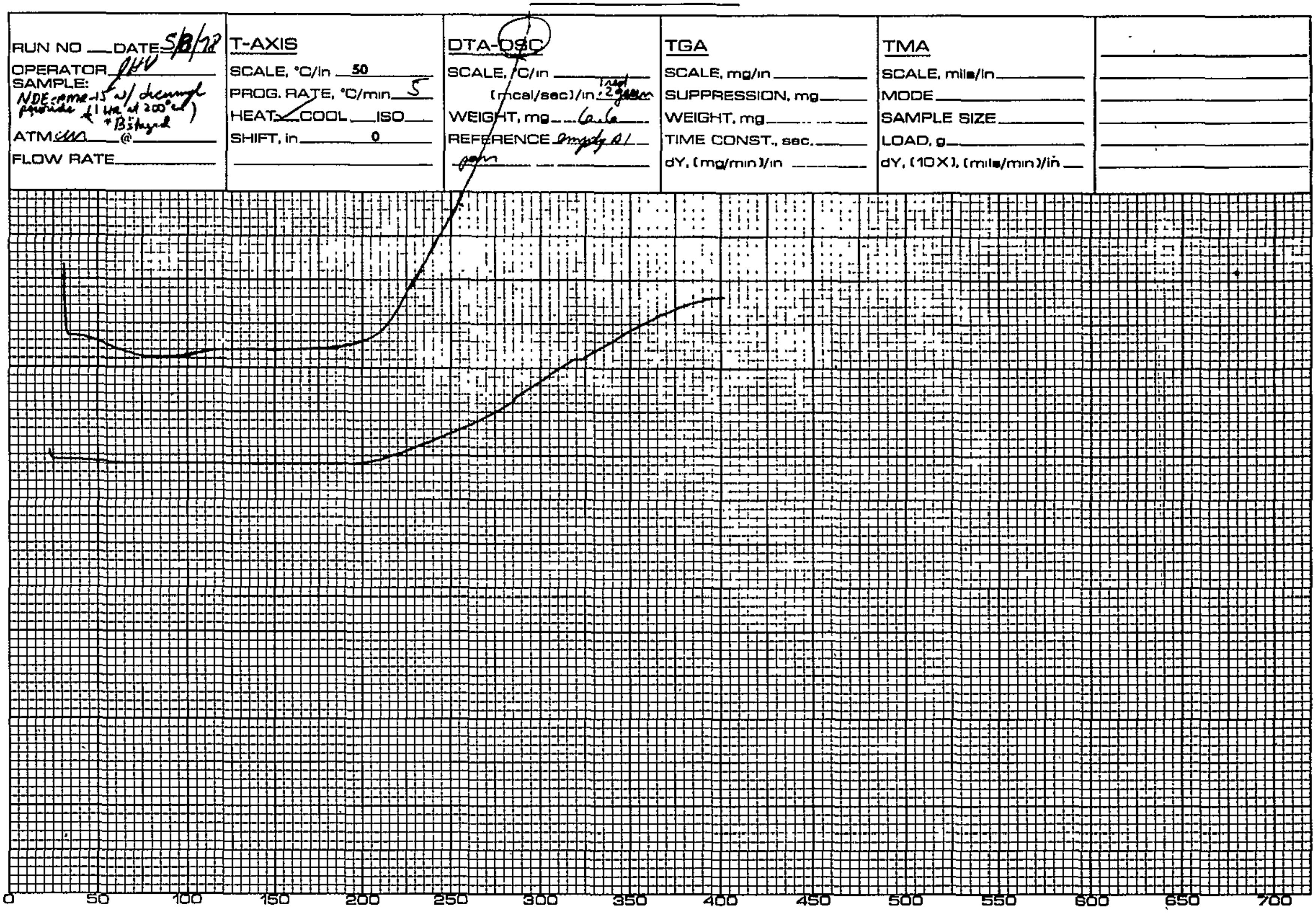

RUN NO ___ DATE 5/8/78
OPERATOR JHV
SAMPLE: NDE-PMR-15 w/ dicumyl peroxide (1 hr at 200°C + B staged)
ATM air @ ___
FLOW RATE ___

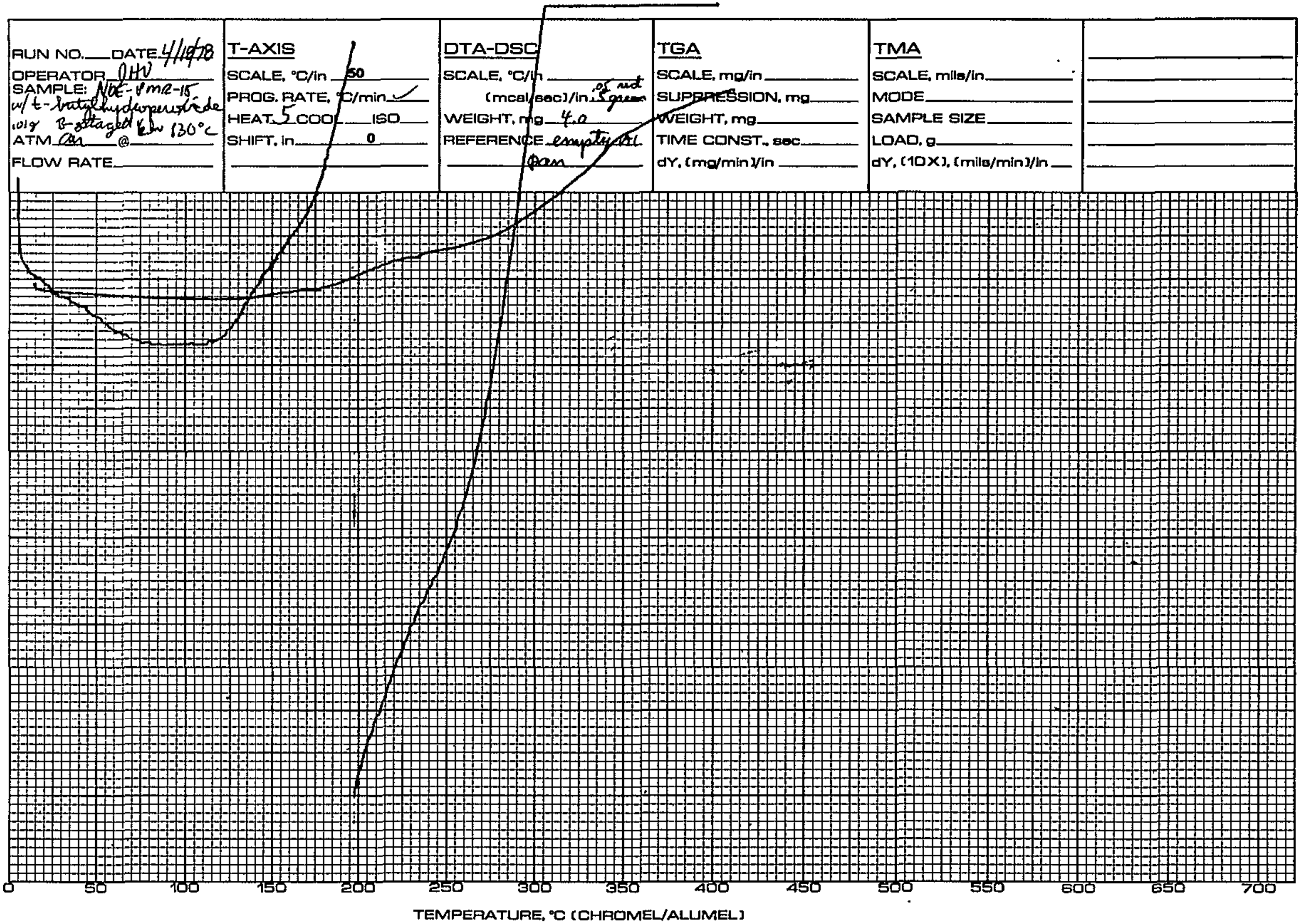
T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 5
HEAT ✓ COOL ___ ISO ___
SHIFT, in 0

DTA-DSC
SCALE, °C/in ___
(mcal/sec)/in [illegible]
WEIGHT, mg 6.6
REFERENCE Empty Al pan

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 ___

FIG. 86 DSC THERMOGRAM OF B STAGED (200°C, 1/2 HR), DCP CATALYZED NDE–PMR–15



RUN NO.__ DATE 4/19/78
OPERATOR JHW
SAMPLE: NDE-PMR-15 w/ t-butylhydroperoxide .01g B-staged 1/2 hr 130°C
ATM Air @
FLOW RATE

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

DTA-DSC
SCALE, °C/in
(mcal/sec)/in .05 red .5 green
WEIGHT, mg 4.0
REFERENCE empty Al pan

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

FIG. 87 DSC THERMOGRAM OF B STAGED (130°C, 1/2 HR), NDE–PMR–15 CONTAINING t–BHP (0.01 g)

RUN NO.__ DATE 5/16/78
OPERATOR JHV
SAMPLE: VCDE-PMR-15-I w/t-butyl hydroperoxide (0.01g)
ATM air @__
FLOW RATE__

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 .5 green .05 red
WEIGHT, mg 2.5
REFERENCE empty Al pan

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__

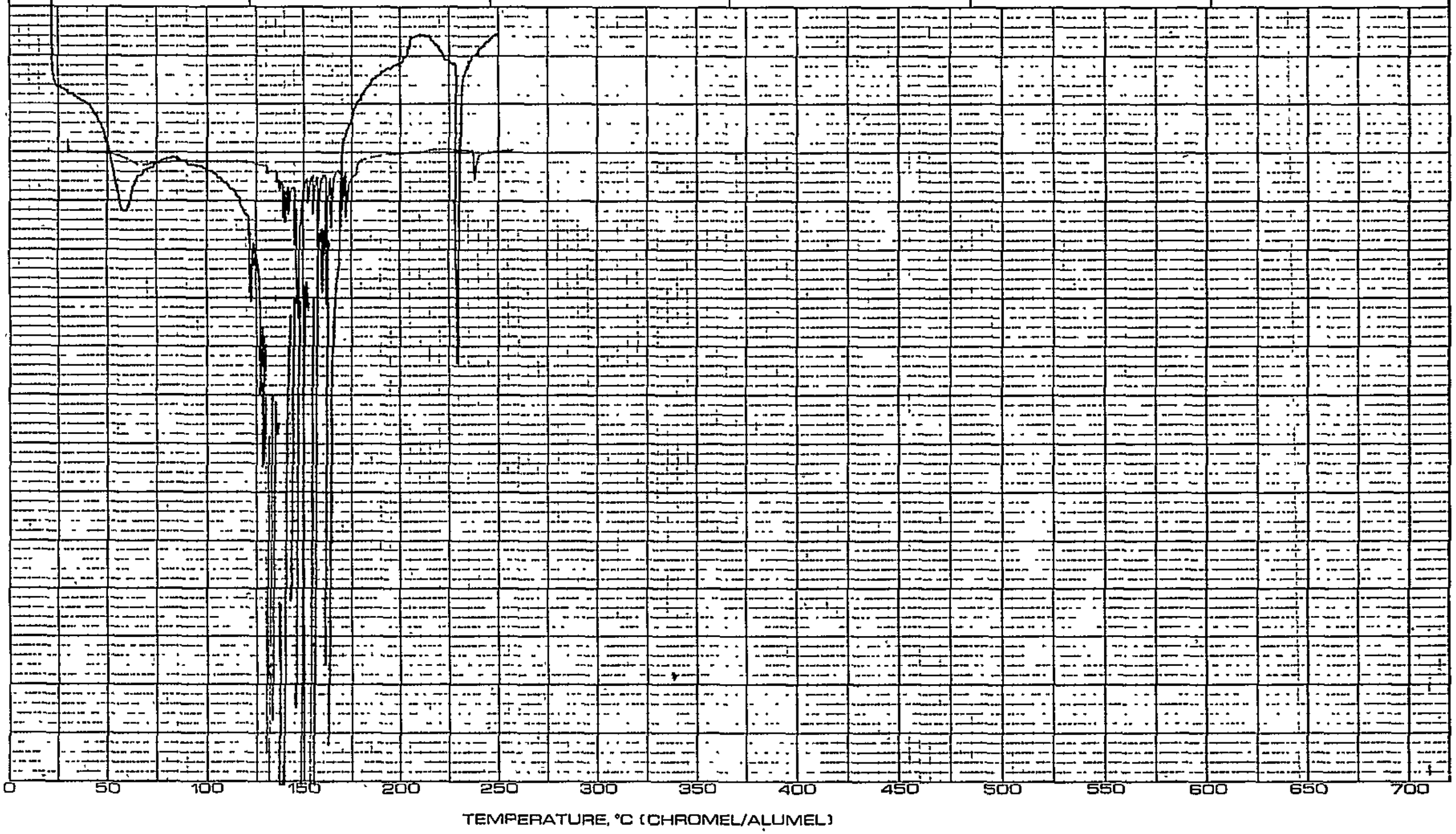


FIG. 88 DSC THERMOGRAM OF t–BUTYLHYDROPEROXIDE CATALYZED MAE–PMR–14 POWDER

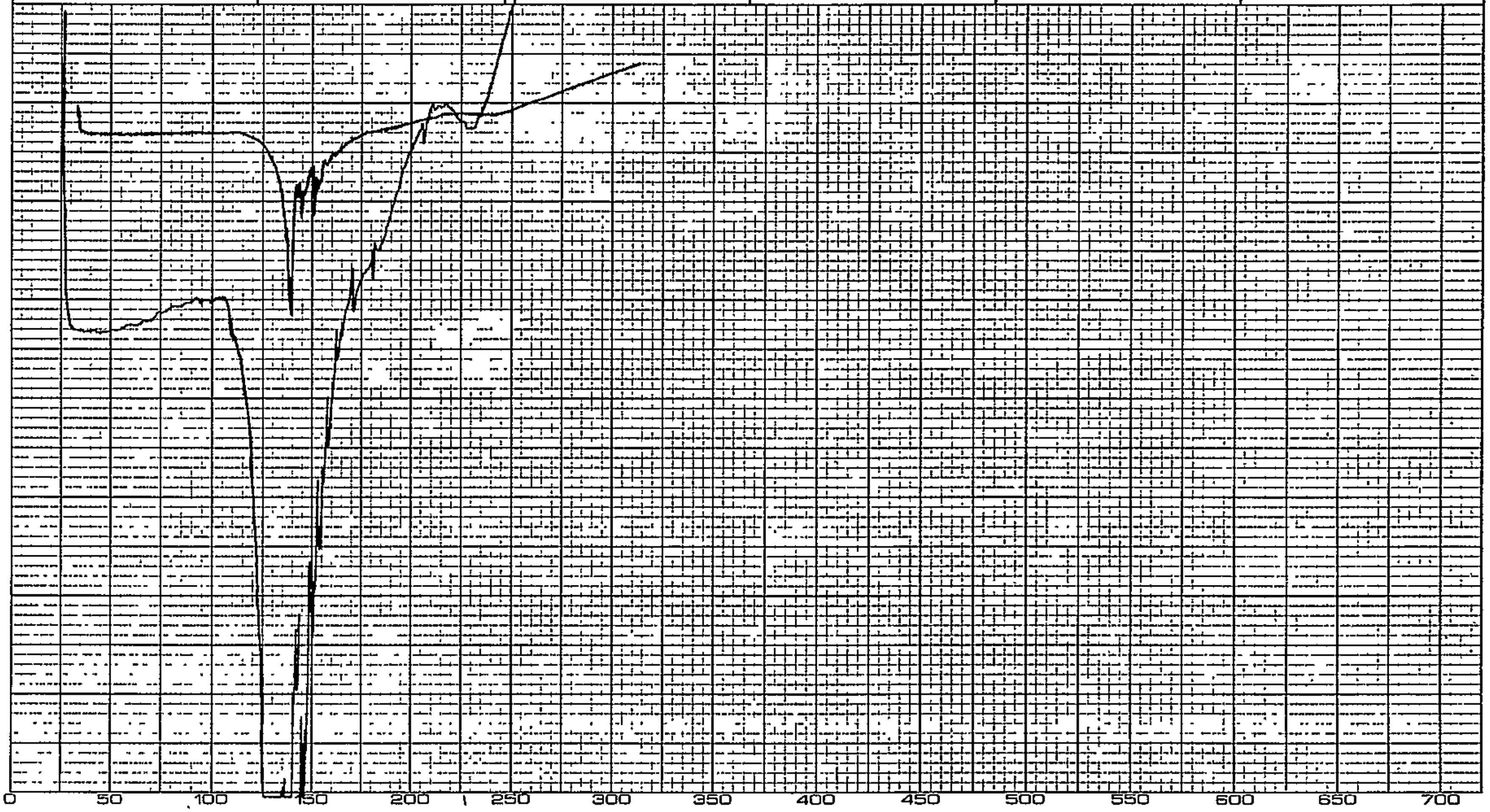
RUN NO.____ DATE 5/11/78
OPERATOR RHW
SAMPLE: MAE-PMR-15-I 41
dimethyldodecylamine
ATM air @______
FLOW RATE______

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 5
HEAT ✓ COOL____ ISO____
SHIFT, in 0

DTA-DSC
SCALE, °C/in .05 mcal
(mcal/sec)/in .5 grad
WEIGHT, mg 4.5
REFERENCE empty Al
pan

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______



TEMPERATURE, °C (CHROMEL/ALUMEL)

FIG. 89 DSC THERMOGRAM OF DIMETHYLDODECYLAMINE CATALYZED MAE–PMR–14 POWDER

79–06–157–32

RUN NO.___ DATE 9/1/78
OPERATOR JHV
SAMPLE: PMR-15
dsc 94
ATM air @___
FLOW RATE 80

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT ✓ COOL ___ ISO ___
SHIFT, in 0

DTA-DSC
SCALE, °C/in ___
(mcal/sec)/in 5 mcal [illegible]
WEIGHT, mg 7.8
REFERENCE empty Al pan

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 ___

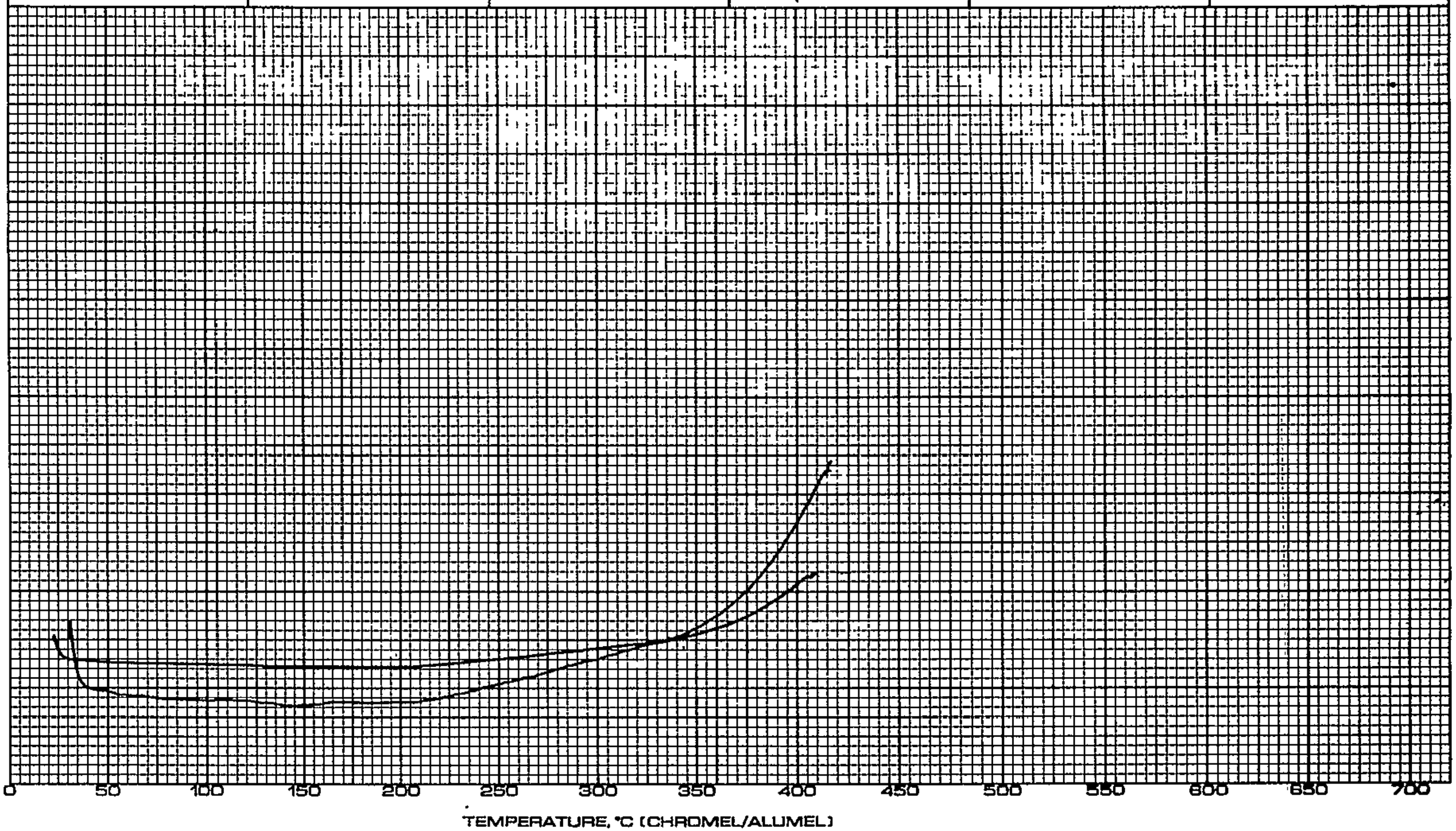


FIG. 90 DSC THERMOGRAM OF PMR–15 CURED AT 600°F, 1 HR

RUN NO.__ DATE 11/30/78
OPERATOR JW
SAMPLE:
NDE-PMR-III-4
(Reprocessed 275°C → 700°C) 1HR
ATM air @
FLOW RATE 2.0

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT ✓ COOL __ ISO __
SHIFT, in 0

DTA-DSC
SCALE, °C/in
(mcal/sec)/in .5 red .2 green
WEIGHT, mg 4.3
REFERENCE empty Al pan

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

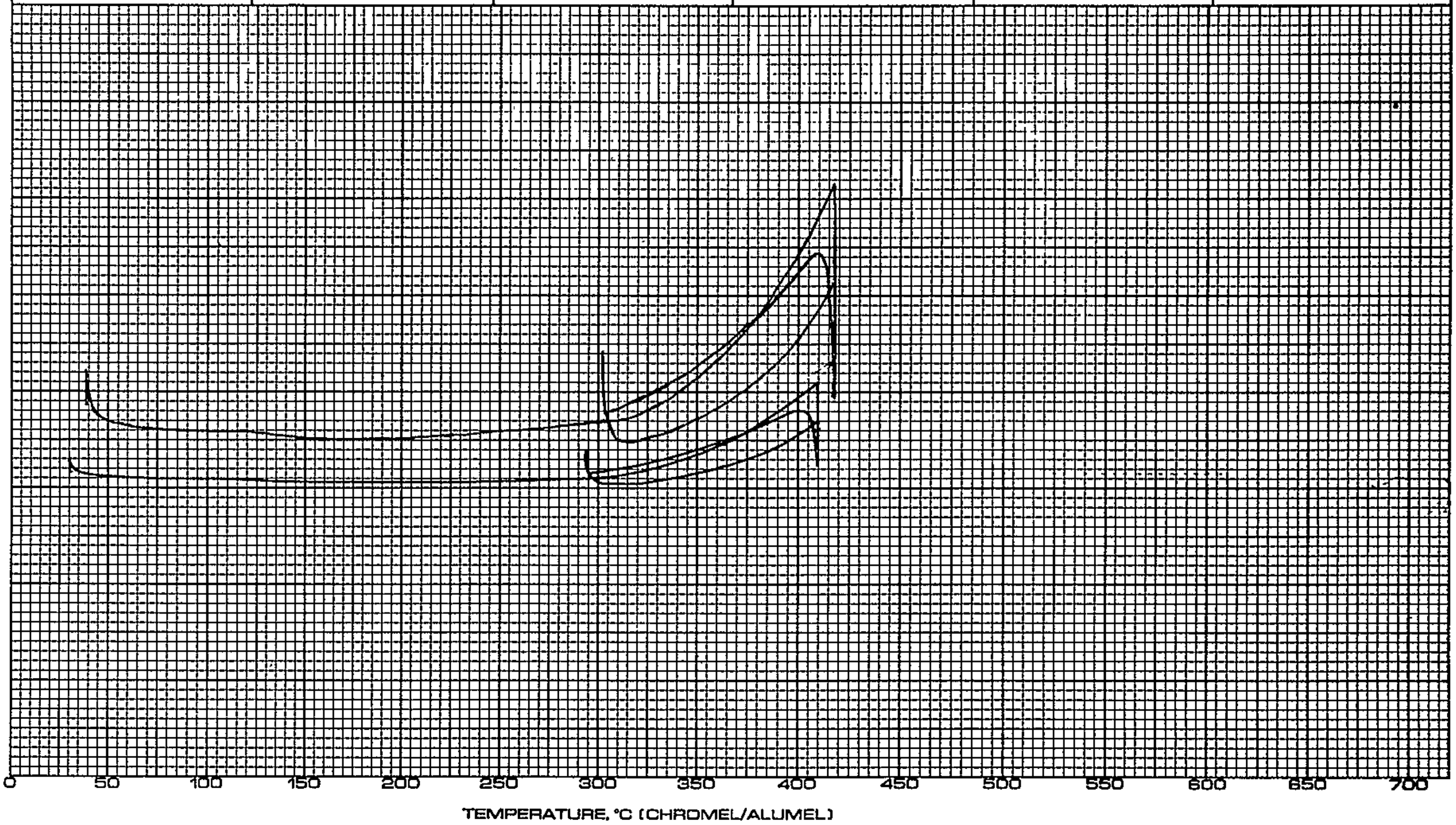
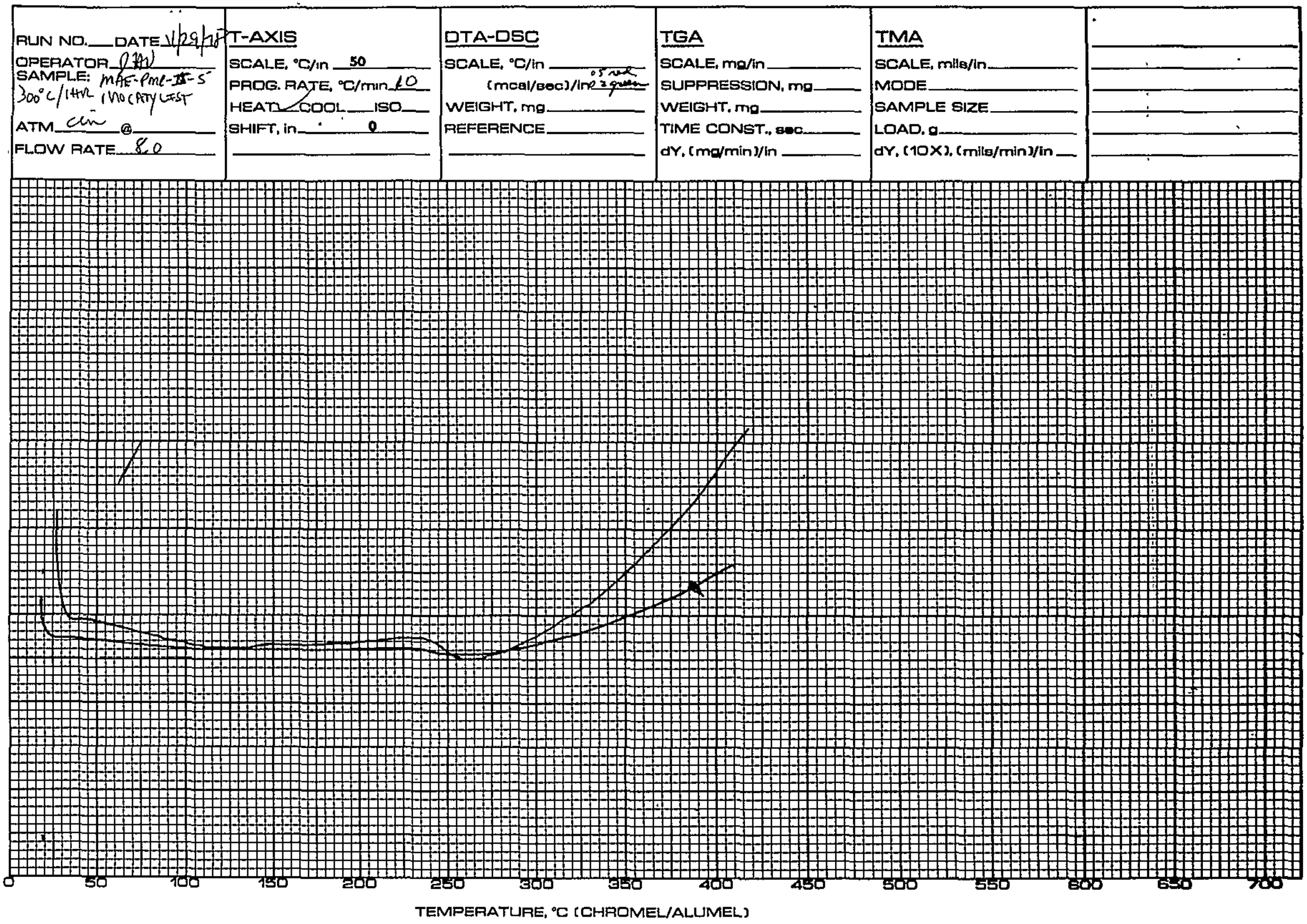


FIG. 91 DSC THERMOGRAM OF UNCATALYZED CURED NDE–PMR–15



RUN NO.__ DATE 1/29/78
OPERATOR JAW
SAMPLE: MAE-PMR-II-5
300°C/1HR 1 NO CATALYST
ATM air @__
FLOW RATE 80

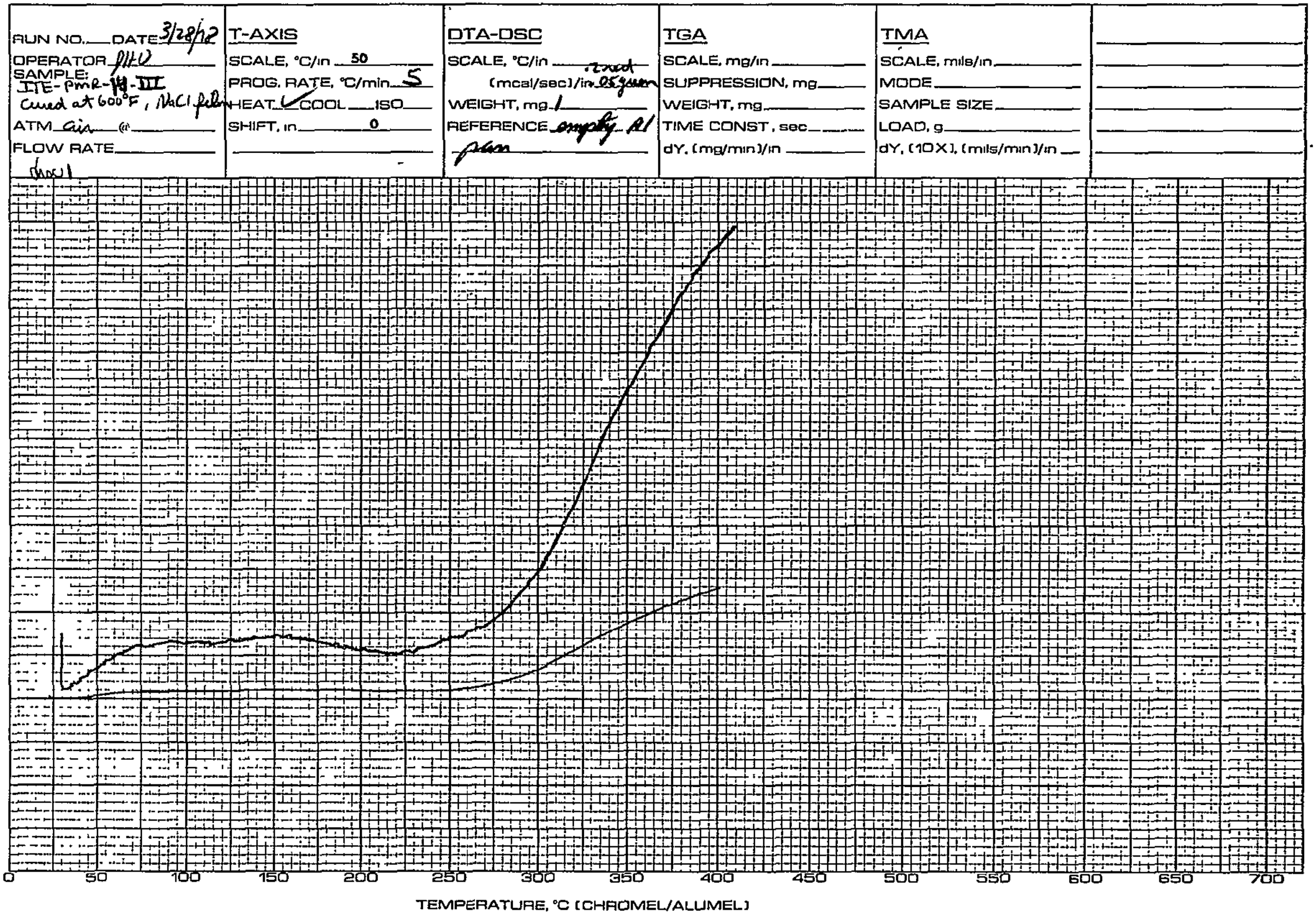
T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT [✓] COOL__ ISO__
SHIFT, in 0

DTA-DSC
SCALE, °C/in __
(mcal/sec)/in 0.5 red 2 green
WEIGHT, mg__
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__

FIG. 92 DSC THERMOGRAM OF UNCATALYZED CURED MAE–PMR–14



RUN NO.__ DATE 3/28/82
OPERATOR JHV
SAMPLE: ITE-PMR-14-III
Cured at 600°F, NaCl film
ATM air @
FLOW RATE
Run 1

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

DTA-DSC
SCALE, °C/in .2 xed
(mcal/sec)/in .05 gram
WEIGHT, mg 1
REFERENCE empty Al pan

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

FIG. 93 DSC THERMOGRAM OF UNCATALYZED ITE–PMR–14–III CURED AT 600°F, 1 HR

79–06–167–33

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