

U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

FE-1724-27

UTILIZATION OF COAL CONVERSION PROCESS
BY-PRODUCTS QUARTERLY REPORT, DECEMBER 26,
1976-MARCH 25, 1977

I. J. Solomon, et al

IIT Research Institute
Chicago, Illinois

May 1977

DISTRIBUTION STATEMENT A

Approved for public release;
Distribution Unlimited

19960223 061

DTIC QUALITY INSPECTED 1

PLASTEC 291158

THE UTILIZATION OF COAL CONVERSION
PROCESS BY-PRODUCTS

Quarterly Report For The
Period December 26, 1976 To March 25, 1977

I. J. Solomon

C. Giori

May 1977

Under Contract No. E(49-18)-1724

PREPARED FOR
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

Fossil Energy Research
Washington, D. C. 20545

REPRODUCED BY
**NATIONAL TECHNICAL
INFORMATION SERVICE**
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

IIT Research Institute
Chicago, Illinois

FOREWORD

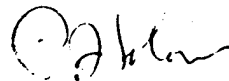
The Quarterly Report on IITRI Project No. C6322, Contract No. E(49-18)-1724 entitled "The Utilization of Coal Conversion Process (CCP) By-Products" covers the time period December 26, 1976 to March 25, 1977. We are pleased to submit this report which covers the progress in the study of the utilization of coal conversion process by-products.

The fractionation and synthesis of monomer studies were performed by W. C. Eisenberg. C. Giori and T. Yamauchi investigated the feasibility of making thermosetting resins from the benzene polycarboxylic acid mixture obtained in the oxidation of CCP by-products. I. J. Solomon was responsible for the technical direction of the program.

Prepared by



C. Giori
Manager
Polymer Research



I. J. Solomon
Chief Scientist

Approved by



M. J. Klein
Director
Chemistry and Chemical
Engineering Research Division

CG:IJS:dfp

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161

TABLE OF CONTENTS

	Page
1. Summary	1
2. Introduction	2
3. Polyesterification of the Organic Extracts Obtained in The Oxidation of CCP By-Products	3
4. Epoxy Cross-Linking of Char Acid Polyesters	7
5. Curing Procedures and Weight Loss Studies	15
6. Infrared Spectroscopy	18
7. Plans for Future Work	19

LIST OF TABLES

Table	Page
1 Preparation of C-1/TEG Bottoms Polyester Prepolymers	4
2 Polyester-Epoxy Curing Studies	8
3 Polyester-Epoxy Curing Studies	10
4 Polyester-Epoxy Curing Studies	12
5 Amine Catalysts Evaluated in Conjunction with C-1/TEG Bottoms Polyesters and Epoxy Cross-linking Agents .	14
6 Weight Loss Study of Molded Resins Cured at 200°C .	16

LIST OF FIGURES

Figure		Page
1	Infrared Spectrum of C-1 Char Acids	20
2	Infrared Spectrum of TEG (tetraethylene glycol) "bottoms" (Dow Chem.)	21
3	Infrared Spectrum of Polyester Prepolymer #18-7	22
4	Infrared Spectrum of Polyester #18-7 in Combina- tion with DER 331 Epoxy (10%-wt) and DETA Catalyst Prior to Curing	23
5	Infrared Spectrum of Polyester #18-7 Cured with DER 331 Epoxy (10%-wt) and DETA Catalyst, (16 hr at 150°C)	24
6	Infrared Spectrum of Polyester #18-7 Cured with DER 331 Epoxy and DETA Catalyst. Sample subjected to thermal aging (110 hr at 150°C)..	25
7	Infrared Spectrum of Polyester #18-7 Cured with DER 331 Epoxy and DETA Catalyst. Sample Sub- jected to thermal aging (110 hr at 150°C, 17 hr at 200°C).....	26

THE UTILIZATION OF COAL CONVERSION PROCESS BY-PRODUCTS

1. SUMMARY

A feasibility study has been initiated which is aimed at the manufacture of low cost, thermosetting, cross-linkable polymers by using the carboxylic acid mixture obtained in the oxidation of the coal conversion process chars. The main criteria utilized in the selection of polymerization approaches are: (1) the polymerization process should be commercially feasible; (2) the co-reactant(s) should be low cost, readily available materials; (3) the polymerization should be relatively insensitive to the composition of the char acid mixture, which may vary from batch to batch; and (4) char acids should be an essential constituent of the final product.

Several polyester compositions were prepared by condensation of char acid extracts with various glycols and subsequently evaluated as molding materials. Among the various glycols investigated, tetraethylene glycol "bottoms", a by-product of the synthesis of ethylene glycol, was found to be a promising co-reactant for polyesterification. Polymerization reactions were conducted under conditions leading to the formation of fusible, partially polymerized resins, which were subsequently cross-linked in a mold with epoxide-functional curing agents in the presence of amine catalysts.

Very encouraging results have been obtained up to this point and it appears that commercially valuable polymers can be produced. Larger scale studies, in which physical properties of the polymer can be obtained, are planned.

2. INTRODUCTION

During the previous quarter, a laboratory study was initiated that was aimed at determining the feasibility of the manufacture of low-cost, thermosetting, cross-linkable polymers by using the carboxylic acid mixture obtained in the oxidation of the coal conversion process chars. Several polyester compositions were prepared by condensation of char acid extracts with various glycols. These polyesters were subsequently evaluated as molding materials. As a general rule, the polymers obtained from the higher molecular weight glycols showed improved flexibility and moldability. Among the various glycols investigated, tetraethyleneglycol "bottoms" (TEG-bottoms, Dow Chemical) was found to be a promising co-reactant for polyesterification. This is a by-product of the synthesis of ethylene glycol, consisting of tetra- and pentaethylene glycol as well as other glycols having a wide molecular weight range. It is a promising co-reactant because of its low cost and its ability to flexibilize the polymerization product by acting as an "internal" plasticizer.

During the present quarter, most of the work has been devoted to the study of polyesters of char acids with TEG bottoms. For this purpose we utilized a combination of char acids (identified as C-1) obtained from various oxidation studies. The average carboxyl group concentration of C-1 char acids as determined by potentiometric titration was found to be 1.27×10^{-2} [COOH] eq/g. The polyesterification reactions were conducted under conditions leading to the formation of fusible, partially polymerized resins. These were subsequently cross-linked with epoxide-functional curing agents in the presence of amine catalysts. A number of small scale polymerization reactions were performed by varying the C-1/TEG bottoms ratio, the polyesterification conditions, the type and concentration of epoxy cross-linker, the type of amine catalyst and the curing temperature and time. Several polyester compositions were evaluated as molding compounds which exhibited very promising properties.

3. POLYESTERIFICATION OF THE ORGANIC EXTRACTS OBTAINED IN THE OXIDATION OF CCP BY-PRODUCTS

Incorporation of unsaturated groups in C-1/TEG "bottoms" polyesters was investigated with the objective of providing an active site for curing by an addition process similar to the one employed with conventional unsaturated (styrene modified) polyesters. Thus, the polyester of TEG with C-1 coal acids was modified by incorporation of various amounts of butenediol during the stage of prepolymer formation. Attempts to induce cross-linking of the unsaturated prepolymers by addition of styrene monomer and benzoyl-peroxide catalyst were only partially successful because of the poor compatibility of the prepolymers with styrene. This approach was abandoned and further work was performed on the curing reaction of the hydroxylfunctional char acid prepolymer with epoxide-functional compounds. Unlike the prepolymers with ethylene glycol studied earlier in this program, the polyesters obtained with TEG exhibited excellent compatibility with the epoxies and good shelf-life.

Polyester prepolymers were prepared by using weight ratios C-1/TEG bottoms of 1:0.3; 1:0.5; 1:1; 1:1.5; and 1:2. The synthesis procedures employed were described in a previous report. Polyesterification reactions were conducted with and without catalyst under various reaction conditions. Some typical polyester compositions are shown in Table 1. The type of product obtained and its degree of polymerization depended upon the presence of a catalyst, the reaction temperature and time, and whether the reaction was conducted at atmospheric or reduced pressure. For uncatalyzed systems and reaction times of approximately 2 hr under nitrogen flow and 2 hr under vacuum at 150°C, it was found that the prepolymers synthesized at weight ratios C-1/TEG bottoms of 1:2 and 1:1.5 were highly viscous liquids; at a ratio 1:1 the prepolymer was semisolid; at lower TEG contents solid prepolymers were obtained. Solid prepolymers were infusible and not suitable

Table 1

Preparation of C-1/TEG bottoms Polyester Prepolymers

Sample I.D.	Solvent	C-1/TEG, btms/cat	Reaction Conditions			Weight Loss g/%	Comments
			Temp °C	N ₂ Flow Hr	Vacuum Hr/mm Hg		
17-14	BuOH	1:0.3: -	156	2	2/0.4	-	Hard resinous product
17-12	"	1:0.51: -	150	2	2/0.4	-	Slightly tacky, brown granules
17-10	"	1:0.68: -	150	2	2/0.4	-	Rubbery material, does not flow at 260°C
17-11	"	1:1: -	150	2	2/0.4	-	Lumpy semisolid, rubbery, does not flow
18-5	none	1:1: -	130	1/2	-	-	Very viscous, reddish black material
18-10	BuOH	1:1: -	150	2 ½	3/0.4	0.1658/4.1	Very viscous, slowly pourable
18-11	BuOH	1:1.25: -	150	3	2 (aspirator) 2/0.4	0.4567/9.3	Tacky, rubbery mass
18-12	"	1:1.25: -	150	2	1 ½/0.2	0.3655/7.4	Very viscous, slowly pourable
18-7	"	1:1.5: -	150	3 ½	½ (aspirator) 3/0.4	0.3834/7.4	Very viscous, very slowly pourable, flows on heating, 120°C
18-16	"	"	150	4	4/0.4	-	Same as above
17-16	BuOH	1:2: -	150	2	2/0.4	-	Very viscous, slowly pourable
18-17	VuOH	1:2: -	150	4	4 ½/0.4	4/0234/11.2	Pourable viscous
19-4	none	1:2.03:0.06	150	5	17 (aspirator)	1.0881/12.6	Infusible rubbery mass
19-6	none	1:2.0:0.092	150	17	-	0.9786/16.9	Tacky rubbery material. Does not flow at 150°C
19-7	none	1:1.975:0.090	120-115	5	-	0.4119/5.5	
			150	17	-	0.4048/5.8	
			150		5/0.4	0.8044/12.4	Tacky, rubbery, does not flow at 150°
17-8*	none	1:2.01:0.090	110	5	-	3.9507/11.9	Tacky semisolid, rubbery does not flow at 150°C
			150	17	-		

Table 1 (cont.)

Preparation of C-1/TEG bottoms Polyester Prepolymers

Sample I.D.	Solvent	C-1/TEG, btms/cat	Reaction Conditions				Weight Loss g/%	Comments
			Temp °C	N ₂ Flow Hr	Vacuum Hr/mm Hg	TIME		
17-9	none	1:2.03:0.091	110-115 150	5 17	-	0.2608/3.5 0.6106/7.55	Very viscous, flows at 120°C	
19-10*	none	1:2.04:-	110-115 150 150	5 17 -	- - 1 (aspirator)	0.4853/5.5 0.3446/4.1 -	Viscous, slowly pourable	
19-12	none	1:2.03:-	115 150	5 17	- -	0.4877/7.9 0.2405/4.2	Tacky, rubbery, intractable, does not flow at 150°	
19-5	none	1:3.06:0.123	150	5	17 (aspirator)	1.9872/24.1	Non tacky, rubbery material, intractable	

* Pure TEG was employed instead of TEG bottoms.

for mixing with epoxies, even at elevated temperatures. In order to maximize the amount of char acids utilized in polymer synthesis and to obtain processable polyesters of low TEG content, experiments were conducted in which polyesterification was interrupted at an earlier stage (lower degree of polymerization). It was possible to synthesize polyesters of low degree of polymerization at weight ratios char acids/TEG bottoms of 1:1.25 and 1:1 which were fusible and compatible with epoxy cross-linking agents. Unfortunately these low molecular weight prepolymers were highly susceptible to void formation during curing as a result of the entrapment of volatile by-products. To a lesser degree, formation of volatile by-products during the curing stage was a problem even with polyesters of higher TEG content and higher degree of polymerization. Thus, a study was initiated to determine the feasibility of synthesizing polyester prepolymers possessing fusibility, compatibility for epoxy cross-linking agents, and reacted to the extent that no voids due to volatile by-products be formed during subsequent curing stages. Long reaction times under vacuum (17 hr at 150°C) in the presence of p-toluenesulfonic acid (p-TSA) as a catalyst gave infusible polymers even at low C-1/TEG ratios (1:3 by weight). Long reaction time at atmospheric pressure under nitrogen flow (5 hr at 110-115°C and 18 hr at 105°C) in the presence of p-TSA as a catalyst at a C-1/TEG ratio of 1:2 gave a highly viscous liquid prepolymer that was compatible with epoxies and suitable for use as molding resin. This prepolymer (#19-9, Table 1) exhibited excellent thermosetting properties with no void formation when cured at 200°C for 17 hr.

4. EPOXY CROSS-LINKING OF CHAR ACID POLYESTERS

The polyester prepolymers obtained from C-1 char acids and TEG bottoms were treated with various cross-linking agents, including Dow epoxy resins DER 331, DER 332 and DER 337 (5,10 and 20%-wt epoxy resin). The curing reaction was catalyzed by addition of diethylenetriamine (DETA), m-phenylene diamine (MPDA), polyoxypropylenediamine (POPDA), DEH 42 (Dow Chemical Co.) and DEH 14 (Dow Chemical Co.). Typical curing experiments with a variety of polyester prepolymers, curing agents and catalysts are shown in Tables 2, 3 and 4. Flexibility was found to increase with decreasing epoxy concentration and with increasing TEG concentration in the polyester prepolymer. DER 331 was preferred because of its lowest cost. DER 337 (a high viscosity epoxy resin having an epoxide equivalent weight of 230-250) gave a cured product considerably less rigid than DER 331 at equivalent epoxy concentrations, therefore, the latter was preferred.

The amines evaluated as cross-linking catalysts are shown in Table 5. All these amines were found to be effective catalysts. The selection of the amine was made on the basis of the rate of curing and strength of the product obtained. In terms of rate of curing, DETA was the most effective of the catalysts evaluated. However, this was a disadvantage with highly viscous polyester prepolymers that required heating to achieve adequate melt flow. Under these conditions, the curing reaction was too fast to allow uniform melt flow. DEH 52 was found to be the most useful catalyst. It allowed efficient mixing with high viscosity polyesters at 120°C and resulted in a cured product noticeably stronger than when other amine catalysts were employed. For these reasons, a curing system consisting of DER 331 epoxy resin and DEH 52 catalyst was selected for further work.

Table 2

Polyester Epoxy Curing Studies

Cured Sample I.D.	Prepolymer		Epoxy/Hardner	Prepolymer Epoxy:Hardner Wt ratio	Reaction Temp. °C	Reaction Conditions		Total Wt. Loss		Comments
	I.D.	Wt ratio C-1/TEG, btms				Hr	%			
18-10B	18-10	1:1	DER 331:DETA	1:0.05:0.01	150	24	0.0798	17.5	Nontacky surface skin (1 hr), rubbery (2 hr), hard rubber (7hr)	
18-10C	"	"	"	1:0.1:0.01	"	"	0.0640	11.6	Fairly hard rubber (1 hr and 2 hr). Overnight: black surface, sl. flexible, tough. Excellent impression	
18-10D	"	"	"	1:0.2:0.02	"	"	0.0531	14.4	Hard rubber (1 hr and 2 hr). Overnight: black surface, barely flexible, tough, excellent mold impression	
18-10A	"	"	"	"	"	"	0.0411	12.5	Stringy gel, non-tacky surface (1 hr), hard rubber (7 hr). Overnight: brownish black, rough surface, flexible, tough, excellent mold impression	
18-15	18-10	1:1	DER 331:DETA	1:0.1:0.011	150	18	0.2734	13.9	Black, smooth surface; flexible. Many pin holes on the bottom side	
18-12A	18-12	1:1.25	DER 331:DETA	1:0.05:0.007	150	6	0.0645	14.9	Dull black surface, very flexible; no pin holes, poor mold impression	
18-12B	"	"	"	1:0.1:0.01	"	"	0.038	8.6	Same as above; fair mold impression	
18-12C	"	"	"	1:0.2:0.02	"	"	0.0314	8.1	Brownish dull black surface, flexible, tough, excellent mold impression.	

Table 2 (cont.)

Polyester Epoxy Curing Studies

Cured Sample I.D.	I.D.	Prepolymer		Epoxy/Hardner	Prepolymer Epoxy:Hardner Wt ratio	Reaction Conditions		Total Wt. Loss		Comments
		C-1/TEG btms	Wt ratio			Temp. °C	Time Hr	%	g	
18-12D	18-12	1:1.25				150	6	0.1246	33.3	Brownish black rough surface; fairly tough, flexible, poor mold impression
18-13A	18-12	1:1.25	DER 331:DETA	1:0.05:0.01		150	17	0.0728	17.2	Dull black surface; flexible, tough, good mold impression
18-13B	"	"	"	1:0.1:0.01		150	"	0.068	16.0	Same as above
18-13C	"	"	"	1:0.2:0.02		"	"	0.0525	15.2	Same as above, less flexible
18-13D	"	"	"	"		"	"	0.0492	17.9	Brownish black rough surface, most flexible of the above

Table 3

Polyester-Epoxy Curing Studies

Sample I.D.	Prepolymer I.D.	Wt ratio		Epoxy/Hardener	Prepolymer: Epoxy:Hardner		Reaction Conditions		Total Weight Loss g %	Comments
		C-1/TEG	btms		wt. ratio	Temp. °C	Time Hr			
18-7A	18-7	1:1.5		DER 331:DETA	1:0.5:0.005	150	18	0.1009	19.5	Dull black rough surface, very flexible, tough, good mold impression
17-7B	"	"		"	1:0.1:0.01	"	"	0.0876	18.8	Same as above
18-7C	"	"		"	1:0.20:0.29	"	"	0.1647	34.2	Black surface, less flexible, very tough, excellent mold impression
18-8A	"	"		DER 331: DEH 52	1:0.05:0.013	100	18	0.0891	21.9	Black surface, very tough barely flexible, excellent mold impression
18-8B	"	"		"	1:0.1:0.03	"	"	0.0977	22.5	Same as above
18-8C	"	"		"	1:0.2:0.06	"	"	0.0793	19.7	Same as above, less flexible
18-9A	18-7	1:1.5		DER 331:MPDA	1:0.05:0.008	100	2	0.1130	23.9	Dull black surface, flexible, tough, excellent mold impression
18-9B	"	"		"	1:0.1:0.01	100	2	0.0842	22.3	Same as above
18-9C	"	"		"	1:0.2:0.019	100	2	0.0565	18.9	Same as above, less flexible
18-15B	18-7	1:1.5		DER 331:DETA	1:0.1:0.01	150	18	0.2999	20.4	Black surface, flexible, tough, pin holes along edge

Table 3 (cont.)

Polyester-Epoxy Curing Studies

Sample I.D.	Prepolymer I.D.	Wt ratio C-1/TEG btms	Epoxy/Hardener	Prepolymer: Epoxy:Hardner wt. ratio	Reaction Temp. OC	Reaction Conditions		Total Weight Loss %	Comments
						Time Hr	£		
18-19A	18-16	1:1.5	DER 337:DETA	1:0.048:0.005	150	18	0.0771	15.6	Dull black surface, flexible, excellent mold impression, no pinholes
18-19B	"	"	"	1:0.103:0.013	"	"	0.0732	15.5	Same as above
18-19C	"	"	"	1:0.202:0.023	"	"	0.0680	15.0	Same as above, less flexible
18-19D	"	"	"	"	"	"	0.0676	18.4	Characteristics similar to 5% DER 337
18-20A	18-16	1:1.5	DER 337:POPPA	1:0.049:0.021	"	"	0.0871	19.4	Dull black surface, flexible, tough, excellent mold impression
18-20B	"	"	"	1:0.1:0.041	"	"	0.0593	15.7	Same as above, less flexible
18-20C	"	"	"	1:0.2:0.07	"	"	0.0944	24.1	Black surface, least flexible

Table 4

Polyester-Epoxy Curing Studies

Sample I.D.	Prepolymer I.D.	Wt ratio C-1/TEG btms	Epoxy-Hardener	Prepolymer: Reaction Conditions		Total Weight Loss %	Comments		
				Epoxy:Hardner wt. ratio	Temp. °C				
18-3A	17-16	1:2	DER 331:MPDA	1:0.2:0.04	150	18	0.0910	21.7	Black surface, very tough and stiff, excellent mold impression
18-3B	"	"	DER 331:DETA	1:0.2:0.06	"	"	0.0848	25.2	More flexible than above
18-6A	"	"	DER 331:DETA	1:0.1:0.04	"	"	0.1292	25.3	Same as above but more flexible
18-6B	"	"	DER 331:DETA	1:0.06:0.006	"	"	0.0818	25.0	Same as above, more flexible
18-18A	18-17	1:2	DER 337:DETA	1:0.051:0.007	150	18	0.108	26.8	Glossy black surface, very flexible, excellent mold impression
18-18B	"	"	"	1:0.108:0.014	"	"	0.1009	26.7	Dull black surface, flexible; excellent mold impression
18-18C	"	"	"	1:0.203:0.020	"	"	0.1148	22.2	Same as above
18-18D	"	"	"	"	"	"	0.0942	31.2	Dull black surface, flexibility same as 18-18A
18-22A	18-17	1:2	DER 337:DEH 52	1:0.05:0.002	"	"	0.1375	26.1	Dull black surface, very flexible, tough, excellent impression
18-22A	18-17	1:2	DER 337:DEH 52	1:0.05:0.002	"	"	0.1375	26.1	Dull black surface, very flexible, tough, excellent impression

Table 4 (cont.)

Polyester-Epoxy Curing Studies

Sample I.D.	Prepolymer I.D.	Wt ratio C-1/IEG btms	Epoxy-Hardener	Prepolymer:		Reaction Conditions		Total Weight Loss %	Comments
				Epoxy:Hardner wt. ratio	Temp. °C	Time Hr	g		
18-22B	18-17	1:2	DER 337:DEH 52	1:0.1:0.025	150	18	0.1350	24.8	Same as above but less flexible
18-22C	"	"	"	1:0.20:0.045	"	"	0.1106	22.7	Same as above, less flexible
18-23A	18-17	1:2	DER 337:POPDA	1:0.051:0.042	150	18	0.1429	29.1	Dull black surface, very flexible, tough, excellent impression
18-23B	"	"	"	1:0.10:0.036	"	"	0.1495	26.0	Same as above, less flexible
18-23C	"	"	"	1:0.199:0.074	"	"	0.1301	23.3	Same as above, less flexible

Table 5

Amine Catalysts Evaluated in Conjunction with
C-1/TEG Bottoms Polyesters And
Epoxy Cross-Linking Agents

<u>Amine</u>	<u>No. of Active H</u>	<u>Amine H Eq. Wt.</u>	<u>PHR¹ for DER 331²</u>	<u>Manufacturer</u>
DETA	5	20.6	10.9	Dow Chem.
MPDA	4	27.03	14.3	Dow Chem.
POPDA ³	4	-	35.0	Jefferson Chem.
DEH 52	5	53	28.0	Dow Chem.
DEH 14	-	-	30-70	Dow Chem.

¹ PHR - parts by weight of 100 parts resin

² DER 331 Epoxide equivalent weight of 186-192 (aver. 189)

³ Polyoxypropylenediamine

5. CURING PROCEDURES AND WEIGHT LOSS STUDIES

Evaluation of curing characteristics and polymer moldability was performed by using a silicone mold. In order to improve the flow properties of highly viscous prepolymers, slightly elevated temperatures were employed for mixing with epoxy curing agents. Three types of heating systems were employed: A Koeffler heating bar, a non-circulating oven and an air-circulating oven. The Koeffler heating bar was the least efficient but was useful to prevent formation of a hard surface "skin" which entrapped volatile by-products. This was generally a problem when a non-circulating oven was used. The air-circulating oven gave the most uniform curing.

Formation of voids resulting in spongy structures was always a problem when polyester prepolymers of low degree of polymerization were used. The tendency of various polyester prepolymers to liberate volatile by-products during curing was evaluated in a weight loss study of three samples, identified as 18-16, 19-9, and 19-10 (Table 6). The weight ratio C-1/TEG bottoms was 1:1.5 for prepolymer 18-16, 1:2 for prepolymers 19-9 and 19-10. Prepolymer 18-16 was prepared by reaction at 150°C for 4 hr under nitrogen flow and 4 hr under vacuum (0.4 mm Hg). Prepolymers 19-9 and 19-10 were prepared by reaction under nitrogen flow at 115°C for 5 hr and at 150°C for 18 hr without vacuum. Prepolymer 19-10, unlike 19-9, was reacted in the absence of an esterification catalyst and with pure TEG instead of TEG bottoms. Molds of these materials were prepared by adding 5, 10 and 20% DER 331 epoxy and DEH 52 as a catalyst. The resins were heat-cured on the Koeffler hot bench at 120°C then in an air-circulating oven at 200°C. Weight losses during curing increase with decreasing the amount of epoxy used as cross-linking agent. Entrapment of volatile by-products, however, was more pronounced at lower TEG contents, presumably because by-product removal was prevented by the formation of an infusible polymer in the early heating stages. In all cases, weight losses during curing were very pronounced. Further curing studies will be performed

Table 6

Weight Loss Study of Molded Resins Cured at 200°C

Cured Sample ID	Prepolymer ID	Initial Weight	4 Hr		8 Hr		12 Hr		16 Hr		Total Wt. Loss	
			g	%	g	%	g	%	g	%	g	%
19-2A	18-16	0.4706	0.0728	15.5	0.0341	7.2	0.0092	1.96	0.0098	2.1	0.1259	26.8
19-2B	"	0.5119	0.0819	16.0	0.0368	7.2	0.0094	1.8	0.0098	1.9	0.1379	26.9
19-2C	"	0.4192	0.0619	14.8	0.0266	6.3	0.0068	1.6	0.0086	2.0	0.1039	24.8
19-2D	"	0.2613	0.0533	20.4	0.0183	7.0	0.0037	1.4	0.0044	1.7	0.0797	30.5
19-3A	"	0.4275	0.0749	17.5	0.0321	7.5	0.0059	1.4	0.006	1.4	0.1189	27.8
19-3B	"	0.4782	0.0784	16.4	0.0325	6.8	0.0075	1.6	0.0073	1.5	0.1257	26.3
19-3C	"	0.3600	0.0518	14.4	0.0227	6.3	0.0058	1.6	0.0055	1.5	0.0858	23.8
19-3D	"	0.2839	0.0555	19.6	0.0192	6.8	0.0044	1.6	0.0045	1.6	0.0836	29.4
19-11A	19-9	0.3982	0.0892	22.4	0.0179	4.5	0.0117	2.9	0.003	0.75	0.1218	30.6
19-11B	"	0.3886	0.0860	22.1	0.0170	4.3	0.0113	2.9	0.0029	0.75	0.1172	30.2
19-11C	"	0.3809	0.0671	17.6	0.0169	4.4	0.0124	3.3	0.0035	0.92	0.0999	26.2
19-11D	"	0.3353	0.0803	23.9	0.0150	4.5	0.0103	3.1	0.0025	0.75	0.1081	32.2
19-13A	19-10	0.4974	0.1388	27.9	0.0307	6.2	0.0041	0.82	0.0044	0.88	0.1780	35.8
19-13B	"	0.5119	0.1324	25.9	0.0292	5.7	0.0036	0.70	0.0141	2.7	0.1793	35.0
19-13C	"	0.3372	0.0850	25.2	0.0129	3.8	0.0005	0.15	0.0105	3.0	0.1055	31.3
19-13D	"	0.3053	0.1050	34.4	0.0147	4.8	0.0001	0.03	0.0092	3.0	0.1290	42.3

by gradually increasing the temperature to determine whether weight losses during curing can be reduced or eliminated.

6. INFRARED SPECTROSCOPY

An attempt was made to study the curing reaction of prepolymer 18-7 (weight ratio C-1/TEG bottoms = 1:1.5) by infrared analysis. A film prepared from a mixture of prepolymer 18-7, DER 331 (10%-wt) and DETA catalyst was subjected to heat curing at 150°C. Subsequently, the same sample was heated at 200°C for 17 hr and 127 hr and IR spectra were taken. The IR spectra of monomeric C-1 carboxylic acids (Figure 1), monomeric TEG-bottoms (Figure 2), polyester prepolymer 18-7 (Figure 3), polyester prepolymer in combination with 10% DER 331 and DETA catalyst prior to curing (Figure 4), and cured 16 hr at 150°C (Figure 5), are included in this report. The IR spectra of samples aged 110 hr at 150°C (Figure 6) and aged 110 hr at 150°C and 17 hr at 200° (Figure 7) are also included. A thorough analysis of these spectra is in progress. A cursory examination reveals that a decrease in the intensity of the -OH absorption band at 2.85 μ compared to the CH₂ stretch band at 3.45 μ takes place during curing due to a decrease in functional group concentration with increasing degree of polymerization. For longer curing times at higher temperatures (Figure 6, 7), the intensity of the 2.85 μ band relative to the 3.45 μ CH₂ stretching band decreases, suggesting the occurrence of chain cleavage reactions leading to regeneration of functional end-groups.

7. PLANS FOR FUTURE WORK

Several polyester compositions obtained from char acid extracts and TEG "bottoms" appear to possess promising properties as molding compounds. In order to assess the commercial feasibility and market potential of these materials it is essential to obtain physical testing data. For this purpose, we are undertaking the synthesis of larger quantities of char acids that will allow scale-up polymerization and fabrication of test specimens for tensile measurements. It is anticipated that the work during the next quarter will be directed primarily to scale-up synthesis and testing of char acid polyesters.

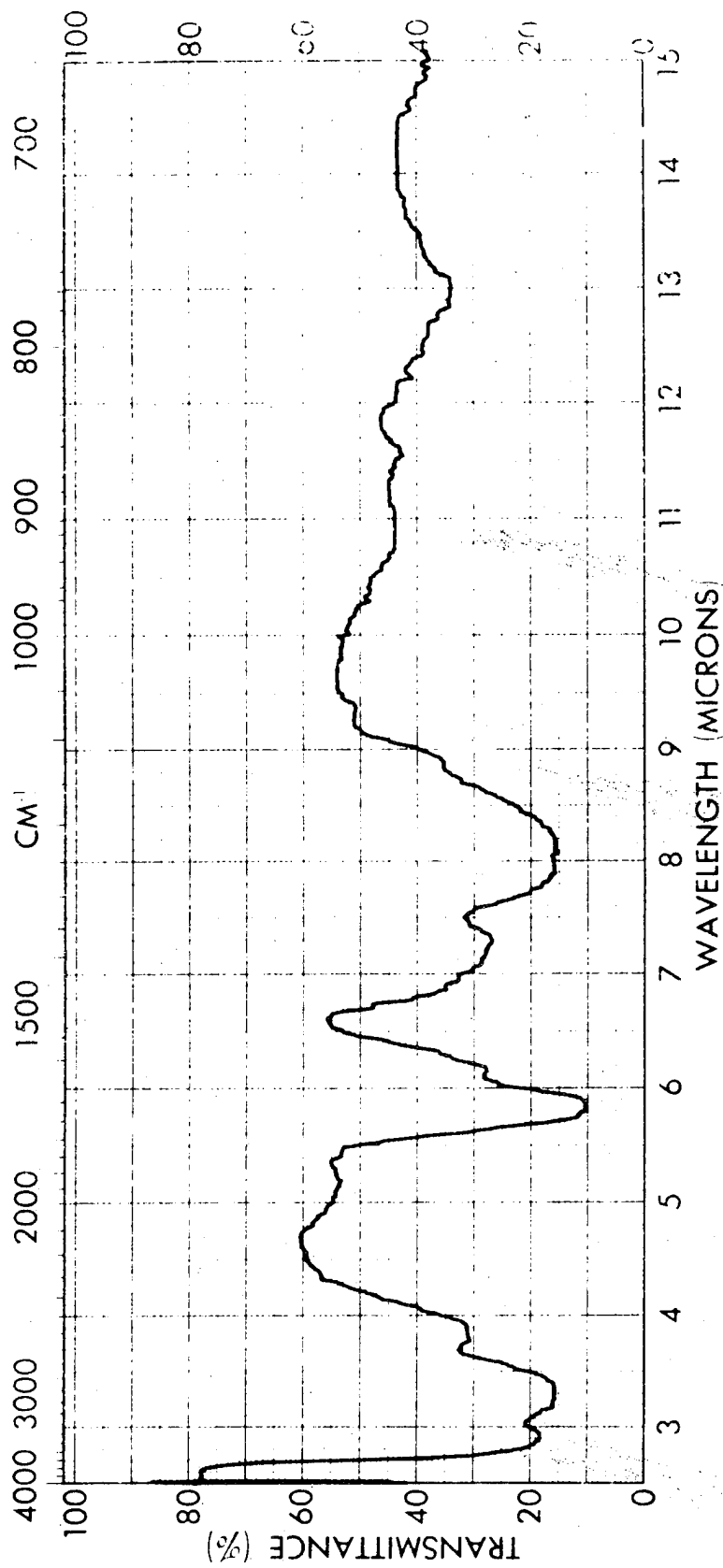


Figure 1
Infrared Spectrum of C-1 Char Acids

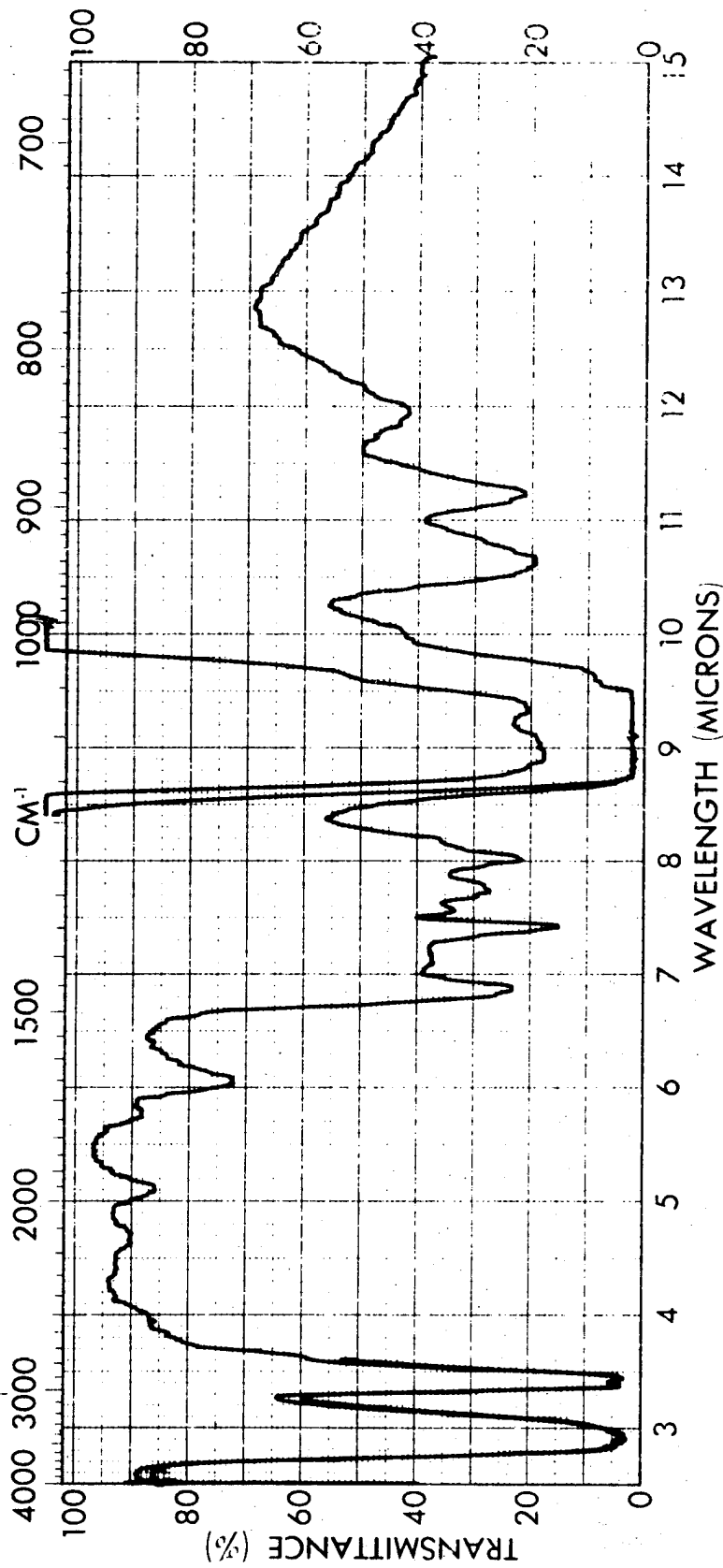


Figure 2

Infrared Spectrum of TEG (tetraethylene glycol) "bottoms" (Dow Chem.)

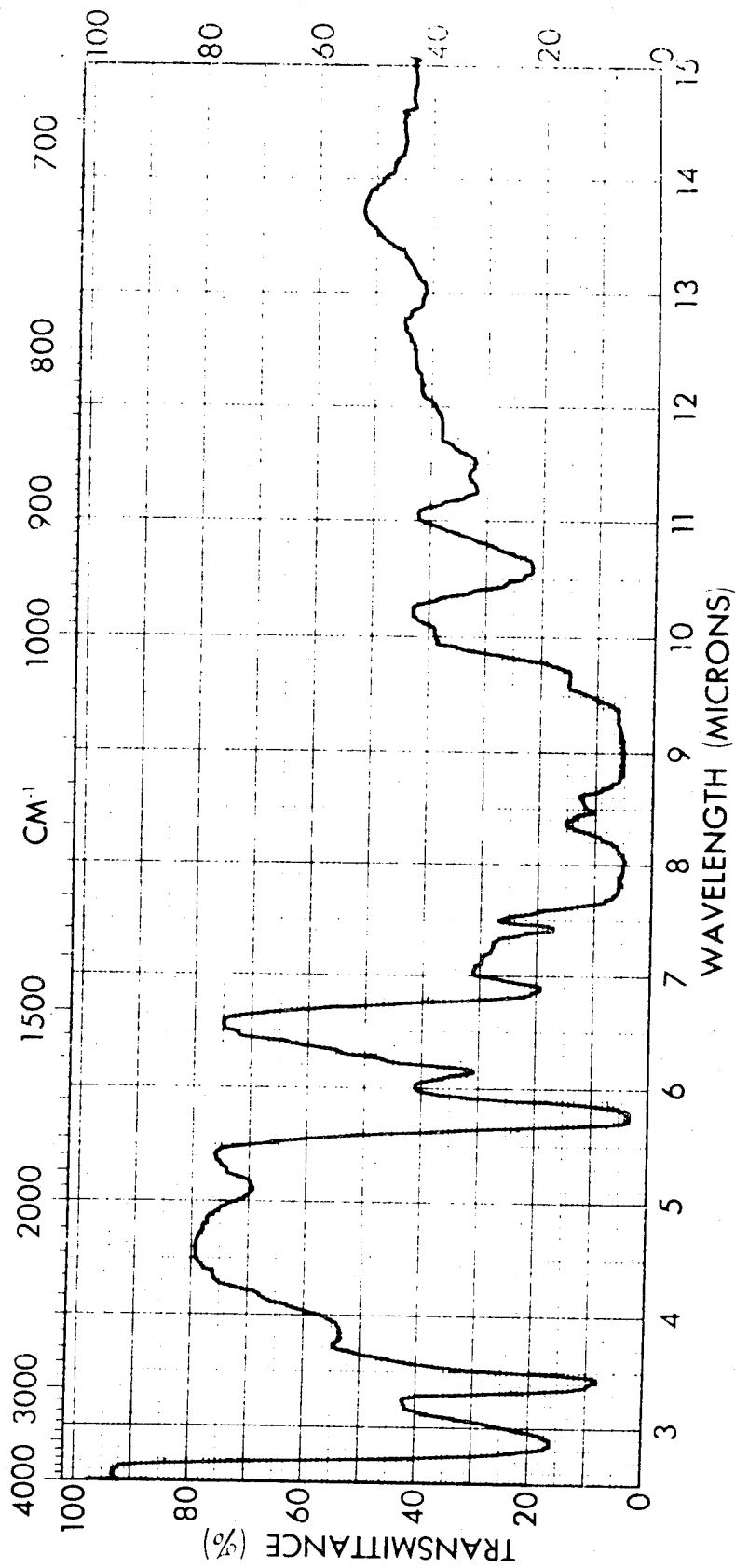


Figure 3

Infrared Spectrum of Polyester Prepolymer #18-7

(C-1/TEG ratio - 1:1.5 by weight)

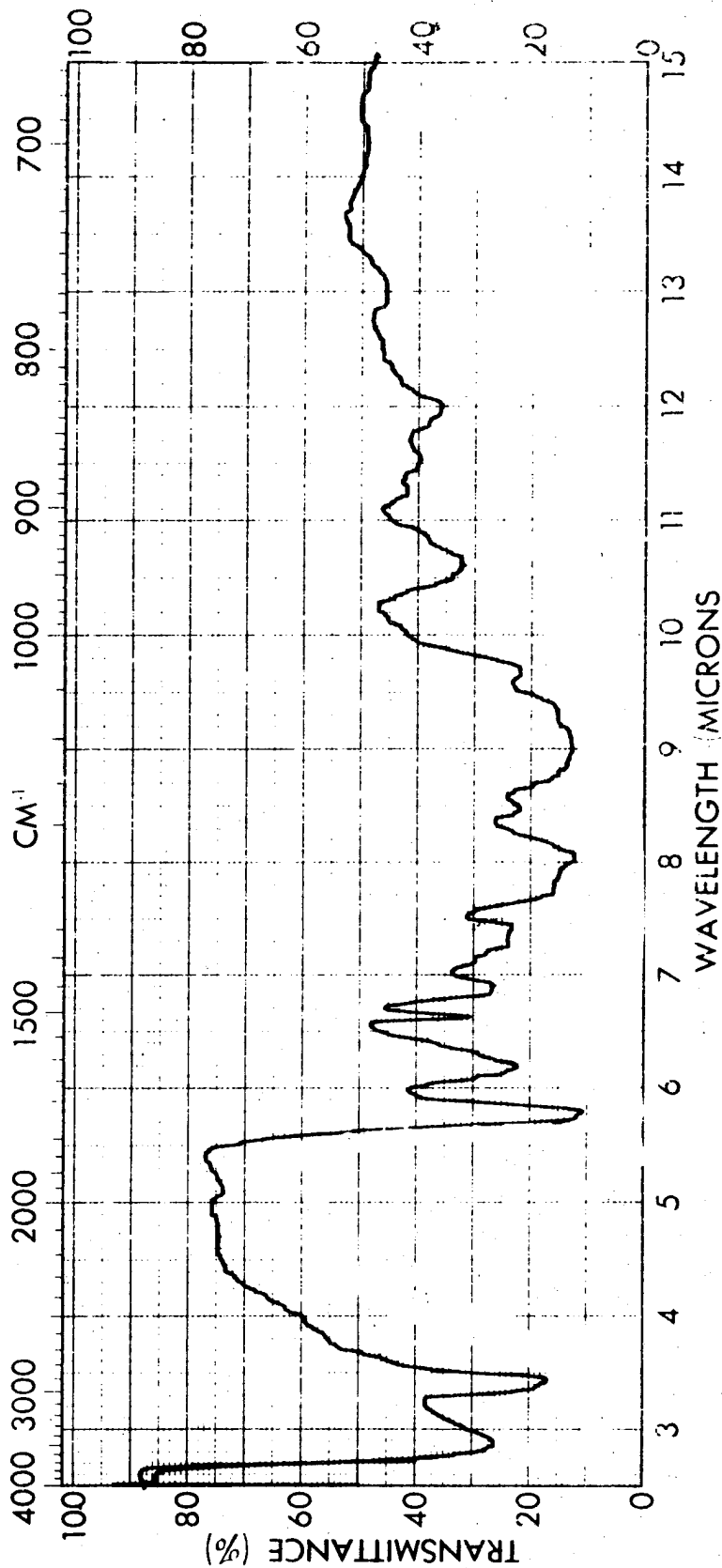


Figure 4

Infrared Spectrum of Polyester #18-7 in Combination with DER 331 Epoxy
(10%-wt) and DETA Catalyst Prior to Curing

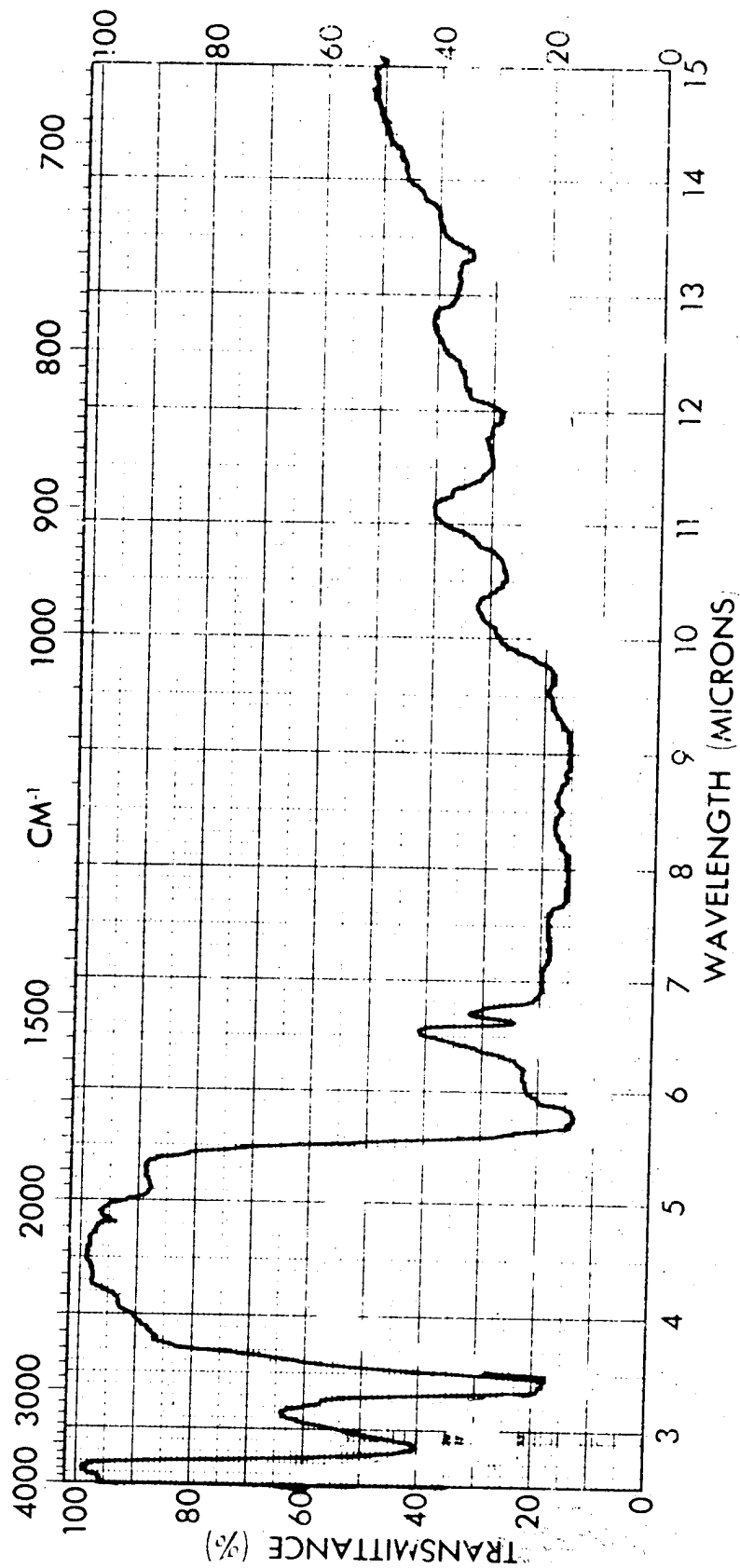


Figure 5

Infrared Spectrum of Polyester #18-7 Cured with DER 331
(10%-wt) and DETA Catalyst (16 hr at 150°C)

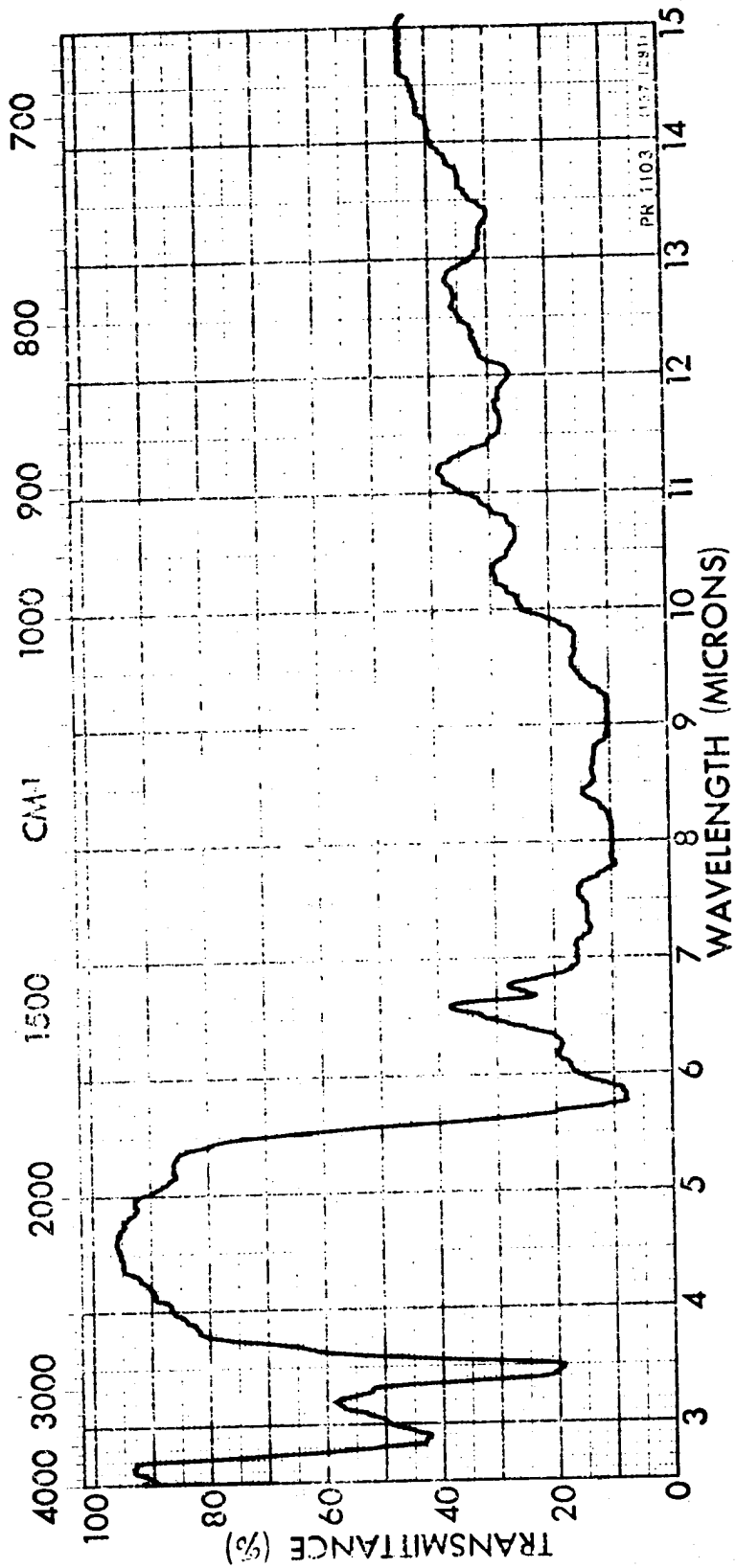


Figure 6

Infrared Spectrum of Polyester #18-7 Cured With DER 331 Epoxy
(10%-wt) and DETA Catalyst. Sample Subjected to Thermal Aging
(110 hr at 150°C).

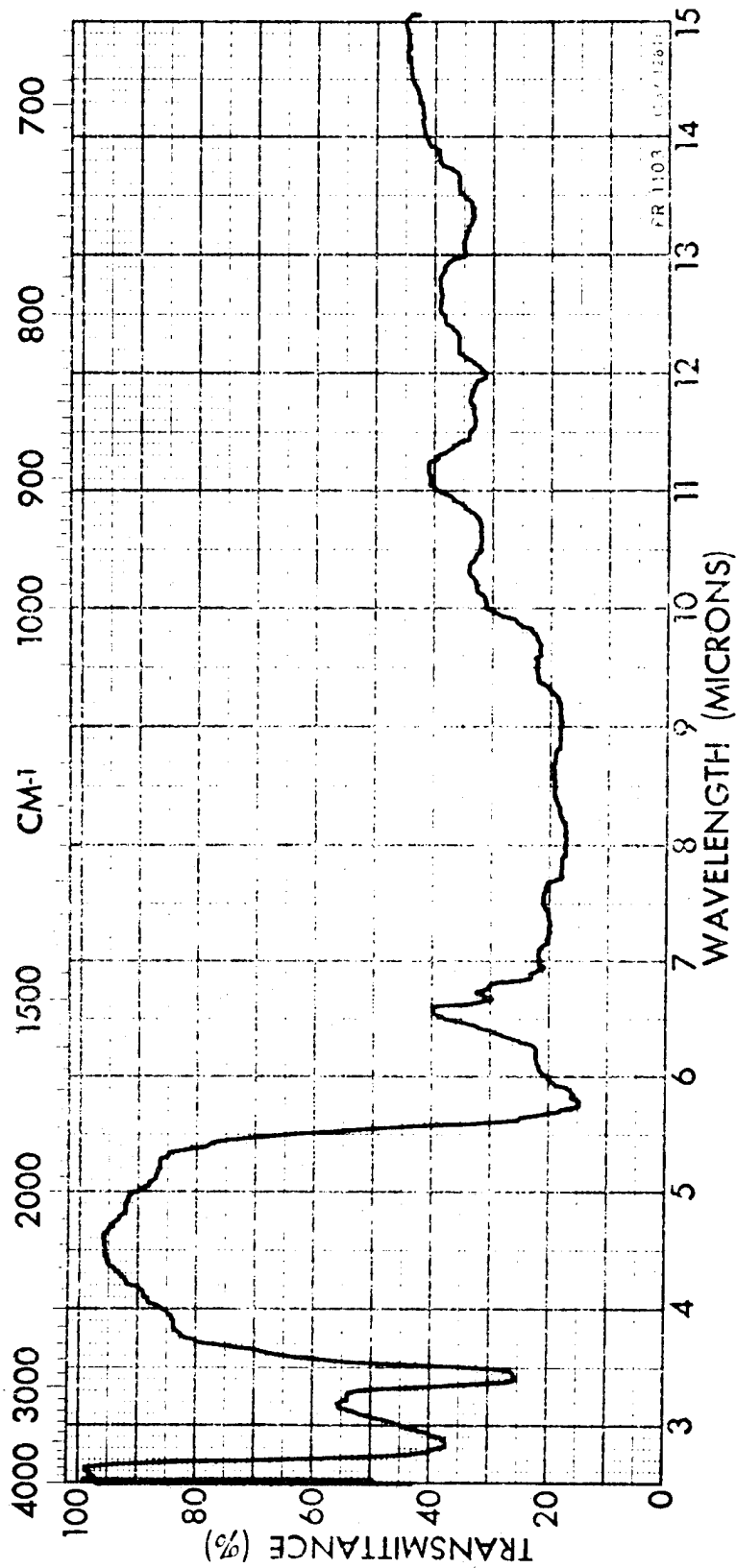


Figure 7

Infrared Spectrum of Polyester #18-7 cured with DER 331 Epoxy and DETA Catalyst
Sample Subjected to Thermal Aging (110 hr at 150°C, 17 hr at 200°C)

