

Pyrolysis of Plastics in a High Vacuum Arc Image Furnace. II

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Synopsis

Samples of glass- and nylon-reinforced CTL 91-LD phenolic and G. E. 124 resin were pyrolyzed in an arc image furnace at high vacuum. Compositions of the various degradation gases are reported. Average molecular weights of these gases were calculated. A description of the mechanism of pyrolysis of G. E. 124 resins is presented. A critique of the method is included.

INTRODUCTION

The purpose of this study is to obtain chemical compositions of pyrolysis gases that would be injected into the boundary layer that surrounds ablating plastics. The results of studies of arc image furnace degradation of nonreinforced and glass-reinforced CTL 91-LD phenolic (a product of Cincinnati Testing and Research Laboratory) in high vacuum were published previously.¹ These studies are extended in the present paper to the nylon-reinforced phenolic and formulation #124 of the General Electric Company Century Series resins. The results of further pyrolyses of the glass-reinforced phenolic are also reported.

EXPERIMENTAL

Apparatus and Methods

The apparatus and analytical techniques that were employed were essentially the same as those that were used in earlier studies.^{1,2} The arc image furnace consisted of a pair of General Electric Company 60-in. diameter searchlight mirrors. The carbon arc source was able to supply a maximum flux of about 400 B.T.U./ft.²-sec. to the 1/2-in. diameter surface. Some modifications were made in the vacuum system, as may be seen by comparison of Figure 1 with Figure 2 of reference 1. In the earlier work, the noncondensable gases were removed from the vicinity of the hot plastic by expansion into a surge volume. These gases were then completely transferred to a sample flask by Toepler pump, and were allowed to stand so that the gases became thoroughly mixed. A *P-V-T* measurement served to determine the total yield of noncondensables. In the present

TABLE I
General Summary (Including Yields of Noncondensable Components and Ammonia)

Run	Exposure time, sec.	Total weight loss, g.	Yield								
			Third fraction, g.	First fraction, moles $\times 10^3$	Second fraction, 10^3 moles $\times 10^3$	H ₂ , moles $\times 10^3$	CO, moles $\times 10^3$	CH ₄ , moles $\times 10^3$	N ₂ , moles $\times 10^3$	NH ₃ , moles $\times 10^3$	
				Glass-reinforced phenolic							
33	5.0	0.2464	0.0421	—	1.705	—	—	—	—	—	0.988
37	10.0	0.3576	0.1100	9.029	1.938	5.581	2.546	0.876	0.028	0.028	0.897
38	10.0	0.3674	0.1209	9.523	2.334	5.913	2.685	0.895	0.028	0.028	0.966
51	10.0	0.3538	0.1144	8.826	2.122	5.436	2.322	1.041	0.026	0.026	1.055
52	10.0	0.3468	0.1099	8.765	2.030	5.337	2.358	1.034	0.035	0.035	1.020
				Nylon-reinforced phenolic							
34	10.0	0.4602	0.0887	7.385	6.548	4.505	2.068	0.805	0.007	0.007	0.785
39	10.0	0.4541	0.1192	7.718	7.072	4.724	2.192	0.787	0.012	0.012	0.859
40	10.0	0.4521	0.1234	8.066	7.051	5.009	2.249	0.791	0.016	0.016	0.858
49	10.0	0.4469	0.1096	7.694	7.035	4.762	2.093	0.824	0.014	0.014	0.763
50	10.0	0.4503	0.1237	7.729	7.597	4.646	2.188	0.881	0.016	0.016	0.823

G. E. 124 resin										
25 ^a	5.0	0.1610	0.0267	3.208	1.623	1.778	1.104	0.327	0.000	0
28	10.0	0.4420	—	8.275	4.659	4.295	3.078	0.893	0.005	0
29	10.0	0.4470	0.1422	8.411	4.582	4.263	3.154	0.988	0.005	0
30	5.0	0.1450	0.0177	4.526	1.535	2.770	1.484	0.268	0.002	0
31	5.0	0.1578	0.0291	4.708	1.536	2.882	1.559	0.268	0.002	0
32 ^b	5.1	—	—	4.935	1.578	3.045	1.624	0.266	0.001	0
35	10.0	0.3370	0.0976	7.604	3.622	4.357	2.616	0.624	0.007	0
36	10.0	0.4105	0.1377	7.917	4.642	4.267	2.873	0.768	0.009	0
41	10.0	0.4393	0.1196	7.929	4.445	4.527	2.816	0.569	0.005	0
42	10.0	0.4486	0.1012	7.976	4.402	4.458	2.896	0.614	0.005	0
53	10.0	0.4497	0.1222	8.499	4.951	4.505	3.179	0.791	0.026	0
54	10.0	0.4475	0.1188	8.459	4.812	4.559	3.104	0.779	0.016	0
56 ^c	10.0	0.3548	0.1207	7.555	4.104	4.216	2.743	0.589	0.002	0

^a Sample from different batch than other runs.

^b Direct expansion of noncondensables into surge volume with diffusion pump not operating.

^c Sample from different batch than other runs.

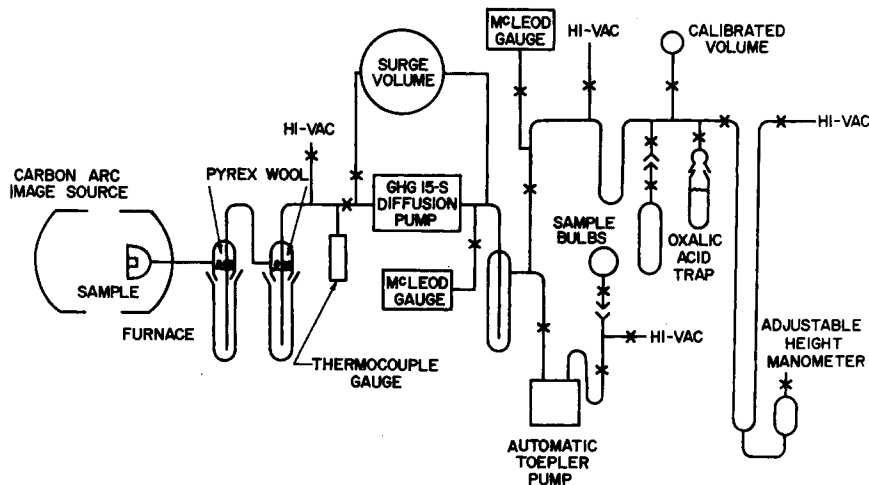


Fig. 1. Arc image furnace vacuum system.

work, the noncondensables were pumped into a pre-evacuated expansion volume, as they formed, with a Consolidated Electro-dynamics Corporation Model GHG 15-S diffusion pump. This pump was able to function against a maximum fore pressure of 5–10 mm. Hg. When transfer was completed, the pump was used to circulate the gases in order to mix them. P - V - T measurements were used to determine yields, but in this case, the pressure was measured in the expansion volume with a McLeod gage. The new procedure was more efficient than the earlier method.

In the earlier work, zero time was defined as the time when the arc became stable. A crude shutter was used to determine zero time in the present work. The quartz dome was covered with a pair of aluminum foil sheets that were supported on cardboard. Before the arc was struck, a long string was attached to each sheet, and the sheets were fastened to each other with masking tape. When the discharge was stable, the cardboard sheets were pulled away from the quartz dome and were allowed to drop to the floor of the furnace housing. Zero time was defined as that when the shutter was withdrawn. Exposure time was the interval between zero time and the instant when the arc was extinguished.

The volatile degradation products were once again divided into three fractions. The first fraction was volatile at liquid nitrogen temperature. The second fraction consisted of the remaining products that were volatile at CO_2 ice-trichloroethylene bath temperature (-78°C .). The third fraction consisted of the balance of the products that were volatile at room temperature. Quantitative analysis of the first fraction was performed by chromatography. Qualitative analyses of second and third fractions were performed by infrared absorption spectroscopy and a combination of chromatography with time-of-flight mass spectroscopy. Quantitative analyses of second and third fractions were performed by mass spectroscopy. Ammonia in second fractions of the phenolics was analyzed by absorption

TABLE II
Detailed Product Analyses for Glass-Reinforced Phenolic

Component	Fraction	Moles $\times 10^3$		
		Run 38	Run 51	Run 52
Hydrogen	1	5.913	5.436	5.337
Methane	1	0.895	1.047 ^a	1.034
Ammonia	2	0.984 ^b	1.055	1.020
Water	3	—	4.931	1.152
Acetylene	2	1.293	0.842	—
Hydrogen cyanide	2	0.231	0.235	—
Carbon monoxide	1	2.685	2.322	2.358
Nitrogen	1	0.028	0.026	0.035
Ethylene	2	0.231	0.307	—
Ethane	2	0.014	0.042	—
Methanol	2	0.005	—	—
Propyne	2	0.035	—	—
Propylene	2	0.072	0.076 ^b	—
Carbon dioxide	2	0.040	0.141	—
Ethanol	2	0.005	—	—
Diacetylene	2	0.093	0.082	—
Vinylacetylene	2	0.044	0.024	—
Butadiene	2	0.012	—	—
Acetone	3	—	0.049	0.058
Isopropanol	3	0.026 ^c	0.225	0.310
2-Pentene-4-yne	2	0.061	—	—
Cyclopentadiene	2	—	0.086	—
Benzene	3	0.135 ^c	0.249 ^b	0.549
Toluene	3	0.019 ^c	0.046 ^b	0.159
Phenylacetylene	3	—	0.011	—
Styrene	3	—	0.007	0.003
Xylenes	3	—	0.030 ^b	0.076
Methylphenyl- acetylene	3	—	0.008	—
Methylstyrene	3	—	0.006	0.002
C ₇ Aromatics	3	—	0.010	0.008
Dimethylstyrene	3	—	0.001	—
Material balance, % ^d		86.8	87.6	—

^a Trace of methane in fraction 2.

^b Parts of component in fractions 2 and 3.

^c In fraction 2.

^d Weight of three volatile fractions compared to total weight loss.

in anhydrous oxalic acid. Total yields of third fractions were determined gravimetrically in small tubes.

Materials

Both reinforced phenolics contained about 40% phenolic by weight. Nylon 66 was used. The 1/2 in. diameter by 1 in. long cylinder samples were machined so that the cloth reinforcement was perpendicular to the circular faces. The G. E. 124 resin samples were machined from cast rods.

TABLE III
Detailed Product Analyses for Nylon-Reinforced Phenolic

Component	Fraction	Moles $\times 10^3$		
		Run 39	Run 49	Run 50
Hydrogen	1	4.724	4.762	4.646
Methane	1	0.787	0.824	0.881
Ammonia	2	2.859	0.763	0.823
Water	3	—	0.026 ^a	3.016
Acetylene	2	2.610	2.096	1.793
Hydrogen cyanide	2	0.580	0.475	1.014
Carbon monoxide	1	2.192	2.093	2.188
Nitrogen	1	0.012	0.014	0.016
Ethylene	2	2.355	2.487	3.480
Ethane	2	0.042	—	0.090
Propyne	2	0.141	—	—
Propylene	2	0.156	0.261	0.338 ^b
Carbon dioxide	2	0.446	0.435	0.408
Propane	2	0.057	—	—
Ethanol	2	0.057	—	—
Diacetylene	2	0.177	0.209	0.131
Vinylacetylene	2	0.134	—	0.106
Butadiene	2	0.106	—	—
Acrolein	2	—	0.839	—
Butylenes	2	—	—	0.069
Acetone	3	—	0.015 ^a	0.137
Isopropanol	3	0.014 ^a	0.011 ^a	0.445
2-Pentene-4-yne	2	0.141	—	—
Cyclopentadiene	2	—	—	0.009
Pentenes	2	—	—	0.009
Benzene	2	0.113	0.168	0.218 ^b
Toluene	2	0.014	0.013	0.097 ^b
Phenylacetylene	3	—	—	0.080
Styrene	2	—	0.001	0.044 ^b
Xylenes	2	—	0.001	0.062 ^b
4-Ethenyl-1-cyclohexane	2	0.002	—	—
Methylphenyl- acetylene	3	—	—	0.016
Methylstyrene	3	—	—	0.008
C ₉ Aromatics	3	—	—	0.010
Dimethylstyrene	3	—	—	0.001
C ₁₀ Aromatics	3	—	—	0.001
Material balance, % ^c		98.5	99.8	102.7

^a In fraction 2.

^b Parts of component in fractions 2 and 3.

^c Weight of three volatile fractions compared to total weight loss.

RESULTS

The results of these experiments are listed in Tables I-IV. Table I contains a general summary of all runs carried out for the three materials, including quantitative analyses for first fractions, and ammonia for the

TABLE IV
Detailed Product Analyses for G. E. 124 Resin

Component	Fraction	Moles $\times 10^3$			
		Run 41	Run 42	Run 54	Run 56
Hydrogen	1	4.527	4.458	4.559	4.216
Methane	1	0.579	0.614	0.779	0.589
Water	3	—	—	3.865	5.435
Acetylene	2	1.551	1.228	—	0.616
Hydrogen cyanide	2	0.018	0.013	—	—
Carbon monoxide	1	2.816	2.896	3.104	2.743
Nitrogen	1	0.005	0.005	0.016	0.002
Ethylene	2	0.573	0.748	—	1.931
Ethane	2	0.044	0.040	—	0.064
Propyne	2	0.053	0.084	—	—
Propylene	3	0.244 ^a	0.291 ^a	0.094	0.220 ^b
Carbon dioxide	2	1.200	1.211	—	0.715
Propane	2	0.071	0.110	—	—
Ethanol	2	0.004	—	—	—
Diacetylene	2	0.102	0.062	—	0.061
Vinyl acetylene	2	0.071	0.066	—	0.031
Butadiene	2	0.049	0.035	—	—
Acrolein	2	0.138	0.176	—	—
Butylenes	2	—	—	—	0.050
Acetone	3	—	—	0.040	0.170 ^b
Propanol	2	0.102	0.128	—	—
Isopropanol	3	—	—	0.028	0.019
2-Pentene-4-yne	2	0.093	0.088	—	—
Cyclopentadiene	2	—	—	—	0.077
Pentenes	2	—	—	—	0.023
<i>n</i> -Pentane	2	—	—	—	0.003
Isopentanes	2	—	—	—	0.049
<i>n</i> -Butanol	3	—	—	0.105	0.033
Benzene	3	0.120 ^a	0.101 ^a	0.186	0.160 ^b
Toluene	3	0.004 ^a	0.003 ^a	0.034	0.020 ^b
Phenol	3	—	—	—	0.017
Phenylacetylene	3	—	—	0.018	0.010
Styrene	3	—	—	0.023	0.006
Xylenes	3	—	—	0.031	0.007
Methylphenol	3	—	—	—	0.007
4-Ethenyl-1-cyclohexane	2	0.031	0.004	—	—
Methylphenyl- acetylene	3	—	—	0.036	0.013
Methylstyrene	3	—	—	0.017	0.006
C ₉ Aromatics	3	—	—	0.009	0.002
Dimethylphenol	3	—	—	—	0.004
Dimethylstyrene	3	—	—	0.004	0.004
C ₁₀ Aromatics	3	—	—	0.003	—
Material balance, % ^c		88.4	82.3	—	101.3

^a In fraction 2.

^b Parts of component in fractions 2 and 3.

^c Weight of three volatile fractions compared to total weight loss.

phenolics. Tables II-IV show quantitative compositions for all experiments where second or third fractions were analyzed. Products are listed in order of increasing molecular weight.

DISCUSSION

Examination of Table I shows that experiments which were carried out for the same exposure time on samples from the same batch had a reasonable degree of reproducibility with respect to total weight loss, total yields of the various fractions, and the specific analyses of noncondensable components and ammonia. The 10-sec. exposure runs for glass phenolic were not very different from the 10-sec. run on the previous study¹ (Table 1, run 4). The specific analyses of the condensables, as listed in Tables II-IV, were quite reproducible for most components, but there were some marked differences. Some of these differences may have been due to different interpretations of the mass spectra from the two different analytical laboratories. In the case of G. E. 124 resin (Table IV), the sample from run 56 is from a different batch than the other samples. It is thought, also, that some of the differences may be due to chemical reactions which occurred between the various products while standing. It is interesting to note that, in some cases, fractions of product formed brown solids while standing, while other fractions, which one might assume to be identical, did not.* The most evident differences are H₂O for the glass phenolic in Runs 51 and 52 and acrolein for the nylon phenolic in Run 49. Mass spectroscopy would be expected to be comparatively inaccurate when applied to fractions which contain a large percentage of water. Tables II-IV also list material balances for all cases where the first and second fractions were analyzed in detail. For glass-reinforced phenolic (Table II, runs 38 and 51), 86.8 and 87.6% of the weight loss was accounted for by the three volatile fractions. It is reasonable that these should be less than 100% since some glass was also lost, and since some products which were not volatile at room temperature were observed on the surface of the quartz dome and on the Pyrex wool filter of the first trap. For nylon-reinforced phenolic (Table III, runs 39, 49, and 50), 98.5, 99.8, and 102.7% of the weight loss appeared in the volatile fractions. These represent extremely good agreement. For G. E. 124 resin (Table IV, runs 41, 42, and 56), 88.4, 82.3, and 101.3% of the total weight loss was accounted for. Sample 56 was not only from a different batch than samples 41 and 42, but mass spectroscopy of the second fractions was carried out in different laboratories. Since a small amount of products are observed on the quartz dome and in

* Recent flash pyrolysis studies of glass-reinforced phenolic in the reaction chamber of a time-of-flight mass spectrometer have shown that sulfur dioxide is a decomposition product; 0.1% sulfur was found by subsequent chemical analysis. It seems likely that sulfur dioxide reacted with ammonia in the presence of water in the traps to form ammonium sulfite. It is also possible that ammonia reacted with some of the carbon dioxide to form ammonium carbonate. Therefore, at least in the case of the glass reinforced phenolic, the reported quantity of ammonia is too low, carbon dioxide may be too low, and sulfur dioxide is completely missing.

TABLE V. Average Product Compositions and Molecular Weights

Component	Moles $\times 10^3$			Mole-%		
	Glass phenolic	Nylon phenolic	G. E. 124	Glass phenolic	Nylon phenolic	G. E. 124
Hydrogen	5.567	4.729	4.383	34.7	23.9	25.1
Methane	0.963	0.818	0.735	6.0	4.1	4.2
Ammonia	0.994	0.818	—	6.2	4.1	—
Water	3.042	3.025	4.650	18.9	15.3	26.6
Acetylene	1.068	2.166	1.132	6.7	10.9	6.5
Hydrogen cyanide	0.233	0.690	0.010	1.5	3.5	0.1
Carbon monoxide	2.478	2.158	2.940	15.4	10.9	16.8
Nitrogen	0.029	0.013	0.009	0.2	0.1	0.1
Ethylene	0.269	2.774	1.084	1.7	14.0	6.2
Ethane	0.028	0.044	0.049	0.2	0.2	0.3
Methanol	0.003	—	—	0.0	—	—
Propyne	0.018	0.047	0.046	0.1	0.2	0.3
Propylene	0.074	0.301	0.304	0.5	1.5	1.7
Carbon dioxide	0.091	0.430	1.042	0.6	2.2	6.0
Propane	—	0.019	0.060	—	0.1	0.3
Ethanol	0.003	0.019	0.001	0.0	0.1	0.0
Diacetylene	0.088	0.172	0.075	0.5	0.9	0.4
Vinylacetylene	0.034	0.080	0.056	0.2	0.4	0.3
Butadiene	0.006	0.035	0.028	0.0	0.2	0.2
Acrolein	—	0.280	0.105	—	1.4	0.6
Butylenes	—	0.023	0.017	—	0.1	0.1
Acetone	0.054	0.142	0.078	0.3	0.7	0.4
Propanal	—	—	0.077	—	—	0.4
Isopropanol	0.281	0.453	0.024	1.7	1.3	0.1
2-Pentene-4-yne	0.032	0.047	0.060	0.2	0.2	0.3
Cyclopentadiene	0.043	0.003	0.026	0.3	0.0	0.1
Pentenes	—	0.003	0.008	—	0.0	0.0
<i>n</i> -Pentane	—	—	0.001	—	—	0.0
Isopentanes	—	—	0.016	—	—	0.1
<i>n</i> -Butanol	—	—	0.069	—	—	0.4
Benzene	0.467	0.178	0.233	2.9	0.9	1.3
Toluene	0.112	0.093	0.029	0.7	0.5	0.2
Phenol	—	—	0.009	—	—	0.1
Phenylacetylene	0.006	0.080	0.014	0.0	0.4	0.1
Styrene	0.005	0.044	0.015	0.0	0.2	0.1
Xylenes	0.053	0.062	0.019	0.3	0.3	0.1
Methylphenol	—	—	0.004	—	—	0.0
4-Ethyl-1-cyclohexane	—	0.001	0.012	—	0.0	0.1
Methylphenylacetylene	0.004	0.016	0.025	0.0	0.1	0.1
Methylstyrene	0.004	0.008	0.012	0.0	0.0	0.1
C ₆ Aromatics	0.009	0.010	0.006	0.1	0.1	0.0
Dimethylphenol	—	—	0.002	—	—	0.0
Dimethylstyrene	0.001	0.001	0.004	0.0	0.0	0.0
C ₁₀ Aromatics	—	0.001	0.002	—	0.0	0.0
Totals	16.059	19.783	17.471	99.9	99.8	99.8

TABLE VI
Average Molecular Weights of Pyrolysis Gases

Average molecular weight of pyrolysis gases, g./mole		
Glass phenolic	Nylon phenolic	G. E. 124
19.08	23.16	22.01

the Pyrex wool of the first trap in all cases, it may be that the material balances for nylon phenolic and run 56 are slightly high. However, it is more probable that those for runs 41 and 42 of the G. E. 124 resin are a little too low. Table V contains the average of all analytical data, and Table VI gives average molecular weights for products which were volatile at room temperature for each plastic for 10-sec. The real molecular weights for stable products would be a little higher because the nonvolatile products have comparatively high molecular weights. Run 56 has been included for G. E. 124 resin, even though it was from a different batch than the other samples because the data were not very different. The differences between decomposition products of glass and nylon reinforced phenolic are interesting. Although most components are produced in quite similar amounts, more CO_2 , HCN, and unsaturated hydrocarbons are produced in

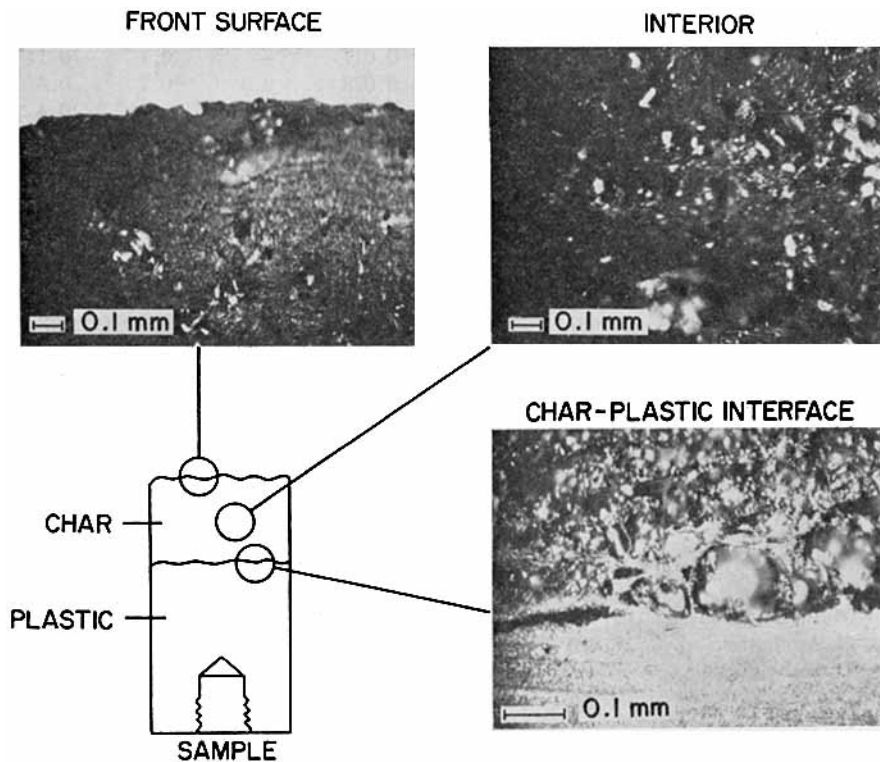


Fig. 2. Microstructure of char from G. E. 124 resin.

the case of nylon. These products are reasonable degradation products of nylon. Gruntfest³ observed similar differences for arc image furnace pyrolyses of nylon- and Refrasil-reinforced CTL 91-LD phenolics.

Barry and Gaulin⁴ studied the ablation of Century Series Resins as a function of pressure and heat flux in several arc plasma facilities and rocket exhaust. Under low pressure and low heat flux conditions, chars were found to contain rather large pores with thick walls with a broad distribution in pore diameter. At high pressures and heat fluxes, chars were more porous with a homogeneous distribution of smaller pores. Pyrolysis studies showed that the chars formed by a two-step process. The first was the production of a highly crosslinked foam at about 350°C., with the evolution of high molecular weight products. This was followed by a further decomposition at higher temperatures to form a more highly carbonaceous char, which was accompanied by the evolution of hydrogen and carbon monoxide. These authors likened the foaming process to the production of polyurethane foams. For slow rates of foaming, small pores have time to break and form larger pores with thick walls. Foaming under vacuum also tends to produce large pores, since the escape of gas is accelerated with the material in a very fluid state. Speeding up the process, with increased pressure, tends to give foams of uniformly fine pore structure, with low density and thin walls, if sufficient foaming volatiles are available.

Arc image furnace pyrolyses are carried out under low pressure and high heat flux conditions. Microscope photographs of three char zones are shown in Figure 2. The region closest to the front surface appears to have a combination of the two types of chars that were described by Barry and Gaulin. While there were a few large pores, a bulk of the char appeared to have rather fine uniform pores. The interior char, however, had the characteristic appearance of the low heat flux, low pressure types. Although the front surface of the char had some small fissures, there were many very large fissures which opened to the sides of the sample between the front surface and the virgin plastic. The chars which were produced in the arc image furnace appeared to be superficially similar to those that were produced by Barry and Sutton⁵ by passing the hot plasma from an air-stabilized arc through the interior of cylindrical test specimens which had been bored.

Barry and Gaulin⁴ pyrolyzed samples of pulverized G. E. 123 resin, a somewhat different formulation from the 124 resin, in an evacuated tube to temperatures slightly below 1000°C. Product analyses was performed for some of the fractions. H₂ was not observed as a reaction product until temperatures of about 600°C. were reached. Although experiments at lower temperatures were of longer duration, it took a variety of times, 167–280 sec., to heat samples from room temperature to the final elevated temperatures. Comparison of the relative yields of H₂ with CO, CH₄, and CO₂ showed that their product picture was most like those of the arc image furnace experiments at about 700°C. These authors showed that the

maximum char temperatures of various parts of low heat flux low pressure chars did not exceed 300–600°C., and predicted that the gases that would be injected into the plasma stream would have compositions similar with tube furnace experiments that were carried out at these temperatures. High heat flux, high pressure chars were shown to exceed 1000°C. Low temperature decomposition products of G. E. 123 resin were also allowed to percolate through a char which was generated from 126 resin while the char was heated to above 2250°C. with an induction heater. Of the available hydrogen, 85% was recovered as H₂, while 86% of the available oxygen was recovered as CO. Very small amounts of CH₄, C₂H₄, and C₂H₂ were formed.

Examination of Table I shows that the rate of loss of weight of 124 resin was higher for the 10-sec. exposure than for 5 sec. Although the rates of formation of CH₄, the second, and third fractions also increased with increased exposure, those for H₂ and CO decreased. Analysis of the various factors leads to the following description of the pyrolysis of G. E. 124 resin in the arc image furnace.

The application of the high heat flux at the front surface of the sample led, initially, to the rapid formation of a highly cross-linked porous char with a comparatively homogeneous distribution of small pores. The presence of vacuum caused larger pores to form in a small fraction of this zone, and some small fissures resulted. As pyrolysis continued, the effective heat flux which reached the lower regions was reduced. Because the formation of the porous char was slower, the vacuum environment caused the more fluid char pores to break and form larger pores with thick walls. The gases were released from these lower temperature regions through large fissures in the cylindrical wall of the sample. For the shorter exposures, the relative quantity of the higher temperature degradation, which led to the formation of H₂ and CO, was more important than for the longer exposures, where the lower temperature degradation processes assumed greater importance. Although the front surface of the sample was probably heated to above 2000°C., the final product picture for the 10-sec. run was more representative of heating at 700°C. It is likely that very short exposures would yield products that are more representative of higher temperature degradation.

Although it was not tested in any systematic fashion, the installation of the C.E.C. Model GHG 15-S diffusion pump did not appear to influence the results of the experiments. It is possible that this pump did not influence the pumping rate appreciably since the 1½ m. length of ½ in. diameter tubing was allowed to remain between the dome and the first trap.* Changing of this tubing would have meant a major modification of the vacuum system. Enlargement at the dome could have caused interference with focussing. Perhaps a cylindrical configuration could have been used instead of spherical. The use of much larger tubing, or pipe, would have

* Photographs and detailed description of apparatus have been given elsewhere.¹

made handling the system more difficult. Another possibility could be to remove the gases through the back. Placement of the vacuum system with respect to the source and furnace housings could then be a problem. It is possible, however, that even very efficient pumping would not change the situation. The pressure at the face of the sample during pyrolysis may be so high compared to the pressure of the surrounding region that very few molecules would find their way back to a region which is hot enough to cause an appreciable change in the initial stable products.

CONCLUSIONS

These studies and the earlier work¹ have shown that it is possible to obtain reasonably reproducible product compositions of high temperature pyrolysis products of plastics with an arc image furnace and with a variety of analytical techniques. Several factors limit the degree of reproducibility that may be achieved. It is very difficult to reproduce focussing of the arc because of the inherent instability of arcs and the cumbersome 60-in. mirror housings. Shuttering is a real problem with the large mirrors. One would suspect that the table-top type of arc image furnace would be superior for such studies. As decomposition progresses, the position of the front surface of the plastic sample will change. This will change the energy input. Illumination of the sample face is not absolutely uniform. Uniformity and quantity of illumination are influenced by the decomposition products that are deposited on the surface of the dome. Since decomposition products arise from regions which are at different temperatures and states of decomposition simultaneously, interpretation of the data is difficult. This difficulty is enhanced by the large number of products. It might be helpful to instrument the samples to determine temperature at a variety of distances from the surface; however, interpretation of data will be difficult because of the other factors.

In order to evaluate the ability of a given plastic to withstand ablation, one must know the precise chemical composition of the gases that are injected into each part of the boundary layer. It is apparent that the composition at any point will be dependent upon local conditions and the history of that point. Therefore, the products which would be evolved from a nonuniformly heated plastic body would vary from point to point. In the case of the Century Series plastics, composition would also be influenced by local pressure. For G. E. 124 resin, at least, the compositions that are reported in this paper are not appropriate for high heat flux and high pressure. For such cases, one should probably assume that all available hydrogen is converted to H_2 and all available oxygen is converted to CO. Since the phenolics do not go through a foaming process during decomposition, the compositions which are reported for those materials are likely to be somewhat more representative of high heat flux, high pressure conditions.

In order to achieve better reproducibility for chemical analyses of the complex mixtures that are produced, one might set up elaborately developed

gas chromatography systems. Analyses of the type that were performed would be required to back up the chromatography because of the complexity of the product picture. Still, it might be difficult or impossible to eliminate chemical reactions between products, and between products and the chromatography apparatus. An improvement over the arc image furnace and similar methods has recently been achieved by flash pyrolysis in the reaction chamber of the Bendix time-of-flight mass spectrometer.⁶ These studies have shown that improved reproducibility results from carrying out analysis soon after the products form. It is also much easier to detect products which would disappear later through chemical reaction.

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Résumé

On a pyrolysé sous vide élevé dans un four à arc des échantillons de résine phénolique CTL 91-LD et de résine G.E. 124, renforcés de verre et de nylon. On décrit les compositions des différents gaz de dégradation. On a calculé les poids moléculaires moyens de ces gaz. On donne une description du mécanisme de pyrolyse des résines GE 124. On ajoute une critique de la méthode.

Zusammenfassung

Proben von glas- und nylonverstärktem CTL-91-LD-Phenol- und G.E.-124-Harz wurden in einem Bogenofen einer Pyrolyse in Hochvakuum unterzogen. Die Zusammensetzung der gasförmigen Abbauprodukte wird mitgeteilt. Das mittlere Molekulargewicht dieser Gase wird berechnet. Eine Beschreibung des Mechanismus der Pyrolyse von G.E.-124-Harzen wird vorgelegt. Eine Kritik der Methode wird gegeben.

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