JOURNAL OF APPLIED POLYMER SCIENCE VOL. 12, PP. 2339–2357 (1968)

Effect of Long-Term Oxidation at 200–300°C on Six Types of Aromatic Amide and Imide Resins

L. C. SCALA, W. M. HICKAM, and I. MARSCHIK,
Research and Development Center, Westinghouse Electric Corporation, Pittsburgh, Pennsylvania 15235

Synopsis

Six types of aromatic amide and imide resins in the form of wire enamels, paper, and film were subjected to thermal and oxidative deterioration at temperatures ranging from 200 to 300°C and for aging periods of 3 and 6 months. No HCN was evolved at any temperature and aging time. The main degradation product was, in all cases, carbon dioxide, in quantities increasing as functions of time and temperature. Other materials evolved were, in approximate order of magnitude, carbon monoxide, water, and nitrogen. Traces of acetonitrile were recovered from a film and a paper sample, while benzene, also in trace quantities, was evolved from the wire enamel samples at temperatures ranging from 250 to 300°C.

INTRODUCTION

It was previously reported that, under certain conditions involving degradation at 360–400°C in the presence of oxygen and with water present in one of the cold traps, traces of HCN were found among the gaseous degradation products from polyamide-imides.[1] The work reported here was carried out in order to determine whether HCN can reasonably be expected among the degradation products when such resins are used in applications involving long exposures to air at relatively high temperatures.

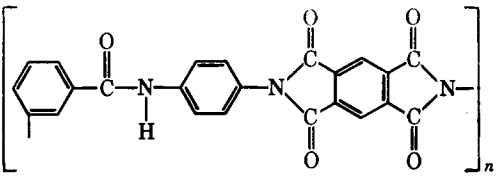
EXPERIMENTAL

Description of Samples

The samples chosen for this investigation were as follows:

AWG #20 Copper Wire Enameled with AI-8 Resin (Westinghouse Experimental Polyimide). The weight of the enamel constituted 3.7% of the weight of the enameled wire. The average weight of the enamel in each sample was 0.036 g. The samples had been post-cured for 0.5 hr at 250°C. The AI-8 resin has the structure I. The enamel build was 3.2–3.4 mils. The color of the enamel before treatment was medium brown bronze.

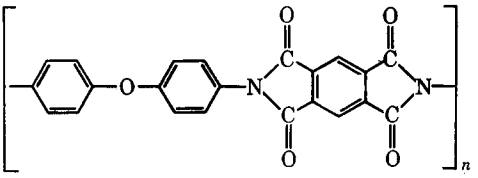
AWG #17 Copper Wire Coated with AI-43 Resin (Westinghouse Experimental Polyimide). The weight of the enamel was 2.1% of the weight



I

of the enameled wire, the average weight of the resin in each sample being 0.02 g. The enamel build was 2.2–2.4 mils. The structure of AI-43 is identical to that of AI-8, except for the replacement of part of the *m*-aminobenzoic derivative with the *p*-aminobenzoic derivative. Its unit molecular weight is 409. The original color of the sample was medium brown bronze.

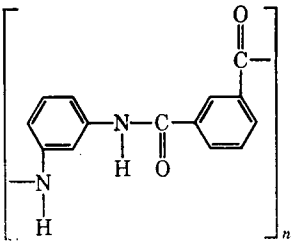
AWG #18 Commercial Copper Wire Coated with DuPont Pyre ML Enamel. The enamel build was 2.5–2.7 mils. The weight of the enamel was 2.4% of the weight of the coated wire, the average weight of ML enamel in each sample being 0.018 g. DuPont Pyre ML enamel may be de-



II

scribed by the structure II. The color of the original enamel was brown-bronze, lighter than the color of AI-8 enameled wire.

DuPont HT-1 Paper, (Nomex), 4 Mils Thick. This material, which has the structure III, was used without any pretreatment. The untreated



III

sample had an off-white color.

DuPont Kapton Film. This was a bright yellow, transparent film, 3 mils thick. The formula describing the DuPont Pyre ML wire enamel can also be applied to characterize the Kapton film, which was used "as received" in this investigation.

AI-7 (Westinghouse Experimental Polyamide-imide Resin). This was a yellow, transparent film, 7 mils thick. Because of the complexity of its structure, AI-7 resin will not be represented by a formula. It can

TABLE I
Composition of Atmosphere on Oxidation of AI-8 Enameled Wire in a Sealed System as a Function of Time and Temperature

Sample identification	Temp., °C	Aging time, mos	Gas, mol/g enamel							
			H_2	N_2	H_2O	CO	CO_2	O_2	C_6H_6	Ar
Initial gas mixture	Room	0	0.0002	—	0.0001	—	0.00003	0.0235	—	0.0178
No. 1	200	3	—	0.0005	0.0008	0.002	0.0038	0.0181	—	0.0178
No. 2		6	—	0.0005	0.0007	—	0.0075	0.0143	—	0.0178
No. 3	225	3	—	0.0005	0.0017	0.0001	0.0125	0.0092	—	0.0178
No. 4		6	—	0.0009	0.0015	0.0001	0.0205	0.0013	—	0.0178
No. 5	250	3	—	0.0009	0.0042	0.00004	0.0226	—	—	0.0178
No. 6		6	—	0.0010	0.0010	0.0001	0.0232	—	0.0001	0.0178
No. 7	275	3	—	0.0010	0.0020	0.00002	0.0239	—	0.0001	0.0178
No. 8		6								
No. 9	300	3	—	0.0011	0.0011	—	0.0268	—	0.0005	0.0178
No. 10		6	—	0.0010	0.0005	0.0002	0.0280	—	0.0007	0.0178

TABLE II
Composition of Atmosphere on Oxidation of AI-43 Enameled Wire in a Sealed System as a Function of Time and Temperature

Sample identification	Temp., °C	Aging time, mos	Gas, mol/g enamel							
			H_2	N_2	H_2O	CO	CO_2	O_2	C_6H_6	Ar
Initial gas mixture	Room	0	0.0004	—	0.0001	—	0.00005	0.0418	—	0.0318
No. 1	200	3	—	0.0026	0.0011	—	0.0058	0.0351	—	0.0318
No. 2		6	—	0.0036	0.0014	—	0.0092	0.0310	—	0.0318
No. 3	225	3	—	0.0035	0.0013	—	0.0126	0.0287	—	0.0318
No. 4		6	—	0.0034	0.0014	—	0.0213	0.0182	—	0.0318
No. 5	250	3	—	0.0040	0.0023	0.00004	0.0305	0.0083	—	0.0318
No. 6		6	—	0.0046	0.0022	0.0004	0.0382	—	0.00002	0.0318
No. 7	275	3	—	0.0048	0.0016	—	0.0389	—	—	0.0318
No. 8		6	—	0.0046	0.0024	0.0003	0.0400	—	0.0001	0.0318
No. 9	300	3	—	0.0051	0.0032	0.0003	0.0402	—	0.0001	0.0318
No. 10		6	—	0.0050	0.0026	0.0004	0.0418	—	0.0002	0.0318

TABLE III
Composition of Atmosphere on Oxidation of DuPont Pyre ML Enameled Wire in a Sealed System as a Function of Time and Temperature

Sample identification	Temp, °C	Aging time, mos	Gas, mol/g enamel							
			H_2	N_2	H_2O	CO	CO_2	O_2	C_6H_6	Ar
Initial gas mixture	Room	0	0.0005	—	0.0001	—	0.00006	0.0467	—	0.0355
No. 1	200	3	0.0001	0.0004	0.0005	—	0.0031	0.0441	—	0.0355
No. 2		6	—	0.0005	0.0008	—	0.0050	0.0397	—	0.0355
No. 3	225	3	—	0.0006	0.0006	—	0.0078	0.0387	—	0.0355
No. 4		6	—	0.0007	0.0011	—	0.0124	0.0315	—	0.0355
No. 5	250	3	—	0.0011	0.0018	—	0.0232	0.0205	—	0.0355
No. 6		6	—	0.0016	0.0023	—	0.0378	0.0044	—	0.0355
No. 7	275	3	—	0.0019	0.0033	—	0.0450	—	—	0.0355
No. 8		6	—	0.0021	0.0024	0.0003	0.0472	—	0.0002	0.0355
No. 9	300	3	—	0.0022	0.0027	0.0001	0.0471	—	0.0002	0.0355
No. 10		6	—	0.0022	0.0021	0.0002	0.0472	—	0.0003	0.0355

TABLE IV
Composition of Atmosphere on Oxidation of Nomex Paper in a Sealed System as a Function of Time and Temperature

Sample identification	Temp, °C	Aging time, mos	Gas, mol/g sample							
			H_2	N_2	H_2O	CO	O_2	Ar	CO_2	C_2H_3N
Initial gas mixture	Room	0	0.0004	—	0.0001	—	0.0400	0.0305	0.00005	—
No. 1	200	3	0.0004	—	0.0011	0.0008	0.0348	0.0305	0.0032	—
No. 2		6	0.0003	0.0001	0.0012	0.0001	0.0295	0.0305	0.0049	0.0001
No. 3	225	3	0.0003	0.0002	0.0026	0.0017	0.0250	0.0305	0.0101	0.0001
No. 4		6	0.0003	0.0001	0.0039	0.0032	0.0058	0.0305	0.0252	0.0001
No. 5	250	3	0.0003	0.0003	0.0066	0.0044	—	0.0305	0.0328	0.0001
No. 6		6	0.0003	0.0002	0.0033	0.0042	—	0.0305	0.0316	0.0002
No. 7	275	3	0.0003	0.0002	0.0052	0.0048	—	0.0305	0.0333	0.0002
No. 8		6	0.0002	0.0001	0.0036	0.0046	—	0.0305	0.0322	0.0002
No. 9	300	3	0.0003	0.0004	0.0037	0.0052	—	0.0305	0.0338	0.0001
No. 10		6	0.0002	0.0002	0.0027	0.0047	—	0.0305	0.0327	0.0002

TABLE V
Composition of Atmosphere on Oxidation of Kapton Film in a Sealed System as a Function of Time and Temperature

Sample identification	Temp, °C	Aging time, mos	Gas, mol/g sample						
			H_2	N_2	H_2O	CO	CO_2	O_2	Ar
Initial gas mixture	Room	0	0.0004	—	0.0002	—	0.00004	0.0381	0.0290
No. 1	200	3	0.0003	0.0006	0.0002	—	0.0001	0.0378	0.0290
No. 2		6	0.0003	0.0005	0.0002	—	0.0002	0.0373	0.0290
No. 3	225	3	0.0003	0.0005	0.0002	—	0.0005	0.0374	0.0290
No. 4		6	0.0003	0.0006	0.0003	—	0.0010	0.0365	0.0290
No. 5	250	3	0.0003	0.0004	0.0006	0.0017	0.0049	0.0310	0.0290
No. 6		6							
No. 7	275	3	0.0002	0.0004	0.0022	0.0057	0.0158	0.0171	0.0290
No. 8		6	0.0002	0.0006	0.0014	0.0077	0.0316	0.0020	0.0290
No. 9	300	3	—	0.0007	0.0026	0.0076	0.0347	—	0.0290
No. 10		6	0.0001	0.0008	0.0014	0.0077	0.0352	—	0.0290

TABLE VI
Composition of Atmosphere on Oxidation of AI-7 Film in a Sealed System as a Function of Time and Temperature

Sample identification	Temp, °C	Aging time, mos	Gas, mol/g sample							
			H_2	N_2	H_2O	CO	CO_2	O_2	C_2H_3N	Ar
Initial gas mixture	Room	0	0.0004	—	0.0001	—	0.00005	0.0400	—	0.0305
No. 1	200	3	0.0002	0.0001	0.0024	0.0010	0.0052	0.0322	0.00009	0.0305
No. 2		6	0.0002	0.0003	0.0021	0.0006	0.0072	0.0281	0.0002	0.0305
No. 3	225	3	0.0004	0.0005	0.0038	0.0018	0.0100	0.0254	0.0003	0.0305
No. 4		6	0.0002	0.0004	0.0046	0.0028	0.0179	0.0160	0.0003	0.0305
No. 5	250	3	0.0001	0.0007	0.0047	0.0043	0.0289	0.0055	0.0003	0.0305
No. 6		6	0.0002	0.0008	0.0032	0.0045	0.0347	0.0002	0.0003	0.0305
No. 7	275	3	0.0002	0.0007	0.0007	0.0048	0.0353	0.0001	0.0003	0.0305
No. 8		6	0.0002	0.0007	0.0050	0.0047	0.0358	—	0.0003	0.0305
No. 9	300	3	0.0002	0.0009	0.0119	0.0047	0.0356	—	0.0002	0.0305
No. 10		6	0.0002	0.0009	0.0035	0.0045	0.0361	—	0.0002	0.0305

TABLE VII
Composition of Atmosphere on Oxidation of AI-8 Enameled Wire in a Sealed System as a Function of Time and Temperature

Sample identification	Temp, °C	Aging time, mos	Gas, mol/unit mol of polymer							O_2 consumed, mol/mol
			H_2	N_2	H_2O	CO	CO_2	O_2	C_6H_6	
Initial gas mixture	Room		0.0953	—	0.0507	—	0.0110	9.5935		—
No. 1	200	3	—	0.2094	0.3100	0.0773	1.5742	7.4164	—	2.1771
No. 2		6	—	0.2004	0.2851	—	3.0802	5.8385	—	3.7550
No. 3	225	3	—	0.2065	0.6814	0.0466	5.1096	3.7800	—	5.8135
No. 4		6	—	0.3706	0.6262	0.0278	8.3923	0.5386	—	9.0549
No. 5	250	3	—	0.3845	1.7248	0.0160	9.2630	—	—	9.5935
No. 6		6	—	0.4090	0.4143	0.0405	9.4818	—	0.0339	—
No. 7	275	3	—	0.4008	0.8348	0.0070	9.7808	—	0.0434	—
No. 8 (broken)		6								
No. 9	300	3	—	0.4372	0.4483	—	10.9804	—	0.1885	—
No. 10		6	—	0.3992	0.1873	0.0883	11.4528	—	0.2896	—

TABLE VIII
Composition of Atmosphere on Oxidation of AI-43 Enameled Wire in a Sealed System as a Function of Time and Temperature

Sample identification	Temp, °C	Aging time, mos	Gas, mol/unit mole of polymer							O_2 consumed, mol/mol
			H_2	N_2	H_2O	CO	CO_2	O_2	C_6H_6	
Initial gas mixture	Room	0	0.1701	—	0.0429	—	0.0204	17.0995	—	—
No. 1	200	3	—	1.0863	0.4434	—	2.3673	14.3616	—	2.7378
No. 2		6	—	1.4789	0.5767	—	3.7223	12.6945	—	4.4049
No. 3	225	3	—	1.4372	0.5211	—	5.1190	11.7575	—	5.3419
No. 4		6	—	1.3722	0.5693	—	8.7080	7.4246	—	9.6749
No. 5	250	3	—	1.6479	0.9247	0.0155	12.4720	3.3951	—	13.7044
No. 6		6	—	1.8826	0.9190	0.1480	15.6128	—	0.0070	17.0995
No. 7	275	3	—	1.9755	0.6634	—	15.9183	—	—	—
No. 8		6	—	1.8716	0.9873	0.1301	16.3571	—	0.0499	—
No. 9	300	3	—	2.0933	1.3260	0.1346	16.4549	—	0.0585	—
No. 10		6	—	2.0569	1.0753	0.1521	17.0888	—	0.1006	—

TABLE IX
Composition of Atmosphere on Oxidation of DuPont Pyre ML Enameled Wire in a Sealed System as a Function of Time and Temperature

Sample identification	Temp, °C	Aging time, mos	Gas, mol/unit mol of polymer							O_2 consumed, mol/mol
			H_2	N_2	H_2O	CO	CO_2	O_2	C_6H_6	
Initial gas mixture	Room	0	0.1776	—	0.0447	—	0.0229	17.8333	—	—
No. 1	200	3	0.0562	0.1494	0.2090	—	1.1724	16.8645	—	0.9688
No. 2		6	—	0.1772	0.3075	—	1.8790	15.1792	—	2.6541
No. 3	225	3	—	0.2372	0.2441	—	2.9521	14.7849	—	3.0484
No. 4		6	—	0.2727	0.4076	—	4.7261	12.0429	—	5.7904
No. 5	250	3	—	0.4057	0.6861	—	8.8536	7.8367	—	9.9966
No. 6		6	—	0.6253	0.8687	—	14.4086	1.6670	—	16.1663
No. 7	275	3	—	0.7338	1.2648	—	17.1579	—	—	17.8333
No. 8		6	—	0.8160	0.9206	0.1322	18.0075	—	0.0875	—
No. 9	300	3	—	0.8343	1.0501	0.0241	17.9597	—	0.0947	—
No. 10		6	—	0.8476	0.7884	0.0695	18.0182	—	0.1219	—

TABLE X
Composition of Atmosphere on Oxidation of Nomex Paper in a Sealed System as a Function of Time and Temperature

Sample identification	Temp, °C	Aging time, mos	Gas, mol/unit mol of polymer							O_2 consumed, mol/mol
			H_2	N_2	H_2O	CO	O_2	CO_2	C_2H_2N	
Initial gas mixture	Room	0	0.0949	—	0.0239	—	9.5236	0.0119	—	—
No. 1	200	3	0.0833	—	0.2621	0.2043	8.2835	0.7418	—	1.2401
No. 2		6	0.0716	0.0261	0.2760	0.0099	7.0302	1.1599	0.0160	2.4935
No. 3	225	3	0.0745	0.0368	0.6244	0.4155	5.9629	2.3966	0.0192	3.5607
No. 4		6	0.0608	0.0346	0.9327	0.7556	1.3843	5.9760	0.0283	8.1393
No. 5	250	3	0.0621	0.0633	1.5754	1.0489	—	7.8007	0.0326	9.5236
No. 6		6	0.0703	0.0540	0.7853	0.9896	—	7.5082	0.0357	—
No. 7	275	3	0.0687	0.0559	1.2319	1.1405	—	7.9120	0.0403	—
No. 8		6	0.0550	0.0297	0.8666	1.0952	—	7.6639	0.0446	—
No. 9	300	3	0.0709	0.0910	0.8880	1.2444	—	8.0441	0.0344	—
No. 10		6	0.0570	0.0478	0.6451	1.1077	—	7.7763	0.0377	—

TABLE XI
Composition of Atmosphere on Oxidation of Kapton Film in a Sealed System as a Function of Time and Temperature

Sample identification	Temp, °C	Aging time, mos	Gas, mol/unit mol of polymer						O_2 consumed, mol/mol
			H_2	N_2	H_2O	CO	CO_2	O_2	
Initial gas mixture	Room	0	0.1450	—	0.0772	—	0.0170	14.5682	—
No. 1	200	3	0.1127	0.2306	0.0929	—	0.0533	14.4443	0.1239
No. 2		6	0.1132	0.1952	0.0914	—	0.0969	14.2472	0.3210
No. 3	225	3	0.1069	0.1759	0.0827	—	0.1756	14.2733	0.2949
No. 4		6	0.1178	0.2150	0.1160	—	0.3713	13.9433	0.6249
No. 5	250	3	0.0966	0.1445	0.2448	0.6660	1.8596	11.8567	2.7115
No. 6 (broken)		6							
No. 7	275	3	0.0767	0.1339	0.8421	2.1772	6.0583	6.5157	8.0525
No. 8		6	0.0670	0.2506	0.5378	2.9361	12.0590	0.7663	13.8019
No. 9	300	3	—	0.2900	1.0042	2.9195	13.2469	—	14.5682
No. 10		6	0.0526	0.3025	0.5413	2.9411	13.4523	—	—

TABLE XII
Composition of Atmosphere on Oxidation of AI-7 Film in a Sealed System as a Function of Time and Temperature

Sample identification	Temp, °C	Aging time, mos	Gas, mol/unit mol of polymer							O_2 consumed, mol/mol
			H_2	N_2	H_2O	CO	CO_2	O_2	C_2H_3N	
Initial gas mixture	Room	0	1.6024	—	0.4016	—	0.2008	160.7002	—	—
No. 1	200	3	0.8032	0.5100	9.7348	3.9196	20.7105	129.3232	0.3614	31.3770
No. 2		6	0.7912	1.2329	8.3854	2.5863	29.1441	112.7050	0.6064	47.9952
No. 3	225	3	1.5622	2.0321	15.3773	7.2127	40.3447	101.9020	1.1526	58.7982
No. 4		6	0.9317	1.6706	18.6664	11.1564	71.7659	63.3805	1.2690	97.3197
No. 5	250	3	0.5582	2.7750	18.7748	17.1041	116.3475	22.0037	1.1928	138.6965
No. 6		6	0.6466	3.4176	13.0359	18.1282	139.1946	0.9197	1.1686	159.7805
No. 7	275	3	0.6747	2.6626	2.8795	19.4214	141.7728	0.2892	1.0361	160.4110
No. 8		6	0.8835	2.6144	20.1442	19.0559	143.7246	—	1.2168	160.7002
No. 9	300	3	0.8996	3.5903	47.9390	18.8752	143.0861	—	0.8353	—
No. 10		6	0.8393	3.5903	14.0158	18.0640	145.0418	—	0.7550	—

be described as the reaction product of *m*-phenylenediamine, isophthaloyl chloride, terephthaloyl chloride, and pyromellitic dianhydride in the molar ratios of 16:9:3:4, respectively. The unit molecular weight is 4016. This

TABLE XIII
Oxygen Balance after Six Months at 300°C

Sample identification	Oxygen added, g	Oxygen recovered as CO_2 and CO, g
AI-8 enameled wire	0.027	0.032
AI-43 enameled wire	0.027	0.027
DuPont Pyre ML enameled wire	0.027	0.027
Nomex paper	0.027	0.025
Kapton film	0.027	0.0275
AI-7 film	0.027	0.026

film had been cured at 150°C for 2 hr and it probably contained traces of solvent (dimethylacetamide). The weight of each free film or paper sample averaged 0.02 g.

Procedure

Weighed samples were placed in Pyrex glass break-off tubes (approximately 43 cc in volume) and the tubes were filled to a pressure of 645 mm Hg with an oxygen:argon mixture. The mass spectrometric analysis of this mixture, was H_2, 0.6 mol-%; O_2, 56.3 mol-%; Ar, 42.9 mol-%; H_2O, 0.1 mol-%; CO_2, 0.1 mol-%.

The filled tubes were sealed, wrapped in heavy aluminum foil, and placed in furnaces at the desired temperatures (200, 225, 250, 275, and 300°C). One set of samples was aged for 3 months and a second set for 6 months at each temperature, at the end of which time the gaseous contents of each tube were analyzed by a mass spectrometer.

Blanks were run to determine the effect of any gas adsorbed on the glass surfaces of the tubes on oxidation rates and gas formation. No effect was detected. A literature search indicated that at the temperatures studied, copper is not appreciably affected by O_2, H_2O, or CO_2.[2,3]

RESULTS

Tables I–VI summarize the compositions of the atmospheres inside the tubes for the six samples at five temperatures and after 3 and 6 months aging, expressed as moles of gas per gram of sample. Tables VII through XII show the same data expressed as moles of gas per unit mole of sample. Table XIII gives the balance between O_2 consumed and O_2 recovered as CO_2 and CO.

Following are comments on each individual sample, based on Tables I–VI and XIII.

AI-8 Enameled Wire

Three Months' Aging. No trace of HCN was found among the gases in the tube at any temperature. No free oxygen remained in the samples at 250°C. Small quantities of nitrogen gas and water were found at all temperatures. Carbon dioxide was evolved in quantities increasing with temperature. Traces of benzene were detected at 275°C; they had increased in quantity at 300°C. The initial traces of H_2 disappeared.

The appearance of the enamel changed slightly at 200, 225, and 250°C, the color becoming progressively darker. At 275°C, the enamel was almost black and was starting to peel from the wire. At 300°C, the enamel was almost black and about 1/5 of it had completely separated from the wire.

Six Months' Aging. The same comments can be made as for the 3-month aging period, except that benzene first appeared at 250°C. The color of the enamel darkened with temperature. The enamel remained intact up to 250°C; at 275°C, it was almost black and had partly fallen off the wire, which looked dull and oxidized. At 300°C, most of the enamel had flaked off the wire in small, black pieces. Parts of the copper wire had become shiny again. Slightly more oxygen was recovered as CO_2 and CO than was originally present as O_2.

AI-43 Enameled Wire

Three Months' Aging. No HCN was evolved. Water appeared in slightly larger quantities than in the AI-8 case, increasing as a function of temperature. Oxygen had disappeared at 275°C and traces of benzene appeared only at 300°C. Carbon dioxide was found in large quantities, increasing with temperature. Nitrogen gas was detected in quantities 4- to 5-fold that in the AI-8 case. The initial traces of H_2 had disappeared at 200°C.

The enamel became darker as the temperature increased. At 200 and 225°C, it remained intact; at 250°C, it was dark and was beginning to sleeve off; at 275°C, the enamel had almost completely sleeved off the wire and had partly broken down into small pieces; at 300°C, practically no enamel was left on the wire, and the pieces appeared to consist of two layers, one darker than the other.

Six Months' Aging. The same comments apply as in the 3-month aging, except that all the effects were magnified. All the oxygen consumed was recovered as CO_2 and CO.

DuPont Pyre ML Enameled Wire

Three Months' Aging. No HCN was evolved at any temperature. The oxygen was completely exhausted at 275°C. Nitrogen gas and water were found present among the degradation gases in about the same molar quantity. Traces of benzene appeared at 300°C. The hydrogen initially present had completely disappeared at 225°C.

The color of the enamel darkened progressively with increasing temperature. The enamel remained intact at 200, 225, and 250°C; at 275°C the enamel started to flake off at either end of the wire and some liquid droplets had appeared on glass walls; at 300°C, most of the enamel had flaked off the wire, the latter appearing dull red in color.

Six Months' Aging. The effect of 6 months' aging was similar to that of the 3 months' aging, but slightly magnified. Benzene first appeared at 275°C. and the amount of CO_2 evolved at 300°C after 3 and 6 months' aging was the same, indicating that maximum CO_2 formation consistent with the system had been reached. Here again, all the oxygen consumed was recovered as CO_2 and CO (traces).

The enamel looked darker at 200 and 225°C, and still adhered to the metal substrate. From 250°C on, the enamel flaked off the conductor at an increasing rate, while becoming progressively darker. At 300°C, most of the coating had left the copper wire.

Nomex

Three Months' Aging. No HCN was evolved. The quantity of hydrogen present in the initial atmosphere remained constant at a very low level. The N_2 evolved was very little, while H_2O and CO were formed in relatively large quantities. All the oxygen had been consumed at 250°C. Carbon dioxide was evolved as usual in quantities increasing as a function of temperature. No benzene was detected, but a new compound made its appearance in trace quantities; namely, acetonitrile C_2H_3N.

The paper became darker as the temperature increased, being almost black at 300°C. However, no fragmentation was observed, the effect of degradation being shown by a very slight amount of shrinkage and curling. At 300°C, a small amount of light yellow distillate was observed on the glass walls.

Six Months' Aging. The same comments apply is in the case of 3 months' aging. The paper became darker at lower temperatures and had shrunk more at 300°C than in the shorter aging time.

Almost all the oxygen consumed could be accounted for as CO_2 and CO.

Kapton Film

Three Months' Aging. Very little N_2 was present at all temperatures. Water was evolved slowly and in relatively small quantities. No HCN, acetonitrile, or benzene was detected. The oxygen was completely exhausted only at 300°C. Carbon monoxide appeared first at 250°C and increased to the largest amount found in any of the previous experiments. The low original level of H_2 remained practically constant at all temperatures and aging periods.

The appearance of the film changed only very slightly up to 250°C; the film started darkening considerably at 275°C, and it was almost black at 300°C. The only other sign of oxidation was curling of the edges.

Six Months' Aging. Approximately the same effect was noted as for the 3 months' aging, except that gas evolution and consumption took place at a faster rate. At 300°C, all the oxygen consumed was accounted for by CO_2 and CO.

The appearance of the film changed more drastically than in the case of the shorter aging period. At 300°C, the film was very dark, curled, and had shrunk to about 1/2 of its original size.

AI-7 Film

Three Months' Aging. No HCN or benzene was detected. Hydrogen originally present in the atmosphere remained constant, while a small amount of N_2 appeared, increasing with temperature. Water was evolved erratically, but generally in relatively large quantities. Carbon monoxide was also evolved in large quantities, which increased with temperature. Oxygen was completely exhausted only at 300°C, while the amount of CO_2 evolved became constant at 275°C. Traces of acetonitrile were found, remaining constant from 225°C on.

The film darkened drastically with temperature. At 225°C, some brown distillate was observed on the glass walls. At 250°C, the film was starting to curl, and at 275–300°C, the film was curled, twisted, and almost black, with some unidentified white crystals deposited on the glass walls.

Six Months' Aging. The 3 months' aging effects were magnified. Oxygen was depleted at 275°C and CO_2 evolution stopped at this temperature. All the oxygen consumed was recovered as CO_2 and CO.

The film was affected by oxidation and heat to a more serious extent. It began to curl at 200°C; it was almost black at 250°C, where some shrinking was evident. At 275 and 300°C, the sample had shrunk by about 1/3 of its original size.

DISCUSSION AND CONCLUSIONS

Within the detection limits of the mass spectrometer (0.5 mol-%), no HCN was detected in any of the six samples, even after six months at 300°C.

Relatively small quantities of nitrogen were evolved from the film and paper samples, but much larger amounts were recovered from the wire enamels, especially AI-43.

Water was evolved in all cases at about the same low level, except in the case of Nomex and AI-7 film, where it appeared in appreciable amounts.

While carbon monoxide was present only in traces in the wire enamel samples, it was evolved in considerable amounts by the paper and film samples.

Hydrogen, which was a part of all the initial atmospheres, disappeared completely in the case of the wire enamels, but it remained at a constant low level in the case of paper and film samples.

Carbon dioxide was the major degradation product, appearing in amounts which increased as functions of aging times and temperatures. Its evolution continued after all the oxygen had disappeared.

No free oxygen remained at 275°C in any of the samples aged six months. In the case of AI-8 wire enamel and Nomex paper, all oxygen was consumed after 3 months at 250°C. The rate of CO and CO_2 evolution was reduced accordingly.

Acetonitrile was first evolved from AI-7 film at 200°C and Nomex paper at 225°C after 3 months. No other material showed this product, which probably arose from the decomposition of residual solvent (DMAC) in these samples.

The presence of benzene in the tubes containing the enameled wire samples is difficult to explain. It cannot derive from solvent traces, since it was not found in the runs at lower temperatures. As it does not appear in the paper and film samples, its presence might be due to the destruction of the polymer, possibly catalyzed by the copper substrate.

In all cases, the oxygen consumed was recovered almost stoichiometrically as CO_2 and CO, neglecting the oxygen already present in the polymer.

In general, the paper and film samples withstood the thermal and oxidative degradation better than the three wire enamels.

The elevated concentration of oxygen in the initial sample atmosphere (about three times that of air) is responsible for the high degree of destruction observed in the samples.

Long-term use of this class of insulating materials at relatively elevated temperatures in the presence of air should not result in the evolution of HCN.

The mechanism of thermal and oxidative degradation still appears to be that postulated previously,[1] that is, a unit-by-unit destruction of the polymer.

The authors are indebted to Drs. Freeman, Frost, and Bower and Mr. Sattler of these Laboratories for their interest and valuable assistance in this work.

References

1. L. C. Scala and W. M. Hickam, *J. Appl. Polym. Sci.*, **9**, 245 (1965).

2. S. L. Archbutt and W. E. Prytherch, *Effects of Impurities in Copper*, British Nonferrous Metals Research Assn. Research Monograph No. 4, London, 1937, pp. 24–35.

3. I. Jenkins, *Controlled Atmospheres for the Heat Treatment of Metals*, Chapman and Hall, London, 1946.

Received April 29, 1968