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**Analysis of Weld-Through Primers
Initial tests using pyrolysis-gas chromatography-
mass spectrometry**

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Science Group: **Health Improvement**

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EXECUTIVE SUMMARY

Objectives

The objective of the work is to provide information on test methods, analytical methods and sampling procedures for determination of thermal degradation products generated during welding involving weld-thro' products and coatings. The information is, amongst other things, intended to aid completion of European Standard prCEN/ISO/TS 15011-5.

Main Findings

Samples of four products were examined by pyrolysis-gas chromatography-mass spectrometry, using a Pyrola 2000 pyrolyser interfaced to an Agilent HP5890/5971 GC-MS system. A standard method of sample preparation was developed which allows easy preparation of samples of a consistent, standard size leading, in turn, to good reproducibility. The sample material is applied to aluminium foil as a film which, when dry, is around 50 µm thick. The dry foil-backed sample is then placed on to a quartz filter and a 1.4 mm circle punched out. The quartz filter material is present to prevent contact (and possible reaction) between the aluminium foil and the platinum pyrolyser filament. During pyrolysis, the samples are heated to the desired temperature for 2 seconds under helium. For these tests, pyrolysis temperatures of 450°C, 650°C and 850°C were used.

Subsequently, pyrolysis tests using similar Pyrola/Agilent equipment at a pyrolysis temperature of 800°C were carried at the Finnish Institute of Occupational Health (FIOH) in Turku, Finland. In addition, FIOH also carried out a series of oven based tests involving heating up the sample (in air) in a glass tube and collecting the evolved material onto various indirect sampling devices. The samples used in the oven tests were much bigger than those used in the pyrolysis tests and were heated from room temperature to 450°C over a time period of about 15 minutes.

The pyrolysis tests carried out showed a good level of agreement between the HSL and FIOH results. In addition, and despite the differences between the techniques, the HSL/FIOH pyrolysis tests and the FIOH oven tests were also found to give broadly similar results, particularly in terms of the range of components observed. It was noted that whilst the oven tests showed significant levels of the various pyrolysis products at the test temperature of 450°C, the amounts of material observed in the pyrolysis test at this temperature were relatively small. The reason for this difference is unclear, but may be due to a combination of the much smaller sample used in pyrolysis and the much shorter heating period. Increasing pyrolyser temperature to 650°C, was generally found to increase the total amount of material produced (by as much as 6 – 10 times). Further increasing pyrolyser temperature to 850°C did not significantly increase the total amount of material produced, but did tend to result in the appearance of many more minor/trace components (including naphthalene and other aromatics).

Recommendations

It is recommended that pyrolysis method, as outlined in this report, should be used in the next stage of the project. This will involve testing of five weld-thro' products by members of the project team, both in the laboratory (using pyrolysis and oven heating technique) and in actual welding tests. Data from the various tests can then be compared with a view to providing input and recommendations on a standard method of analysis for incorporation into European Standard prCEN/ISO/TS 15011-5.

1 INTRODUCTION

This project was carried out in partnership with The Welding Institute (TWI), Cambridge, the Finnish Institute of Occupational Health (FIOH), Turku, Finland, FORCE Technology, Denmark and Arcelor, France/Belgium.

The objective of the work is to provide information on test methods, analytical methods and sampling procedures for determination of thermal degradation products generated during welding involving weld-thro' products and coatings. The information is, amongst other things, intended to aid completion of European Standard prCEN/ISO/TS 15011-5.

This report summarises initial tests to develop a laboratory testing procedure for identification of thermal breakdown products generated by weld-thro' paints and primers on heating. This forms part of Work Package 2 (WP2) of the project.

The objectives for WP2 are:

- To use various pyrolysis techniques to identify components produced by heating of weld-thro products.
- To examine and compare the results obtained by different test procedures and equipment on the amounts and composition of the thermal degradation products.
- To produce recommendations for a standard test procedure for testing of weld-thro' products.

The first tests were carried out on two samples provided by FIOH, one 'two-component epoxy' shop-primer and one 'water-based acrylic' top paint. Subsequently, tests were carried out on two more samples, a 'water-based acrylic' shop primer and a 'two-component oxirane ester' top paint. These samples were supplied as thin films on glass and aluminium foil. On application, the film thickness was 100 μm , however this is reduced to around 50 μm when dry.

The samples were tested using a pyrolyser interfaced to a gas chromatograph (GC) equipped with a mass spectrometer (MS) detector. The same samples will also be tested by FIOH using pyrolysis and a combination of oven and various indirect sampling/analytical techniques.

2 TESTING METHOD

2.1 EQUIPMENT

In these initial tests, samples of the weld-thro products were tested using a Pyrola 2000 pyrolyser interfaced to an Agilent HP5890 GC equipped with an HP5971 MS detector. This particular pyrolyser is mounted directly on to the 'normal' split-splitless injector of the GC (Figure 1) and is capable of heating samples to over 1000°C. The sample is placed on a calibrated platinum filament assembly (Figure 2). This filament is then placed inside the body of the pyrolyser surrounded by a heated (typically to 175°C) glass liner (Figure 3). When the GC is ready, the pyrolyser is started and an electrical current is passed through the filament. This heats up to the test temperature in just a few milliseconds (ms) and maintains it at that temperature for, typically, two seconds (Figure 4). Thermal degradation products are carried by the GC carrier gas (helium) from the pyrolysis chamber to the GC via a short heated transfer line. The rapid heating process focuses the degradation products at the front end of the chromatographic column producing good resolution of even the most volatile components.

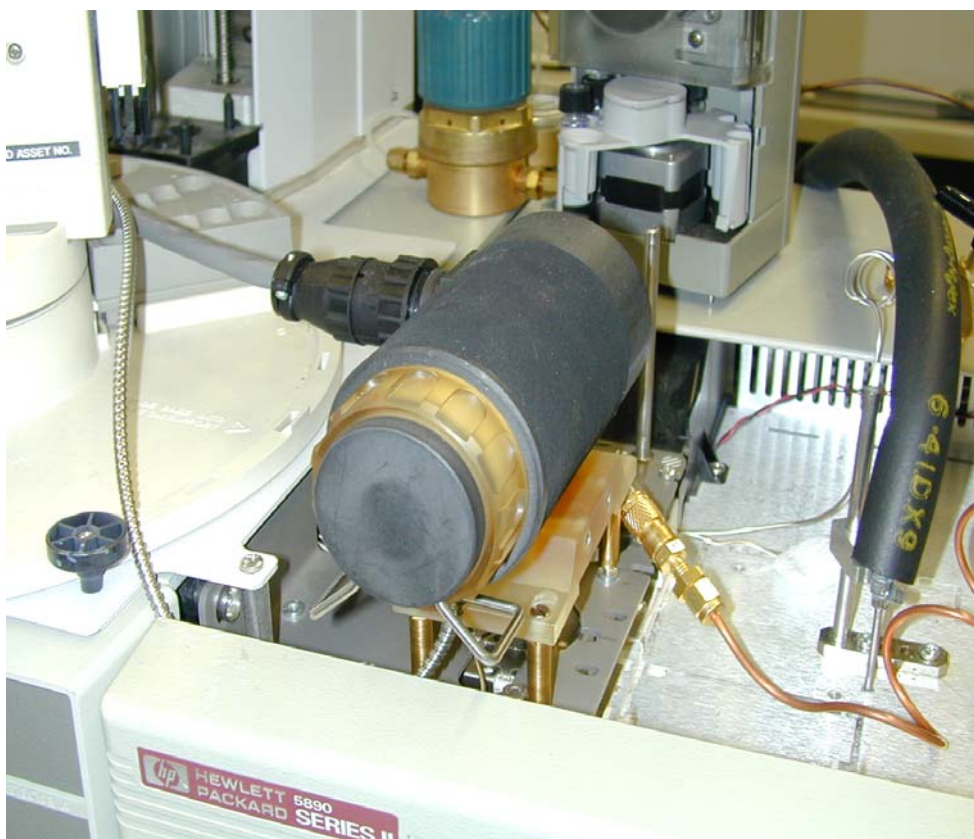


Figure 1: Pyrola 2000 pyrolyser mounted on Agilent GC-MS



Fig. 2: Pyrola 2000 - Platinum filament and sample

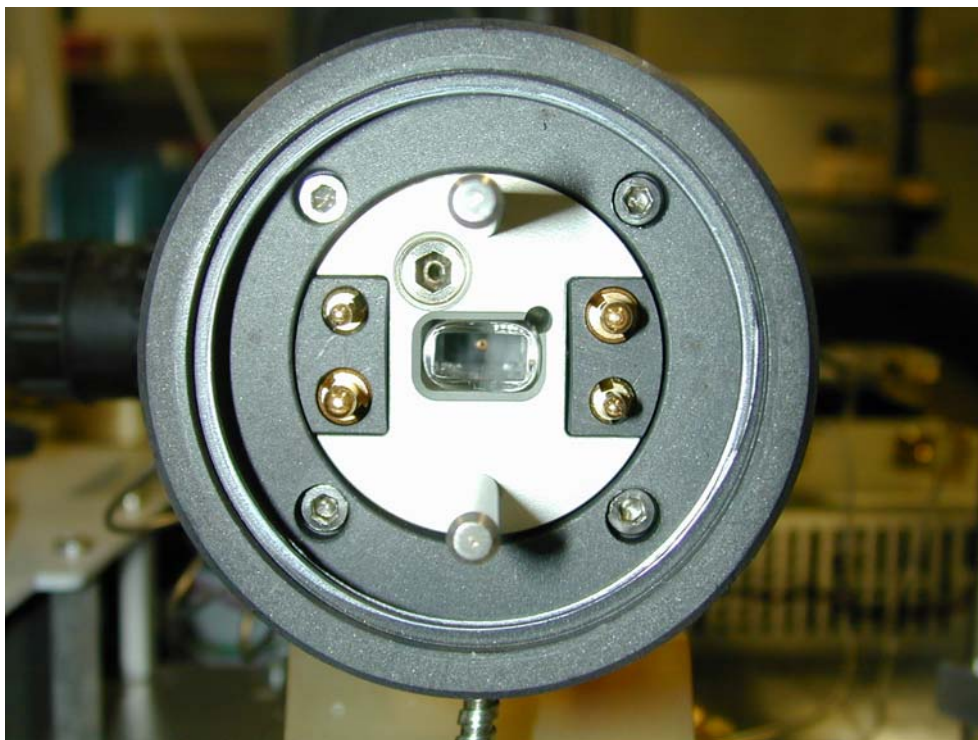


Figure 3: Pyrola 2000 - Heated glass liner

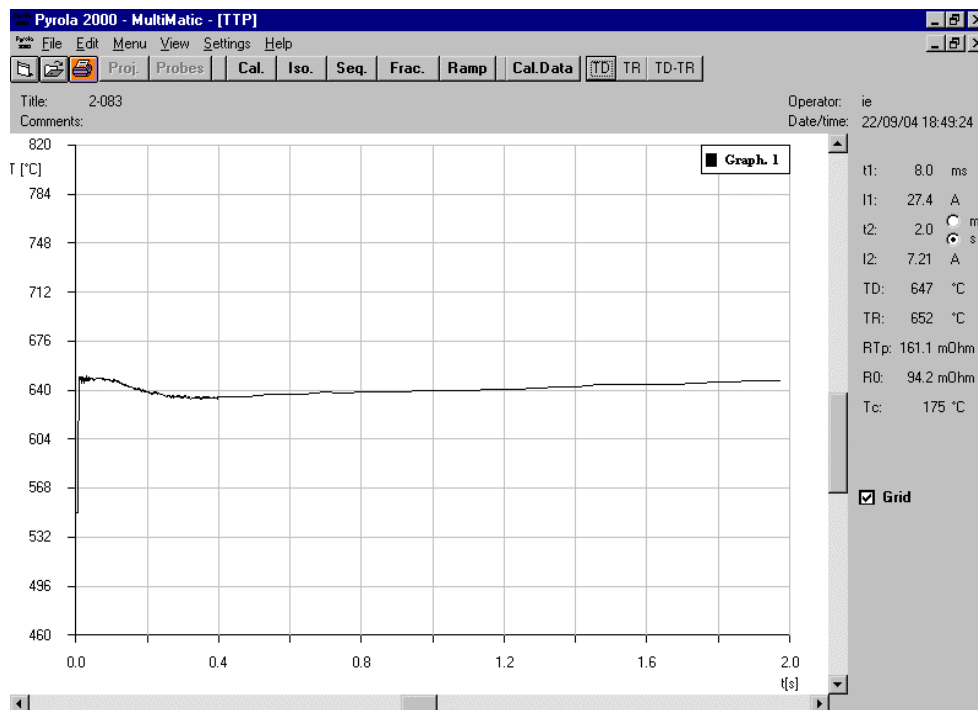


Figure 4: Pyrola 2000 - Plot of typical heating program

2.2 ADVANTAGES & DISADVANTAGES

This direct pyrolysis technique has advantages and disadvantages over procedures employing indirect sampling and analysis – ie where the sample is heated and the thermal degradation products, as with actual welding tests, are collected onto various sampling media for later laboratory analysis.

2.1

Advantages

- Method is quick, simple and reproducible;
- Method is capable of showing components covering a wide range of volatilities and has excellent sensitivity;
- Method gives a good idea of the relative concentrations of many components in a single analysis.

2.2.2 Disadvantages

- The sample is heated in helium rather than air;
- Despite the heated liner and transfer line, some higher boiling point compounds may be lost or reduced in intensity;
- Components which can't be analysed by GC may be lost.

2.3 CHROMATOGRAPHIC CONDITIONS

The chromatographic conditions used for the tests were as follows:-

Column:- 30 m × 0.25 mm HP-5 (0.25 µm film thickness);

Carrier gas:- Helium

Carrier flow rate:- 2 ml/min (initial pressure = 16.9 psi);

Injector:- Split-splitless (split on);

Injector temperature:- 250°C;

Temperature program:- 50°C for 5 minutes; 5°C/min to 75°C; 12.5°C to 200°C; 25°C/min to 300°C; 300°C for 6 minutes;

Run time:- 30 minutes;

Detector 'Solvent' delay:- 30 seconds;

Detector range:- 20 – 400 amu.

2.4 PYROLYSIS

Prior to the tests, the platinum filament was calibrated over a temperature range of 350°C – 1000°C using the calibration procedure described in the manufacturers literature.

The test samples were pyrolysed at temperatures of 450°C, 650°C or 850°C. One of the tests was carried out with a heating duration of 5 seconds, the remainder with a heating duration of 2 seconds. In all cases the heated glass liner was maintained at 175°C. The pyrolysis conditions used in each test are given with the results.

3 PYROLYSIS TESTS

3.1 TEST PRODUCTS

The four products examined in the initial tests were as follows:-

Product F – A two-component epoxy shop primer;

Product M – A one-component water based acrylate top paint.

Product G – A one-component water based acrylic shop primer;

Product I – A two-component oxirane ester top paint;

The products were applied to glass and aluminium substrates using a metal roller by scientists at FIOH, and allowed to dry thoroughly at room temperature before testing. On application the paint thickness was 100 μm which, on drying, was reduced to around 50 μm .

In the case of the glass mounted samples, a small amount (*ca.* 50 – 200 μg) of the dry paint was scraped off the glass and deposited directly on the platinum filament for testing.

In the case of the foil mounted samples, 1.4 mm circles were punched out of the foil using a metal borer and placed on the platinum filament. This technique should be able to produce replicate samples much more easily than is the case with the glass mounted material.

3.2 PYROLYSIS TESTS

3.2.1 Product F

The following tests were carried out with Product F:-

- **Sample F1:-** Sample material taken from glass slide and pyrolysed at 450°C (*max.* 455°C) for 2 seconds.
- **Sample F2:-** Sample material taken from glass slide and pyrolysed at 650°C (*max.* 658°C) for 2 seconds.
- **Sample F3:-** 1.4 mm circle punched from foil-mounted sample and pyrolysed at 650°C (*max.* 655°C) for 2 seconds.
- **Sample F4:-** 1.4 mm circle punched from foil-mounted sample and pyrolysed at 450°C (*max.* 453°C) for 2 seconds.
- **Sample F5:-** 1.4 mm circle punched from foil-mounted sample and pyrolysed at 650°C (*max.* 653°C) for 5 seconds.
- **Sample F6:-** 1.4 mm circle punched from foil-mounted sample and pyrolysed at 850°C (*max.* 855°C) for 2 seconds.
- **Sample F7:-** 1.4 mm circle punched from unpainted foil and pyrolysed at 650°C (*max.* 655°C) for 2 seconds.

3.3 PRODUCT M

The following tests were carried out with Product M:-

- **Sample M1:-** 1.4 mm circle punched from foil-mounted sample and pyrolysed at 650°C (*max. 658°C*) for 2 seconds.
- **Sample M2:-** 1.4 mm circle punched from foil-mounted sample and pyrolysed at 650°C (*max. 658°C*) for 2 seconds.
- **Sample M3:-** 1.4 mm circle punched from foil-mounted sample and pyrolysed at 450°C (*max. 451°C*) for 2 seconds.
- **Sample M4:-** Sample M3 left in pyrolyser and re-pyrolysed at 650°C (*max. 650°C*) for 2 seconds.
- **Sample M5:-** 1.4 mm circle punched from foil-mounted sample and pyrolysed at 850°C (*max. 850°C*) for 2 seconds.
- **Sample M6:-** 1.4 mm circle punched from foil-mounted sample with quartz filter underlay and pyrolysed at 650°C (*max. 655°C*) for 2 seconds.
- **Sample M7:-** 1.4 mm circle punched from unpainted foil and pyrolysed at 650°C (*max. 658°C*) for 2 seconds.

3.4 PRODUCT G

The following tests were carried out with Product G:-

- **Sample G1:-** 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 650°C for 2 seconds.
- **Sample G2:-** 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 850°C for 2 seconds.
- **Sample G3:-** 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 450°C for 2 seconds.

3.5 PRODUCT I

The following tests were carried out with Product I:-

- **Sample I1:-** 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 650°C for 2 seconds.
- **Sample I2:-** 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 850°C for 2 seconds.
- **Sample I3:-** 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 450°C for 2 seconds.

4 RESULTS

4.1 PRODUCT F

The chromatograms obtained from the six samples of Product F were generally found to contain in excess of 50 components, however many of these were present in amounts of rather less than 1%. The main components in all six samples were styrene, butyl acrylate, an aliphatic methacrylate ester, bisphenol-A, a group of unidentified high (>300 amu) molecular weight aromatics and a component with a retention time of 16.6 minutes and a mass spectrum similar to that of an acetoamidophenol compound.

The chromatogram obtained from Sample F3, a foil mounted sample of Product F heated to 650°C, is shown in Figure 5.

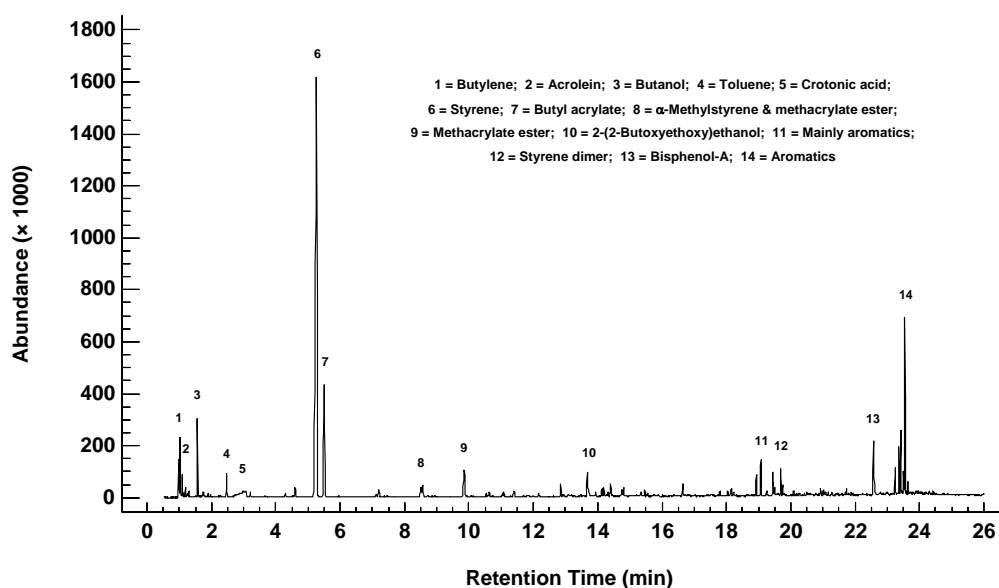


Figure 5: Product F – Foil Mounted Sample at 650°C

Table 1 shows the peak areas for the forty or so largest components in the Total Ion Chromatogram (TIC) for each of the six test samples.

Table 2 shows these peak areas converted to a percentage of the total peak area. These data are based on the assumption that all components give an equal detector response, and, while this is unlikely to be the case, the data are still useful as an estimate of the proportions of each compound present.

Table 3 lists the twelve main components in the three foil sample tests run at 450°C, 650°C and 850°C.

Table 1: Product F – TIC Peak Areas

COMPONENT	RT (min)	F1 450°C†	F2 650°†	F3 650°C†	F4 450°C†	F5 650°C‡	F6 850°C†
Isobutylene	1.02	57	526	2251	98	2629	5931
Acrolein	1.11	139	391	966	105	1101	1519
Allyl alcohol	1.18	35	84	257	59	288	232
Butyraldehyde	1.29	-	88	156	-	141	467
n-Butanol	1.57	298	866	3300	267	3686	2787
Benzene	1.58	-	47	149	-	165	625
Acrylic acid	1.85	-	-	-	-	-	1418
Toluene	2.48	68	352	1243	85	1297	1817
Crotonic acid	2.74	236	1067	3412	48	3329	3524
Butyl acetate	3.21	-	97	277	-	277	152
Ethylbenzene	4.29	-	81	288	-	256	1529
m/p-Xylene	4.52	-	12	110	-	120	222
Phenylacetylene	4.75	-	-	-	-	-	269
Styrene	5.23	3228	16296	49194	3841	49012	48576
Butyl acrylate	5.50	765	3837	10390	715	10062	4987
Trimethylbenzene	6.38	-	-	20	-	54	399
4-Methylstyrene	7.19	-	250	685	-	713	829
Propylbenzene	7.43	-	-	88	-	107	263
α-Methylstyrene	8.51	-	287	776	-	767	2203
Butyl methacrylate	8.57	-	268	1106	-	1160	448
Methacrylate ester	9.84	460	982	3004	598	3157	1848
β-Methylstyrene	10.02	-	-	125	-	150	245
Indene	10.58	-	25	65	-	-	896
α-Ethylstyrene	11.02	-	75	197	-	212	1090
DEG butyl ether (S)	13.51	265	624	2216	6795	2912	1159
Naphthalene	13.58	-	-	25	-	19	477
Methyl naphthalenes	15.2/4	-	-	-	-	-	289
“Acetamidophenol”	16.65	364	391	702	1291	876	796
Toluene dimer	17.80	-	40	198	9	209	520
Styrene dimer	19.68	94	330	1301	134	1346	947
Bisphenol-A	22.58	523	975	3599	749	4046	3991
Aromatics	23 - 24	2038	4782	15492	3407	15985	7456
TOTAL PEAK AREA		8207	32383	100891	16910	103198	97117

† = glass mounted sample; ‡ = foil mounted sample; # = foil mounted sample heated for 5 seconds; (S) = solvent

Table 2: Product F – TIC Peak Areas (%)

COMPONENT	RT (min)	F1 450°C†	F2 650°†	F3 650°C‡	F4 450°C‡	F5 650°C#	F6 850°C‡
Isobutylene	1.02	0.7%	1.6%	2.2%	0.5%	2.5%	6.1%
Acrolein	1.11	1.6%	1.2%	1.0%	0.6%	1.1%	1.6%
Allyl alcohol	1.18	0.4%	0.3%	0.3%	0.3%	0.3%	0.2%
Butyraldehyde	1.29	-	0.3%	0.2%	-	0.1%	0.5%
n-Butanol	1.57	3.5%	2.6%	3.2%	1.5%	3.5%	2.8%
Benzene	1.58	-	0.1%	0.1%	-	0.2%	0.6%
Acrylic acid	1.85	-	-	-	-	-	1.4%
Toluene	2.48	0.8%	1.1%	1.2%	0.5%	1.2%	1.9%
Crotonic acid	2.74	2.8%	3.3%	3.4%	0.3%	3.2%	3.6%
Butyl acetate	3.21	-	0.3%	0.3%	-	0.3%	0.2%
Ethylbenzene	4.29	-	0.2%	0.3%	-	0.2%	1.6%
m/p-Xylene	4.52	-	0.0%	0.1%	-	0.1%	0.2%
Phenylacetylene	4.75	-	-	-	-	-	0.3%
Styrene	5.23	37.7%	49.7%	48.4%	21.1%	47.1%	49.6%
Butyl acrylate	5.50	8.9%	11.7%	10.2%	3.9%	9.7%	5.1%
Trimethylbenzene	6.38	-	-	0.0%	-	0.1%	0.4%
4-Methylstyrene	7.19	-	0.8%	0.7%	-	0.7%	0.8%
Propylbenzene	7.43	-	-	0.1%	-	0.1%	0.3%
α-Methylstyrene	8.51	-	0.9%	0.8%	-	0.7%	2.2%
Butyl methacrylate	8.57	-	0.8%	1.1%	-	1.1%	0.5%
Methacrylate ester	9.84	5.4%	3.0%	3.0%	3.3%	3.0%	1.9%
β-Methylstyrene	10.02	-	-	0.1%	-	0.1%	0.2%
Indene	10.58	-	0.1%	0.1%	-	-	0.9%
α-Ethylstyrene	11.02	-	0.2%	0.2%	-	0.2%	1.1%
DEG butyl ether (S)	13.51	3.1%	1.9%	2.2%	37.3%	2.8%	1.2%
Naphthalene	13.58	-	-	0.0%	-	0.0%	0.5%
Methyl naphthalenes	15.2/4	-	-	-	-	-	0.3%
“Acetamidophenol”	16.65	4.2%	1.2%	0.7%	7.1%	0.8%	0.8%
Toluene dimer	17.80	-	0.1%	0.2%	0.1%	0.2%	0.5%
Styrene dimer	19.68	1.1%	1.0%	1.3%	0.7%	1.3%	1.0%
Bisphenol-A	22.58	6.1%	3.0%	3.5%	4.1%	3.9%	4.1%
Aromatics	23 - 24	23.8%	14.6%	15.2%	18.7 %	15.4%	7.6%
TOTAL PEAK AREA		100%	100%	100%	100%	100%	100%

† = glass mounted sample; ‡ = foil mounted sample; # = foil mounted sample heated for 5 seconds; (S) = solvent

Table 3: Product F – Main Components

COMPONENT	RT (min)	F4 450°C†	F2 650°C†	F3 850°C†	Mean Value
Styrene	5.23	21.1%	48.4%	49.6%	39.7%
Aromatics	23 - 24	18.7%	15.2%	7.6%	13.9%
DEG butyl ether	13.51	37.3%	2.2%	1.2%	13.6%
Butyl acrylate	5.50	3.9%	10.2%	5.1%	6.4%
Bisphenol-A	22.58	4.1%	3.5%	4.1%	3.9%
Isobutylene	1.02	0.5%	2.2%	6.1%	2.9%
“Acetamidophenol”	16.65	7.1%	0.7%	0.8%	2.9%
Methacrylate ester	9.84	3.3%	3.0%	1.9%	2.7%
n-Butanol	1.57	1.5%	3.2%	2.8%	2.5%
Crotonic acid	2.74	0.3%	3.4%	3.6%	2.4%
Toluene	2.48	0.5%	1.2%	1.9%	1.2%
Acrolein	1.11	0.6%	1.0%	1.6%	1.0%
TOTAL PEAK AREA		98.9%	94.3%	86.2%	93.1%

- The data in Tables 1 to 3 produced the following observations:-
- The main components in all six samples were very similar;
- The composition of pyrolysis products obtained from the two glass mounted samples was very similar to the two corresponding foil mounted samples;
- The total peak areas for the 650°C and 850°C foil mounted samples were very similar and significantly (around six times) greater than was observed in the corresponding 450°C sample;
- The samples heated to 450°C, both glass and foil mounted, showed significantly fewer components than the corresponding samples heated to 650°C;
- The foil mounted sample heated to 850°C, whilst showing a similar total peak area to the corresponding 650°C sample, shows an increase in the number of minor/trace components (including naphthalene and other aromatics);
- The twelve most abundant components in the foil mounted sample heated to 450°C account for around 99% of the total chromatographic peak area. This decreases to around 94% for the equivalent sample heated to 650°C and to around 86% for the sample heated to 850°C;
- The foil sample heated to 650°C for five seconds (Sample F5) gave very similar results, both in terms of total peak area and composition, to the one heated to a similar temperature for two seconds (Sample F3).

4.2 PRODUCT M

The chromatograms obtained from the six samples of Product M were generally found to contain in excess of 50 components, but, once again, many of these were present in amounts of rather less than 1%. The main components in all six samples were styrene, butyl acrylate, methyl methacrylate, a group of unidentified high (>300) molecular weight aromatics and the “acetamidophenol” compound at 16.6 minutes.

The chromatogram obtained from Sample M2, a foil mounted sample of Product M heated to 650°C, is shown in Figure 6.

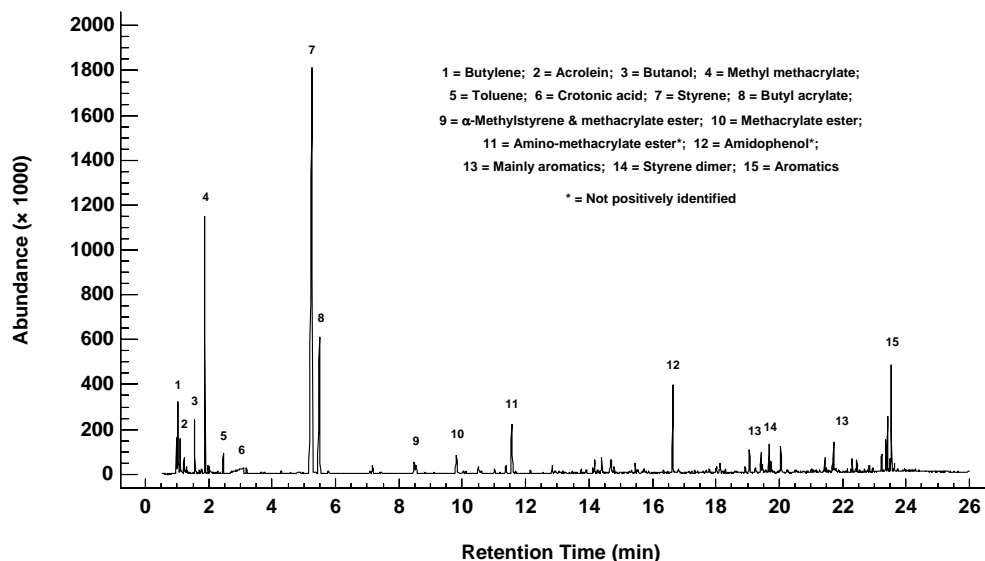


Figure 6: Product M – Foil Mounted Sample at 650°C

Table 4 shows the peak areas for the forty or so largest components in the TIC for each of the six test samples.

Table 5 shows these same peak areas converted to a percentage of the total peak area.

Table 6 lists the twelve main components in the three foil mounted test samples run at 450°C, 650°C and 850°C.

The previous tests with Product F showed no significant differences in the fume composition generated from glass and foil mounted samples. Consequently, in this set of tests only foil mounted samples were run.

The sample with the quartz filter underlay was run because at higher temperatures the aluminium foil can react with the platinum of the filament and shorten its life. Consequently, it was thought that one way of preventing this might be to place a thin underlay of quartz between the aluminium and the platinum.

Table 4: Product M – TIC Peak Areas

COMPONENT	RT (min)	M1 650°C‡	M2 650°†	M3 450°C‡	M4 650°C*	M5 850°C‡	M6 650°C*
Isobutylene	1.02	3773	3171	-	3477	8004	2858
Acrolein	1.11	1414	1312	125	1009	1393	1179
Allyl alcohol	1.18	76	49	-	55	146	37
Butyraldehyde	1.29	171	116	-	109	390	110
Methacrylonitrile	1.30	-	-	-	-	136	-
n-Butanol	1.57	2136	2056	108	1879	1461	2295
Benzene	1.58	143	120	-	108	444	140
Acrylic acid	1.85	285	396	-	78	1500	299
Methyl methacrylate	1.88	11557	10851	768	8110	9796	9483
Toluene	2.48	1109	1163	76	931	1442	1254
Crotonic acid	2.74	3794	3713	52	2963	4804	4189
Butyl acetate	3.21	156	423	-	331	193	401
Ethylbenzene	4.29	223	225	-	223	1506	260
m/p-Xylene	4.52	20	35	-	-	40	17
Phenylacetylene	4.75	-	-	-	-	231	-
Styrene	5.23	61652	61298	2596	47391	60802	62285
Butyl acrylate	5.50	13844	14779	562	10902	6415	12557
Trimethylbenzene	6.38	61	80	-	48	501	65
4-Methylstyrene	7.19	640	954	-	847	914	981
Propylbenzene	7.43	223	82	-	111	361	73
α-Methylstyrene	8.51	938	1083	-	1053	2668	1109
Butyl methacrylate	8.57	655	857	-	771	332	1035
Methacrylate ester	9.84	1910	2075	197	1099	1300	1961
β-Methylstyrene	10.02	199	227	-	187	330	233
Indene	10.58	10	-	-	10	854	20
α-Ethylstyrene	11.02	280	335	-	259	1409	324
DMAE methacrylate	11.59	3780	4873	686	1359	2574	3451
Naphthalene	13.58	-	26	-	-	496	10
Methyl naphthalenes	15.2/4	-	-	-	-	287	10
"Acetamidophenol"	16.65	3364	6789	6547	-	5116	3674
Toluene dimer	17.80	199	270	-	166	467	190
Styrene dimer	19.68	1125	1514	57	1438	1031	1521
Bisphenol-A	22.58	617	-	-	-	-	-
Aromatics	23 - 24	12876	13207	1945	10975	5819	16842
TOTAL PEAK AREA		8207	123866	125291	7172	95886	118046

‡ = foil mounted sample; × = previous sample re-heated; * = foil sample with quartz filter underlay

Table 5: Product M – TIC Peak Areas (%)

COMPONENT	RT (min)	M1 650°C‡	M2 650°‡	M3 450°C‡	M4 650°C*	M5 850°C‡	M6 650°C*
Isobutylene	1.02	3.0%	2.4%	-	3.6%	6.5%	2.2%
Acrolein	1.11	1.1%	1.0%	0.9%	1.1%	1.1%	0.9%
Allyl alcohol	1.18	0.1%	0.0%	-	0.1%	0.1%	0.0%
Butyraldehyde	1.29	0.1%	0.1%	-	0.1%	0.3%	0.1%
Methacrylonitrile	1.30	-	-	-	-	0.1%	-
n-Butanol	1.57	1.7%	1.6%	0.8%	2.0%	1.2%	1.8%
Benzene	1.58	0.1%	0.1%	-	0.1%	0.4%	0.1%
Acrylic acid	1.85	0.2%	0.3%	-	0.1%	1.2%	0.2%
Methyl methacrylate	1.88	9.1%	8.2%	5.6%	8.5%	8.0%	7.4%
Toluene	2.48	0.9%	0.9%	0.6%	1.0%	1.2%	1.0%
Crotonic acid	2.74	3.0%	2.8%	0.4%	3.1%	3.9%	3.3%
Butyl acetate	3.21	0.1%	0.3%	-	0.3%	0.2%	0.3%
Ethylbenzene	4.29	0.2%	0.2%	-	0.2%	1.2%	0.2%
m/p-Xylene	4.52	0.0%	0.0%	-	-	0.0%	0.0%
Phenylacetylene	4.75	-	-	-	-	0.2%	-
Styrene	5.23	48.5%	46.4%	18.9%	49.4%	49.4%	48.3%
Butyl acrylate	5.50	10.9%	11.2%	4.1%	11.4%	5.2%	9.7%
Trimethylbenzene	6.38	0.0%	0.1%	-	0.0%	0.4%	0.1%
4-Methylstyrene	7.19	0.5%	0.7%	-	0.9%	0.7%	0.8%
Propylbenzene	7.43	0.2%	0.1%	-	0.1%	0.3%	0.1%
α-Methylstyrene	8.51	0.7%	0.8%	-	1.1%	2.2%	0.9%
Butyl methacrylate	8.57	0.5%	0.6%	-	0.8%	0.3%	0.8%
Methacrylate ester	9.84	1.5%	1.6%	1.4%	1.1%	1.1%	1.5%
β-Methylstyrene	10.02	0.2%	0.2%	-	0.2%	0.3%	0.2%
Indene	10.58	0.0%	-	-	0.0%	0.7%	0.0%
α-Ethylstyrene	11.02	0.2%	0.3%	-	0.3%	1.1%	0.3%
DMAE methacrylate	11.59	3.0%	3.7%	5.0%	1.4%	2.1%	2.7%
Naphthalene	13.58	-	0.0%	-	-	0.4%	0.0%
Methyl naphthalenes	15.2/4	-	-	-	-	0.2%	0.0%
"Acetamidophenol"	16.65	2.6%	5.1%	47.7%	-	4.2%	2.9%
Toluene dimer	17.80	0.2%	0.2%	-	0.2%	0.4%	0.1%
Styrene dimer	19.68	0.9%	1.1%	0.4%	1.5%	0.8%	1.2%
Bisphenol-A	22.58	0.5%	-	-	-	-	-
Aromatics	23 - 24	10.1%	10.0%	14.2%	11.4%	4.7%	13.1%
TOTAL PEAK AREA		100%	100%	100%	100%	100%	100%

‡ = foil mounted sample; × = previous sample re-heated; * = foil sample with quartz filter underlay

Table 6: Product M – Main Components

COMPONENT	RT (min)	M3 450°C [†]	M2 650°C [†]	M5 850°C [†]	Mean Value
Styrene	5.23	18.9%	46.4%	49.4%	38.2%
“Acetamidophenol”	16.65	47.7%	5.1%	4.2%	19.0%
Aromatics	23 - 24	14.2%	10.0%	4.7%	9.6%
Methyl methacrylate	1.88	5.6%	8.2%	8.0%	7.3%
Butyl acrylate	5.50	4.1%	11.2%	5.2%	6.8%
DMAE methacrylate	11.59	5.0%	3.7%	2.1%	3.6%
Isobutylene	1.02	-	2.4%	6.5%	3.0%
Crotonic acid	2.74	0.4%	2.8%	3.9%	2.4%
Methacrylate ester	9.84	1.4%	1.6%	1.1%	1.4%
n-Butanol	1.57	0.8%	1.6%	1.2%	1.2%
Acrolein	1.11	0.9%	1.0%	1.1%	1.0%
α-Methylstyrene	8.51	-	0.8%	2.2%	1.0%
TOTAL PEAK AREA		99.0%	94.8%	89.4%	94.4%

The data in Tables 4 to 6 produced the following observations:-

- The main components in all six samples were very similar;
- The composition of the pyrolysis products showed obtained from Product M was also fairly similar to that of Product F. The main difference was the presence of methyl methacrylate, a substance not observed in Product F, and the absence of bisphenol-A, a significant component in Product F;
- The total peak areas for the 650°C and 850°C samples were very similar and significantly (around fifteen times) greater than was observed in the 450°C sample;
- Total peak areas for the 650°C and 850°C samples were a little higher than for the corresponding samples of Product F, whilst that for the 450°C sample was somewhat lower;
- The sample heated to 450°C showed significantly fewer components than the corresponding samples heated to 650°C;
- The sample heated to 850°C, whilst showing a similar total peak area to the corresponding 650°C sample, shows an increase in the number of minor/trace components (including naphthalene and other aromatics);
- Sample M4, heated to 650°C, after first heating to 450°C shows a decrease in total peak area of around 20%, when compared with Samples M1 and M2. Despite this loss however, the composition of the fume produced by all three 650°C samples is very similar;

- The twelve most abundant components in the foil mounted sample heated to 450°C account for around 99% of the total chromatographic peak area. This decreases to around 95% for the equivalent sample heated to 650°C and to around 89% for the sample heated to 850°C;
- Sample M6, heated to 650°C with a quartz underlay in place, produced very similar results, both in terms of total peak area and composition, to Samples M1 and M2.

4.3 PRODUCT G

The chromatograms obtained from the three samples of Product G were generally found to contain in excess of 30 components, but many of these were present in amounts of rather less than 1%. The main components in the three samples were styrene and various acrylate/methacrylate esters.

The chromatogram obtained from Sample G1, a foil mounted sample of Product G heated to 650°C, is shown in Figure 7.

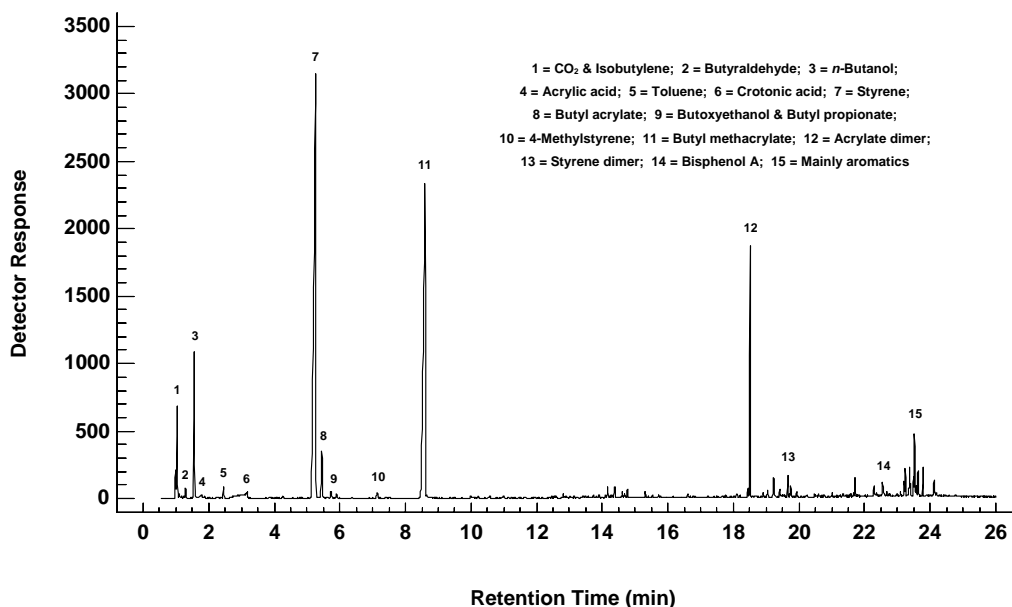


Figure 7: Product G – Heated to 650°C

Table 7 shows the peak areas for the thirty or so largest components in the TIC for each of the three test samples. Table 8 shows these same peak areas converted to a percentage of the total peak area (these data are based on the assumption that all components give an equal detector response, and, while this is not the case, the data are still useful as an estimate of the proportions of each compound present). Table 9 lists the ten largest components in order of abundance.

The data in Tables 7 to 9 produced the following observations:-

- The main components in all three samples were similar;
- The total peak area for the sample heated to 450°C was around 10 times lower than for the corresponding samples heated to 650°C and 850°C;

- The sample heated to 450°C showed significantly fewer components than the corresponding samples heated to 650°C and 850°C;
- Some of the acrylate/methacrylate esters showed a significant drop in abundance between 650°C and 850°C. This fall was accompanied by significant rises in styrene and many of the minor components.

Table 7: Product G – TIC Peak Areas

COMPONENT	RT (min)	G3 450°C	G1 650°C	G2 850°C	Mean Value
Isobutylene	1.02	140	9250	41300	16900
Acrolein	1.10	50	490	1000	510
Isoprene	1.14	10	110	1100	405
Allyl alcohol	1.18	15	130	370	170
Acetic acid	1.24	65	230	330	210
Butyraldehyde	1.30	25	1150	2200	1130
Butanol	1.56	1300	15200	14500	10300
Benzene	1.57	-	360	1300	550
Acrylic acid	1.79	-	760	2000	920
Toluene	2.46	-	1400	3100	1500
Crotonic acid	3.18	-	6300	15000	7100
Styrene	5.25	1400	128000	179000	103000
Butyl acrylate	5.45	130	7800	4000	3980
Butoxyethanol	5.73	270	1200	1400	960
Butyl propionate	5.90	-	660	300	320
Trimethylbenzene	6.42	-	65	740	270
4-Methylstyrene	7.14	-	1150	1800	980
Propylbenzene	7.46	-	110	410	170
α -Methylstyrene	8.53	-	530	4950	1830
Butyl methacrylate	8.60	1800	96000	48000	48600
Phenol	8.65	-	390	890	425
β -Methylstyrene	10.02	-	340	930	425
2-Ethylhexanol	10.26	210	310	260	260
4-Phenyl-1-butene	10.56	-	85	2200	760
Indene	10.58	-	330	610	310
α -Ethylstyrene	11.02	-	350	2900	1080
Naphthalene	13.60	-	-	1900	630
"Cyclic hydrocarbon"	14.40	-	1800	5400	2400
Methylnaphthalenes	15.2/15.4	-	65	1250	440
Isopropenylphenol	15.33	-	760	1300	690
Toluene dimer	17.80	-	170	490	220
"Acrylate dimer"	18.53	24200	26700	13500	21500
Styrene dimer	19.68	85	1950	1450	1160
Bisphenol A	22.57	200	2300	2800	1770
High MW aromatics	23 - 24	2350	23600	13600	13200
TOTAL PEAK AREA		32250	330045	372280	244860

Table 8: Product G – TIC Peak Areas (%)

COMPONENT	RT (min)	G3 450°C	G1 650°C	G2 850°C	Mean Value
Isobutylene	1.02	0.4%	2.8%	11.1%	6.9%
Acrolein	1.10	0.2%	0.1%	0.3%	0.2%
Isoprene	1.14	0.0%	0.0%	0.3%	0.2%
Allyl alcohol	1.18	0.0%	0.0%	0.1%	0.1%
Acetic acid	1.24	0.2%	0.1%	0.1%	0.1%
Butyraldehyde	1.30	0.1%	0.3%	0.6%	0.5%
Butanol	1.56	4.0%	4.6%	3.9%	4.2%
Benzene	1.57	-	0.1%	0.3%	0.2%
Acrylic acid	1.79	-	0.2%	0.5%	0.4%
Toluene	2.46	-	0.4%	0.8%	0.6%
Crotonic acid	3.18	-	1.9%	4.0%	2.9%
Styrene	5.25	4.3%	38.8%	48.1%	42.0%
Butyl acrylate	5.45	0.4%	2.4%	1.1%	1.6%
Butoxyethanol	5.73	0.8%	0.4%	0.4%	0.4%
Butyl propionate	5.90	-	0.2%	0.1%	0.1%
Trimethylbenzene	6.42	-	0.0%	0.2%	0.1%
4-Methylstyrene	7.14	-	0.3%	0.5%	0.4%
Propylbenzene	7.46	-	0.0%	0.1%	0.1%
α -Methylstyrene	8.53	-	0.2%	1.3%	0.7%
Butyl methacrylate	8.60	5.6%	29.1%	12.9%	19.8%
Phenol	8.65	-	0.1%	0.2%	0.2%
β -Methylstyrene	10.02	-	0.1%	0.2%	0.2%
2-Ethylhexanol	10.26	0.7%	0.1%	0.1%	0.1%
4-Phenyl-1-butene	10.56	-	0.0%	0.6%	0.3%
Indene	10.58	-	0.1%	0.2%	0.1%
α -Ethylstyrene	11.02	-	0.1%	0.8%	0.4%
Naphthalene	13.60	-	-	0.5%	0.3%
"Cyclic hydrocarbon"	14.40	-	0.5%	1.5%	1.0%
Methylnaphthalenes	15.2/15.4	-	0.0%	0.3%	0.2%
Isopropenylphenol	15.33	-	0.2%	0.3%	0.3%
Toluene dimer	17.80	-	0.1%	0.1%	0.1%
"Acrylate dimer"	18.53	75.0%	8.1%	3.6%	8.8%
Styrene dimer	19.68	0.3%	0.6%	0.4%	0.5%
Bisphenol A	22.57	0.6%	0.7%	0.8%	0.7%
High MW aromatics	23 - 24	7.3%	7.2%	3.7%	5.4%
TOTAL PEAK AREA		100.0%	100.0%	100.0%	100.0%

Table 9: Product G – Main Components

COMPONENT	RT (min)	G3 450°C	G1 650°C	G2 850°C	Mean Value
Styrene	5.25	4.3%	38.8%	48.1%	42.0%
Butyl methacrylate	8.60	5.6%	29.1%	12.9%	19.9%
"Acrylate dimer"	18.53	75.0%	8.1%	3.6%	8.8%
Isobutylene	1.02	0.4%	2.8%	11.1%	6.9%
High MW aromatics	23 - 24	7.3%	7.2%	3.7%	5.4%
Butanol	1.56	4.0%	4.6%	3.9%	4.2%
Crotonic acid	3.18	-	1.9%	4.0%	2.9%
Butyl acrylate	5.45	0.4%	2.4%	1.1%	1.6%
"Cyclic hydrocarbon"	14.40	-	0.5%	1.5%	1.0%
α -Methylstyrene	8.53	-	0.2%	1.3%	0.8%
TOTAL PERCENTAGE		97.0%	95.6%	91.2%	93.5%

4.4 PRODUCT I

The chromatograms obtained from the three samples of Product I were generally found to contain in excess of 20 components, but many of these were present in amounts of rather less than 1%. The main components in the three samples were phthalic anhydride, chlorendic anhydride and hexachlorocyclopentadiene. It was also noted that, after heating, the samples all left a white residue on the quartz liner of the pyrolyser.

The chromatogram obtained from Sample I1, a foil mounted sample of Product I heated to 650°C, is shown in Figure 8.

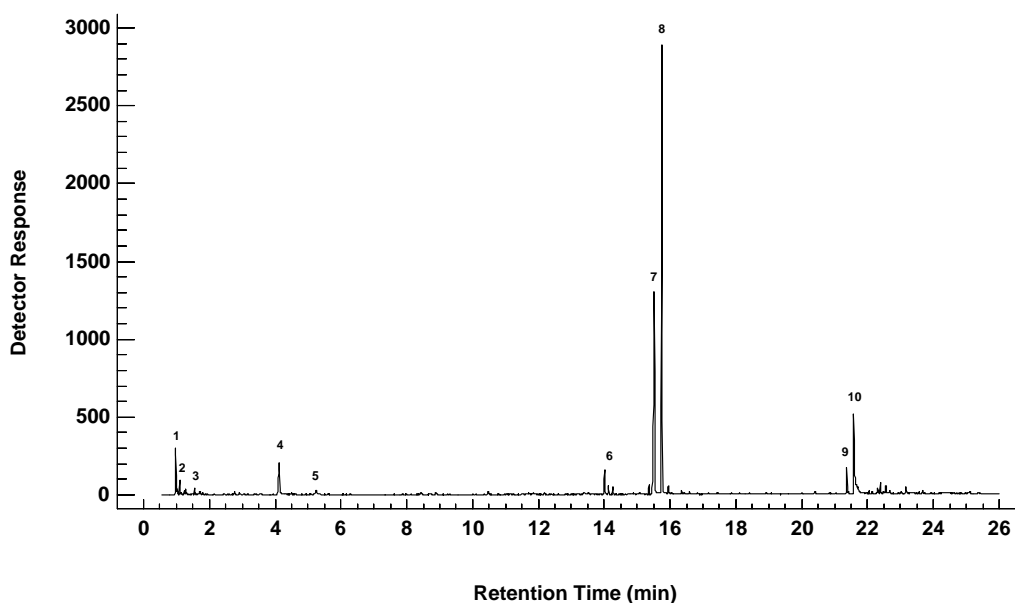
**Figure 8: Product I – Heated to 650°C**

Table 10 shows the peak areas for the twenty or so largest components in the TIC for each of the three test samples. Table 11 shows these same peak areas converted to a percentage of the total peak area. Table 12 lists the ten largest components in order of abundance.

- The data in Tables 10 to 12 produced the following observations:-
- Unlike many of the other primer and paint samples tested, the total peak areas at the three test temperature were all very similar;
- Whilst the main components observed in all the three samples were very similar, their relative amounts do show a marked temperature dependence (particularly in the case of the three main components - phthalic anhydride, chlorendic anhydride and hexachlorocyclopentadiene);
- At 450°C, chlorendic anhydride is the main component, but as the pyrolysis temperature is increased to 650°C and 850°C, the proportion of this particular compound decreases. At the same time however, the proportion of phthalic anhydride and hexachlorocyclopentadiene increases significantly, as does the numbers and amounts of the various minor/trace components. This indicates that the chlorendic anhydride is undergoing some form of thermal breakdown producing, in the main, phthalic anhydride and hexachlorocyclopentadiene.

Table 10: Product I – TIC Peak Areas

COMPONENT	RT (min)	I3 450°C	I1 650°C	I2 850°C	Mean Value
Propylene	1.00	-	-	3800	1270
Isobutylene	1.02	-	260	3300	1190
Acrolein	1.10	90	910	3200	1400
Cyclopentadiene	1.18	-	30	1200	410
Methylpentane	1.28	60	370	1700	710
Butanol	1.55	390	330	440	390
Benzene	1.57	15	80	2700	930
Toluene	2.48	-	30	1200	410
Maleic anhydride	4.16	940	6300	10000	5750
Ethylbenzene	4.29	-	90	430	175
m/p-Xylene	4.52	-	200	470	225
Styrene	5.20	-	85	930	340
o-Xylene	5.26	40	930	1600	860
Ethylphenol	6.29	-	150	430	195
Trichlorocyclopentadienes	10.5/11.8	55	610	710	460
Indene	10.57	-	-	680	225
Tetrachlorocyclopentadiene	14.01	710	2700	3050	2150
Pentachlorocyclopentadienes	14.1/14.3	280	1450	1550	1090
"Chloropyridine"	15.36	-	780	800	525
Phthalic anhydride	15.52	29600	30100	50500	36700
Hexachlorocyclopentadiene	15.75	2850	41900	34500	26400
Palmitic acid	21.37	990	2300	2600	1960
Chlorendic anhydride	21.58	87500	10800	4300	34200
TOTAL PEAK AREA		123520	100405	130090	118005

Table 11: Product I – TIC Peak Areas (%)

COMPONENT	RT (min)	I3 450°C	I1 650°C	I2 850°C	Mean Value
Propylene	1.00	-	-	2.9%	1.1%
Isobutylene	1.02	-	0.3%	2.5%	1.0%
Acrolein	1.10	0.1%	0.9%	2.5%	1.2%
Cyclopentadiene	1.18	-	0.0%	0.9%	0.4%
Methylpentane	1.28	0.0%	0.4%	1.3%	0.6%
Butanol	1.55	0.3%	0.3%	0.3%	0.3%
Benzene	1.57	0.0%	0.1%	2.1%	0.8%
Toluene	2.48	-	0.0%	0.9%	0.4%
Maleic anhydride	4.16	0.8%	6.3%	7.7%	4.9%
Ethylbenzene	4.29	-	0.1%	0.3%	0.2%
m/p-Xylene	4.52	-	0.2%	0.4%	0.2%
Styrene	5.20	-	0.1%	0.7%	0.3%
o-Xylene	5.26	0.0%	0.9%	1.2%	0.7%
Ethylphenol	6.29	-	0.1%	0.3%	0.2%
Trichlorocyclopentadienes	10.5/11.8	0.0%	0.6%	0.5%	0.4%
Indene	10.57	-	-	0.5%	0.2%
Tetrachlorocyclopentadiene	14.01	0.6%	2.7%	2.3%	1.8%
Pentachlorocyclopentadienes	14.1/14.3	0.2%	1.4%	1.2%	0.9%
"Chloropyridine"	15.36	-	0.8%	0.6%	0.5%
Phthalic anhydride	15.52	24.0%	30.0%	38.8%	31.1%
Hexachlorocyclopentadiene	15.75	2.3%	41.7%	26.5%	22.4%
Palmitic acid	21.37	0.8%	2.3%	2.0%	1.7%
Chlorendic anhydride	21.58	70.8%	10.8%	3.3%	29.0%
TOTAL PEAK AREA		100.0%	100.0%	100.0%	100.0%

Table 12: Product I – Main Components

COMPONENT	RT (min)	I3 450°C	I1 650°C	I2 850°C	Mean Value
Phthalic anhydride	15.52	24.0%	30.0%	38.8%	31.1%
Chlorendic anhydride	21.58	70.8%	10.8%	3.3%	29.0%
Hexachlorocyclopentadiene	15.75	2.3%	41.7%	26.5%	22.4%
Maleic anhydride	4.16	0.8%	6.3%	7.7%	4.9%
Tetrachlorocyclopentadiene	14.01	0.6%	2.7%	2.3%	1.8%
Palmitic acid	21.37	0.8%	2.3%	2.0%	1.7%
Acrolein	1.10	0.1%	0.9%	2.5%	1.2%
CO ₂ /Propylene	1.00	-	-	2.9%	1.1%
Isobutylene	1.02	-	0.3%	2.5%	1.0%
Pentachlorocyclopentadienes	14.1/14.3	0.2%	1.4%	1.2%	0.9%
TOTAL PERCENTAGE		99.6%	96.4%	89.7%	95.1%

4.5 SAMPLE BLANKS

As stated in Section 3.2, two samples of unpainted aluminium foil were also tested at 650°C (Samples F7 and M7). These produced chromatograms with no significant peaks present.

However, it was noted that some of the sample chromatograms did show evidence of one or 'transient' components which are probably due to contamination during sample handling. These include carboxylic acids (such as palmitic (C₁₆) and stearic (C₁₈) acid), squalene (an unsaturated high molecular weight aliphatic hydrocarbon) and other compounds which could not be positively identified.

5 INTER LABORATORY COMPARISON

The four products were also analysed by FIOH to provide an inter laboratory comparison for the heating tests. FIOH analysed all four products by pyrolysis (using a similar Pyrola-Agilent system to that used at HSL) and also conducted a set of oven heating tests on Products F and M. These oven tests involve a different heating technique to those at HSL in which a larger sample of 30 – 40 mg is heated in a glass tube to a temperature of 450 – 490°C in a stream of air. The components produced are sampled onto a combination of XAD-2 tubes (vapour) and glass fibre filters (particulate). Chromatograms showing the results from both fractions were supplied.

5.1 PRODUCT F

The main components identified by FIOH in their pyrolysis tests with Product F were styrene, butylene, methacrylic acid, bisphenol-A, butyl acrylate, α -methylstyrene, butanol and toluene. This shows good agreement with the HSL results (see Table 3).

In the oven heating tests, the main components identified on the XAD-2 chromatograms were styrene, butyl butenoate/methylstyrene/phenol, 2-(2-butoxyethoxy)ethanol (solvent), higher molecular weight aromatics, butyl acrylate, benzaldehyde, toluene & various substituted alkylbenzenes. On the glass fibre filter chromatograms the main components were bisphenol-A, surfynol and higher molecular weight aromatics. When compared with the HSL data, this produced the following observations:-

- Overall, the components identified in the FIOH chromatograms are fairly similar to those observed in the HSL tests (see Table 3);
- Although styrene is the biggest component in both HSL and FIOH chromatograms, some of the other components appear rather more prominent in the FIOH data;
- Perhaps because of their heavier sample loading, the FIOH chromatograms contain a greater number of minor/trace components;
- Because of the need to include a solvent delay, the FIOH chromatograms do not show components more volatile than toluene. Consequently, it is not possible to confirm the presence of any of the more volatile components identified in the HSL results, such as isobutylene, n-butanol and acrolein.

5.2 PRODUCT M

The main components identified by FIOH in their pyrolysis tests with Product M were styrene, surfynol, butylene, methyl methacrylate, methacrylic acid, butyl acrylate, α -methylstyrene, toluene and butanol. It was noted that the “surfynol” peak was not positively identified, and it seems likely that this component was the same as that identified in the HSL data as an “amidophenol”. This difference in identification is probably being due to the two MS search routines having problems obtaining a reliable match for this particular compounds. This is quite often a problem with pyrolysis or heating experiments, which produce compounds which are either very obscure or very similar in nature, and thus difficult to positively identify. In this case for example, apart from the acetamidophenol/surfynol peak, there are also a number of acrylate/methacrylate compounds. Despite this, the FIOH data generally shows good agreement with the HSL results (see Table 6).

The main components identified in the FIOH XAD-2 chromatograms were styrene, butyl acrylate, benzaldehyde, methylstyrene/MMA esters, higher molecular weight aromatics, methacrylic acid, diethyldimethylsuccinonitrile, toluene & various lower molecular weight aromatic compounds. On the glass fibre filter chromatograms the main components were identified as surfynol together with various medium and higher molecular weight aromatics.

A comparison of the HSL and FIOH chromatograms produces a similar set of conclusions to those obtained with Product F. Once again, styrene is the largest component in both HSL and FIOH data, but several of the secondary components are more prominent in the FIOH chromatograms. The main difference between the two sets of results however, is the absence of methyl methacrylate, one of the main components identified at HSL, in the FIOH data. Looking at the relative retention times for toluene and methyl methacrylate on the HSL chromatograms, it is clear that this particular compound has been 'lost' in the solvent delay on the FIOH chromatograms (together with other less prominent components such as isobutylene, n-butanol and acrolein).

5.3 PRODUCT G

The main components identified by FIOH in their pyrolysis tests with Product G were styrene, butyl methacrylate, acrylate dimer, butylene, methacrylic acid, butanol and α -methylstyrene. This shows good agreement with the HSL results (see Table 9).

5.4 PRODUCT I

The main components identified by FIOH in their pyrolysis tests with Product I were phthalic anhydride, tetra-, penta- and hexachlorocyclopentadienes, butadiene, maleic anhydride, benzene and low molecular weight alkenes. This shows reasonably good agreement with the HSL results (see Table 12), with the main differences being a lack of butadiene in the HSL data and a lack of chlorendic anhydride in the FIOH data. However, in the case of the chlorendic anhydride, it should be noted that the FIOH test was carried out at 800°C and the HSL data did show that the proportion of this component fell significantly at higher pyrolysis temperatures.

6 SUMMARY & CONCLUSIONS

In the initial experiments described in this report, the samples were examined using either a GC-mounted pyrolyser (HSL and FIOH) or by heating in a glass oven tube with various indirect sampling methods (FIOH only).

In the case of the pyrolysis tests, the HSL samples were heated over a range of three temperatures ranging from 450 to 850°C, whilst the FIOH samples were heated to a temperature of 800°C. In all cases the samples were heated very rapidly (2 seconds) in an inert atmosphere of helium. Both laboratories used very similar equipment (Pyrola 2000 pyrolyser and Agilent GC-MS) and chromatographic conditions, and, generally, obtained a good level of agreement in their results.

In the case of the oven tests carried out by FIOH, the samples were only heated to 450°C, but were much larger and heated more slowly (several minutes) in air. Despite these differences, the oven tests gave broadly similar results to the HSL/FIOH pyrolysis tests, particularly in terms of the range of components observed.

It was noted that the FIOH oven tests produced significant levels of the various pyrolysis products at the test temperature of 450°C. By comparison, the amounts of material generated by the HSL method at 450°C were relatively small, possibly due to a combination of the much smaller sample and the much shorter heating period. However, by increasing the pyrolyser temperature to 650°C, the total amount of material produced by pyrolysis increased by 6 – 10 times. A further increase in pyrolyser temperature to 850°C did not significantly increase the total amount of material produced, but did result in the appearance of many more minor/trace components (including naphthalene and other aromatics).