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**Analysis of Weld-Through Thin Organic Coatings  
Pyrolysis and Resistance Welding Tests**

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Science Group: **Health Improvement**

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# EXECUTIVE SUMMARY

## Objectives

- To carry out welding and pyrolysis tests to identify components produced by heating of four weld-thru products - two thin organic coatings (TOC) and two oils.
- To examine and compare the results obtained by the 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 these weld-thru products.

## Main Findings

- The two TOC products were found to generate a variety of volatile organic components when heated. These include methyl methacrylate and ethyl acrylate in Product W and isophorone diisocyanate (IPDI) in Product X. The presence of IPDI (together with much smaller amounts of TDI) in the fume generated from Product X may be of particular interest as isocyanates due to their sensitising properties and low occupational exposure limits, both in the UK and elsewhere.
- The two TOC products show generally good correlation between the components observed in the pyrolysis and welding tests, particularly for the main components of interest, ie the methyl methacrylate and ethyl acrylate in Product W and isophorone diisocyanate (IPDI) in Product X.
- In the case of Product X, the main difference between the chromatographic results is a lack of C<sub>20/30</sub> aliphatic hydrocarbons in the welding test material – a difference also observed in the case of the two oils. At the same time however, analysis of particulate from the welding tests shows a significantly higher organic content in the material being generated by these three products. One possibility therefore, is the missing semi-volatile C<sub>20/30</sub> hydrocarbon material is being incorporated into the particulate phase of the fume, possibly as higher molecular weight non-volatile components.
- In the case of the two oils, neither of the welding tests was found to generate very much in the way of volatile organic material (or even CO), with emissions from both being mainly in the form of particulate. The C<sub>20/30</sub> components which formed the majority of the material observed in the pyrolysis tests were not observed in any of the chromatographic analyses of the welding samples. The proportion (and amount) of organic material in the particulate generated by the two oils differed quite significantly. The reason for this is not clear, but may be due to the relative thickness of the oil layer on the steel test strips.
- Correlation between pyrolysis and welding results for this selection of thin organic coatings was noticeably better than for the weld-thru primers examined previously. This is probably mainly due to the welding technique used. The previous tests employed various forms of arc welding, a higher temperature and more aggressive technique than the resistance welding technique used in this study. In particular, it is probably significant that the heating cycle in resistance welding is much more like that used in the pyrolyser, albeit carried out under air rather than helium.

## Recommendations

- For the two TOC products tested, laboratory testing, using pyrolysis, can provide a similar level of information on the composition of the fume produced on heating to the resistance welding tests. The main advantages of the pyrolysis test method is that is quicker, easier to set up and more reproducible than the welding tests, and hence can be done at significantly lower cost.
- In the case of TOCs, it is recommended that samples should be supplied as finished coatings on steel plate, and that pyrolysis testing be carried out on flakes of the finished coating material scraped from the surface of the metal with a flat blade.
- A pyrolysis temperature of 650°C – 700°C is sufficient.

# 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-through products and coatings. The information is, amongst other things, intended to aid completion of European Standard prCEN/ISO/TS 15011-5. This standard will provide a testing procedure for weld-through products with the objective of improving the quality of information provided by manufacturers on their Material Safety Data Sheets (MSDSs). This will enable users to produce a more informed risk assessment and hence help to reduce instances of ill health caused by occupational exposure to weld-through products.

This report summarises the results of pyrolysis and resistance welding tests carried out on a selection of four weld-through products, two thin organic coatings and two oils, to identify the components generated on heating. This work forms part of Work Package 2 (WP2) of the project.

The objectives of 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 recommendation for a standard test procedure for testing of weld-thro products.

The four samples were supplied by Arcelor, Belgium. The two thin organic coatings were supplied as pieces of finished steel plate, the two oils as bulk products.

The pyrolysis test procedure is based on that described previously for weld-through primers (Project Report OMS/2005/16). The samples were tested using a pyrolyser interfaced to a gas chromatograph (GC) equipped with a mass spectrometer (MS) detector. Similar pyrolysis tests will also be carried out by Arcelor and FIOH.

## 2 TEST METHOD

### 2.1 EQUIPMENT

The testing protocol and equipment has been described previously (Project Report OMS/2005/16), but is basically as follows:-

Samples of the various primers are heated in a Pyroly 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 and is capable of heating samples to over 1000°C. The sample is placed on a calibrated platinum filament assembly, which is placed inside the body of the pyrolyser surrounded by a heated (175°C) glass liner. 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 two seconds. 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 focusses the degradation products at the front end of the chromatographic column producing good resolution of even the most volatile components.

### 2.2 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.

### 2.3 PYROLYSIS

The test samples were pyrolysed at nominal temperatures of 500°C, 650°C and 800°C.

### 3 TEST SAMPLES

The four products examined in these tests were as follows:-

- **Product W:-** This is an acrylic-based thin organic coating (TOC) intended for use on steel;
- **Product X:-** This is an epoxy-based TOC intended for use on steel;
- **Product Y:-** This is an oil intended for use on steel (with Product X);
- **Product Z:-** This is an oil intended for use on steel (with Product W);

The two TOCs were supplied as finished coatings a few microns thick on typical pieces of steel plate. The TOC was removed from the surface steel by gently scraping with a straight blade, and a small sample (< 1 mg) was then placed directly onto the platinum filament for analysis.

The two oil samples were diluted in dichloromethane (DCM) to give a 10% v/v solution. 2  $\mu$ l of this solution was then applied directly onto the platinum filament using a 10  $\mu$ l syringe. The DCM solvent was then left to evaporate at room temperature, leaving approximately 0.2  $\mu$ l (ca. 160  $\mu$ g) of the sample oil on the filament for analysis.

## 4 PYROLYSIS TESTS

The tests carried out on the four test products were as follows:-

### 4.1 PRODUCT W

- *Sample W1*:- Sample pyrolysed at 470°C for 2 seconds;
- *Sample W2*:- Sample pyrolysed at 660°C for 2 seconds;
- *Sample W3*:- Sample pyrolysed at 780°C for 2 seconds.

### 4.2 PRODUCT X

- *Sample X1*:- Sample pyrolysed at 580°C for 2 seconds;
- *Sample X2*:- Sample pyrolysed at 680°C for 2 seconds;
- *Sample X3*:- Sample pyrolysed at 820°C for 2 seconds.

### 4.3 PRODUCT Y

- *Sample Y1*:- 2 µl of 10% v/v solution left for solvent to evaporate, then pyrolysed at 500°C for 2 seconds;
- *Sample Y2*:- 2 µl of 10% v/v solution left for solvent to evaporate, then pyrolysed at 660°C for 2 seconds;
- *Sample Y3*:- 2 µl of 10% v/v solution left for solvent to evaporate, then pyrolysed at 810°C for 2 seconds.

### 4.4 PRODUCT Z

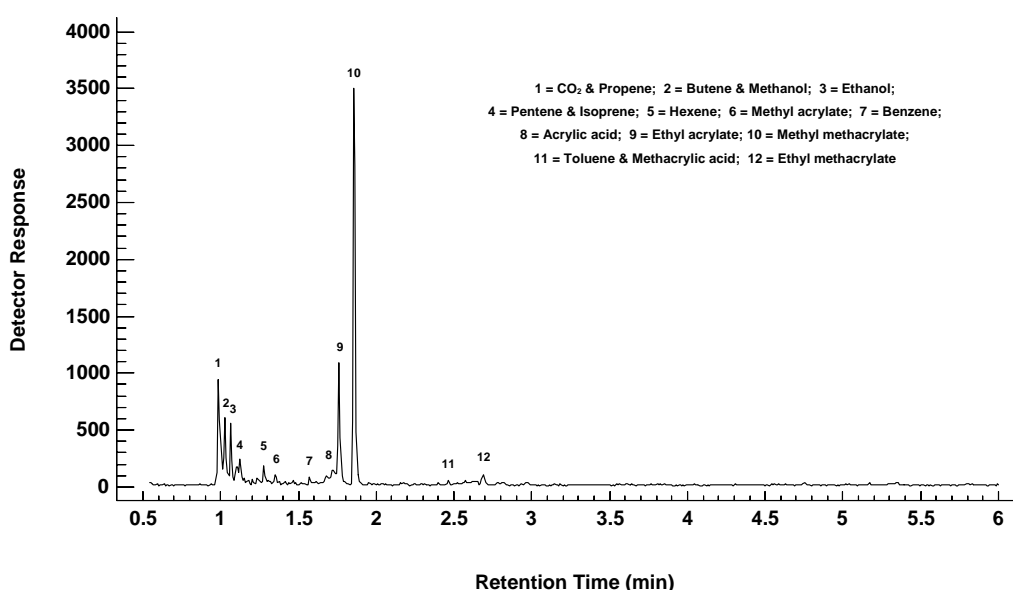
- *Sample Z1*:- 2 µl of 10% v/v solution left for solvent to evaporate, then pyrolysed at 510°C for 2 seconds;
- *Sample Z2*:- 2 µl of 10% v/v solution left for solvent to evaporate, then pyrolysed at 650°C for 2 seconds;
- *Sample Z3*:- 2 µl of 10% v/v solution left for solvent to evaporate, then pyrolysed at 820°C for 2 seconds.

## 5 PYROLYSIS TEST RESULTS

### 5.1 PRODUCT W

The chromatograms obtained from the three samples of Product W were generally found to contain around a dozen components, however many of these were present in amounts of rather less than 1%. The main components in the three samples were methyl methacrylate, ethyl acrylate, propylene, butylene and ethanol. During pyrolysis the samples deposited a metallic grey/black residue on the glass liner surrounding the filament. This deposit became more pronounced as pyrolysis temperature increased.

The chromatogram obtained from Sample W3, heated to 780°C, is shown in Figure 1.



**Figure 1: Product W – Heated to 780°C**

Table 1 shows the peak areas for the ten largest components in the Total Ion Chromatogram (TIC) for each of the three tests. In Table 2, the peak areas of the ten largest components have been converted to a percentage of the total peak area and are listed in order of abundance. The data in Table 2 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.

The data in Tables 1 and 2 produced the following observations:-

- The main components in all three samples were very similar;
- The largest component at all three temperatures was methyl methacrylate;
- The total peak area for the sample heated to 470°C was significantly lower than for the corresponding samples heated to 660°C and 780°C;

- The sample heated to 470°C showed significantly fewer components than the corresponding samples heated to 660°C and 780°C.
- The ten most abundant components in the sample heated to 470°C account for the whole of the chromatographic peak area. This decreases to around 98% for the sample heated to 660°C and 95% for the sample heated to 780°C.

**Table 1: Product W – TIC Peak Areas**

COMPONENT	RT (min)	TEST W1 (470°C)	TEST W2 (660°C)	TEST W3 (780°C)	MEAN VALUE
CO <sub>2</sub> + Propylene	0.99	215	505	1220	645
Butylene + Methanol	1.03	175	335	650	385
Ethanol	1.06	535	535	490	520
Pentene	1.10	-	-	115	40
Isoprene	1.12	-	-	220	75
Hexene	1.28	-	35	170	70
Methyl acrylate	1.35	-	85	120	70
Benzene	1.57	-	-	60	20
Acrylic acid	1.70	-	65	300	120
Ethyl acrylate	1.78	420	1270	1030	905
Methyl methacrylate	1.87	1030	2560	3870	2490
Methacrylic acid	2.63	60	215	230	170
Ethyl methacrylate	2.75	45	130	130	100
Methacrylate trimer	21.70	45	155	200	130
<b>TOTAL PEAK AREA</b>		<b>2530</b>	<b>5890</b>	<b>8800</b>	<b>5740</b>

**Table 2: Product W – Main Components**

COMPONENT	RT (min)	TEST W1 (470°C)	TEST W2 (660°C)	TEST W3 (780°C)	MEAN VALUE
Methyl methacrylate	1.87	40.8%	43.4%	43.8%	43.4%
Ethyl acrylate	1.78	16.6%	21.6%	11.7%	15.8%
CO <sub>2</sub> + Propylene	0.99	8.5%	8.6%	13.9%	11.2%
Ethanol	1.06	21.2%	9.1%	5.6%	9.1%
Butylene + Methanol	1.03	6.9%	5.7%	7.4%	6.7%
Methacrylic acid	2.63	2.4%	3.7%	2.6%	3.0%
Methacrylate trimer	21.70	1.8%	2.6%	2.3%	2.3%
Acrylic acid	1.70	-	1.1%	3.4%	2.1%
Ethyl methacrylate	2.75	1.8%	2.2%	1.5%	1.7%
Isoprene	1.12	-	-	2.5%	1.3%
<b>TOTAL PERCENTAGE</b>		<b>100.0%</b>	<b>98.0%</b>	<b>94.7%</b>	<b>96.6%</b>

## 5.2 PRODUCT X

The chromatograms obtained from the three samples of Product X were generally found to contain in excess of 30 components, but most of these were present in amounts of rather less than 1%. By far the largest component in all three samples was an aliphatic hydrocarbon envelope covering an approximate range of  $C_{20} - C_{30}$ . The most significant of the minor components were  $C_3 - C_7$  alkenes, benzene, ethyl acrylate and two isomers of isophorone diisocyanate (IPDI). During pyrolysis the samples deposited a white residue on the glass liner surrounding the filament. As with Product W, this deposit became more pronounced as pyrolysis temperature increased.

The chromatogram obtained from Sample X3, heated to 820°C, is shown in Figure 2.

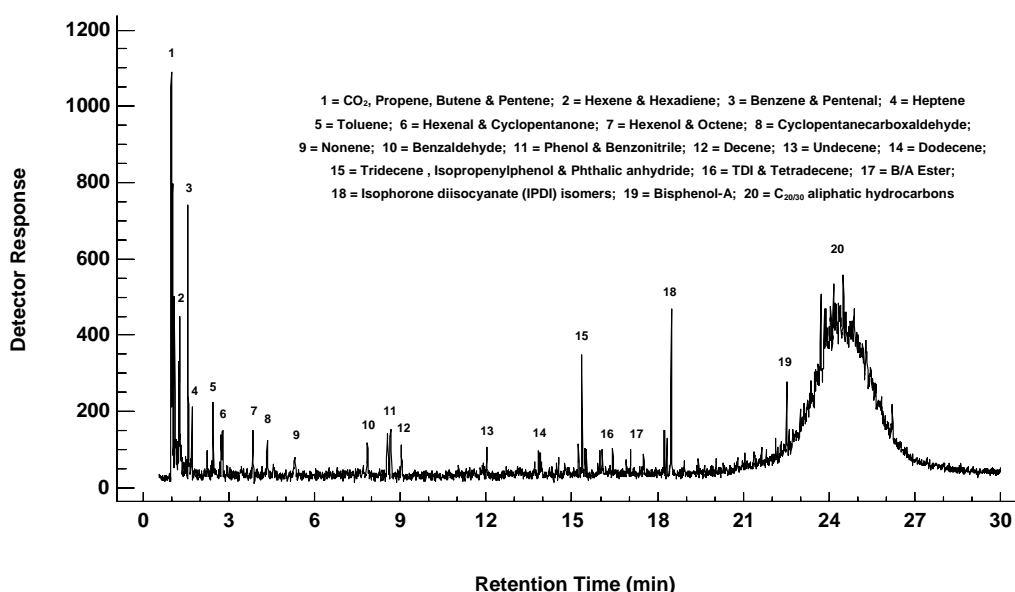


Figure 2: Product X – Heated to 820°C

Table 3 shows the peak areas for the forty or so largest components in the TIC for each of the three test samples. Table 4 shows the peak areas of the ten largest components converted to a percentage of the total peak area and listed in order of abundance.

The data in Tables 3 and 4 produced the following observations:-

- The pyrolysis products generated by all three samples were fairly similar and dominated by the  $C_{20/30}$  aliphatic hydrocarbon envelope, which make up between 85 and 97% of the total mass of material. This pattern of hydrocarbons closely resembles that observed in the two oil samples (see Sections 5.3 and 5.4). Whilst these hydrocarbons make originate from the TOC itself, another possibility is that the sample plate supplied for testing also incorporates a coating of oil.
- Increasing pyrolysis temperature causes a decrease in the proportion of the  $C_{20/30}$  aliphatic hydrocarbon material and a corresponding increase in the amounts of the various minor components.

**Table 3: Product X – TIC Peak Areas**

COMPONENT	RT (min)	TEST X1 (580°C)	TEST X2 (680°C)	TEST X3 (820°C)	MEAN VALUE
CO <sub>2</sub> & Propylene	0.99	130	490	1870	830
Butylene	1.02	60	160	960	390
Pentene	1.09	45	95	440	190
Isoprene	1.11	-	35	220	85
Hexadiene	1.24	30	100	170	100
Hexene	1.27	25	35	280	110
Benzene	1.56	5	200	880	360
Pentenal	1.58	130	170	270	190
Heptene	1.71	-	-	190	65
Toluene	2.45	-	70	190	90
Hexenal	2.75	20	25	100	50
Cyclopentanone	2.78	35	55	220	105
Hexenol	3.83	100	110	290	170
Cyclopentanecarboxaldehyde	4.34	85	110	200	130
Benzaldehyde	7.85	55	110	200	120
Phenol	8.54	60	110	300	155
Benzonitrile	8.66	-	110	300	135
C <sub>10-15</sub> alkenes	9.0-17.6	-	-	785	260
Isopropenylphenol	15.35	85	140	410	210
Phthalic anhydride	15.46	140	85	110	110
Tolylene diisocyanate	15.98	70	55	85	70
Benzoic acid esters	17.1/18.3	35	80	210	110
Isophorone diisocyanates	18.2/18.5	580	630	810	675
Bisphenol-A	22.52	190	65	300	185
C <sub>20-30</sub> aliphatic hydrocarbons	22-28	68000	28000	58000	51500
<b>TOTAL PEAK AREA</b>		<b>69900</b>	<b>31000</b>	<b>67800</b>	<b>56200</b>

**Table 4: Product X – Main Components**

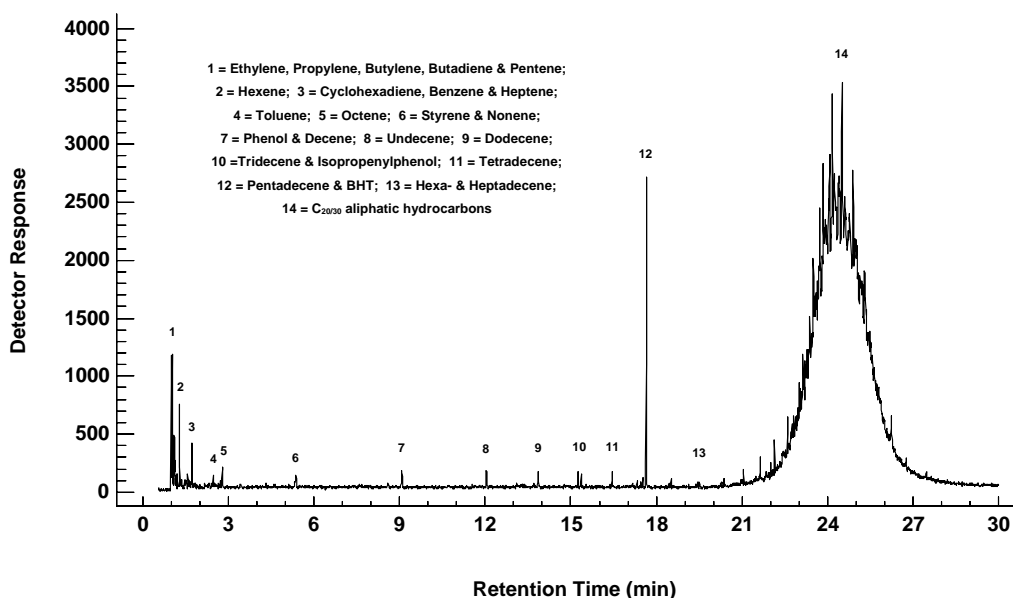
COMPONENT	RT (min)	TEST X1 (580°C)	TEST X2 (680°C)	TEST X3 (820°C)	MEAN VALUE
C <sub>20-30</sub> aliphatic hydrocarbons	22-28	97.3%	90.2%	85.6%	91.3%
CO <sub>2</sub> /Propylene	0.99	0.2%	1.6%	2.8%	1.5%
IPDI isomers	18.2/18.5	0.8%	2.0%	1.2%	1.2%
C <sub>4</sub> Alkene	1.02	0.1%	0.5%	1.4%	0.7%
Benzene	1.56	0.0%	0.6%	1.3%	0.6%
"Alkenes"	9.0-17.6	-	-	1.2%	0.5%
Isopropenylphenol	15.35	0.1%	0.5%	0.6%	0.4%
C <sub>5</sub> Alkene	1.09	0.1%	0.3%	0.6%	0.3%
Pentenal	1.58	0.2%	0.5%	0.4%	0.3%
Bisphenol-A	22.52	0.3%	0.2%	0.4%	0.3%
<b>TOTAL PERCENTAGE</b>		<b>99.1%</b>	<b>96.5%</b>	<b>95.5%</b>	<b>97.1%</b>

- The ten most abundant components in the sample heated to 580°C account for over 99% of the total chromatographic peak area. This decreases slightly, to around 97%, for the sample heated to 680°C and to around 96% for the sample heated to 820°C.
- Although none of the minor components is ever present in amounts greater than 3% w/w, they do include some potentially important components with regard to toxicity, most notably isocyanates in the form of IPDI and tolylene diisocyanate (TDI).

### 5.3 PRODUCT Y

The chromatograms obtained from the three samples of Product Y were generally found to contain in excess of 20 components, but most of these were present in amounts less than 0.1%. By far the largest component in all three samples was an aliphatic hydrocarbon envelope covering an approximate range of C<sub>20</sub> – C<sub>30</sub>. The most significant of the minor components was butylated hydroxytoluene (BHT), a commonly used anti-oxidant.

The chromatogram obtained from Sample Y3, heated to 810°C, is shown in Figure 3.



**Figure 3: Product Y – Heated to 810°C**

Table 5 shows the peak areas for the twenty or so largest components in the TIC for each of the three test samples. Table 6 shows the peak areas of the ten largest components converted to a percentage of the total peak area and listed in order of abundance.

The data in Tables 5 and 6 produced the following observations:-

- The pyrolysis products generated by all three samples were fairly similar and are dominated by the C<sub>20/30</sub> aliphatic hydrocarbon envelope, which make up between 97 and 99% of the total mass of material;
- Increasing pyrolysis temperature causes a small decrease in the proportion of the C<sub>20/30</sub> aliphatic hydrocarbon material and a corresponding increase in the amounts of the

remaining minor components. However, apart from BHT, none of these minor, mainly alkene, components is ever present in amounts greater than 0.3% w/w;

- The ten most abundant components account for over 99% of the total chromatographic peak area in all three samples.

**Table 5: Product Y – TIC Peak Areas**

COMPONENT	RT (min)	TEST Y1 (500°C)	TEST Y2 (660°C)	TEST Y3 (810°C)	MEAN VALUE
Ethylene	0.97	-	210	850	355
Propylene	0.99	-	200	800	335
Butylene & Butadiene	1.02	-	230	1150	460
Pentene	1.09	-	170	430	200
Isoprene	1.11	-	60	160	75
Hexene	1.27	-	140	90	75
Cyclohexadienes	1.45/1.60	-	35	230	90
Benzene	1.56	-	40	190	75
Heptene	1.71	-	130	390	175
Toluene	2.45	-	-	130	45
Octene	2.77	-	90	270	120
Styrene	5.28	-	-	90	30
Nonene	5.32	-	140	270	135
Phenol	8.56	45	60	100	70
C <sub>10/18</sub> alkenes	9.0-20.2	-	1280	2410	1230
Isopropenylphenol	15.35	-	60	135	65
Butylated hydroxytoluene	17.65	3700	2700	3400	3270
C <sub>20/30</sub> aliphatic hydrocarbons	20-28	360000	380000	330000	357000
<b>TOTAL PEAK AREA</b>		<b>364000</b>	<b>386000</b>	<b>341000</b>	<b>364000</b>

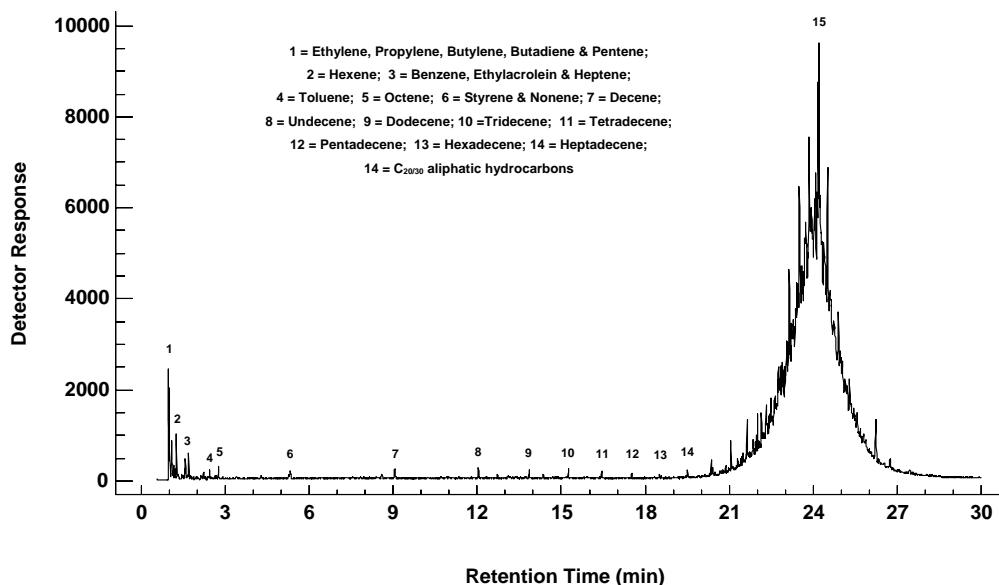
**Table 6: Product Y – Main Components**

COMPONENT	RT (min)	TEST Y1 (500°C)	TEST Y2 (660°C)	TEST Y3 (810°C)	MEAN VALUE
C <sub>20/30</sub> aliphatic hydrocarbons	20-28	98.97%	98.56%	96.75%	98.13%
Butylated hydroxytoluene	17.65	1.02%	0.70%	1.00%	0.90%
C <sub>10/18</sub> alkenes	9.05	-	0.33%	0.71%	0.34%
Butylene & Butadiene	1.02	-	0.06%	0.34%	0.13%
Ethylene	0.97	-	0.05%	0.25%	0.10%
Propylene	0.99	-	0.05%	0.23%	0.09%
Pentene	1.09	-	0.04%	0.13%	0.06%
Heptene	1.71	-	0.03%	0.11%	0.05%
Nonene	5.32	-	0.04%	0.08%	0.04%
Octene	2.77	-	0.02%	0.08%	0.03%
<b>TOTAL PERCENTAGE</b>		<b>99.99%</b>	<b>99.90%</b>	<b>99.67%</b>	<b>99.86%</b>

## 5.4 PRODUCT Z

The chromatograms obtained from the three samples of Product Z were generally found to contain in excess of 20 components, but most of these were present in amounts less than 0.1%. Although the chromatograms were very similar to those obtained from Product Y, consisting mainly of a large  $C_{20/30}$  aliphatic hydrocarbon envelope. The one main difference was the absence of any BHT (or other anti-oxidant).

The chromatogram obtained from Sample Z3, heated to 820°C, is shown in Figure 4.



**Figure 4: Product Z – Heated to 820°C**

Table 7 shows the peak areas for the twenty or so largest components in the TIC for each of the three test samples. Table 8 shows the peak areas of the ten largest components converted to a percentage of the total peak area and listed in order of abundance.

The data in Tables 7 and 8 produced the following observations:-

- The pyrolysis products generated by all three samples were fairly similar and are dominated by the  $C_{20/30}$  aliphatic hydrocarbon envelope, which make up between 97 and 99% of the total mass of material;
- Increasing pyrolysis temperature causes a very slight decrease in the proportion of the  $C_{20/30}$  aliphatic hydrocarbon material and a corresponding increase in the amounts of the remaining minor, mainly alkene, components. However, none of these minor components is ever present in amounts greater than 0.3% w/w;
- The ten most abundant components account for over 99% of the total chromatographic peak area in all three samples.

**Table 7: Product Z – TIC Peak Areas**

COMPONENT	RT (min)	TEST Z1 (510°C)	TEST Z2 (650°C)	TEST Z3 (820°C)	MEAN VALUE
Ethylene	0.97	-	620	1600	740
Propylene	0.99	-	100	1600	565
Butylene & Butadiene	1.02	-	440	2100	845
Pentene	1.09	-	520	1100	540
Isoprene	1.11	-	80	210	95
Cyclopentadiene	1.17	-	-	170	55
Hexene	1.27	-	360	980	445
C <sub>6/8</sub> n-alkanes	1.3/1.8/2.9	-	490	-	165
Cyclohexadienes	1.45/1.60	-	-	230	75
Benzene	1.56	-	-	310	105
Ethylacrolein	1.59	420	640	-	355
Heptene	1.71	-	260	640	300
Toluene	2.45	-	-	210	70
Octene	2.77	-	290	420	235
Ethylbenzene	4.29	-	-	140	45
Styrene	5.28	-	110	400	170
Nonene	5.32	-	300	250	185
C <sub>10/18</sub> alkenes	9.0-20.2	-	965	1810	925
Methylstyrenes	9.05-9.23	-	140	420	185
C <sub>20/30</sub> aliphatic hydrocarbons	20-28	830000	950000	720000	833300
<b>TOTAL PEAK AREA</b>		<b>830000</b>	<b>955000</b>	<b>733000</b>	<b>839000</b>

**Table 8: Product Z – Main Components**

COMPONENT	RT (min)	TEST Z1 (510°C)	TEST Z2 (650°C)	TEST Z3 (820°C)	MEAN VALUE
C <sub>20/30</sub> aliphatic hydrocarbons	20-28	99.95%	99.44%	98.28%	99.27%
C <sub>10/18</sub> alkenes	9.0-20.2	-	0.10%	0.25%	0.11%
Butylene & Butadiene	1.02	-	0.05%	0.29%	0.10%
Ethylene	0.97	-	0.06%	0.22%	0.09%
Propylene	0.99	-	0.01%	0.22%	0.07%
Pentene	1.09	-	0.05%	0.15%	0.06%
Hexene	1.27	-	0.04%	0.13%	0.05%
Ethylacrolein	1.59	0.05%	0.07%	-	0.04%
Heptene	1.71	-	0.03%	0.09%	0.04%
Octene	2.77	-	0.03%	0.06%	0.03%
<b>TOTAL PERCENTAGE</b>		<b>100.00%</b>	<b>99.88%</b>	<b>99.68%</b>	<b>99.86%</b>

## 6 TOXICITY OF COMPONENTS

The data in Tables 1 to 8 take no account of the toxicity of the individual compounds. However, as with the weld-thro' primer products analysed previously, the peak area data can be modified to highlight more toxically significant components by dividing the peak area by an appropriate exposure limit (in mg/m<sup>3</sup>).

### 6.1 PRODUCT W

Modifying the data from Product W in this way indicates that, when toxicity is taken into account, ethyl acrylate is probably the most important component present. This is due to an exposure limit which is 10 times lower than that for methyl methacrylate. The data also display an increase in total 'toxicity' with temperature.

Despite this however, most of the components generated by Product W have relatively high exposure limits or are only present in quite small amounts, so the 'toxicity' of the VOCs generated by this product are fairly low compared with the weld-thro' primers examined previously.

### 6.2 PRODUCT X

The modified peak area data from Product X indicate that, when toxicity is taken into account, the IPDI and C<sub>20/30</sub> aliphatic hydrocarbon components are probably the most important components present. In the case of the hydrocarbons, this is not surprising since they make up around 90% of the pyrolysis products. In the case of the IPDI however, this importance is due to the very low exposure limits assigned to isocyanates, since the component itself only makes up around 1% of the material generated on heating.

The only other components contributing significantly to the overall VOC 'toxicity' figure are TDI, pentenal, benzene and hexenal. The modified data for Product X show little evidence of any temperature dependence over the range of temperatures tested.

### 6.3 PRODUCT Y

The modified peak area data from Product Y indicate that the C<sub>20/30</sub> aliphatic hydrocarbons, which make up around 98% of the pyrolysis material, are also the only significant component present with regard to toxicity. The data also show no significant temperature dependence.

### 6.4 PRODUCT Z

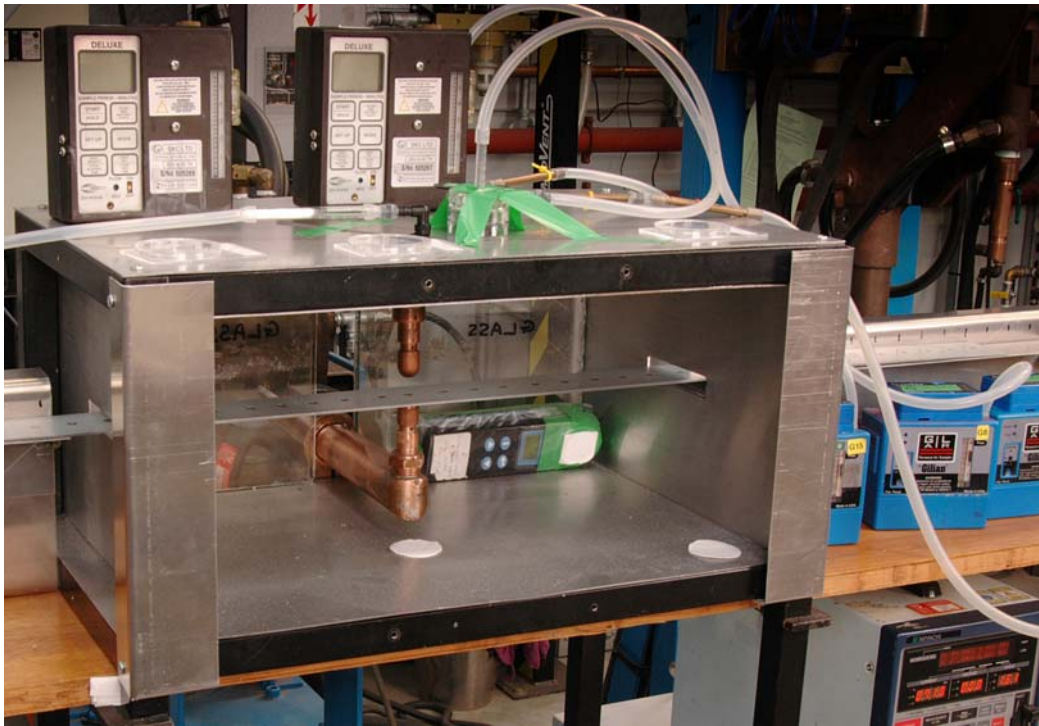
The modified peak area data from Product Z indicate that, like Product Y, the C<sub>20/30</sub> aliphatic hydrocarbons making up the vast majority of the observed pyrolysis material are also the only significant component present with regard to toxicity. Also, and once again like Product Y, the data show no significant temperature dependence.

## 7 RESISTANCE WELDING TESTS

Resistance welding tests, comprising around 200 spot welds, were carried out on metal strips coated with the following products:-

- **Test WT-1:-** Product X strips
- **Test WT-2:-** Product Y strips
- **Test WT-3:-** Product W strips
- **Test WT-4:-** Product Z strips

The welding tests were carried out inside a semi-sealed metal and glass chamber, approximately 50 cm × 30 cm × 20 cm in size (see Figure 5). The metal strips (approximately 5 cm wide and 1.2 m long) were fed into the chamber through a slot, and 50 spot welds applied, one every 2.5 cm. For each product, this process was repeated on a total of four strips (making a total of 200 welds in all). Full details of the welding tests are given in Appendix 1.



**Figure 5: Resistance Welding Test Chamber**

During welding, a number of air sampling devices were used to measure the concentration of various components inside the chamber. The sampling devices used were as follows:-

- **Automated Thermal Desorption (ATD) Tubes** – Tenax for volatile organic compounds (VOC) and Carboxen for highly volatile organic compounds (HVOC);
- **DNPH Filters** – For formaldehyde;

- **Quartz filters** – For total particulate (including organic/elemental carbon content);
- **GF/A filter + XAD-2 tube** – For polycyclic aromatic hydrocarbons (PAH);
- **2-MP filter** – For isocyanates (Product X only);
- **Real-time CO monitor.**

## 7.1 ATD TUBE SAMPLES

The Tenax and Carboxen ATD tubes were analysed by ATD using a combination of GC-FID and GC-MS to give the results shown in Table 9. These are a combination of the results from the three samples taken during each test. It should be noted that all samplers were fitted with a GF/A pre-filter in order to prevent the ingress of particulate matter onto the sample tube.

**Table 9: ATD Samples – VOC Results**

COMPONENT (ppm)	Test WT-1 (PRODUCT X)	Test WT-2 (PRODUCT Y)	Test WT-3 (PRODUCT W)	Test WT-4 (PRODUCT Z)	Blank*
Propane / Propene	0.44	0.04	0.36	0.18	-
Butane / Butene	0.33	0.07	0.41	0.20	-
Ethanol	-	-	0.94	-	-
Acetone	0.37	0.11	0.15	0.30	0.10
Hexadiene	0.31	-	-	-	-
Pentenal	0.18	-	< 0.01	< 0.01	-
Methyl acrylate	-	-	0.05	-	-
Ethyl acetate	-	-	0.10	-	-
Methyl propionate	-	-	0.04	-	-
Methyl isobutyrate	-	-	0.06	-	-
Benzene	0.66	0.06	0.04	0.04	< 0.01
C <sub>7/8</sub> alkenes	0.09	-	-	0.03	-
Ethyl acrylate	-	-	1.68	-	-
Methyl methacrylate	-	-	3.03	-	-
Ethyl methacrylate	-	-	0.03	-	-
Toluene	0.19	< 0.01	0.03	0.06	< 0.01
Hexenal	0.13	-	-	-	-
Cyclopentanone	0.06	-	-	-	-
Xylene	-	0.03	-	0.01	-
Hexenol	0.13	-	-	-	-
Cyclopentanecarboxaldehyde	0.06	-	-	-	-
Phenol	0.12	-	-	-	-
Benzaldehyde	0.11	-	-	-	< 0.01
Benzonitrile	0.24	-	-	-	-

\* = Welding area blank samples

The ATD results in Table 9 produced the following observations:-

- VOC concentrations on the two tests with the oiled strips (WT-2 and WT-4) were very low with the only measureable components being BTEX and some low molecular weight aliphatic hydrocarbons;
- Product W generated significant concentrations of methyl methacrylate and ethyl acrylate, together with lower concentrations of ethanol and various other acrylic esters and aliphatic/aromatic hydrocarbons. These results correlate very well with those obtained from the pyrolysis tests (see Table 2).
- Product X showed the presence of benzene and toluene, together with a number of other aliphatic and aromatic components, including propylene, butylene, pent/hexenal, cyclopentanone, hexenol, cyclopentanecarboxaldehyde, phenol, benzaldehyde and benzonitrile. Several of these are quite unusual components, but all were observed in the pyrolysis test chromatograms, albeit as relatively minor components when compared with the C<sub>20/30</sub> hydrocarbon oil envelope (see Figure 2).

## 7.2 DNPB SAMPLES

The DNPB samples were analysed for the presence of formaldehyde by high performance liquid chromatography (HPLC). However, the resulting chromatograms showed no detectable amounts of formaldehyde in any of the samples.

## 7.3 QUARTZ FILTER SAMPLES

The quartz filter samples were analysed in two ways – gravimetrically, to give a total particulate concentration, and by coulometry, to determine the amount of carbon, both elemental (soot) and organic, in the particulate. It should be noted that the ‘organic carbon’ test cannot identify actual organic components present, it merely gives a total mass of organic carbon present in the particulate. The results of the various analyses are given in Table 10.

**Table 10: Quartz Filter Samples – Particulate/Carbon Results**

COMPONENT (ppm)		Test WT-1 (PRODUCT X)	Test WT-2 (PRODUCT Y)	Test WT-3 (PRODUCT W)	Test WT-4 (PRODUCT Z)
Total Particulate	Mass (mg)	1.890	1.916	2.569	1.504
	Concentration (mg/m <sup>3</sup> )	45.8	32.6	37.7	23.6
Total Carbon Particulate	Mass (mg)	1.059	1.427	0.269	0.536
	Concentration (mg/m <sup>3</sup> )	25.6	24.3	3.9	8.4
	% of Total Mass	56%	75%	10%	36%
Elemental Carbon (Soot) Particulate	Mass (mg)	0.035	0.010	0.008	0.006
	Concentration (mg/m <sup>3</sup> )	0.8	0.2	0.1	0.1
	% of Total Mass	2%	1%	< 1%	< 1%
Organic Carbon Particulate	Mass (mg)	1.024	1.417	0.261	0.529
	Concentration (mg/m <sup>3</sup> )	24.8	24.1	3.8	8.3
	% of Total Mass	54%	74%	10%	35%
Non-carbonaceous Particulate	% of Total Mass	44%	25%	90%	64%

The results in Table 10 produced the following observations:-

- The total particulate concentrations generated by the two coatings (WT-1 and WT-3) are around 50% greater than for their associated oil (WT-2 and WT-4).
- The particulate generated by Products X and Y, the TOC (WT-1) and oil (WT-2), contains a significantly higher proportion of organic material than that generated by Products W and Z. Conversely, the proportion of inorganic material in particulate generated by Products X and Y is markedly lower.
- The elemental carbon (soot) content of the particulate in all four products is very low (less than 2%).

#### 7.4 GF/A FILTER + XAD-2 TUBE SAMPLES

The GF/A filter/XAD-2 tube samples were analysed for the presence of PAHs and other semi-volatile components by GC-MS (in single ion monitoring (SIM) and SCAN mode respectively).

The PAH results are shown in Table 11. As with previous welding tests, the main PAH present is naphthalene, but the concentrations, even of naphthalene, are very low.

**Table 11: GF/A Filter & XAD-2 Tube Samples – PAH Results**

TEST	PRODUCT	PAH COMPONENTS ( $\mu\text{g}/\text{m}^3$ )
WT-1	Product X	Naphthalene (5)
WT-2	Product Y	Naphthalene (10); Pyrene (1)
WT-3	Product W	Naphthalene (10); Pyrene (1)
WT-4	Product Z	Naphthalene (9); Pyrene (1)

Additional analysis of the samples in SCAN mode did not detect the presence of any other semi-volatile organic components in the four samples.

#### 7.5 2-MP FILTER SAMPLES

The 2-MP filter sample taken in Test WT-1 (Product X) was analysed for the presence of isocyanates by HPLC (using mass spectrometry to confirm the identity of any isocyanate components observed).

The analysis showed the presence of two isomers of isophorone diisocyanate (IPDI). Also present, but at very much lower levels, were both isomers of tolylene diisocyanate (TDI). These results match up very well with the isocyanate components observed in the pyrolysis tests with Product X (see Tables 3 and 4) in which both IPDI and TDI were observed.

The combined concentration of the two isomers of IPDI (as isocyanate (NCO)) in Test WT-1 was found to be  $0.48 \text{ mg}/\text{m}^3$ . The concentration of TDI was too low to be accurately measured, but was estimated to be at least 20 times less (ie less than  $0.02 \text{ mg}/\text{m}^3$ ).

By way of comparison, the current UK short term (15-minute) exposure limit for isocyanate is 0.07 mg/m<sup>3</sup> (as NCO), whilst the 8-hour time weighted average (TWA) exposure limit is 0.02 mg/m<sup>3</sup> (also as NCO). Thus, the isocyanate concentration measured in this test would appear to be quite significant.

## 7.6 REAL TIME CO MONITOR

Real time carbon monoxide (CO) concentrations inside the test chamber during Tests WT-1, WT-2 and WT-3 were measured using a Trollex TX 6521 CO monitor. The resulting CO concentration data obtained from the three tests is shown in Figures 6 to 8.

The data show significantly higher CO concentrations being generated during welding of the two TOC products compared with just oil (Product Y). Peak CO concentrations for the three tests are around 8 ppm for Product W, 3 ppm with Product X and 1 ppm with Product Y. The detection limit (and resolution) of the Trollex monitor is 1 ppm.

The mean CO concentrations for the three products, averaged over the individual test periods, are 2.3 ppm (Product W), 1.7 ppm (Product X) and less than 0.1 ppm (Product Y). Although the average concentrations for the two TOCs are quite similar, it should be noted that the test with the Industry product includes significantly more 'down time' (mainly for electrode cleaning), which has the effect of lowering the average concentration.

Possibly the main point of interest from these experiments is that the mean CO concentrations measured during the various tests were not significantly greater than those observed for some of the main VOCs (see Table 9). Thus, it would appear that for these products, and under these test conditions, carbon monoxide is not necessarily the predominant component generated during welding.

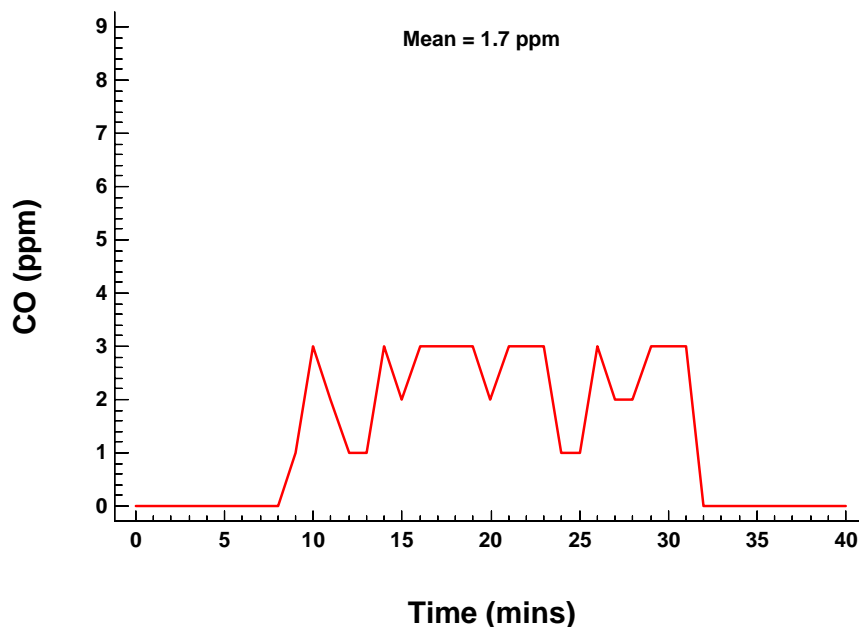
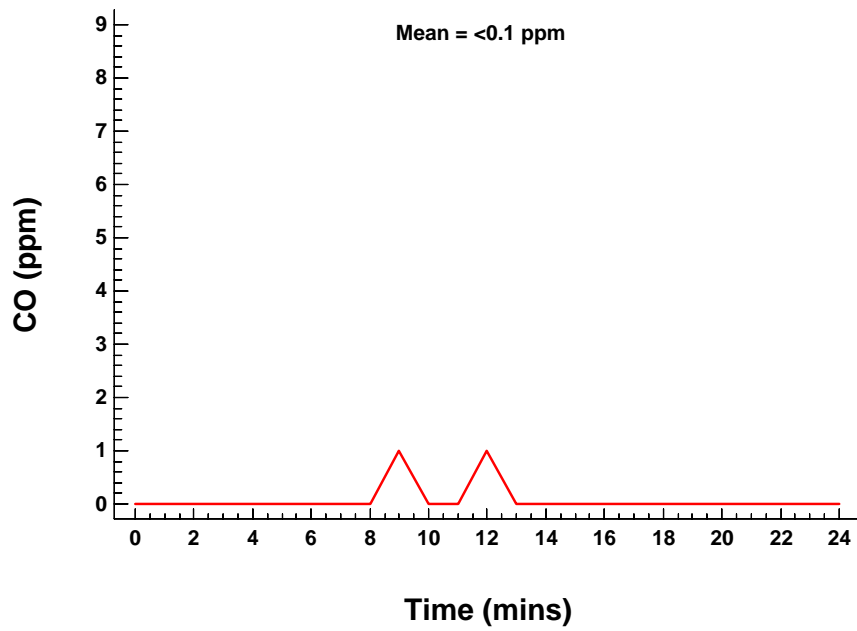
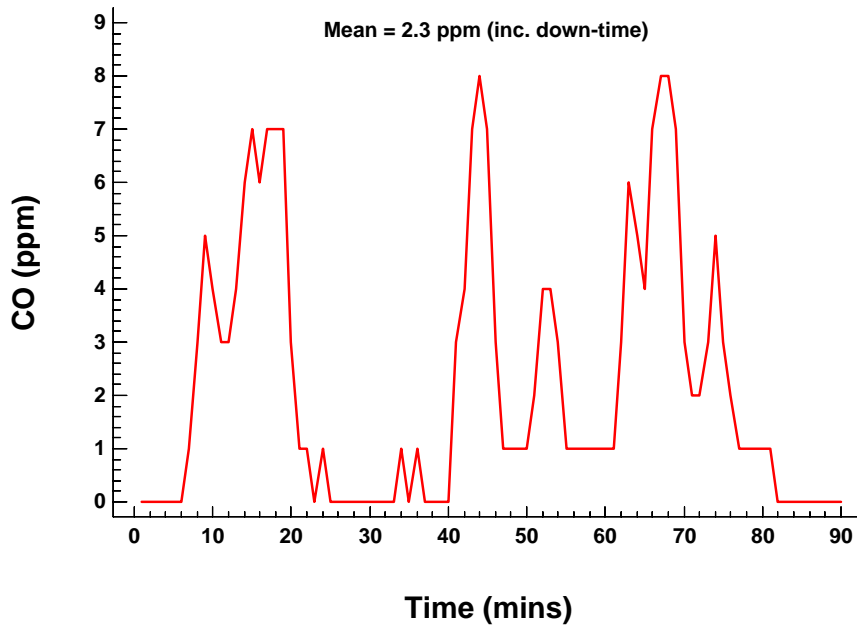


Fig. 6: Test WT-1 (Product X) – CO Concentration



**Fig. 7: Test WT-2 (Product Y) – CO Concentration**



**Fig. 8: Test WT-3 (Product W) – CO Concentration**

## 8 SUMMARY & CONCLUSIONS

A summary of the results obtained from the pyrolysis and welding tests carried out on the four products is given in Table 12.

**Table 12: Pyrolysis & Welding Tests - Summary of Results**

PRODUCT	TEST METHOD	MAIN COMPONENTS	SECONDARY COMPONENTS	MINOR/TRACE COMPONENTS
Product W	Pyrolysis	Methyl methacrylate	<u>Ethyl acrylate</u> ; CO <sub>2</sub> ; Propylene; Ethanol; Butylene; Methanol	Other acrylic acids & esters; Isoprene
	Resistance Welding	CO; Methyl methacrylate	<u>Ethyl acrylate</u> ; Propylene; Ethanol; Butylene	Other acrylic & aliphatic esters; Benzene; Toluene; Naphthalene
Product X	Pyrolysis	<u>C<sub>20/30</sub> alkanes</u>	CO <sub>2</sub> ; Propylene; Benzene; <u>IPDI isomers</u>	C <sub>4/13</sub> alkenes; Hexadiene; Pent/hexenal; Hexenol; Cyclopentanone; Phenols; C'pentanecarboxaldehyde; Benzaldehyde; Benzoxazole; TDI; Bisphenol-A
	Resistance Welding	CO; Benzene; Propylene; Butylene; <u>IPDI</u> ; Hexadiene	Pent/hexenal; Toluene; Hexenol; Phenol; Benzaldehyde; Benzoxazole	C <sub>7/8</sub> alkenes; Cyclopentanone; C'pentanecarboxaldehyde; TDI
Product Y	Pyrolysis	<u>C<sub>20/30</sub> alkanes</u>	BHT	C <sub>2/16</sub> alkenes
	Resistance Welding	-	CO; C <sub>3/8</sub> alkenes; <u>Benzene</u> ; Xylene	Toluene; Naphthalene
Product Z	Pyrolysis	<u>C<sub>20/30</sub> alkanes</u>	-	C <sub>2/16</sub> alkenes
	Resistance Welding	-	C <sub>3/8</sub> alkenes; <u>Benzene</u> ; Toluene	Xylene; Naphthalene

Components underlined in bold are probably the most significant in each test if toxicity is taken into account (see Section 6)

Comparison of the pyrolysis and welding results for the four products produced the following observations:-

- The two TOC products show generally good correlation between the components observed in the pyrolysis and welding tests, particularly for the components of interest with regard to toxicity, ie methyl methacrylate and ethyl acrylate in Product W and IPDI in Product X.
- The presence of IPDI (and much lower amounts of TDI) in the welding samples generated from Product X is of particular importance as isocyanates are regarded as highly toxic substances with sensitising properties and very low occupational exposure limits, both in the UK and elsewhere.

- In the case of Product X, the main difference between the chromatographic results is a lack of C<sub>20/30</sub> aliphatic hydrocarbons in the welding test material – a difference also observed in the case of the two oils. At the same time however, analysis of particulate from the welding tests shows a significantly higher organic content in the material being generated by Product X and the two oils. One possibility therefore, is the missing semi-volatile C<sub>20/30</sub> hydrocarbon material in these three products is being incorporated into the particulate phase of the fume, possibly as even higher molecular weight non-volatile organic material. Unfortunately, as stated in Section 7.3, the coulometric test does not identify the actual organic components present.
- In the case of the two oils, neither of the welding tests was found to generate very much in the way of volatile organic material (or even CO), with emissions from both being mainly in the form of particulate. As previously mentioned, the C<sub>20/30</sub> components which formed the majority of the material observed in the pyrolysis tests were not observed in any of the chromatographic analyses of the welding samples. The main difference in the fume collected from the two products was that the proportion (and amount) of organic material in the particulate collected from Product Y was far greater than for Product Z. The reason for this is not clear, but, as the pyrolysis tests on the two oils appear to give very similar results, may be related to the relative thickness of the oil layer on the two sets of metal strips.
- Overall, the correlation between pyrolysis and welding results for this selection of thin organic coatings is better than for the weld-thro' primers examined previously. This is probably due to the welding technique used rather than to the products themselves. In the case of the five primers, the welding techniques used were various forms of arc welding, a higher temperature and more aggressive technique than the resistance welding method used with the TOCs. The better correlation of results is also probably not unrelated to the fact that the heating process involved in resistance welding much more closely resembles that which occurs in the pyrolyser, albeit that heating takes place in air rather than helium.

## 8.1 RECOMMENDED TEST CONDITIONS

From the results and observations detailed in this report, the following test conditions have been found to give a reasonable representation of the main volatile organic components produced during resistance welding through thin organic coatings:-

**Test Equipment:** Pyrola 2000 pyrolyser interfaced to Agilent 5890/5971 GC-MS

**Sample Type (TOC):** < 1 mg of finished coating removed from metal substrate

**Sample Type (oil/liquid):** 2 µl of 10% solution of oil/liquid in dichloromethane

**Pyrolyser Liner/Interface Temperature:** 175°C

**Pyrolysis Temperature:** 650°C – 700°C

**Heating Period:** 2 seconds

**GC Inlet:** Spilt (50 – 100 ml/min)

## 9 APPENDIX 1: SPOT WELDING OF TOC STEELS

The following paragraphs give details of the four resistance welding tests carried out by Steve Westgate at TWI, Cambridge.

### 9.1 MATERIALS

The test materials used were as follows:-

- **Test WT-1** - Product X coated steel;
- **Test WT-2** - Product Y coated steel;
- **Test WT-3** - Product W coated steel;
- **Test WT-4** - Zinc coated steel plus Product Z.

### 9.2 WELDING EQUIPMENT

The welding equipment used was as follows:-

- Miyachi 1000 Hz mfdc supply and Martin scissors gun;
- Electrodes F16 type B profile remachined with 5.5 mm tip with 40 mm face radius. (A2/2ISO 5821) Electrodes bedded in with 20 welds on uncoated steel with a similar total thickness to the test strips;
- Current measured with a Miyachi MM336 current meter (actual current measured 300A lower than set value on the power supply).

### 9.3 WELDING CONDITIONS

The welding conditions (as defined by Arcelor) were as follows:-

- Electrode force 2.5 kN;
- Squeeze time 40 cycles (increased from 20 cycles on the machine used to ensure force > 2.4kN at onset of current and checked with a squeeze analyser);
- Weld time - 8 cycles;
- Hold time - 5 cycles;
- Welding rate - 30 spots/min;
- 300 welds made in each test.

The welding current was set up by conducting a weld growth curve experiment to determine the splash point. The test welds were then made at a current 500 A lower than the splash current. The weld size was checked to ensure it was not less than  $4.5\sqrt{t}$ . The measured currents used in each of the tests were as follows:-

- **Test WT-1** (Product X) - 7.45 kA
- **Test WT-2** (Product Y) - 9.1 kA
- **Test WT-3** (Product W) - Started at 7.9kA (but modified during the test)
- **Test WT-4** (Product Z) - 7.2kA

#### **9.4 MODIFICATIONS FOR TEST WT-3**

Some welding problems were encountered during Test WT-3, using the strips coated with Product W. This required the following modifications to be made to the welding parameters as the test progressed.

The Product W coated strips displayed such a high resistance that breakthrough was unreliable and the electrodes quickly became contaminated. In order to start the test strip without splash the surfaces were abraded for the first weld. The shunted welds in the test strips gave less problems but did occasionally produce slight splash effects. Current was reduced by 200 A, but splashing and slight sticking still began to occur more frequently after about 100 welds. Electrodes were abraded after 150 welds and the setting modified to try to stabilise weldability. Squeeze time was increased to 60 cycles and 2 cycles of upslope was added in an effort to reduce the effect of the high initial resistance. The test was completed at the modified setting, but it was necessary to stop and dress the electrodes from time to time to minimise the incidence of splash. Even under these conditions, the weld quality was still only around the minimum required weld size.

## 10 PREVIOUS REPORTS

### **HSL Report OM/2005/15**

Analysis of weld-through primers

Initial tests using pyrolysis-gas chromatography-mass spectrometry

Ian Pengelly

### **HSL Report OM/2005/16**

Analysis of weld-through primers

Laboratory tests using pyrolysis-gas chromatography-mass spectrometry

Ian Pengelly

### **HSL Report OM/2006/09**

Analysis of weld-through primers

Arc Welding Tests

Ian Pengelly