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**Analysis of Weld-Through Primers  
Arc Welding Tests**

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Science Group: **Health Improvement**

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## EXECUTIVE SUMMARY

### Objectives

- To identify components produced during arc welding of five weld-through primers.
- To examine and compare the results of the welding tests with those obtained from laboratory testing, by pyrolysis, on the same five products.
- To produce recommendations for a standard test procedure for testing of weld-through products.

### Main Findings

- Three different arc welding techniques, Metal Active Gas (MAG), Manual Metal Arc (MMA) and Tungsten Inert Gas (TIG) were used. The test data showed that fume composition was dependent on welding method. TIG welding tended to generate the highest concentrations of volatile organic compounds (VOCs), whilst MAG and MMA welding produced more particulate. The main components identified in the TIG welding tests were generally similar to those produced by MAG and MMA, but with some significant variations in relative and absolute concentrations. In particular, concentrations of formaldehyde, phenols and polycyclic aromatic hydrocarbons (PAHs), especially the higher molecular weight, more toxically significant PAHs, tended to be higher with TIG welding. The higher VOC concentrations in TIG welding also tended to result in a greater variety of components, but, at the same time, give better agreement between welding and pyrolysis results. Differences in heat input did not appear to have a significant effect on fume composition.
- The welding samples frequently contained compounds, in particular commonly used solvents such as acetone, cyclohexane and dichloromethane, which probably originate from the surrounding work area rather than the welding process. The presence of these interfering substances represents an added complication when assessing the results of the welding tests. Pyrolysis should not be subject to this type of interference as heating takes place in an instrument system which is not open to the outside atmosphere.
- Correlation between welding and pyrolysis test data for the five test primers is very variable. The best correlation tended to occur for those products giving higher overall emissions. However, with all five products it was found that there were significant components detected in the pyrolysis tests that were not present in the welding tests (and vice versa).
- Sampling deficiencies may have been at least partly responsible for the absence of some of the very volatile compounds, such as propylene, butylene and butadiene, from the welding tests. If so, it may be possible to improve this situation by employing alternative sampling media for these particular components.
- The proportion of semi-volatile compounds detected in the welding tests also appeared to be significantly lower than in the pyrolysis tests. The reason for this remains unclear, however there is evidence from analysis of the particulate that some or all of these 'lost' semi-volatile compounds are being incorporated into the particulate fraction, either by condensation or adsorption.

- A significant difference between pyrolysis and welding results was observed with Product B. Several major components detected in the welding tests, in particular methyl isobutyl ketone, methoxypropyl acetate and methoxypropanol, were not observed in the pyrolysis tests. These components are often found in paint thinners, and it is suspected that these may have been used in the application of the primer to the welding test pieces. This illustrates the need to ensure that sample material analysed by pyrolysis is consistent with that used on the primed welding test pieces.
- Some of the differences in emissions may be due to differences in the heating environment between welding and pyrolysis, particularly in the case of arc welding. Pyrolysis testing is performed in a totally inert, helium, atmosphere, whereas arc welding takes place in a much more aggressive oxidising atmosphere. This might well be expected to lead to a greater proportion of oxidised components and smaller, more volatile, components in the welding tests. Indeed, even amongst the various welding methods used, heating conditions appear to be sufficiently different to produce some significant variations in fume composition and emissions.
- When comparing pyrolysis and welding results, the fact that some compounds are much more toxic than others mean that not all merit equal ranking. For example, the presence of carboxylic acids in some welding samples, but not in the corresponding pyrolysis data is not too significant an omission. By contrast, components such as acroleins have low exposure limits and hence extremely important for any risk assessment. It is therefore important that any highly toxic compounds present in the fume are identified, even at low concentrations.
- The test data have shown that many compounds can be emitted during welding over shop primers and it would be impractical to present them all on a Material safety Data Sheet (MSDS). A toxicity ranking system might therefore be of use in establishing those data that should be included. Ideally, such a system would take into account both toxicity and concentration, perhaps by dividing concentration by the occupational exposure limit of the compound.
- The test results indicate that, overall, pyrolysis would be the preferred technique for generating MSDS data. Whilst correlation between pyrolysis and welding data was variable, pyrolysis testing did successfully identify all the toxically significant compounds detected in welding. In addition, sampling and detection problems meant that some compounds, mainly semi-volatiles, were much more easily identified by pyrolysis. Pyrolysis testing also offers the prospect of good reproducibility between laboratories and at a cost that is less than half of that for a welding test. Furthermore, previous work has indicated that representative results may be obtained from pyrolysis at a single test temperature of 850°C.
- In order to minimise the risk of failure to identify important degradation products, the welding tests employed a very comprehensive sampling protocol. To reduce the sampling regime employed during the welding tests, it would therefore be desirable to have information on the likely degradation products before the welding tests are performed. The easiest way to generate such data is probably pyrolysis. Consequently, some form of pyrolysis testing would probably need to be carried out as an integral part of any welding test procedure.

## Recommendations

- Pyrolysis offers a reproducible and cost effective solution for generation of emissions data for weld-thro shop primers. The equipment required for pyrolysis testing is significantly less specialised and more readily available than that required for welding tests. Consequently, pyrolysis testing can be initiated and performed more rapidly than welding and requires fewer resources, resulting in a significantly lower lead/turnaround time and cost per test.
- Representative results can be obtained from a single pyrolysis test at either 650°C or 850°C. For a single pyrolysis test, the recommendation for arc welding through this type of primer product is to use a pyrolysis temperature of 850°C.
- Where thinners have been mixed with the primer during the spraying process, it is recommended that pyrolysis is carried out on primer samples removed from finished products to fully characterise emissions, rather than the actual raw material.
- Experimental problems and higher costs make welding tests a less attractive solution for generating emissions data for weld-thro shop primers. In particular, welding tests require more specialist knowledge, equipment and facilities, which tends to both increase costs and be less readily available.
- Laboratory testing can never fully reproduce actual welding conditions. Consequently, there may be occasions where welding tests are also justified. However, in order to reduce sampling requirements during these welding tests, it is desirable to have information on the likely degradation products. In such instances, it is recommended that pyrolysis be used as a screening procedure prior to the welding tests.

# 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 laboratory analyses carried out following welding tests carried out at TWI, Cambridge. These tests were carried out on a selection of five weld-through primers (WTP) 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 recommendations for a standard test procedure for testing of weld-thro products.

The welding tests were carried out on samples of steel plate coated with the primers and supplied by FORCE Technology, Denmark and by the Finnish Institute of Occupational Health (FIOH) in Turku.

During each welding test, six air samples were taken using different devices to collect components of interest in the fume. These samples were subsequently analysed at HSL, Buxton using standard methods of analysis.

The welding test results were then compared with those obtained from pyrolysis testing carried out previously on the same five WTP samples. Full details of the pyrolysis tests are given in Project Report OMS/2005/16.

## 2 TEST METHOD

### 2.1 HOOD

A test hood fabricated of aluminium was constructed at TWI. This is shown in Figure 1 with the access door open and the test piece and various sampling devices in position. Pre-filters for the various sampling tubes can be seen inside the hood, as can the welding torch and a test piece. During testing, the hood is suspended above the test piece using an appropriate bracket.



**Figure 1: Welding Test Hood with Sampling Devices in Position**

### 2.2 TEST MATERIAL

The test pieces were made from carbon steel measuring 500 mm × 200 mm × 10 mm, the optimum size determined by heat flow calculations. They were pre-prepared by shot blasting and painted with shop primers, according to manufacturers' instructions. The shop primers examined are shown in Table 1, together with a brief description of their type and typical application thickness.

Five test pieces each of Product A, Product B and Product C were supplied for testing. In addition, 500 mm lengths of 50 mm × 12 mm bright mild steel bar stock, degreased with acetone and allowed to dry at room temperature, were employed as blank test pieces.

Only three test pieces coated with Product E were supplied, although an unpainted sample of the base material was supplied as a blank. Subsequently, five test pieces coated with Product D were also received.

**Table 1: Welding Test Products**

PRODUCT	MAKER	MATERIAL DESCRIPTION	SOLIDS CONTENT (%)	THICKNESS (µm)
A	1	Low zinc, solvent borne, ethyl silicate shop-primer(2-component)	25	15-25
B	1	Epoxy Polyamide pigmented with zinc phosphate shop-primer (2-component)	22	15-25
C	2	Alkyd shop-primer (1-component)	40	30
D	3	Water based, low zinc, ethyl silicate shop-primer (2-component)	36	15
E	4	Low zinc, solvent borne, ethyl silicate shop-primer (2-component)	56	15

### 2.3 WELDING TESTS

The welding test programme is shown in Table 2.

**Table 2: Welding Test Program**

TEST	PRODUCT	PROCESS	D* (mm)	SHIELD GAS	CURRENT (A)	VOLTAGE (v)	TS <sup>†</sup> (mm/min)	AT <sup>‡</sup> (s)
1.1	None (B/M Steel)	MAG	1.2	Ar/20%CO <sub>2</sub> /2%O <sub>2</sub>	254	28.0	300	78
1.2	Product A	MAG	1.2	Ar/20%CO <sub>2</sub> /2%O <sub>2</sub>	246	27.8	300	84
1.3	Product B	MAG	1.2	Ar/20%CO <sub>2</sub> /2%O <sub>2</sub>	251	28.0	300	82
1.4	Product C	MAG	1.2	Ar/20%CO <sub>2</sub> /2%O <sub>2</sub>	252	27.8	300	79
1.5	Product D	MAG	1.2	Ar/20%CO <sub>2</sub> /2%O <sub>2</sub>	247	28.5	300	84
1.6	Product E	MAG	1.2	Ar/20%CO <sub>2</sub> /2%O <sub>2</sub>	251	27.8	300	79
2.1	None (B/M Steel)	MMA	5.0	-	285	32.6	300	81
2.2	Product A	MMA	5.0	-	312	36.7	300	71
2.3	Product B	MMA	5.0	-	300	34.9	300	73
2.4	Product C	MMA	5.0	-	300	35.5	300	81
2.5	Product D	MMA	5.0	-	312	35.1	300	76
2.6	Product E	MMA	5.0	-	292	34.6	300	80
3.1	None (B/M Steel)	TIG	-	Argon	149	10.6	58	472
3.2	Product A	TIG	-	Argon	149	10.7	58	490
3.3	Product B	TIG	-	Argon	150	10.4	58	477
3.4	Product C	TIG	-	Argon	150	11.5	58	485
3.5	Product D	TIG	-	Argon	152	11.6	58	374
3.6	Product E	TIG	-	Argon	151	11.4	58	477
3.7	Product A	TIG	-	Argon	150	11.5	40	199
3.8	Product B	TIG	-	Argon	155	10.9	40	710
3.9	Product C	TIG	-	Argon	151	11.4	40	488

\* = Consumable diameter; † = Travel Speed; ‡ = Arcing Time

**Table 2: Welding Test Program (continued)**

TEST	PRODUCT	PROCESS	D* (mm)	SHIELD GAS	CURRENT (A)	VOLTAGE (v)	TS† (mm/min)	AT‡ (s)
3.10	Product D	TIG	-	Argon	152	11.6	40	551
3.11	Product E	TIG	-	Argon	-	-	-	-
3.12	Product E Blank	TIG	-	Argon	150	12	58	471
3.13	None (BMS)	TIG	-	Argon	150	12	40	501
4.1	Product A	TIG	-	Argon	150	12	162	137
4.2	Product B	TIG	-	Argon	150	12	81	495
4.5	Product C	TIG	-	Argon	150	12	81	353
4.6	Product D	TIG	-	Argon	150	12	81	353

\* = Consumable diameter; † = Travel Speed; ‡ = Arcing Time

### 2.3.1 MAG Welding

Metal Active Gas (MAG) welding tests were carried out on a blank and each type of coated test piece at approximately 250 A, 28 v with a traverse speed of 300 mm/min and an Ar/20%CO<sub>2</sub>/2%O<sub>2</sub> shielding gas supplied at a flow rate of 15 l/min. The contact tip to workpiece distance (CTWD) was 18 mm and the contact tip was 5 mm inside the gas shroud, which was 17 mm in diameter. The MAG welding wire was 1.2 mm diameter to EN440 G3 Si1. These welding conditions provided a heat input of 1.12 kJ/mm.

### 2.3.2 MMA Welding

Manual Metal Arc (MMA) welding tests were performed on a blank and each type of coated test piece using ESAB OK 33.80 welding consumables to EN 499: E42ARR73 and employing dc+ polarity. The electrodes were 5 mm diameter and were deposited at approximately 300 A, 36 v with a traverse speed of 300 mm/min. These welding parameters gave a heat input of 1.73 kJ/mm.

### 2.3.3 TIG Welding

Tungsten Inert Gas (TIG) welding tests were carried out at approximately 150 A, 12 v with dc- polarity and argon shielding gas at 10 l/min. The tungsten electrode was 2.4mm diameter and extended 3 mm outside the gas shroud, which was 9 mm diameter.

In Tests 3.1 to 3.6 and Test 3.12 the traverse speed was 58 mm/min, giving a heat input of 1.1 kJ/mm (similar to that employed in the MAG welding tests).

In Tests 3.7 to 3.11 and Test 3.13 the traverse speed was 40 mm/min, giving a heat input of 1.7 kJ/mm, similar to that employed in the MMA tests.

The remaining test pieces were used to further investigate the effects of heat input. In Test 4.1, using coating ZS 15890, the traverse speed was 162 mm/min giving a heat input of 0.4 kJ/mm, whilst in Tests 4.2 to 4.5, using the other four coatings, the traverse speed was 81 mm/min giving a heat input of 0.8 kJ/mm.

### **2.3.4 Additional Welding Information**

A problem occurred at the start of welding in Test 3.9. In this case, the ceramic gas shroud cracked and fell onto the test piece causing the tungsten electrode to melt. However, on restarting welding proceeded satisfactorily.

Problems were present generally when test pieces sprayed with Product C were welded. Gross visual porosity occurred during MAG welding (Test 1.4), and there were indications of porosity just beneath the surface during MMA welding (Test 2.4). Very sooty deposits were obtained in Tests 3.4, 3.9, 4.5 and slag islands were observed at frequent regular intervals. These islands were easily detached accidentally after welding but their former positions can be identified by the “bright spots” on the relevant welds. The problems associated when welding with Product C were believed to arise from the thicker application of this primer, as welding proceeded satisfactorily with all other test pieces.

## **2.4 SAMPLING DEVICES**

The following sampling devices were employed during the welding tests. These were analysed for the specified substances using the techniques described below.

### **2.4.1 Tenax ATD Tube**

One Tenax automatic thermal desorption (ATD) tube fitted with a GF/A (glass fibre) pre-filter, at a nominal sampling rate of 100 ml/min, for collection of volatile organic compounds.

Sample tubes were desorbed at 250°C in a Perkin Elmer TurboMatrix ATD and the collected components separated and identified using a Perkin Elmer TurboMass gas chromatography-mass spectrometry (GC-MS) system.

### **2.4.2 Chromosorb-106 ATD Tube**

One Chromosorb-106 ATD tube fitted with a GF/A (glass fibre) pre-filter, at a nominal sampling rate of 100 ml/min, for collection of volatile organic compounds.

Sample tubes were desorbed at 200°C in a Perkin Elmer TurboMatrix ATD and the collected components separated and identified using a Perkin Elmer TurboMass GC-MS system.

### **2.4.3 DNPH Filter**

One 2,4-dinitrophenylhydrazine (DNPH) coated filter with an uncoated pre-filter, at a nominal 125 ml/min, for collection of aldehydes and other carbonyl compounds.

Sample filters were desorbed in acetonitrile and the resulting components separated using a Waters Millennium high performance liquid chromatography (HPLC) system equipped with a diode array detector (DAD). Formaldehyde was identified and quantified by peak area.

### **2.4.4 PAH Tube/Filter**

One XAD-2 adsorbent tube with a GF/A pre-filter, at a nominal 500 ml/min, for collection of polycyclic aromatic hydrocarbons (PAHs).

Both tubes and filters were desorbed in dichloromethane and the collected components separated and identified using a Hewlett Packard HP 6890/5973 GC-MS system. Peak areas of PAH components were measured and their concentrations were determined.

#### **2.4.5 Phenol Tube/Filter**

One XAD-7 tube with a GF/A pre-filter, at a nominal sampling rate of 125 ml/min, for collection of phenols.

Sample tubes were desorbed with methanol and the resulting components separated and analysed using a Hewlett Packard HP 6890/5973 GC-MS system. Peak areas for phenols were measured and their concentrations determined.

#### **2.4.6 Quartz Filter**

One quartz filter in an IOM sampling head, at a nominal sampling rate of 2.2 l/min, for collection of total particulate.

The filters were analysed gravimetrically for total welding fume (TWF) using a Sartorius RC 210 balance.

After weighing the sample filters were cut in half. The particulate on each half-filter was analysed for its carbon content using a Ströhlein Coulomat 702 coulometric analyser. This instrument is capable of distinguishing between, and measuring, organic carbon, ie organic molecules, and elemental carbon, ie soot, in a particulate sample. Unfortunately, whilst the coulometric analysis can determine the amount of organic carbon present in a sample, it is not able to identify individual unknown organic components in the same way as a chromatography-based analysis. Consequently, it is not able to determine the composition of any organic material detected in the particulate.

In order to try and determine the composition of the organic material the following additional analysis on the remaining filter halves was carried out:-

- i) The filter halves from the MAG and MMA tests (excluding 1.5 and 2.5) were examined by solvent extraction into dichloromethane followed by GC-MS.
- ii) A selection of the remaining filters halves (mainly from the TIG tests) were examined by pyrolysis. 2 mm circles were cut from the fume filters and pyrolysed at a temperature of 650 - 850°C. Any components released during heating were then identified by GC-MS.

## 3 TEST RESULTS

### 3.1 TENAX TUBES

The results of the Tenax tube samples are summarised in Table 3. It was noted that both the steel and enclosure “blanks” generally contained some, or all, of a variety of common organic solvents, including acetone, isooctane, cyclopentane, cyclohexane, dichloromethane and trichloroethane. Whilst the precise origin of these compounds remains unclear, and varied from day to day, the results indicate that these are “background” components probably generated somewhere within the surrounding work area and not by the shop-primer product under test. Consequently, and in order to clarify the results, the data in Table 3 have been “blank corrected” to include only those compounds present at concentrations significantly higher than those in the corresponding steel and enclosure “blanks”.

**Table 3: Tenax Tube Results**

TEST	SAMPLE	COMPONENTS FOUND (ppm)
1.1	Bright Steel (MAG)	-
1.2	Product A (MAG)	Ethanol (0.004); IPA (0.004)
1.3	Product B (MAG)	MiBK (0.25); Acetic acid (0.02); Xylene (0.02); Benzene (0.02); MPA (0.02); MPrOH (0.01); Phenol (0.01); Benzyl chloride (0.01)
1.4	Product C (MAG)	Ethylacrolein (0.58); Benzene (0.24); Hexanoic acid (0.14); Hexanal (0.10); Methylacrolein (0.06); Toluene (0.06); Xylene (0.05); Acetic acid (0.05); Phenol (0.05); Heptane (0.05); Heptanones (0.05); Hexenal (0.04); Pentanoic acid (0.04); Pentane (0.04); Pentanol (0.03); Pentanal (0.02); Propanoic acid (0.02); DCM (0.02); Styrene (0.01); IPA (0.01); Acrolein (0.01); Propanol (0.01); Isooctane (0.01); Naphthalene (0.01); Phthalic anhydride (0.01)
1.5	Product D (MAG)	-
1.5(B)	Product D Blank (MAG)	-
1.6	Product E (MAG)	Butanoic acid (0.06); Benzene (0.04); IPA (0.04); Butanol (0.02); Propanol (0.01)
EB-1	Enclosure Blank 1	-
FB-1	Field Blank	-
2.1	Bright Steel (MMA)	-
2.2	Product A (MMA)	IPA (0.01); Ethanol (0.01)
2.3	Product B (MMA)	MiBK (0.24); Xylene (0.02); MPA (0.02); MPrOH (0.02); Benzyl chloride (0.02); Acrolein (0.01); Phenol (0.01)
2.4	Product C (MMA)	Ethylacrolein (0.71); Benzene (0.36); Acetone (0.29); Hexanal (0.24); Hexanoic acid (0.23); Xylene (0.14); Pentane (0.13); Heptanones (0.12); Acetic acid (0.10); Heptane (0.09); Methylacrolein (0.08); Phenol (0.07); Octane (0.06); Toluene (0.06); Pentanoic acid (0.05); Acrolein (0.04); Hexenal (0.04); Pentanol (0.04); Pentanal (0.03); Propanoic acid (0.03); Isoprene (0.02); Benzyl alcohol (0.01); Propanol (0.01); Naphthalene (0.01); Phthalic anhydride (0.01)
2.5	Product D (MMA)	-
2.6	Product E (MMA)	Butanoic acid (0.12); IPA (0.08); Butanol (0.06); Benzene (0.06); Propanol (0.01)
EB-2	Enclosure Blank 2	-
3.1	Bright Steel (TIG-58)	-
3.2	Product A (TIG-58)	Ethanol (0.01)

**Table 3: Tenax Tube Results (continued)**

TEST	SAMPLE	COMPONENTS FOUND (ppm)
3.3	Product B (TIG-58)	MiBK (0.19); Benzene (0.18); Acetic acid (0.15); Phenol (0.05); Xylene (0.02); MPA (0.02); Benzyl chloride (0.02); MPrOH (0.01); Propanoic acid (0.01); Hexanoic acid (0.01)
3.4	Product C (TIG-58)	Benzene (4.36); Ethylacrolein (0.75); Hexanoic acid (0.47); Xylene (0.34); Acetic acid (0.31); Phenol (0.22); Toluene (0.61); Ethylhexanoic acid (0.33); Phthalic anhydride (0.20); Methylacrolein (0.17); Hexanal (0.16); Propanoic acid (0.16); Naphthalenes (0.16); Heptanones (0.16); Pentanoic acid (0.14); Heptanal (0.14); Octane (0.13); Heptane (0.10); Nitrophenol (0.09); Pentane (0.07); Hexenal (0.05); Pentanol (0.05); Benzyl alcohol (0.04); Hexane (0.04); Styrene (0.04); Pentanal (0.03); Ethanol (0.03); Acrolein (0.02); Pentanone (0.02); Isoprene (0.01); Propanol (0.01)
3.5	Product D (TIG-58)	-
3.6	Product E (TIG-58)	Butanoic acid (0.12); Acetic acid (0.09); Benzene (0.08); Butanol (0.06); Toluene (0.04); Ethanol (0.04); IPA (0.03); Propanol (0.02); Phenol (0.01); Propanoic acid (0.01)
EB-3	Enclosure Blank 3	-
3.7	Product A (TIG-38)	IPA (0.004)
3.8	Product B (TIG-38)	MiBK (0.37); Benzene (0.34); Toluene (0.26); Acetic acid (0.21); Phenol (0.14); Benzyl chloride (0.05); Xylene (0.04); MPA (0.03); Propanoic acid (0.03); MPrOH (0.03); Styrene (0.02); Acrolein (0.01); Pentanoic acid (0.01); Hexanoic acid (0.01); Nitrophenol (0.01); Benzyl alcohol (0.01)
3.9 (1)	Product C (TIG-38)	Benzene (2.14); Ethylacrolein (0.61); Acetic acid (0.44); Toluene (0.29); Xylene (0.26); Hexanoic acid (0.25); Methylacrolein (0.13); Pentane (0.13); Hexanal (0.11); Propanoic acid (0.11); Heptanones (0.11); Acrolein (0.11); Phenol (0.10); Phthalic anhydride (0.10); Ethylhexanoic acid (0.09); Octane (0.09); Heptane (0.07); Naphthalenes (0.07); Pentanoic acid (0.07); Nitrophenol (0.05); Hexenal (0.04); Pentanol (0.03); Pentanal (0.02); Ethanol (0.02); Pentanone (0.02); Styrene (0.01); Butadiyne (0.01); Butadiene (0.003)
3.9 (2)	Product C (TIG-38)	Benzene (5.56); Ethylacrolein (0.88); Toluene (0.84); Hexanoic acid (0.42); Phthalic anhydride (0.40); Acetic acid (0.37); Ethylhexanoic acid (0.30); Xylene (0.27); Phenol (0.25); Naphthalenes (0.24); Methylacrolein (0.21); Hexanal (0.17); Heptanal (0.17); Propanoic acid (0.14); Heptanones (0.14); Pentanoic acid (0.13); Octane (0.13); Heptane (0.10); Nitrophenol (0.10); Pentane (0.08); Hexenal (0.06); Pentanol (0.04); Styrene (0.03); Acrolein (0.02); Ethanol (0.01); Butadiyne (0.002); Butadiene (0.001)
3.10	Product D (TIG-58)	-
3.12	Product D Blank (TIG-58)	-
3.13 (1)	Bright Steel (TIG-38)	-
3.13 (2)	Bright Steel (TIG-38)	-
4.1	Product A (TIG-162)	Toluene (0.14); Ethanol (0.01)
4.2	Product B (TIG-81)	MiBK (0.31); Toluene (0.12); Benzene (0.09); Phenol (0.04); Xylene (0.04); MPrOH (0.03); Benzyl chloride (0.02); MPA (0.02); Propanoic acid (0.01)
4.5	Product C (TIG-81)	Benzene (2.39); Acetic acid (0.42); Ethylacrolein (0.39); Toluene (0.34); Xylene (0.26); Hexanoic acid (0.21); Phenol (0.12); Naphthalenes (0.12); Acetone (0.10); Heptanones (0.10); Hexanal (0.10); Propanoic acid (0.09); Ethylhexanoic acid (0.09); Octane (0.07); Methylacrolein (0.07); Pentane (0.06); Pentanoic acid (0.06); Hexane (0.05); Heptane (0.05); Phthalic anhydride (0.05); Nitrophenol (0.04); Acrolein (0.03); Benzotrile (0.03); Pentanol (0.03); Hexenal (0.02); Pentanal (0.02); Styrene (0.02); Ethanol (0.01); Pentanone (0.01); Butadiyne (0.001); Butadiene (0.001)
4.6	Product D (TIG-81)	-
EB-4	Enclosure Blank 4	-

Abbreviations:- IPA = Isopropanol; MiBK = Methyl isobutyl ketone; MPA = Methoxypropyl acetate; MPrOH = Methoxypropanol

The results in Table 3 produced the following observations:-

- The components observed in the samples from Product A were generally very similar to the corresponding steel “blanks”. The only consistent difference was the presence of small amounts of ethanol and isopropanol.
- The samples from Product B were found to contain the following characteristic compounds – methyl isobutyl ketone (MiBK), acetic acid, xylene, methoxypropanol, methoxypropyl acetate, phenol and benzyl chloride. Of these only xylene, phenol and benzyl chloride were present amongst the components observed in the pyrolysis tests. Whilst the components identified in the five welding tests carried out with Product B were generally similar, the relative proportions of the different components was observed to vary quite markedly from test to test. For example, the proportion of MiBK in the MAG and MMA tests was significantly higher than in the three TIG tests, whilst the levels of formaldehyde and low molecular weight carboxylic acids tended to be higher in the TIG tests.
- The samples from Product C showed both the greatest variety and highest concentrations of components. Of these, benzene and ethylacrolein were generally the two main components, but numerous other aldehydes, ketones and aliphatic/aromatic hydrocarbons were also present. The components produced by the different welding techniques are fairly similar, although the concentrations produced by the TIG welding experiments are generally higher than those by MAG or MMA. With respect to the two main components, benzene and ethylacrolein, it was noted that whilst the former was the main component in the three TIG tests, the latter was the main component in the MAG and MMA tests. In fact, concentrations of ethylacrolein remain fairly similar in all five tests, but concentrations of benzene in the TIG tests are over ten times greater than those in the MAG and MMA samples.
- The samples from Product D showed little or no significant difference from the corresponding steel “blanks”. Pyrolysis tests with this particular product identified styrene as the major component generated on heating. However, concentrations were generally fairly low, and no styrene was detected in any of the Tenax tube samples collected during welding.
- The samples from Product E showed the presence of low levels of butanoic acid, benzene, isopropanol, butanol and propanol.

### **3.2 C-106 TUBES**

The results of the C-106 tube samples are summarised in Table 4. Once again, it was noted that both the steel and enclosure “blanks” generally contained a similar variety of organic solvents to those observed in the Tenax tubes. As stated in Section 3.1, these solvents appear to be “background” components probably generated somewhere within the surrounding work area rather than by the shop-primer product under test. Consequently, like the Tenax tube data in Table 3, the data in Table 4 have been “blank corrected” to include only those compounds present at concentrations significantly higher than those in the corresponding steel and enclosure “blanks”.

Overall, the components observed in the from the C-106 tubes are very similar to those in the Tenax tubes. Consequently, the observations and overall conclusions for this group of samples are also broadly similar in Section 3.1.

**Table 4: Chromosorb-106 Tube Results**

TEST	SAMPLE	COMPONENTS FOUND (ppm)
1.1	Bright Steel (MAG)	-
1.2	Product A (MAG)	Ethanol (0.03); IPA (0.01)
1.3	Product B (MAG)	MiBK (0.09); MeOPROH (0.005)
1.4	Product C (MAG)	Ethylacrolein (0.24); Benzene (0.10); Hexanal (0.08); Methylacrolein (0.03); Pentane (0.03); MEK (0.02); Heptane (0.02); Pentenol (0.02); Toluene (0.02); Heptenes (0.02); Acrolein (0.01); Octane (0.01); Pentanol (0.01); Pentanal (0.01); Butyraldehyde (0.01)
1.5	Product D (MAG)	-
1.5(B)	Product D Blank (MAG)	-
1.6	Product E (MAG)	Butyraldehyde (0.04); Ethanol (0.03); IPA (0.02)
EB-1	Enclosure Blank 1	-
2.1	Bright Steel (MMA)	-
2.2	Product A (MMA)	Ethanol (0.04); IPA (0.01)
2.3	Product B (MMA)	MiBK (0.11); MeOPROH (0.01)
2.4	Product C (MMA)	Ethylacrolein (0.31); Hexanal (0.29); Acetone (0.18); Benzene (0.15); Toluene (0.10); MEK (0.06); Acrolein (0.04); Heptane (0.04); Pentenol (0.04); Heptenes (0.04); Methylacrolein (0.03); Pentanal (0.03); Butyraldehyde (0.02); Octane (0.02); Butadiene (0.01); Pentanol (0.01); Pentane (0.01)
2.5	Product D (MMA)	-
2.6	Product E (MMA)	Butyraldehyde (0.08); IPA (0.06); Ethanol (0.06); Butanol (0.02)
EB-2	Enclosure Blank 2	-
3.1	Bright Steel (TIG-58)	-
3.2	Product A (TIG-58)	Toluene (0.11); Ethanol (0.07)
3.3	Product B (TIG-58)	Acetic acid (0.15); MiBK (0.07); MeOPROH (0.004)
3.4	Product C (TIG-58)	Benzene (1.59); Acetic acid (0.38); Ethylacrolein (0.28); Toluene (0.22); Hexanal (0.15); Ethanol (0.15); Pentane (0.10); MEK (0.08); Acrolein (0.07); Methylacrolein (0.07); Butadiyne (0.05); Butyraldehyde (0.05); Heptane (0.04); Butadiene (0.04); Pentenol (0.04); Pentanal (0.03); Octane (0.03); Pentanol (0.02)
3.5	Product D (TIG-58)	-
3.6	Product E (TIG-58)	Ethanol (0.20); IPA (0.06); Butyraldehyde (0.04); Benzene (0.03); Butanol (0.02); Butanoic acid (0.01)
EB-3	Enclosure Blank 3	-
3.7	Product A (TIG-38)	HCHO (0.78); Ethanol (0.08); Nitromethane (0.04); IPA (0.01)
3.8	Product B (TIG-38)	HCHO (0.18); MiBK (0.12); Benzene (0.10); Toluene (0.07); MEK (0.02); Acrolein (0.02); Butyraldehyde (0.01); MePROH (0.01)
3.9 (1)	Product C (TIG-38)	Toluene (0.07)
3.9 (2)	Product C (TIG-38)	Benzene (4.16); Acetic acid (0.78); Toluene (0.66); Ethylacrolein (0.59); HCHO (0.30); Hexanal (0.25); Pentane (0.19); Methacrolein (0.13); MEK (0.13); Hexane (0.11); Butyraldehyde (0.10); Pentenol (0.09); Pentanal (0.06); Ethanol (0.06); Butadiyne (0.06); Pentanol (0.04); Butadiene (0.03)
3.10	Product D (TIG-38)	-
3.12	Product E Blank (TIG-58)	-
3.13 (1)	Bright Steel (TIG-38)	-
3.13 (2)	Bright Steel (TIG-38)	-
4.1	Product A (TIG-162)	Ethanol (0.05)

**Table 4: Chromosorb-106 Tube Results (continued)**

TEST	SAMPLE	COMPONENTS FOUND (ppm)
4.2	Product B (TIG-81)	MiBK (0.11); Toluene (0.08); Benzene (0.04); MEK (0.02)
4.5	Product C (TIG-81)	Benzene (1.41); Acetic acid (0.40); HCHO (0.20); Ethylacrolein (0.19); Toluene (0.16); Hexanal (0.13); Acrolein (0.12); Xylenes (0.11); Phenol (0.10); Pentene (0.10); Pentane (0.09); MEK (0.06); Naphthalene (0.06); Ethanol (0.04); Methacrolein (0.04); Heptanones (0.04); Butyraldehyde (0.04); Phenylacetylene (0.04); Pentenol (0.03); Pentanal (0.03); Heptane (0.03); Ethylhexanoic acid (0.02); Hexanoic acid (0.02); Styrene (0.02); Octane (0.02); Butadiyne (0.02); Pentanol (0.02); Pentanoic acid (0.01); Butadiene (0.01)
4.6	Product D (TIG-81)	-

### 3.3 DNPH FILTERS

The formaldehyde results obtained from the DNPH filters are given in Table 5. Although most of the samples showed evidence of other compounds, these were not quantified as, with some exceptions, for example acetone, these components are difficult to positively identify and therefore probably better addressed by the Tenax and Chromosorb tube samples.

**Table 5: Formaldehyde Sample Results (ppm)**

TEST	SAMPLE	HCHO	TEST	SAMPLE	HCHO
FB-1	Field Blank	N/D	3.3	Product B (TIG/58)	0.027
1.1	Bright Steel (MAG)	N/D	3.4	Product C (TIG/58)	1.153
1.2	Product A (MAG)	N/D	3.5	Product D (TIG/58)	N/D
1.3	Product B (MAG)	N/D	3.6	Product E (TIG/58)	0.073
1.4	Product C (MAG)	0.012	3.7	Product A (TIG/38)	N/D
1.5	Product D (MAG)	N/D	3.8	Product B (TIG/38)	0.184
1.6	Product E (MAG)	N/D	3.9 (1)	Product C (TIG/38)	0.599
EB-1	Enclosure Blank 1	N/D	3.9 (2)	Product C (TIG/38)	0.933
2.1	Bright Steel (MMA)	N/D	3.10	Product D (TIG/38)	N/D
2.2	Product A (MMA)	N/D	3.12	Prod. E Blank (TIG/58)	N/D
2.3	Product B (MMA)	N/D	3.13 (1)	Bright Steel (TIG/38)	N/D
2.4	Product C (MMA)	0.008	3.13 (2)	Bright Steel (TIG/38)	N/D
2.5	Product D (MMA)	N/D	4.1	Product A (TIG/162)	0.007
2.6	Product E (MMA)	N/D	4.2	Product B (TIG/81)	0.053
3.1	Bright Steel (TIG/58)	0.015	4.5	Product C (TIG/81)	1.372
3.2	Product A (TIG/58)	N/D	4.6	Product D (TIG/81)	N/D

The results in Table 5 produced the following observations:-

- Samples generated using MAG and MMA welding techniques were found to contain little or no formaldehyde;
- Samples generated using the various TIG welding techniques contained markedly higher levels of formaldehyde than the corresponding MAG and MMA samples. This is interesting since it indicates that formaldehyde concentration is directly affected by

welding technique, something which is much less obvious in the case of the other higher aldehydes observed in the ATD samples;

- The samples from Product C, particularly those generated by TIG welding, show significantly higher levels of formaldehyde than corresponding samples using the other four shop-primer coatings. This observation is consistent with results from the ATD tubes which all showed much higher levels of other aldehydes in the Product C samples.

### 3.4 PAH SAMPLES

The results obtained from GC-MS analysis of the PAH samples are given in Table 6. The limit of detection for the method was estimated to be around 1 µg/m<sup>3</sup>.

**Table 6: PAH Sample Results**

TEST	SAMPLE	PAH COMPONENTS (µg/m <sup>3</sup> )
1.1	Bright Steel (MAG)	Naphthalene (4)
1.2	Product A (MAG)	Naphthalene (4)
1.3	Product B (MAG)	Naphthalene (4)
1.4	Product C (MAG)	Naphthalene (44)
1.5	Product D (MAG)	Naphthalene (6)
1.6	Product E (MAG)	Naphthalene (4)
FB-1	Field Blank	-
2.1	Bright Steel (MMA)	Naphthalene (4)
2.2	Product A (MMA)	Naphthalene (4)
2.3	Product B (MMA)	Naphthalene (4)
2.4	Product C (MMA)	Naphthalene (32)
2.5	Product D (MMA)	Naphthalene (3)
2.6	Product E (MMA)	Naphthalene (8)
3.1	Bright Steel (TIG/58)	Naphthalene (8)
3.2	Product A (TIG/58)	Naphthalene (4)
3.3	Product B (TIG/58)	Naphthalene (24); Fluorene (8)
3.4	Product C (TIG/58)	Naphthalene (384)
3.5	Product D (TIG/58)	Naphthalene (3)
3.6	Product E (TIG/58)	Naphthalene (8)
3.7	Product A (TIG/38)	Naphthalene (8)
3.8	Product B (TIG/38)	Naphthalene (64); Fluorene (8); Phenanthrene (4)
3.9 (1)	Product C (TIG/38)	Naphthalene (260); Acenaphthylene (4); Fluorene (24)
3.9 (2)	Product C (TIG/38)	Naphthalene (80); Acenaphthylene (8); Acenaphthene (8); Fluorene (152); Phenanthrene (28); Fluoranthene (8); Pyrene (4); Benzo(a)anthracene (4); Chrysene (92); Benzo(b/k)fluoranthene (16); Indeno(123-cd)pyrene (4); Benzo(ghi)perylene (4)
3.10	Product D (TIG/38)	Naphthalene (3)
3.12	Product E Blank (TIG/58)	Naphthalene (4)
3.13 (1)	Bright Steel (TIG/38)	Naphthalene (4)
3.13 (2)	Bright Steel (TIG/38)	-
4.1	Product A (TIG/162)	Naphthalene (4)
4.2	Product B (TIG/81)	-
4.5	Product C (TIG/81)	Naphthalene (420); Acenaphthylene (8); Fluorene (44); Phenanthrene (8); Chrysene (8)
4.6	Product D (TIG/81)	Naphthalene (4)

The results in Table 6 produced the following observations:-

- Naphthalene, the lightest of the EPA-16 compounds, was the only PAH detected in the great majority of the 26 samples analysed.
- Samples generated using the various TIG welding techniques contained markedly higher levels of naphthalene than the corresponding MAG and MMA samples;
- The various Product C samples, in particular those generated using TIG welding techniques, show significantly higher levels of naphthalene than corresponding samples generated in the presence of the other shop-primers. Some of the Product C TIG samples also show the presence of other, heavier PAH components, in particular fluorene, phenanthrene and chrysene.

### 3.5 PHENOL SAMPLES

Results for phenol and bisphenol-A from the combined XAD-7 tube and GF/A filter head samplers are given in Table 7.

**Table 7: Phenol Sample Results**

TEST	SAMPLE	PHENOL (ppm)	BISPHENOL-A (ppm)	PHENOL* (ppm)
1.1	Bright Steel (MAG)	-	BDL	BDL
1.2	Product A (MAG)	-	BDL	BDL
1.3	Product B (MAG)	BDL	BDL	0.01
1.4	Product C (MAG)	BDL	BDL	0.05
1.5	Product D (MAG)	BDL	BDL	BDL
1.6	Product E (MAG)	-	BDL	BDL
FB-1	Field Blank	BDL	BDL	BDL
2.1	Bright Steel (MMA)	BDL	BDL	BDL
2.2	Product A (MMA)	BDL	BDL	BDL
2.3	Product B (MMA)	BDL	BDL	0.01
2.4	Product C (MMA)	BDL	BDL	0.07
2.5	Product D (MMA)	BDL	BDL	BDL
2.6	Product E (MMA)	BDL	BDL	BDL
3.1	Bright Steel (TIG/58)	BDL	BDL	BDL
3.2	Product A (TIG/58)	BDL	-	BDL
3.3	Product B (TIG/58)	BDL	BDL	0.05
3.4	Product C (TIG/58)	0.21	0.06	0.22
3.5	Product D (TIG/58)	BDL	BDL	0.01
3.6	Product E (TIG/58)	BDL	BDL	BDL
3.7	Product A (TIG/38)	BDL	0.08	BDL
3.8	Product B (TIG/38)	0.19	0.06	0.14
3.9 (1)	Product C (TIG/38)	BDL	0.06	0.10
3.9 (2)	Product C (TIG/38)	0.26	0.06	0.25
3.10	Product D (TIG/38)	BDL	BDL	BDL
3.12	Prod. E Blank (TIG/58)	BDL	BDL	BDL
3.13 (1)	Bright Steel (TIG/38)	BDL	BDL	BDL
3.13 (2)	Bright Steel (TIG/38)	BDL	BDL	BDL
4.1	Product A (TIG/162)	BDL	BDL	BDL
4.2	Product B (TIG/81)	BDL	BDL	0.04
4.5	Product C (TIG/81)	BDL	BDL	0.12
4.6	Product D (TIG/81)	BDL	BDL	BDL

BDL = Below Detection Limit; \* = Result from corresponding Tenax tube sample

The instrument detection limit for this analysis was estimated to be around 0.8 µg/sample, which equates to an airborne concentrations of around 0.17 ppm for phenol and around 0.07 ppm in the case of bisphenol-A. As can be seen from the results, most of the samples contain less than this. Of the few samples with a phenolic content which did exceed the detection limit, none exceeded the estimated limit for reliable quantitation (around 0.4 ppm in the case of phenol and 0.18 ppm in the case of bisphenol-A).

These rather poor detection limits indicate that, for phenol at least, the ATD tube samples probably provides a rather more sensitive method of determination (see column marked with asterisk in Table 6). The data do show however, reasonably good correlation between the two methods.

The results in Table 7 produced the following observations:-

- Samples generated using the various TIG welding techniques contained markedly higher levels of the two phenolic compounds than the corresponding MAG and MMA samples. This is in agreement with the results obtained from the ATD sample tubes.
- Only samples generated from Products B and C were found to generate measurable levels of the two phenols.

### **3.6 QUARTZ FILTERS**

The gravimetric (total particulate) and coulometric (carbon) analysis results obtained from the quartz filter samples are given in Table 8. These results produced the following observations:-

- Samples generated using the various TIG welding techniques produced significantly lower levels of total particulate than the corresponding MAG and MMA samples;
- At the same time, the concentration of organic (and elemental) carbon in the particulate collected from TIG welding was significantly greater than in corresponding MAG and MMA samples. Consequently, the proportion of organic carbon in the TIG samples is much greater than MAG and MMA;
- The data indicate that, in general, as welding speed increases, the concentration of organic carbon in the TIG welding particulate decreases;
- The proportion of organic material in the particulate is generally significantly greater for Products B and C than for Products A, D and E. At the same time, it is apparent that the proportion of organic carbon in the particulate generated from welding of the unpainted samples of bright steel samples is also amongst the highest of the various samples. The reason for this is unclear, but would tend to indicate the presence of some organic material, possibly oil residue, on the metal.
- The higher organic content in the particulate generated by Products B and C may be an explanation for the significant discrepancies observed in the semi-volatile content of the pyrolysis and welding results. For example, Product C showed a high proportion of phthalic anhydride in the pyrolysis tests, but very little in the welding fume. Unfortunately however, the coulometric analysis is not able to identify the organic components present, only to determine that the material is organic in nature. Nevertheless, this observation does tend to support the supposition that a significant proportion of the semi-volatile material observed in the pyrolysis tests is incorporated into the welding fume particulate.

**Table 8: Gravimetric & Carbon Results (Quartz Filters)**

TEST	SAMPLE	T/P (mg/m <sup>3</sup> )	O/C (mg/m <sup>3</sup> )	E/C (mg/m <sup>3</sup> )	T/C (mg/m <sup>3</sup> )	O/C (% w/w)
1.1	Bright Steel (MAG)	177	4.3	0.1	4.4	2%
1.2	Product A (MAG)	204	2.8	-	2.8	1%
1.3	Product B (MAG)	142	3.5	0.2	3.7	2%
1.4	Product C (MAG)	239	5.5	0.2	5.7	2%
1.5	Product D (MAG)	223	7.3	0.9	8.2	3%
1.6	Product E (MAG)	220	3.6	0.1	3.6	2%
2.1	Bright Steel (MMA)	114	3.2	0.6	3.7	3%
2.2	Product A (MMA)	150	2.2	0.5	2.7	1%
2.3	Product B (MMA)	137	2.7	0.4	3.1	2%
2.4	Product C (MMA)	180	7.3	0.5	7.8	4%
2.5	Product D (MMA)	115	6.7	1.0	7.6	6%
2.6	Product E (MMA)	179	2.8	0.4	3.2	2%
3.1	Bright Steel (TIG/58)	11	4.3	1.1	5.3	38%
3.2	Product A (TIG/58)	45	3.8	0.8	4.6	8%
3.3	Product B (TIG/58)	27	7.6	3.9	11.5	28%
3.4	Product C (TIG/58)	80	19.2	7.9	27.0	24%
3.5	Product D (TIG/58)	63	4.3	1.1	5.4	7%
3.6	Product E (TIG/58)	51	1.9	0.9	2.8	4%
3.7	Product A (TIG/38)	66	4.0	0.7	4.7	6%
3.8	Product B (TIG/38)	54	15.3	7.0	22.3	28%
3.9	Product C (TIG/38)	99	21.1	5.4	26.6	21%
3.10	Product D (TIG/38)	80	6.3	0.9	7.3	8%
3.13	Bright Steel (TIG/38)	26	10.3	1.2	11.5	40%
4.1	Product A (TIG/162)	32	3.4	0.8	4.2	11%
4.2	Product B (TIG/81)	39	6.1	2.7	8.8	16%
4.5	Product C (TIG/81)	58	9.3	2.7	11.9	16%
4.6	Product D (TIG/81)	25	3.6	0.9	4.5	14%

T/P = Total Particulate; O/C = Organic Carbon; E/C = Elemental Carbon; T/C = Total Carbon

Solvent extraction and GC-MS analysis of the MAG/MMA filters failed to identify any of the organic components present in the collected fume. Consequently, it was decided to examine a selection of the remaining filters using an alternative method of analysis, thermal desorption using the pyrolysis-GC-MS system. This technique was to prove much more successful, generating the components shown in Table 9.

Of particular interest amongst the components in Table 9 are the phenolic and semi-volatile amine components observed with Product B and the benzoic acid and phthalic anhydride components observed with Product C. Also of interest are the very volatile alkenes identified in several of the samples. All of these are compounds that were identified as significant components in the laboratory heating tests, but were lacking, or even absent, from the welding samples. These results therefore provide evidence that the lack of semi-volatile components in particular may be due, at least in part, to being incorporated into the particulate fraction of the fume.

**Table 9: Quartz Filters by Thermal Desorption (Pyrolysis)**

TEST	SAMPLE	O/C (mg/m <sup>3</sup> )	COMPONENTS DETECTED
1.5	Product D (MAG)	7.3	C <sub>6</sub> – C <sub>9</sub> Carboxylic acids (15%); C <sub>4</sub> – C <sub>8</sub> Alkenes (13%); Benzene (8%); Toluene (2%); Other (62%)
2.5	Product D (MMA)	6.7	C <sub>6</sub> – C <sub>9</sub> Carboxylic acids (42%); C <sub>4</sub> – C <sub>8</sub> Alkenes (14%); Benzene (5%); Other (39%)
3.3	Product B (TIG/58)	7.6	Phenol (21%); Isopropenylphenol (18%); C <sub>4</sub> – C <sub>8</sub> Alkenes (14%); DMAA* (7%); Benzene (4%); Styrene (3%); Bisphenol-A (2%); Toluene (2%); Other (29%)
3.8	Product B (TIG/38)	15.3	Bisphenol-A (36%); DMAA* (36%); Isopropenylphenol (7%); BP-A† (7%); C <sub>4</sub> – C <sub>8</sub> Alkenes (6%); Phenol (3%); Other (5%)
3.9	Product C (TIG/38)	21.1	Benzoic acid (15%); Phthalic anhydride (14%); BA/D‡ (4%); Ethylacrolein (4%); C <sub>5</sub> – C <sub>6</sub> Alkenes (4%); Other (63%)
3.10	Product D (TIG/38)	6.3	C <sub>4</sub> – C <sub>8</sub> Alkenes (23%); Benzene (10%); Toluene (6%); Styrene (3%); Other (58%)
3.13	Bright Steel (TIG/38)	10.3	C <sub>4</sub> – C <sub>8</sub> Alkenes (38%); Styrene (9%); Benzene (3%); Phthalic anhydride (3%); Toluene (2%); Other (45%)
4.2	Product B (TIG/81)	6.1	C <sub>4</sub> – C <sub>8</sub> Alkenes (27%); Isopropenylphenol (14%); Phenol (14%); DMAA* (6%); Benzene (6%); Bisphenol-A (1%); Other (32%)
4.5	Product C (TIG/81)	9.3	Benzoic acid (21%); Phthalic anhydride (14%); Ethylacrolein (8%); BA/D‡ (7%); C <sub>4</sub> – C <sub>6</sub> Alkenes (5%); Benzene (5%); Phenol (2%); Other (38%)

O/C = Organic Carbon; \* = Dimethylalkylamines (~C<sub>12</sub>); † = Bisphenol-A derivatives; ‡ = Benzoic acid derivatives

### 3.7 SUMMARY OF RESULTS

Overall, the results from all five samples produced the following observations:-

- Concentrations of the various volatile organic components are highly dependent on the welding technique being used. The highest concentrations tend to occur with the TIG welding samples, with the MAG and MMA tests giving broadly similar, but lower, results. Conversely, the MAG and MMA techniques generate much higher levels of particulate.
- The welding test results from Products A and D gave extremely low VOC concentrations (less than 0.05 ppm), making comparison with the pyrolysis tests for these products quite difficult.
- The welding samples from Products B and E showed higher VOC concentrations (up to 0.5 ppm). These samples contained most of the VOCs observed in the laboratory heating tests for these two products. However, there were also a number of additional components, for example, methyl isobutyl ketone, methoxypropyl acetate and methoxypropanol with Product B. The origin of these particular compounds is unknown, however they are often found in paint thinners or cleaning solvents.
- The highest VOC concentrations, up to 8 ppm, occurred in the welding samples from Product C. In addition, these emissions contained a fairly high proportion of more toxic components, in particular ethylacrolein, benzene and formaldehyde.

- The lack of highly volatile components, such as propylene, in the welding samples is probably due to limitations in the capture efficiency of such compounds with the two ATD sorbents used (Tenax and Chromosorb-106). In any future tests, a combination of Tenax and Carboxen-1000 will be used instead.
- The lack of semi-volatiles in the welding samples may also be due to deficiencies in the sampling/analytical methods, however another significant factor appears to be the presence of high levels of particulate in the welding fume. The latter observation appears to be supported by the results from Product C in particular, which show levels of phthalic anhydride to be significantly lower in the MAG and MMA samples (which generate much higher levels of fume than the TIG samples). In addition, Products B and C, which show significant levels of semi-volatile material in the pyrolysis tests, have the highest proportion of organic carbon in the particulate. Subsequent analysis (by thermal desorption) of the particulate does indicate the presence of some of the 'missing' semi-volatile components in the particulate.
- Analysis of the welding samples also showed the presence of numerous solvents, including cyclohexane, dichloromethane, isooctane and various aliphatic hydrocarbons as interferences, probably originating from other processes occurring in the vicinity of the welding tests. Also prominent in all the welding samples, probably as a consequence of being used to clean the metal plates, was acetone. These occurrences highlight one clear advantage of the heating tests, namely that they are much less prone to interference or contamination from external sources.

## 4 COMPARISON OF PYROLYSIS & WELDING RESULTS

A summary of the welding results, together with a comparison with the results from the laboratory heating tests carried out by the three participating laboratories, is shown in Table 10. A more detailed individual comparison of the welding test results and the HSL pyrolysis results follows in Tables 11 to 15.

**Table 10: Summary of Pyrolysis and Welding Test Results**

Product	Laboratory Heating Test Results	Welding Test Results
	Main Components*	Main Components†
A	Propylene; Isopropanol; Acetone; Ethanol	Ethanol; Isopropanol (< 0.05 ppm)
B	Bisphenol A (& fragments); Phenol; Alkylphenols; Alkylamines; Alkenes; Toluene; Aromatics; Acrolein	Methyl isobutyl ketone; Acetic acid; Benzene; Methoxypropyl acetate; Methoxypropanol; Phenol; Bisphenol-A; Xylene; Naphthalene; Benzyl chloride (up to 0.5 ppm)
C	Phthalic anhydride; Benzoic acid/esters; Ethyl/methylacrolein; Pentanol; Benzene; Alkenes	Ethyl/methylacrolein; Aldehydes (C <sub>1</sub> -C <sub>6</sub> ); Carboxylic acids (C <sub>2</sub> -C <sub>8</sub> ); Benzene; Toluene; Xylene; Phenol; n-Alkanes (C <sub>4</sub> -C <sub>8</sub> ); Heptanone; Pentanol; Styrene; Acrolein; Propanol; Naphthalene; Bisphenol-A; Phthalic anhydride; PAHs (up to 6 ppm)
D	Styrene; Butadiene; Toluene; Ethylbenzene; Methylstyrenes; Benzene; Aromatics	n-Alkanes (C <sub>5</sub> -C <sub>10</sub> ); Toluene (< 0.02 ppm)
E	Propylene; Isopropanol; Butyraldehyde; Alkenes; Acetaldehyde; Ethanol; Tertiary amines	Carboxylic acids (C <sub>2</sub> -C <sub>4</sub> ); Alcohols (C <sub>2</sub> -C <sub>4</sub> ); Benzene; Toluene (up to 0.2 ppm)

\* = Combination of all three laboratories; † = Under MAG, MMA and TIG welding conditions

### 4.1 PRODUCT A

Tables 11 and 12 summarise the results obtained from the pyrolysis and welding tests carried out with Product A.

**Table 11: Product A – Summary of Results (I)**

Component	TPA* at 850°C	Welding Tests (ppm)				
		MAG	MMA	TIG/38	TIG/58	TIG/81
Propylene	8.3 (57%)	-	-	-	-	-
IPA & Acetone	2.8 (19%)	0.01 (24%)	0.01 (20%)	0.01 (11%)	-	-
Acetaldehyde	1.6 (11%)	-	-	-	-	-
Ethanol	1.2 (8%)	0.03 (73%)	0.04 (78%)	0.08 (88%)	0.07 (39%)	0.05 (26%)
Toluene	0.2 (2%)	-	-	-	0.11 (61%)	0.14 (73%)
Other	0.5 (3%)	-	-	-	-	-
<b>Total †</b>	15 (100%)	0.04 (98%)	0.05 (98%)	0.09 (99%)	0.18 (99%)	0.19 (99%)
Naphthalene	-	0.00 (2%)	0.00 (2%)	0.00 (1%)	0.00 (1%)	0.00 (1%)
Other	-	-	-	-	-	-
<b>Total ‡</b>	-	0.00 (2%)	0.00 (2%)	0.00 (1%)	0.00 (1%)	0.00 (1%)

† = Total for components identified in pyrolysis tests; ‡ = Total for components found in welding tests but not observed in pyrolysis tests;

\* = Total Ion Chromatographic Peak Area (TPA) for pyrolysis test

**Table 12: Product A - Summary of Results (II)**

	Pyrolysis	MAG	MMA	TIG*
<b>Major Components</b>	Propylene	Ethanol	Ethanol	Ethanol
<b>Harmful Components †</b>	Acetaldehyde (B)	-	-	-
<b>Concentration ‡</b>	15	< 0.1 ppm	< 0.1 ppm	0.2 ppm

\* = Three levels of heat input; † = Components with low exposure limits and/or high toxicity (A = Major component; B = Secondary Component; C = Minor Component; D = Trace Component); ‡ = Total Concentration (TIC Peak Area or ppm)

The very low emissions obtained from all the tests with Product A make any comparison between pyrolysis and welding tests difficult. The main difference apparent from the data above is a lack of propylene in the welding samples, although this is probably due to the poor collection efficiency for this particular component onto either Tenax and C-106. There are also some variations in the composition and concentration of the fume generated by the different welding techniques.

Overall however, the conclusions from both the pyrolysis and welding testing of this product are essentially the same. These are that the levels of volatile organic emissions generated by Product A are both very low and of fairly low toxicity.

#### 4.2 PRODUCT B

Tables 13 and 14 summarise the results obtained from the pyrolysis and welding tests carried out with Product B.

**Table 13: Product B – Summary of Results (I)**

Component	TPA* at 850°C	Welding Tests (ppm)				
		MAG	MMA	TIG/38	TIG/58	TIG/81
<b>Bisphenol-A</b>	16 (18%)	-	-	0.16 (10%)	-	-
<b>Phenol</b>	13 (15%)	0.01 (4%)	0.01 (4%)	0.17 (10%)	0.04 (8%)	0.04 (7%)
<b>C<sub>2</sub> – C<sub>4</sub> alkenes</b>	10 (11%)	-	-	-	-	-
<b>Isopropenylphenol</b>	9 (10%)	-	-	-	-	-
<b>Bisphenol-A fragments</b>	9 (10%)	-	-	-	-	-
<b>Dimethylalkylamines</b>	4 (5%)	-	-	-	-	-
<b>Acetone</b>	4 (4%)	-	-	-	-	-
<b>Cresols</b>	2 (3%)	-	-	-	-	-
<b>Allyl alcohol</b>	2 (2%)	-	-	-	-	-
<b>Toluene</b>	2 (2%)	-	-	0.17 (10%)	-	0.10 (17%)
<b>Acrolein</b>	1 (2%)	-	0.01 (4%)	0.02 (1%)	-	-
<b>Benzene</b>	1 (2%)	0.02 (7%)	-	0.22 (14%)	0.18 (29%)	0.07 (11%)
<b>Other</b>	15 (16%)	0.03 (11%)	0.04 (14%)	0.12 (8%)	0.04 (6%)	0.06 (12%)
<b>Total †</b>	88 (100%)	0.06 (22%)	0.06 (22%)	0.86 (53%)	0.27 (43%)	0.27 (48%)
<b>Methyl isobutyl ketone</b>	-	0.17 (61%)	0.18 (65%)	0.25 (15%)	0.13 (21%)	0.21 (36%)
<b>C<sub>2</sub>-C<sub>6</sub> carboxylic acids</b>	-	0.02 (7%)	-	0.24 (15%)	0.16 (26%)	0.01 (1%)
<b>Formaldehyde</b>	-	-	-	0.18 (11%)	0.03 (4%)	0.05 (9%)
<b>Methoxypropyl acetate</b>	-	0.02 (7%)	0.02 (7%)	0.03 (2%)	0.02 (3%)	0.02 (3%)
<b>Methoxypropanol</b>	-	0.01 (3%)	0.02 (6%)	0.02 (1%)	0.01 (1%)	0.02 (3%)
<b>Other</b>	-	0.00 (0%)	0.00 (0%)	0.03 (2%)	0.01 (1%)	0.00 (0%)
<b>Total ‡</b>	-	0.22 (78%)	0.27 (78%)	0.75 (47%)	0.62 (57%)	0.30 (52%)

† = Total for components identified in pyrolysis tests; ‡ = Total for components found in welding tests but not observed in pyrolysis tests;  
\* = Total Ion Chromatographic Peak Area (TPA) for pyrolysis test

**Table 14: Product B - Summary of Results (II)**

	<b>Pyrolysis</b>	<b>MAG</b>	<b>MMA</b>	<b>TIG*</b>
<b>Major Components</b>	Bisphenol-A	MiBK	MiBK	MiBK
<b>Harmful Components</b> †	Bisphenol-A (A)			Benzene (B)
	Phenol (B)	Benzene (B)	Phenol (B)	Phenol (B)
	Alkylphenols (B)			Formaldehyde (B)
	Acrolein (D)	Phenol (B)	Acrolein (B)	Bisphenol-A (B)
	Benzene (D)			Acrolein (D)
<b>Concentration</b> ‡	88	0.3 ppm	0.3 ppm	0.6 – 1.6 ppm

\* = Three levels of heat input; † = Components with low exposure limits and/or high toxicity (A = Major component; B = Secondary Component; C = Minor Component; D = Trace Component); ‡ = Total Concentration (TIC Peak Area or ppm)

The data in Tables 13 and 14 show significant differences between the pyrolysis and welding tests results for Product B, both in the overall composition of the fume and with regard to toxicity.

The pyrolysis tests show the presence of significant amounts of a number of semi-volatile (mainly phenolic) components which, for the most part, were not observed in the welding samples. The reasons for this are unknown, but the main possibilities are probably:-

- A combination of poor sampling efficiency and/or analytical deficiencies for these components and/or;
- Thermal/chemical degradation to smaller organic compounds - caused by the extreme conditions in the welding arc.

Heating tests on the particulate collected on the quartz filters did show evidence of the presence of the ‘missing’ semi-volatile phenols and amines, so perhaps the most likely explanation for their ‘loss’ is that they are condensing out into the particulate fraction.

Conversely, the welding samples show the presence of a number of more volatile components not observed in the welding tests. These additional components, mainly solvents, but also including formaldehyde in the three TIG tests, make up around half of the total measured concentration in the TIG tests and over three-quarters in the MAG and MMA tests. The origin of these components is unknown, although MiBK, methoxypropyl acetate and methoxypropanol are often found in brush thinners. Consequently, one obvious possibility is that such a thinning product has been used during the preparation of the metal sheets coated with this particular shop-primer. If this is indeed the case, it highlights the need to make sure that any testing, whether by pyrolysis or by welding, is carried out on samples prepared in a consistent manner.

These differences in fume composition also lead to significant differences between the pyrolysis and welding tests with regard to toxicity. As mentioned above, the pyrolysis tests are characterised by the presence of various, relatively toxic, phenolic components, in particular bisphenol-A. These phenolic components are virtually absent from the welding samples, which are instead characterised by significant levels of various, less toxic, solvents such as MiBK.

Overall, it is clear that the correlation between pyrolysis and arc welding tests for Product B is probably the poorest of the five products tested.

### 4.3 PRODUCT C

Tables 15 and 16 shows a summary of the results obtained from the pyrolysis (at 850°C) and welding tests carried out with Product C.

**Table 15: Product C – Summary of Results (I)**

Component	TPA*	Welding Tests (ppm)				
	at 850°C	MAG	MMA	TIG/38	TIG/58	TIG/81
Phthalic anhydride	26 (26%)	0.01 (1%)	0.01 (0%)	0.10 (1%)	0.20 (2%)	0.05 (1%)
C <sub>3</sub> – C <sub>4</sub> alkenes	10 (10%)	-	-	-	-	-
Benzoic acid	9 (9%)	-	-	-	-	-
Benzoic acid esters	6 (6%)	-	-	-	-	-
Ethylacrolein	6 (6%)	0.41 (29%)	0.51 (21%)	0.60 (7%)	0.52 (6%)	0.29 (5%)
Formaldehyde	5 (5%)	0.01 (1%)	0.01 (0%)	0.93 (11%)	1.15 (14%)	1.37 (23%)
Benzene	5 (5%)	0.17 (12%)	0.26 (11%)	3.15 (39%)	2.98 (36%)	1.90 (32%)
Pentenol	4 (4%)	0.01 (1%)	0.04 (2%)	0.05 (1%)	0.02 (0%)	0.02 (0%)
Methylacrolein	2 (2%)	0.05 (3%)	0.06 (2%)	0.13 (2%)	0.12 (2%)	0.06 (1%)
Benzaldehyde	2 (2%)	-	-	-	-	0.06 (1%)
Other	26 (25%)	0.23 (17%)	0.52 (22%)	1.20 (15%)	1.31 (15%)	1.03 (17%)
<b>Total †</b>	<b>102 (100%)</b>	<b>0.89 (63%)</b>	<b>1.40 (58%)</b>	<b>6.16 (75%)</b>	<b>6.29 (75%)</b>	<b>4.77 (78%)</b>
C <sub>2</sub> -C <sub>6</sub> carboxylic acids	-	0.21 (15%)	0.35 (14%)	1.00 (12%)	1.04 (12%)	0.72 (12%)
C <sub>5</sub> -C <sub>8</sub> alkanes	-	0.12 (8%)	0.25 (10%)	0.30 (4%)	0.25 (3%)	0.16 (3%)
Phenol	-	0.05 (4%)	0.07 (3%)	0.26 (3%)	0.21 (3%)	0.12 (2%)
Heptanone	-	0.05 (4%)	0.12 (5%)	0.11 (1%)	0.16 (2%)	0.10 (2%)
Hexenal	-	0.04 (3%)	0.17 (7%)	0.02 (0%)	0.03 (0%)	0.01 (0%)
Other	-	0.05 (4%)	0.07 (3%)	0.32 (4%)	0.41 (4%)	0.14 (2%)
<b>Total ‡</b>	<b>-</b>	<b>0.52 (37%)</b>	<b>1.02 (42%)</b>	<b>2.01 (25%)</b>	<b>2.10 (25%)</b>	<b>1.25 (22%)</b>

† = Total for components identified in pyrolysis tests; ‡ = Total for components found in welding tests but **not** observed in pyrolysis tests;  
\* = Total Ion Chromatographic Peak Area (TPA) for pyrolysis test

**Table 16: Product C - Summary of Results (II)**

	Pyrolysis	MAG	MMA	TIG*
<b>Major Components</b>	Phthalic anhydride	Ethylacrolein	Ethylacrolein	Benzene
<b>Harmful Components †</b>	Ph. anhydride (A)	Ethylacrolein (A)	Ethylacrolein (A)	Benzene (A)
	Ethylacrolein (B)	Benzene (B)	Benzene (B)	Formaldehyde (B)
	Formaldehyde (B)	Phenol (C)	Phenol (C)	Ethylacrolein (C)
		Formaldehyde (D)	Formaldehyde (D)	Phenol (C)
	Benzene (B)	Ph. anhydride (D)	Ph. anhydride (D)	Ph. anhydride (D)
<b>Concentration ‡</b>	102	1.4 ppm	2.4 ppm	6.0 – 8.4 ppm

\* = Three levels of heat input; † = Components with low exposure limits and/or high toxicity (A = Major component; B = Secondary Component; C = Minor Component; D = Trace Component); ‡ = Total Concentration (TIC Peak Area or ppm)

The data in Tables 15 and 16 show similarities, but also some significant differences between the pyrolysis and welding tests results in the case of Product C. The pyrolysis tests show the presence of significant amounts of phthalic anhydride and benzoic acid components which were much less prominent, or absent altogether in the welding samples. Also missing are propylene and butylene. The reasons for this are unknown, but, once again, the two main possibilities are poor sampling/analytical efficiency and/or thermal/chemical degradation of some or all of these components. Amongst the semi-volatile components, it is interesting to note that the phthalic

anhydride is present in all five welding samples, but noticeably more abundant in the TIG samples, which produce less particulate. By contrast, the various benzoic acid-based components, which are less volatile, are absent from all five welding samples. One explanation for the apparent lack of semi-volatiles in the welding samples is that the material is adsorbed onto the particulate. If this is the case, it seems likely that the less volatile the component, the greater the likelihood of this occurring, and indeed the data in Table 14 would seem to be consistent with this. Subsequent thermal desorption tests also showed evidence of the presence of the 'missing' benzoic acid and phthalic anhydride components in the particulate collected during welding.

In the welding tests, two of the main components observed are benzene and ethylacrolein, two components also observed in the pyrolysis tests. The data in Table 14 show the proportion of benzene in the TIG samples to be significantly greater than in the MAG and MMA tests, whilst the proportion of ethylacrolein is significantly lower. However, looking at the concentrations of the two components shows levels of ethylacrolein to be fairly similar in all five welding samples and it is actually only the benzene which is changing significantly, with concentrations in the TIG samples over ten times those observed in the MAG/MMA tests.

The lack of propylene and butylene in the welding samples is, as previously mentioned, probably due to the poor collection efficiency for this particular component onto either Tenax and C-106. The components observed in the welding samples but not in the pyrolysis tests are comprised mainly of low molecular weight carboxylic acids and alkanes, together with lesser amounts of phenol, heptanone and hexenal. These additional components make up around a quarter of the total measured concentration in the TIG tests and around 40% in the MAG and MMA tests. Once again, the origin of these components, in particular that of phenol, is unknown, although in this case they do not appear consistent with solvents commonly used as thinners.

With regard to toxicity, the components of most importance identified in this particular product are probably the various unsaturated ketones (acroleins, etc), phthalic anhydride, benzene and formaldehyde. Of these, all were present in both the pyrolysis and welding samples, although levels of anhydride, particularly in the MAG and MMA tests are significantly reduced. Of the components observed only in the welding tests, only phenol has a particularly low exposure limit, however this is a fairly minor component (typically around 2 – 3% of the total measured VOC concentration).

Overall, whilst the composition of the volatile organic emissions observed in the various tests varies quite markedly, the overall conclusions are quite similar, namely:-

- Volatile organic emissions from Product C are the highest of the five products tested and contain a fairly high proportion of relatively toxic components, in particular benzene, ethylacrolein, formaldehyde and phthalic anhydride (although, as stated above, the relative proportions of these 'toxic' components is highly dependent on the test method used).

#### **4.4 PRODUCT D**

Tables 17 and 18 summarise the results obtained from the pyrolysis and welding tests carried out with Product D.

**Table 17: Product D – Summary of Results (I)**

Component	TPA* at 850°C	Welding Tests (ppm)				
		MAG	MMA	TIG/38	TIG/58	TIG/81
<b>CO<sub>2</sub> &amp; Propylene</b>	12.5 (33%)	-	-	-	-	-
<b>Styrene</b>	11.5 (30%)	-	-	-	-	-
<b>Butadiene</b>	3.7 (10%)	-	-	-	-	-
<b>Toluene</b>	2.5 (7%)	-	-	-	-	-
<b>Ethylbenzene</b>	1.2 (3%)	-	-	-	-	-
<b>Benzene</b>	0.9 (2%)	-	-	-	-	-
<b>Methylstyrenes</b>	0.8 (2%)	-	-	-	-	-
<b>Other</b>	4.6 (12%)	0.12 (100%)	-	-	-	-
<b>Total †</b>	38 (100%)	0.12 (100%)	-	-	-	-
<b>Acetic acid</b>	-	-	0.03 (100%)	0.02 (100%)	0.02 (25%)	-
<b>Methylcyclohexane</b>	-	-	-	-	0.06 (75%)	0.16 (100%)
<b>Total ‡</b>	-	-	0.03 (100%)	0.02 (100%)	0.08 (100%)	0.16 (100%)

† = Total for components identified in pyrolysis tests; ‡ = Total for components found in welding tests but not observed in pyrolysis tests;  
\* = Total Ion Chromatographic Peak Area (TPA) for pyrolysis test

**Table 18: Product D - Summary of Results (II)**

	Pyrolysis	MAG	MMA	TIG*
<b>Major Components</b>	Styrene	-	-	-
	Propylene	-	-	-
<b>Harmful Components †</b>	Styrene (A)	-	-	-
	Butadiene (B)	-	-	-
	Benzene (C)	-	-	-
<b>Concentration ‡</b>	38	0.1 ppm	< 0.1 ppm	0.1 ppm

\* = Three levels of heat input; † = Components with low exposure limits and/or high toxicity (A = Major component; B = Secondary Component; C = Minor Component; D = Trace Component); ‡ = Total Concentration (TIC Peak Area or ppm)

The data in Tables 17 and 18 show that whilst the pyrolysis tests showed the presence of a number of components, including styrene and butadiene, the welding tests were little different from those obtained from the corresponding steel “blanks”, or even the field blanks. Pyrolysis (and oven) tests at FIOH showed the presence of similar components to those identified in the pyrolysis tests at HSL, so the reasons for the lack of volatile organics, particularly styrene, in the welding samples is unclear. One possibility is that the pyrolysis tests were conducted using a rather larger mass of sample than the other tests. However, given the very low detection limits achievable by GC-MS analysis of ATD tubes, it still seems strange that no styrene was detected in any of the samples.

This lack of components in the welding samples results in a significant difference in the overall conclusions from the various tests. The pyrolysis tests conclude that levels of volatile organic emissions from Product D are fairly low, but identifies styrene, butadiene and benzene as being of possible importance with regard to the toxicity of the fume. The conclusions from the welding tests however, are that the levels of volatile organic emissions from Product D are very low and of fairly low toxicity (with no evidence of styrene, butadiene or benzene).

## 4.5 PRODUCT E

Tables 19 and 20 summarise the results obtained from the pyrolysis and welding tests carried out with the Temaweld product.

**Table 19: Product E – Summary of Results (I)**

Component	TPA* at 850°C	Welding Tests (ppm)		
		MAG	MMA	TIG/58
Propylene	14.5 (54%)	-	-	-
C <sub>16</sub> - C <sub>20</sub> alkenes	2.7 (10%)	-	-	-
Butyraldehyde	2.6 (10%)	0.02 (13%)	0.04 (15%)	0.02 (3%)
Isopropanol	2.5 (9%)	0.03 (19%)	0.07 (25%)	0.06 (10%)
Acetaldehyde	1.4 (5%)	-	-	-
Ethanol	0.9 (3%)	0.02 (9%)	0.03 (11%)	0.20 (33%)
Tertiary amines	0.4 (1%)	-	-	-
Benzene	0.3 (1%)	0.02 (12%)	0.03 (11%)	0.06 (9%)
Other	1.7 (6%)	0.02 (10%)	0.05 (17%)	0.07 (12%)
<b>Total †</b>	<b>27 (100%)</b>	<b>0.11 (63%)</b>	<b>0.22 (78%)</b>	<b>0.41 (68%)</b>
C <sub>2</sub> - C <sub>4</sub> carboxylic acids	-	0.06 (37%)	0.06 (22%)	0.12 (19%)
Formaldehyde	-	-	-	0.07 (12%)
Other	-	-	-	0.01 (2%)
<b>Total ‡</b>	<b>-</b>	<b>0.06 (37%)</b>	<b>0.06 (22%)</b>	<b>0.20 (32%)</b>

† = Total for components identified in pyrolysis tests; ‡ = Total for components found in welding tests but not observed in pyrolysis tests;  
\* = Total Ion Chromatographic Peak Area (TPA) for pyrolysis test

**Table 20: Product E - Summary of Results (II)**

	Pyrolysis	MAG	MMA	TIG
<b>Major Components</b>	Propylene	C <sub>2</sub> - C <sub>4</sub> carboxylic acids Isopropanol	Isopropanol C <sub>2</sub> - C <sub>4</sub> carboxylic acids	Ethanol C <sub>2</sub> - C <sub>4</sub> carboxylic acids
<b>Harmful Components †</b>	Benzene (D)	Benzene (B)	Benzene (B)	Formaldehyde (B) Benzene (B)
<b>Concentration ‡</b>	Low/Medium	0.2 ppm	0.3 ppm	0.6 ppm

† = Components with low exposure limits and/or high toxicity (A = Major component; B = Secondary Component; C = Minor Component; D = Trace Component); ‡ = Total Concentration (TIC Peak Area or ppm)

The data in Tables 19 and 20 show, once again, some significant differences between the pyrolysis and welding results. As with the previous samples, the main differences are a lack of very volatile (propylene) and semi-volatile (C<sub>16</sub> - C<sub>20</sub> alkenes and tertiary amines) in the welding samples, with the most likely explanation being, as previously mentioned, deficiencies in the sampling/analytical methods. The welding samples also show the presence of low molecular weight carboxylic acids, none of which were seen in the pyrolysis tests. The reason for the presence of these acids is unknown, however similar compounds were observed in the welding samples generated from several of the other primers. Formaldehyde was observed in the one TIG test carried out, but not in the MAG, MMA or pyrolysis tests.

With regard to toxicity, probably the only component of any significance is benzene, which was observed in the pyrolysis tests and in all three welding tests. However, concentrations are low, particularly in the case of the pyrolysis test in which it was only classified as a trace component.

Consequently, whilst the results of the pyrolysis and welding tests clearly show some significant differences, the main conclusions are fairly similar, namely:-

- The levels of fume generated by this product are fairly low;
- Most of the VOCs generated by this product are of fairly low toxicity;
- Taking toxicity into account, benzene is probably the only component of any significance, however levels are generally very low.

## 5 DISCUSSION

The main objective of this work was to establish a method for generating emissions data for arc welding over shop primers for inclusion in MSDSs. These data are used to assess the risks to health that can arise from using these products and are dependent mainly on the composition and concentration of the emissions. The method used must therefore be fit for this purpose, accurately identify the components emitted and, if possible, give relative emission rates that may be encountered during welding. One way of providing such data is to carry out welding tests on metal coated with the relevant primer. However, the work here has shown that welding tests are costly to perform and, if the emission products vary with process or temperature, or both, many tests will be required, making welding-generated data prohibitively expensive. An alternative is to test the primer using a laboratory-based pyrolysis technique. Providing good correlation between welding and pyrolysis generated data could be demonstrated, it would be much less expensive to generate the data in pyrolysis tests. On the basis of the work carried out during this project, it is estimated that the cost of pyrolysis testing is less than half of those for welding tests. Pyrolysis tests also have the advantage that can be performed quickly and easily and, if necessary, at different temperatures. For a single temperature heating test, our previous work recommended a pyrolysis temperature of 800-850°C.

The data from the welding tests described in this report clearly show that fume composition is dependent on the welding method used. In the case of most VOCs, the highest concentrations occurring during TIG welding, with MAG and MMA welding giving similar, but lower, results. Higher VOC concentrations also appeared to generate a greater variety of components, but, at the same time, show better agreement between welding and pyrolysis results. This may indicate some sampling deficiencies in the welded tests, particularly in the case of some very volatile components, for example propylene, butylene and butadiene.

The compounds generated during MMA and MAG welding with heat inputs of 1.1 and 1.7kJ/mm were generally similar, indicating that these differences in heat input were not significant to the composition of the emissions. The compounds identified in TIG welding tests were generally similar to those from MMA and MAG welding also, although the relative and absolute concentrations differed. In particular, the concentrations of formaldehyde, phenols and PAHs tended to be higher with TIG welding and larger numbers of higher molecular weight PAHs were observed.

It was found that the welding samples frequently contained compounds thought to have originated from the surrounding workplace atmosphere, in particular commonly used solvents such as acetone, cyclohexane and dichloromethane. The presence of these interfering substances obviously represents an added complication when interpreting the results of the welding tests. This problem does not occur with pyrolysis tests as heating takes place within a sealed instrument system. Consequently, by placing less demand on interpretation of results, pyrolysis testing should result in better reproducibility between laboratories.

Correlation between welding and pyrolysis data for these five products is clearly very variable. It was best for the two products with medium/high emissions (Products B and C), but even for these two products there were some major components generated in pyrolysis tests that were not observed in the welding tests (and vice versa). It is possible however, that sampling deficiencies may have been at least partly responsible for the absence of very volatile compounds from the welding tests and it may be possible to improve this situation by employing sorbent tubes with better retention characteristics for very volatile compounds, possibly in series with the Tenax tubes.

Semi-volatile compounds also tend to be far less prominent in the welding samples than in the pyrolysis samples. The reason for this remains unclear, however there is evidence from the organic carbon content of the particulate component of the welding fume, that some or all of these 'lost' semi-volatile compounds are being incorporated into the particulate fraction, either by condensation or adsorption. The latter scenario is supported by the greater abundance of semi-volatiles observed in the TIG welding samples, which generate far lower overall levels of particulate. However, at the same time it was observed that the amount of organic particulate in the TIG welding samples is higher than in the corresponding MAG and MMA samples. This clearly indicates that welding using MAG and MMA generates noticeably less of the semi-volatile components than using TIG.

A major difference between pyrolysis and welding results was observed when welding over Product B. Several of the major components generated during welding, in particular methyl isobutyl ketone, methoxypropyl acetate and methoxypropanol, were not observed in the pyrolysis tests. Instead, all three are believed to have originated from paint thinners, possibly used in the application of the primer. This illustrates the need to ensure that pyrolysed sample material is consistent with that actually present on the primed metal used in welding. One solution to this particular problem could be to use material removed from a finished primed plate for pyrolysis testing. However, this approach is not without problems of its own, as demonstrated by the pyrolysis results from Product D, which was found to generate misleadingly high emissions of the various components. This was probably due to the sample being much bigger than the aluminium foil mounted samples used in the case of the other four primers.

It seems likely that some of the differences in emissions may be due to differences in the heating environment between welding and pyrolysis, particularly in the case of arc welding. Pyrolysis testing is performed in a totally inert, helium, atmosphere, whereas arc welding takes place in a much more aggressive oxidising atmosphere. Consequently, it would not be too surprising if these more extreme heating conditions did not lead to some differences in the observed emissions. In particular a greater proportion of oxidised components and smaller, more volatile, components in the welding tests might be expected. Indeed, even amongst the various arc welding methods used, heating conditions appear to be sufficiently different to produce some significant variation in fume composition and emissions.

Thus far, correlation between welding and pyrolysis data has been considered only in terms of the extent to which the compounds generated by one reflected those generated by the other. However, not all compounds merit equal ranking because some are much more toxic than others. For example, the presence of carboxylic acids in some welding samples, but not in the corresponding pyrolysis data is not too significant an omission from a risk assessment point of view. Conversely, acroleins, which were present in emissions from several primers, have low exposure limits and are therefore extremely important to any risk assessment. Consequently, it is important that any highly toxic compounds present in the fume are identified by whatever technique is employed to generate the MSDS data. From this aspect, pyrolysis appears to be the superior technique as, by virtue of its superior ability to identify and detect components, it is probably less likely to miss any of the components generated on heating.

The results generated have shown that many compounds can be emitted during welding over shop primers and it would be impractical to present them all on a MSDS. A toxicity ranking system might therefore be of use in establishing those data that should be presented on a MSDS. Ideally, such a system would take into account both toxicity and concentration, perhaps by dividing concentration by the occupational exposure limit of the compound.

Overall, pyrolysis would probably be the preferred technique for generating the data required for MSDSs. Although correlation between pyrolysis and welding data was variable, pyrolysis did successfully identify all the toxically significant compounds generated in the welding tests. In addition, sampling and detection problems meant that some compounds, mainly semi-volatiles, could be identified using the pyrolysis method but were not found in the welding tests. Pyrolysis also offers the prospect of good reproducibility between laboratories and a cost that is less than half of that for a welding test. Furthermore, previous work has indicated that representative results may be obtained from pyrolysis at a single test temperature of 850°C.

It was necessary to employ a very comprehensive sampling protocol in the welding tests in order to minimise the risk of failure to identify an important degradation product. Even so, compounds were identified by pyrolysis that had not been identified in the welding tests, although it is possible that these same compounds were not generated in the more oxidising welding atmosphere. To reduce the sampling regime employed during the welding tests, it would be desirable to have information on the likely degradation products before the welding tests are performed. However, the best way to generate these data is by pyrolysis, thus requiring pyrolysis testing to be carried out as an integral part of the welding test procedure.

Thus far, the project has only investigated emissions generated from arc welding through shop primers. Clearly however, the ISO test standard (ISO/15011-5) will need to cover a much broader range of products and welding conditions. Further work will therefore be carried out, as part of the present project, to examine the methodology with regard to generating emissions data from resistance welding through thin organic coatings, sealants, adhesives, oils, etc. This will have the objective of providing additional input into the proposed test standard.

## 6 SUMMARY & CONCLUSIONS

Welding and pyrolysis testing was carried out to generate fume emissions data for a range of weld-thru shop primers. This had the objective of producing input towards a standard test procedure for generating fume emissions data for inclusion on MSDSs. In particular, the investigation looked at the effect on emissions of using different arc welding processes, with different heat inputs, and of variations in pyrolysis temperature. When making recommendations for the proposed test method, it is necessary to take into account several factors, the most important of which is probably correlation between welding and pyrolysis results. However, other important factors including costs, practicality and reproducibility of the test procedure must also be considered.

The work carried out thus far has produced the following conclusions:-

- Pyrolysis has been shown to be a reproducible and cost effective solution for generation of emissions data for weld-thru shop primers. The equipment required is also rather less specialised and more readily available than that required for welding tests.
- Experimental problems and higher costs make welding tests a less attractive solution for generating emissions data for weld-thru shop primers. In particular, welding tests require more specialist knowledge, equipment and facilities, which tends to both increase costs and be less readily available.
- Laboratory testing can never fully reproduce actual welding conditions, and hence there may be occasions where welding tests are justified. However, in order to reduce the sampling requirements during welding, it is desirable to have information on the likely degradation products. The best way of doing this would be to use pyrolysis as a screening procedure prior to commencement of the welding tests.
- Correlation between welding and pyrolysis data was rather variable, but tended to be best under conditions producing high emissions and/or a large range of degradation products. From an occupational hygiene perspective however, it is important to note that the most toxically significant components identified in the welding emissions were also always present in the pyrolysis test data.
- Pyrolysis was performed in an interference-free environment, generating more reproducible results and requiring less analyst interpretation than some of the welding test data.
- Pyrolysis testing can be set up and performed more rapidly than welding testing and requires fewer resources, resulting in a significantly lower lead/turnaround time and cost per test.
- Representative results can be obtained from a single pyrolysis test at either 650°C or 850°C. For a single pyrolysis test, the recommendation for arc welding through this type of product is to use a pyrolysis temperature of 850°C.
- Where thinners have been mixed with the primer during the spraying process, it is necessary to pyrolyse primer samples removed from finished products to fully characterise emissions, rather than the actual raw material.

## 7 PREVIOUS REPORTS

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

Analysis of weld-thro' primers

Initial tests using pyrolysis-gas chromatography-mass spectrometry

Ian Pengelly

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

Analysis of weld-thro' primers

Laboratory tests using pyrolysis-gas chromatography-mass spectrometry

Ian Pengelly