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Fume emissions from resistance welding through adhesives and sealants

Prepared by **TWI Limited**
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Fume emissions from resistance welding through adhesives and sealants

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Modern fabrication practice, especially in the motor industry, can involve resistance welding through adhesives and sealants. During welding, fumes are generated that may be harmful to health and may be breathed by workers in the work area. At present, little is known about the concentration or composition of the fumes emitted, making it difficult to assess the risks to health arising from the activity, as required by the Control of Substances Hazardous to Health (COSHH) Regulations 1999. The Health and Safety Executive (HSE) required that TWI generate fume composition data for resistance welding through a representative range of epoxy based adhesives and polybutadiene based interweld sealants, with the objective of developing sufficient information for comprehensive risk assessment. If possible, it was intended that a marker compound should be identified, to enable simplified monitoring of exposure to fumes in the workplace.

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EXECUTIVE SUMMARY

Background

Modern fabrication practice, especially in the motor industry, can involve resistance welding through adhesives and sealants. During welding, fumes are generated that may be harmful to health and may be breathed by workers in the work area. At present, little is known about the concentration or composition of the fumes emitted, making it difficult to assess the risks to health arising from the activity, as required by the Control of Substances Hazardous to Health (COSHH) Regulations 1999. The Health and Safety Executive required that TWI generate fume composition data for resistance welding through a representative range of epoxy based adhesives and polybutadiene based interweld sealants, with the objective of developing sufficient information for comprehensive risk assessment. If possible, it was intended that a marker compound should be identified, to enable simplified monitoring of exposure to fumes in the workplace.

Objectives

- To generate fume composition and, where possible, concentration data for resistance welding through adhesives and sealants.

- To identify, if possible, fume marker compounds, enabling simplified exposure measurements in the workplace.

Approach

Test pieces, made using zinc coated sheet materials, together with either epoxy based adhesives or polybutadiene based sealants, were resistance welded inside a specially constructed sampling chamber. All materials and welding conditions were selected to be typical of modern practice in the motor industry. The fumes emitted were collected, using sampling equipment that could also be used for workplace monitoring, and analysed to determine the compounds generated. Where possible, the approximate concentrations of compounds were estimated, and possible marker compounds for measuring exposure in the workplace were identified.

Main Conclusions

1. The most harmful compounds identified in terms of their occupational exposure limits were benzene and 1,3 butadiene. Small concentrations of acrylonitrile were present in some samples from tests employing adhesives. Compared to the level of total welding fume, the concentrations of these compounds were low.

2. The concentrations of the individual high molecular weight (carcinogenic) PAHs was very low, less than 1µg/m^3. The PAH composition comprised mainly naphthalene, the remainder being other low molecular weight PAHs.

3. Phenol was the preferred marker compound for the adhesives examined and benzothiazole or one of the thiophenes identified for the sealants.

1. INTRODUCTION

Modern fabrication practice in the motor industry involves resistance welding through adhesives and sealants. Typically, the adhesives are epoxy resin based products whilst the sealants contain polybutadiene. Either product may be added to welded joints to improve structural strength or prevent the ingress of dust and water. During welding, fumes and gases are generated that may be harmful to health and may be breathed by workers in the vicinity. At present, little is known about the concentration or composition of the fumes emitted, making it difficult to assess the risks to health arising from the activity, as required by the Control of Substances Hazardous to Health (COSHH) Regulations 1999. The Health and Safety Executive required TWI to generate data on fume composition, and where possible concentration, for resistance welding through a range of adhesives and sealants, with the objective of developing sufficient information for comprehensive risk assessment. Particular attention was to be placed upon the identification of possible carcinogenic emissions such as benzene, 1,3 butadiene and high molecular weight polycyclic aromatic hydrocarbons (PAHs). If possible, it was intended that marker compounds should be identified, to simplify monitoring of workplace exposure.

2. OBJECTIVES

- To generate fume composition and, where possible, concentration data for resistance welding through adhesives and sealants.

- To identify, if possible, fume marker compounds, enabling simplified exposure measurements in the workplace.

3. EXPERIMENTAL APPROACH

Test pieces were prepared by applying adhesive or sealant between strips of zinc coated steel that had been cut from sheets commonly used for fabrication in the motor industry. The test pieces were made either from 0.8mm or 2.0mm thick materials and were resistance welded inside a specially constructed sampling chamber. Those made with the thinner material were welded using Splash conditions whilst a Non-Splash condition was employed with the thicker material. The hotter Splash condition was expected to increase the amount of fume generated when welding the thinner material, thus ensuring sufficient fume for analysis. The thicker material, which demands a greater heat input for welding, was expected to yield sufficient fume for analysis without the use of Splash conditions. To provide a link between the results for the two conditions and to aid interpretation, an additional test was performed where the thinner material was also welded under Non-Splash conditions.

The chamber served to concentrate the fume and prevent contamination from the surrounding atmosphere. Each test consisted of sampling the particulate fume and gases generated while up to 200 spot welds were made on test pieces fed through slots in the sides of the chamber. Twenty welds were made on each test piece, at 25mm spacing, at a rate of about 30 welds per minute, requiring up to 10 test pieces for each test. As welding of each test piece was completed, it was moved forward of the electrodes and stacked within the chamber to allow sampling of emissions occurring at lower temperatures. Sampling continued for ten minutes after welding had been completed to ensure that these emissions were captured fully. Each test lasted between 25 and 40 minutes, depending upon the number of welds made. The fumes and gases generated were collected using a range of samplers and subsequently analysed in the laboratory. The work examined the emissions generated by welding through three types of adhesive and two types of sealant commonly used in the motor industry (Table 1). Two trials, without the use of adhesive or sealant, were carried out to establish baseline data.

4. EXPERIMENTAL DETAILS

4.1. TEST PIECES

Each test piece consisted of two strips of sheet steel approximately 90cm long. They were placed one upon the other, with the adhesive or sealant between (Figure 1). For the 0.8mm thick material, the upper strip was 16mm wide whilst with the 2.0mm material it was 19mm. In both cases the lower strip was 38mm wide. Thus the test pieces resembled a joint that would be commonly welded during motor vehicle fabrication. Immediately prior to preparation of the test piece, the sheet materials were degreased by wiping with paper impregnated with acetone and allowed to dry, as assessed visually. A 3mm diameter bead of adhesive or sealant was deposited centrally along the length of the lower strip and the upper strip placed on it. The strips were pressed together, manually, until the adhesive or sealant just emerged from the sides of the upper strip. The top strip was then secured permanently to the bottom strip with a resistance weld at each end. This procedure gave an adhesive/sealant thickness of approximately 0.3 to 0.5mm. Welding and sampling commenced within one hour of preparing the test pieces, primarily to prevent premature setting of the two-part adhesive examined (Section 4.3.1).

4.2. SAMPLING CHAMBER

The sampling chamber is shown in Figure 2. It was 50cm wide by 25cm deep by 25cm high and fitted between the throat gap of the resistance welder. The sides, top and bottom were fabricated from a PETG copolymer, which was not expected to react easily with any Splashed metal from the resistance welding process. Much of the copolymer was protected during welding by lining the back, front and bottom of the enclosure with nickel foil. The slots placed in the sides of the chamber were designed not only to allow the test pieces to pass through for welding but also to allow them to be retained in the chamber after welding. The samplers entered the chamber through holes in the top (Fig 3). Figure 4 shows their relative positions with respect to the welding arm.

4.3. MATERIALS

4.3.1. Adhesives and Sealants

Formulations for the adhesives used are shown in Table 2. The formulations are generic for epoxy based adhesives used in the motor industry and represent the most widely used types. ESP1 was a hot setting single part product. From the manufacturer’s data, it had an average particle size of around 50µm and remained of paste consistency until heated to temperatures of around 100°C or higher. It will gel in 60 seconds when heated to 150°C and cures fully in 5 minutes. ESP2 was also a hot setting single part product but with smaller particle size. The particle size was around 10µm and it set more slowly than ESP1. The gel time was 5 minutes at 150°C with full cure occurring in 15 minutes. Product E3 was a two-part adhesive, which set in 16 hours at room temperature, or in 10 minutes at 100°C. The particle size was around 10µm.

Different particle sizes can affect joint properties, the welding parameters employed and the quantities of adhesive used. Adhesives with larger particles distribute stresses in the joint over a wider area, giving a stronger joint. However, the larger particle size results in a thicker layer of adhesive, requiring a greater rate of use than products with a smaller particle size and demanding somewhat different welding conditions because of the thicker, electrically insulating, layer.

The sealants were commercial products. Consequently the exact formulation was not available. Product A was a low strength, and Product B a medium strength, interweld sealer containing polybutadiene (information obtained from telephone conversation with supplier). The Material Safety Datasheet (MSDS) supplied with the low strength product indicated that it contained calcium oxide dispersed in oil at the 5-10% level and di(benzothiazol-2-yl) disulphide at the 1-5% level. The medium strength product was reported to contain less than 5% calcium oxide (90%) paste and less than 5% dibenzothiozyl sulphide. No other compositional information was available.

4.3.2. Test piece steels

The steels employed for the test pieces were iron/zinc alloy coated low carbon steels of 0.8 and 2.0mm thickness (TWI batch numbers 4R857 and 4R858 respectively). The total coating weight on the 0.8mm steel was 90gm/m^2, including both sides, but was not specified for the 2.0mm product.

4.4. WELDING

The work was conducted on a 103 kVA Olofström Automation scissors type welding gun with a 4kN force and 16kA short circuit current capacity. The throat length of the gun was 560mm and the throat gap 300mm. The electrode holders operated through the centre of the top and bottom panels of the sampling chamber and the test pieces were welded at approximately the centre point of the chamber.

The electrodes used were Cu/1%Cr/0.1%Zr, 16mm diameter caps with a truncated cone tip. The tip diameter was 6mm when welding the 0.8mm strips and 8mm for the 2mm strips. The welding parameters used during the work depended on the material thickness being joined, the adhesive/sealant used, and whether a Splash or Non-Splash condition was required. These are listed in Tables 3 and 4.

At the start of testing, the electrodes were aligned and the welding condition set up for welding the appropriate material. 50 welds were then made close to the Splash condition, to bed in the electrodes. This was repeated whenever new electrodes were needed. The test pieces were guided by a brass block, with guide pins on the lower electrode, to enable the welds to be made in the centre of the top strip.

4.5. SAMPLING AND ANALYSIS

4.5.1. Sampling

The following samples were taken during the welding operations:

i) Two Tenax ATD tubes with GF/A (glass fibre) pre-filters for collection of volatile organic compounds (VOCs). The nominal sampling rate was 100 ml/min. One tube was for use as a spare during analysis, if required.

ii) One Tenax ATD tube with GF/A pre-filter for collection of benzene. The nominal sampling rate was100 ml/min.

iii) One Molecular Sieve 13X ATD tube with GF/A pre-filter and drying cartridge for collection of 1,3-butadiene. The nominal sampling rate was100 ml/min.

iv) One DNPH (dinitrophenylhydrazine) coated filter with GF/A prefilter for collection of aldehydes and other carbonyl compounds. The nominal sampling rate was 100 ml/min.

v) One XAD-2 adsorbent tube with GF/A filter in an IOM head for collection of polycyclic aromatic hydrocarbons (PAH). The nominal sampling rate was 2 l/min;

vi) One pre-weighed membrane filter (mixed cellulose ester) in an IOM head for collection of total welding fume (TWF) and zinc. The nominal sampling rate was 2 l/min.

vii) One silica gel adsorbent tube with GF/A pre-filter for collection of phenols. The nominal sampling rate was 1 l/min.

4.5.2. Analysis

i) The Tenax tubes were analysed semi-quantitatively for VOCs by thermal desorption and gas chromatography-mass spectrometry (GC-MS). Sample tubes were desorbed at 250°C in a Perkin Elmer ATD 400 and the resulting components separated and identified using a Hewlett Packard HP5890/5970 GC-MS system. Peak areas of the main components were measured and relative concentrations in the various samples determined (1).

ii) The Tenax tubes were analysed quantitatively for benzene by thermal desorption and gas chromatography using a flame ionisation detector (GC-FID). Sample tubes were desorbed at 250°C in a Perkin Elmer ATD 400 and the resulting components separated using a Perkin Elmer Autosystem dual-column GC-FID system. The benzene peak was identified and quantified by peak area (1).

iii) The Molecular Sieve 13X tubes were analysed quantitatively for 1,3-butadiene by thermal desorption and GC-FID. Sample tubes were desorbed at 250°C in a Perkin Elmer ATD 400 and the resulting components separated using a Perkin Elmer Autosystem GC-FID system. The 1,3-butadiene peak was identified and quantified by peak area (2).

iv) The DNPH filters were analysed quantitatively for aliphatic aldehydes by solvent desorption and liquid chromatography (HPLC). Sample filters were desorbed in acetonitrile and the resulting components separated using a Waters Millennium HPLC system equipped with a diode array detector (DAD). Aldehyde peaks were identified and quantified by peak area (3), (4).

v) The XAD-2 tubes and GF/A filters were analysed quantitatively for PAHs by solvent desorption and GC-MS. Sample tubes/filters were desorbed in dichloromethane and the resulting components separated and identified using a Hewlett Packard HP6890/5973 GC-MS system. Peak areas of the PAH components were measured and concentrations of these components determined. The samples were also analysed qualitatively for the presence of other semi-volatile components (5).

vi) The membrane filters were first analysed gravimetrically for TWF using a Mettler AT21 balance (6). The filters were then extracted into 10% hydrochloric acid and the zinc content determined by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) (7).

vii) The silica gel tubes were analysed semi-quantitatively for phenols by solvent desorption and GC-MS. Sample tubes were desorbed in methanol and the resulting components separated and identified using a Hewlett Packard HP5890/5971 GC-MS system. Peak areas of any phenolic components were measured and the relative concentrations in the various samples determined (8).

5. RESULTS

5.1. GENERAL

From Tables 3 and 4, 13 tests were required to complete the work programme. However, sixteen tests were performed, tests 1, 2 and 7 being discarded, either because of sampling or welding difficulties. The sampling procedures were considered to be generally satisfactory, with the exception of using cellulose ester filters for the collection of total welding fume samples. These filters had been chosen because of their 'low analytical blank' properties but they were sometimes ignited by stray sparks from the welding. They were replaced subsequently by Non-flammable quartz filters (Section 5.7).

5.2. VOLATILE ORGANIC COMPOUNDS

The main volatile organic compounds generated are shown in Table 5, with acetone being by far the largest component in most of the samples. The main observation from the results was that the different adhesives generate fume of widely differing volatile composition, although some components, such as benzene, toluene and various aliphatic alkanes were common to all or most of the samples. Estimates of the concentrations of some the larger components were obtained from the GC-FID chromatograms obtained from the benzene analyses (see paragraph 5.3 and Table 7).

Overall, the results of these analyses may be summarised, qualitatively, as follows:

- Components generated by the welding process itself (without any adhesive being present) included acetone, benzene, toluene, xylene and C_{8-10} alkanes.

- Components generated whilst welding with ESP 1 adhesive included, in addition to those listed above for the welding process itself, styrene, phenol, naphthalene and cresol.

- Components generated whilst welding with ESP 2 adhesive were characterised by a significant dependence on the welding conditions used. However, in addition to those listed above for the welding process itself, they included styrene, phenol, naphthalene, cyanocyclohexene, indene, cresol, benzofuran and acrylonitrile. By far the greatest variety of components, and the highest concentrations, were found to occur under Splash welding conditions with the thinner material.

- Components generated whilst welding with E3, the 2-part adhesive, included, in addition to those for the welding process itself, styrene, phenol, naphthalene and, under Non-Splash conditions with the thicker material, methylpyrazine (a compound with an aromatic ring containing two nitrogen atoms).

- Components generated whilst welding with Sealant A included, in addition to those for the welding process itself, styrene, numerous low molecular weight alkenes, dienes and trienes, various monoterpenes, the most abundant of which was limonene, and naphthalene. Under Non-Splash conditions with the 2mm thick material, benzothiazoles were also observed, as were butylated hydroxytoluenes, the last a commonly used anti-oxidant.

- Components generated whilst welding with Sealant B included, in addition to those for the welding process itself, styrene, thiophenes, benzonitrile, indene and naphthalene. Under Non-Splash conditions, benzothiazoles and butylated hydroxytoluenes were also observed, as with Sealant A.

5.3. BENZENE

The benzene contents of the various samples are shown in Table 6. Benzene was detected in all samples with concentrations ranging between 0.02 ppm and 2.16 ppm. The highest concentrations, for any given set of conditions, were found when using Sealant B, followed by Sealant A and then the epoxy adhesive products, which all generated fairly similar concentrations. Overall, Sealant B, welded under Splash conditions, gave the highest benzene concentration.

For the tests in which an adhesive or sealant had been used, significantly higher levels of benzene were observed when welding with Splash conditions. Differences in benzene concentration between Splash and Non-Splash conditions ranged between 2.5 and 11 times, with the biggest percentage differences occurring when using adhesive ESP 2 and the lowest with ESP 1.

5.4. 1,3-BUTADIENE

The 1,3-butadiene contents of the various samples are also shown in Table 6. Butadiene was detected in all samples with concentrations ranging between 0.04 ppm in the absence of a sealant or adhesive to 5.69 ppm with Sealant A. The highest concentrations, irrespective of the welding conditions, found when using Sealant A, were followed by those with Sealant B and then by the epoxy adhesives. Adhesive ESP2, which contained an addition of butadiene rubber, did not generate substantially higher levels of 1,3 butadiene than the other adhesives.

Unlike for benzene, the results did not show any consistent trend in concentration between Splash and Non-Splash conditions. In the case of adhesives ESP 1 and E3 2-Part, higher 1,3-butadiene concentrations were observed under Splash conditions, whilst the sealants gave higher concentrations (significantly higher in the case of Sealant A) under Non-Splash conditions. The concentrations generated with adhesive ESP 2 showed no significant difference either way.

5.5. ALDEHYDES

The aldehydic content of the various samples is shown in Table 8. Only two aldehydes, formaldehyde and acetaldehyde were identified, the concentrations of both being extremely low in most of the tests. Only two tests, Tests 9 and 10, with adhesives ESP 2 and E3 2-Part under Splash conditions, showed formaldehyde concentrations in excess of 0.05 ppm. Acetaldehyde levels were generally slightly higher, with concentrations up to 0.88 ppm. Again Tests 9 and 10 gave the two highest concentrations, although this time Test 10 with adhesive E3 2-part gave the highest result. Overall, the results indicated that, for the most part, aldehydes are not significant components of the fume generated by these particular adhesives and sealants, the exceptions being ESP 2 and E3 2-Part under Splash conditions.

5.6. POLYCYCLIC AROMATIC HYDROCARBONS

The results for the EPA-16 PAHs are shown in Table 9. The highest concentrations of polycyclic aromatic hydrocarbons (PAHs) were observed in the various samples taken under Splash welding conditions, although, even then, naphthalene was the only component to exceed a concentration 100 µg/m³. These results are consistent with those observed with the Tenax tube samples (Tables 5 and 7), with a general pattern of results that mirror those for benzene (Table 6). In all tests, by far the largest PAH component was naphthalene, with acenaphthylene, fluorene and phenanthrene making up most of the remainder. Higher molecular weight PAHs (greater than 226) were not detected in the test samples, meaning that the concentrations of these components, if present at all, were less than 1 µg/m³.

Other components observed in the sample chromatograms were generally consistent with those already observed in the Tenax tube samples, comprising medium molecular weight aliphatic/aromatic hydrocarbons and esters, benzothiazoles (Sealants A and B) and butylated hydroxytoluenes (Sealant A).

5.7. TOTAL WELDING FUME

The total welding fume (TWF) results from the various samples are shown in Table 10. Tests 3, 4, 5 and 6 were sampled using mixed cellulose ester filters but these were replaced with quartz filters for the remainder of the tests (Section 5.1). TWF concentrations ranged between 7 mg/m³ and 944 mg/m³. The high filter loadings lead to greatly increased back-pressures on the pumps so that some of the sample volumes were subject to greater error than the 5-10% normally be expected. This, in turn, meant that some of the TWF (and zinc) concentrations were also subject to a greater degree of error and uncertainty than would usually be the case. Nevertheless, it is clear from the results in Table 10 that TWF concentrations inside the sampling chamber were typically in excess of 100 mg/m³, sometimes considerably in excess. The two samples taken during welding of test pieces without adhesive showed filter loadings of between 3.7 and 5.1 mg, indicating that a significant proportion of the particulate collected on the filters is due to the welding process itself, rather than the presence of any adhesive.

The highest filter loadings were obtained in the tests using adhesives ESP 2 and E3 2-Part under Splash conditions. There appeared to be no consistent trend in filter loading between Splash and Non-Splash conditions. In the case of tests with ESP 2 and E3 2-Part, higher loadings were observed under Splash conditions, whilst in the remaining tests higher concentrations were obtained under Non-Splash conditions.

5.8. ZINC

The zinc concentrations in the various samples are also shown in Table 10. These varied between 0.2 mg/m^3 and 18.2 mg/m^3, although, as mentioned in paragraph 5.7, the concentrations were subject to a greater degree of error and uncertainty than usual.

The results did not show any discernible patterns between the different adhesive types, although comparison of samples taken under Splash and Non-Splash conditions generally showed the proportion of zinc to be greater in the former. The two samples taken with no adhesive in use showed loadings of between 24 and 197 µg, indicating that a significant proportion of the particulate collected on the filters was due to the welding process itself, rather than the presence of any adhesive.

5.9. PHENOLS

The main phenolic compounds identified were phenol, o-cresol, p-cresol, isopropylphenol (IPP) and butylated hydroxyphenol (BHT) - the last being a common anti-oxidant. The peak areas for these compounds, which were measured and normalised to take account of the differing sample volumes, are shown in Table 11.

Phenol was detected in seven of the thirteen samples, cresols in five, IPP in four and BHT in four. Phenol, cresol and IPP were only detected in those samples involving the use of adhesives, whilst the BHT was only found where sealants had been used. The results show that higher concentrations of phenols were obtained under Non-Splash conditions with adhesives ESP 1 and E3 2-part, whereas with ESP 2 the opposite was true. Both of the sealants gave higher concentrations of BHT compounds under Non-Splash conditions. These analyses here were only semi-quantitative but previous results (Table 7) indicate phenol concentrations to be no more than 0.8 ppm.

6. DISCUSSION

Fumes and gases were generated by resistance welding through adhesives and sealants, employing test pieces designed to resemble production welding. The welding was carried out in a specially constructed sampling chamber where the fumes were collected and analysed subsequently in the laboratory. High concentrations of fumes and gases were measured but this was expected because the chamber had been employed to deliberately concentrate the fume, permitting detection of compounds that would be present at low concentrations in the workplace. It is impossible to predict workplace exposure levels from the data generated but it is expected that the relative concentrations of compounds observed in the tests will be maintained in the workplace.

The largest gas concentrations measured came from acetone. However, it seems probable that the acetone, and most of the aliphatic alkanes measured, were derived mainly from the solvent used to degrease the test pieces rather than from the adhesives and sealants. Consequently, degreasing with acetone can be expected to give rise to high levels of acetone relative to the other fume components. However, if acetone is not used, its presence in small concentrations relative to the other compounds is expected. In the present case acetone was employed to remove oils from the test pieces, giving confidence that fume components arose only from degradation of adhesives or sealants. It is not believed that degreasing with acetone will generally be employed in the motor industry, although there may be a degreasing requirement when using adhesives for other applications.

The generation of benzene, toluene and xylene was common to most tests, including those conducted without an adhesive or sealant, although the levels were higher when adhesives and sealants were used. This may indicate that some oil remained on the test pieces and was a source of benzene etc on welding. The concentrations of benzene and toluene tended to be highest when sealants had been used. The use of the two part adhesive was characterised by larger concentrations of ethyl benzene and xylene, whilst the concentrations of phenol and cresol were higher with all of the epoxy adhesives examined. The sealants generated BHT but no phenol. Emissions from the sealants were also characterised by enhanced concentrations of 1,3 butadiene, as well as the benzene mentioned earlier. Only the adhesives generated formaldehyde and acetaldehyde.

The PAH composition was comprised mainly of naphthalene (typically 70-85% of the total PAH concentration), with most of the rest being lower molecular weight types. The concentration of PAHs was generally low with only naphthalene exceeding a concentration of 100μg/m^3 and the concentration of high molecular weight PAHs (greater than 226) being less than 1μg/m^3. It is the higher molecular weight compounds, i.e. those with molecular weights above 226, which are generally regarded as being carcinogenic, so the risk of exposure to carcinogenic PAHs is low.

The TWF concentrations were generally high. In the two tests (Tests 8 and 9) where Splash and Non-Splash conditions were directly comparable, the Splash condition generated substantially more fume. However, when Splash and Non-Splash conditions were compared for the different material thicknesses, and hence welding conditions, there was no clear correlation between a particular condition and the amount of fume generated. Clearly the concentration of some components is enhanced by Splash conditions (benzene) whilst the concentration of others remains essentially the same (phenol). If the concentration of total welding fume is used to normalise the concentrations of the other components measured, their concentrations are invariably low. For example, from Table 7, the highest concentration of phenol was 0.7ppm (Test 6) but the associated TWF concentration was 84mg/m^3. Of the various volatile compounds identified, benzene and 1,3 butadiene were the most harmful in terms of exposure limit, the levels of both being notably higher in the tests involving sealants. The level of benzene in Test 13, with Sealant B, was 2.16ppm and the level of 1,3 butadiene in Test 15, with Sealant A, was 5.69ppm but the corresponding TWF concentrations were 177 and 140 mg/m^3 respectively.

Volatile phenolic compounds, such as phenol and cresol, were more easily observed on the Tenax tube samples. Consequently, in any future tests, it is recommended that the presence of phenols be determined using the ATD tubes, and the silica gel tubes be deleted from the sampling procedure.

It was not possible to select one marker compound that was suitable for all five of the adhesives and sealants examined. For the individual adhesives, possible markers included the following:

- ESP 1 - Phenol; Styrene; Naphthalene.
- ESP 2 - Phenol; Styrene; Naphthalene.
- E3 2-Part - Phenol; Xylene; Styrene.
- Sealant A - 1,3-Butadiene; Styrene; Naphthalene; Benzothiazole; Thiophene; Methylthiophene.
- Sealant B - 1,3-Butadiene; Styrene; Naphthalene; Benzothiazole; Thiophene; Methylthiophene.

Of the compounds listed above, all but 1,3-butadiene can be collected using standard Tenax ATD tubes and analysed by gas chromatography. Although not the largest component, phenol would probably be the component of choice for the three adhesives and benzothiazole and/or one of the thiophenes for the sealants, mainly because they are less likely to be affected by interferences from other sources.

7. SUMMARY AND CONCLUSIONS

Resistance welding, employing Splash and Non-Splash conditions, was performed on test pieces made using zinc coated steel sheet and interweld adhesives and sealants. The test pieces and welding procedures were designed to be representative of industrial practice in the motor industry. During welding through the adhesives and sealants, which was performed in a specially constructed chamber so as to concentrate and isolate the emissions, the fumes and gases generated were collected and subsequently analysed. From the results the following conclusions may be drawn:

1. The most harmful compounds identified in terms of their occupational exposure limits were benzene and 1,3 butadiene. The levels of both, in particular 1,3-butadiene, were notably higher in tests involving the sealants. Small concentrations of acrylonitrile were present in some samples from tests employing adhesives. The concentrations of these compounds were low compared to the level of total welding fume.

2. The concentrations of the individual high molecular weight (carcinogenic) PAHs was very low, less than 1µg/m^3. The PAH composition comprised mainly naphthalene, the remainder being other low molecular weight PAHs.

3. No significant amounts of any aldehydic components were detected.

4. The TWF concentration showed little correlation with the use of an adhesive or sealant.

5. Although with identical welding conditions and materials, Splash generated more fume than Non-Splash welding conditions, overall there was no consistent pattern in the relative concentrations of the various components between Splash and Non-Splash conditions.

6. Phenol was the preferred marker compound for the adhesives examined and benzothiazole or one of the thiophenes identified for the sealants.

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7. Internal HSL method.

8. Internal HSL method.

Table 1 Test piece compositions and welding conditions

Adhesive/sealant	Generic type	Plate thickness mm	Welding conditions
Epoxy ESP1	Hot setting, single part, large particle size (50µm)	0.8	Splash
		2.0	Non-Splash
Epoxy ESP2	Hot setting, single part, small particle size (10µm)	0.8	Splash
		0.8	Non-Splash
		2.0	Splash
Epoxy E3	Room temperature setting, two part, small particle size (10µm)	0.8	Splash
		2.0	Non Splash
Sealant A	Low strength, polybutadiene	0.8	Splash
		2.0	Non Splash
Sealant B	Medium strength, polybutadiene	0.8	Splash
		2.0	Non Splash
Blank	No adhesive or sealant	0.8	Splash
		2.0	Non Splash

Table 2 Adhesive formulations

Compound	%m/m		
	ESP 1	ESP 2	E3
Diglycidyl Ether of Bisphenol A	43	56	39
Amine accelerator	4	1	
Guanidine	2	5	
Calcium carbonate	48	31	15
Talc	2	-	4
Amorphous silica	1	1	3
Titanium dioxide	1	-	
Butadiene rubber	-	6	
Aminopolyamide	-	-	39

Table 3 Resistance welding conditions for 0.8mm thick material

Adhesive/sealant	Welding time, cycles		Welding current, kA		Condition
	Pulse 1	Pulse 2	Pulse 1	Pulse 2	
ESP 1	5	7	7.0	11.0	Splash
ESP 2	5	7	7.0	10.5	Splash
ESP 2	5	7	7.0	9.5	Non-Splash
E3	5	7	7.0	10.5	Splash
Sealant A	5	7	7.0	11.6	Splash
Sealant B	5	7	7.0	11.8	Splash
Blank	10	0	9.7	0.0	Splash

The following parameters were constant for each test:
Electrode tip diameter, 6mm; electrode force, 2.5kN; squeeze time, 60 cycles; cool time, 0 cycles, hold time, 10cycles.

Table 4 Resistance welding conditions for 2.0mm thick material

Adhesive/sealant	Welding time, cycles		Welding current, kA		Condition
	Pulse 1	Pulse 2	Pulse 1	Pulse 2	
ESP 1	10	15	8.5	11.0 to 9.2	Non-splash
ESP 2	10	15	8.5	11.3 to 10.4	Non-splash
E3	10	15	8.5	11.4 to 10.8	Non-splash
Sealant A	10	15	8.5	10.5	Non-splash
Sealant B	10	15	8.5	10.5	Non-splash
Blank	20	0	11.0	0.0	Non-splash

The following parameters were constant for each test:
Electrode tip diameter, 8mm; electrode force, 4kN; squeeze time, 60 cycles; cool time, 0 cycles, hold time, 10cycles.

Table 5 VOC Results – Component Peak Areas

Test	Adhesive	Conditions*	Components Identified
3	None	2.0/100/NS	Main components: Acetone; hexane; benzene; toluene; xylene; styrene; C_{8-10} alkanes. Minor components: Aliphatic/aromatic hydrocarbons.
11	None	0.8/100/S	Main components: Acetone; C_{8-10} alkanes. Minor components: Aliphatic/aromatic hydrocarbons; benzene; toluene; xylene.
4	ESP 1	2.0/80/NS	Main components: Acetone; allyl alcohol; benzene; toluene; styrene; phenol; C_{8-10} alkanes. Minor components: Dichloromethane; xylene; cresol; naphthalene; aliphatic/aromatic hydrocarbons.
14	ESP 1	0.8/100/S	Main components: Acetone; benzene; toluene; styrene; phenol; naphthalene; C_{8-10} alkanes. Minor components: Aliphatic alkanes/alkenes/dienes; xylene; benzofuran; indene; cresol; low MW PAHs.
5	ESP 2	2.0/100/NS	Main components: Acetone; isopropylamine; C_{8-10} alkanes; dioxane. Minor components: Aliphatic/aromatic hydrocarbons.
8	ESP 2	0.8/100/NS	Main components: Acetone; cyanocyclohexene; high MW aliphatic hydrocarbons. Minor components: Benzene; toluene; xylene; C_{6-10} alkanes; propylene glycol; phenol; naphthalene.
9	ESP 2	0.8/100/S	Main components: Acetone; benzene; toluene; xylene; styrene; acrylonitrile; phenol; cyanocyclohexene; indene; cresol; benzofuran; naphthalene; high MW aliphatic hydrocarbons. Minor components: Aliphatic/aromatic hydrocarbons; nitriles; benzaldehyde.
6	E3 2-Part	2.0/100/NS	Main components: Acetone; xylene; isopropylamine; methylpyrazine; phenol. Minor components: C_{6-10} alkanes; pyrazine; benzene; toluene; styrene; cresol; aliphatic/aromatic hydrocarbons.

Test	Adhesive	Conditions*	Components Identified
10	E3 2-Part	0.8/100/S	Main components: Acetone; benzene; toluene; xylene; styrene; C_{6-10} alkanes; high MW aliphatic hydrocarbons. Minor components: Aliphatic/aromatic hydrocarbons; phenol; indene; naphthalene.
15	Sealant A	2.0/100/NS	Main components: Acetone; hexane; benzene; toluene; xylene; styrene; limonene; benzoalkenes; benzothiazoles; butylated hydroxytoluenes. Minor components: Aliphatic alkanes/alkenes/dienes/trienes; thiophenes; monoterpenes; phenol; aromatic hydrocarbons.
12	Sealant A	0.8/100/S	Main components: Acetone; benzene; toluene; xylene; styrene; isoprene; C_{5-10} alkanes/alkenes/dienes/trienes; monoterpenes (including limonene); naphthalene. Minor components: Aliphatic/aromatic hydrocarbons; thiophenes.
16	Sealant B	2.0/100/NS	Main components: Acetone; benzene; toluene; thiophenes; xylene; styrene; benzothiazoles; butylated hydroxytoluenes. Minor components: Aliphatic alkanes/alkenes/dienes/trienes; phenol; benzonitrile; indene; naphthalene; benzothiophene; aromatic hydrocarbons.
13	Sealant B	0.8/100/S	Main components: Acetone; benzene; toluene; styrene; thiophenes; benzonitrile; indene; naphthalene. Minor components: Aliphatic/aromatic hydrocarbons.
Blank	None	-	Main components: None

* = Sheet thickness (in mm); No. of Welds; Splash/Non-Splash

Table 6 Benzene and 1,3-Butadiene Results

Test Number	Adhesive Used	Welding Conditions*	Benzene (ppm)	1,3-Butadiene (ppm)
3	None	2.0/100/NS	0.03	0.11
11	None	0.8/100/S	0.02	0.04
4	ESP 1	2.0/80/NS	0.09	0.18
14	ESP 1	0.8/100/S	0.23	0.52
5	ESP 2	2.0/100/NS	0.05	0.33
8	ESP 2	0.8/100/NS	0.05	0.26
9	ESP 2	0.8/100/S	0.55	0.33
6	E3 2-Part	2.0/100NS	0.09	0.13
10	E3 2-Part	0.8/100/S	0.29	0.21
15	Sealant A	2.0/100/NS	0.18	5.69
12	Sealant A	0.8/100/S	1.05	1.04
16	Sealant B	2.0/100/NS	0.63	1.68
13	Sealant B	0.8/100/S	2.16	1.18
Blank	-	-	< 0.02	< 0.05

* = Sheet thickness (in mm); No. of Welds; Splash/Non-Splash

Table 7 VOCs – Estimates of Concentration by GC-FID

Component	Test 3	Test 11	Test 4	Test 14	Test 5	Test 8	Test 9	Test 6	Test 10	Test 15	Test 12	Test 16	Test 13	Blank
Acetone	1.35	0.74	0.51	1.62	0.61	1.25	0.77	0.59	0.48	0.99	0.86	0.39	3.14	<0.01
Benzene	0.03	0.02	0.09	0.23	0.05	0.05	0.55	0.09	0.29	0.18	1.05	0.63	2.16	ND
Toluene	0.05	0.05	0.07	0.14	0.04	0.10	0.30	0.10	0.22	1.26	1.11	0.28	0.15	ND
Trimethylhexane	0.02	0.09	0.01	0.04	0.09	0.03	0.04	0.04	0.08	0.03	0.15	0.05	< 0.01	ND
Ethylbenzene	< 0.01	< 0.01	0.01	0.01	0.01	0.02	0.04	0.55	0.26	0.05	0.09	0.06	0.08	ND
Xylenes	0.01	< 0.01	0.02	0.03	0.02	0.04	0.06	2.21	0.80	0.37	0.15	0.13	0.10	ND
Styrene	< 0.01	< 0.01	0.02	0.03	0.01	< 0.01	0.08	0.01	0.05	0.12	0.25	0.08	0.26	ND
Phenol	ND	ND	0.33	0.09	0.30	0.03	0.11	0.71	0.02	0.01	ND	ND	ND	ND
o-Cresol	ND	ND	0.02	< 0.01	0.02	ND	0.03	0.05	< 0.01	ND	ND	ND	ND	ND
Limonene	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.27	0.08	ND	ND	ND
Naphthalene	0.01	< 0.01	0.01	0.03	0.01	0.01	0.07	0.01	0.03	0.02	0.05	0.03	0.12	ND

Table 8 Aldehyde Results

Test Number	Adhesive Used	Welding Conditions*	Formaldehyde (ppm)	Acetaldehyde (ppm)
3	None	2.0/100/NS	ND	0.04
11	None	0.8/100/S	ND	ND
4	ESP 1	2.0/80/NS	0.05	0.20
14	ESP 1	0.8/100/S	0.05	0.23
5	ESP 2	2.0/100/NS	ND	0.15
8	ESP 2	0.8/100/NS	< 0.03	ND
9	ESP 2	0.8/100/S	0.75	0.44
6	E3 2-Part	2.0/100NS	ND	0.18
10	E3 2-Part	0.8/100/S	0.21	0.88
15	Sealant A	2.0/100/NS	ND	0.04
12	Sealant A	0.8/100/S	ND	ND
16	Sealant B	2.0/100/NS	ND	ND
13	Sealant B	0.8/100/S	ND	0.06
Blank	-	-	ND	ND

* = Sheet thickness (in mm); No. of Welds; Splash/Non-Splash; ND = Not Detected

Table 9 PAH Results

Test Number	Adhesive Used	Welding Conditions*	PAH Concentrations (µg/m³)				
3	None	2.0/100/NS	NA	ACL	AC	FL	PH
			15	ND	ND	ND	ND
			AN	FA	PY	Others	
			ND	ND	ND	ND	
11	None	0.8/100/S	NA	ACL	AC	FL	PH
			16	ND	ND	ND	ND
			AN	FA	PY	Others	
			ND	ND	ND	ND	
4	ESP 1	2.0/100/NS	NA	ACL	AC	FL	PH
			29	6	ND	ND	ND
			AN	FA	PY	Others	
			ND	ND	ND	ND	
14	ESP 1	0.8/100/S	NA	ACL	AC	FL	PH
			157	50	ND	14	14
			AN	FA	PY	Others	
			7	7	7	ND	
5	ESP 2	2.0/100/NS	NA	ACL	AC	FL	PH
			5	ND	ND	ND	ND
			AN	FA	PY	Others	
			ND	ND	ND	ND	
8	ESP 2	0.8/100/NS	NA	ACL	AC	FL	PH
			43	ND	ND	ND	ND
			AN	FA	PY	Others	
			ND	ND	ND	ND	
9	ESP 2	0.8/100/S	NA	ACL	AC	FL	PH
			228	50	ND	14	14
			AN	FA	PY	Others	
			14	7	7	ND	
6	E3 2-Part	2.0/100/NS	NA	ACL	AC	FL	PH
			10	ND	ND	ND	ND
			AN	FA	PY	Others	
			ND	ND	ND	ND	

Table 9 PAH Results continued.

Test Number	Adhesive Used	Welding Conditions*	PAH Concentrations (µg/m³)				
10	E3 2-Part	0.8/100/S	NA	ACL	AC	FL	PH
			155	32	ND	13	13
			AN	FA	PY	Others	
			7	ND	ND	ND	
15	Sealant A	2.0/100/NS	NA	ACL	AC	FL	PH
			48	5	ND	ND	5
			AN	FA	PY	Others	
			5	ND	ND	ND	
12	Sealant A	0.8/100/S	NA	ACL	AC	FL	PH
			360	20	ND	ND	ND
			AN	FA	PY	Others	
			ND	ND	ND	ND	
16	Sealant B	2.0/100/NS	NA	ACL	AC	FL	PH
			93	5	ND	10	10
			AN	FA	PY	Others	
			10	ND	ND	ND	
13	Sealant B	0.8/100/S	NA	ACL	AC	FL	PH
			968	80	24	32	16
			AN	FA	PY	Others	
			16	8	8	ND	
Blank	-	-	NA	ACL	AC	FL	PH
			ND	ND	ND	ND	ND
			AN	FA	PY	Others	
			ND	ND	ND	ND	

* = Sheet thickness (in mm); No. of Welds; Splash/Non-Splash; ND = Not Detected

NA - Naphthalene (MW = 128); ACL - Acenaphthylene (152); AC - Acenaphthene (154);
FL - Fluorene (166); PH - Phenanthrene (178); AN - Anthracene (178); FA - Fluoranthene (202); PY - Pyrene (202); BAAN - Benzo(a)anthracene (226); CHR - Chrysene (226);
BBKFA - Benzo(b)fluoranthene & Benzo(k)fluoranthene (252); BAP - Benzo(a)pyrene (252);
IP - Indeno(1,2,3-c,d)pyrene (276); DBAHA - Dibenzo(a,h)anthracene (278); BGHIP = Benzo(g,h,i)perylene (278).

Table 10 TWF and Zinc Results

Test Number	Adhesive Used	Welding Conditions*	TWF		Zinc		
			(mg)	(mg/m³)	(µg)	(mg/m³)	(%)
3	None	2.0/100/NS	5.13	85	24	0.40	0.5
11	None	0.8/100/S	3.68	147	197	7.87	5.4
4	ESP 1	2.0/80/NS	7.93	944	153	18.2	1.9
14	ESP 1	0.8/100/S	4.33	140	428	15.3	9.9
5	ESP 2	2.0/100/NS	5.67	138	50	1.22	0.9
8	ESP 2	0.8/100/NS	0.19	7	5	0.19	2.8
9	ESP 2	0.8/100/S	18.25	913	306	15.3	1.7
6	E3 2-Part	2.0/100NS	3.38	84	21	0.53	0.6
10	E3 2-Part	0.8/100/S	17.97	580	287	9.25	1.6
15	Sealant A	2.0/100/NS	5.86	140	46	1.10	0.8
12	Sealant A	0.8/100/S	3.66	122	122	4.06	3.3
16	Sealant B	2.0/100/NS	7.25	177	60	1.46	0.8
13	Sealant B	0.8/100/S	5.86	234	323	12.9	5.5
Blank	-	-	-	-	-	-	-

* = Sheet thickness (in mm); No. of Welds; Splash/Non-Splash

Table 11 Phenol Results - Normalised Peak Areas

Test Number	Adhesive Used	Welding Conditions*	Phenol	o-Cresol	p-Cresol	IPP	BHT
3	None	2.0/100/NS	ND	ND	ND	ND	ND
11	None	0.8/100/S	ND	ND	ND	ND	ND
4	ESP 1	2.0/80/NS	59503	3634	ND	14160	ND
14	ESP 1	0.8/100/S	15529	ND	ND	ND	206
5	ESP 2	2.0/100/NS	23009	2020	ND	2150	ND
8	ESP 2	0.8/100/NS	3193	ND	ND	ND	ND
9	ESP 2	0.8/100/S	28212	8600	ND	1274	ND
6	E3 2-Part	2.0/100NS	65190	4840	1053	9759	ND
10	E3 2-Part	0.8/100/S	4924	ND	ND	ND	ND
15	Sealant A	2.0/100/NS	ND	ND	ND	ND	83228
12	Sealant A	0.8/100/S	ND	ND	ND	ND	7146
16	Sealant B	2.0/100/NS	ND	ND	ND	ND	32611
13	Sealant B	0.8/100/S	ND	ND	ND	ND	586
Blank	-	-	ND	ND	ND	ND	ND

* = Sheet thickness (in mm); No. of Welds; Splash/Non-Splash; ND = Not Detected

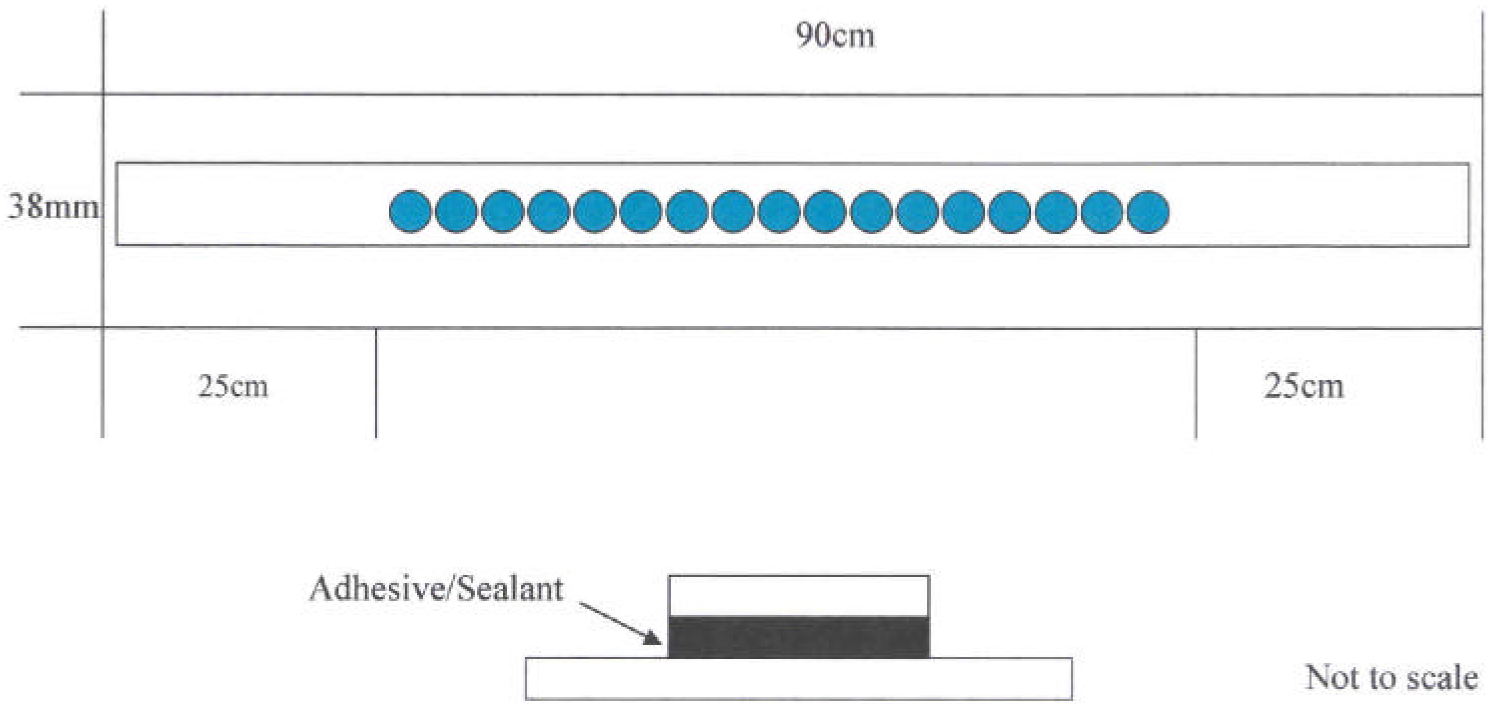

Fig.1. Configuration of test pieces

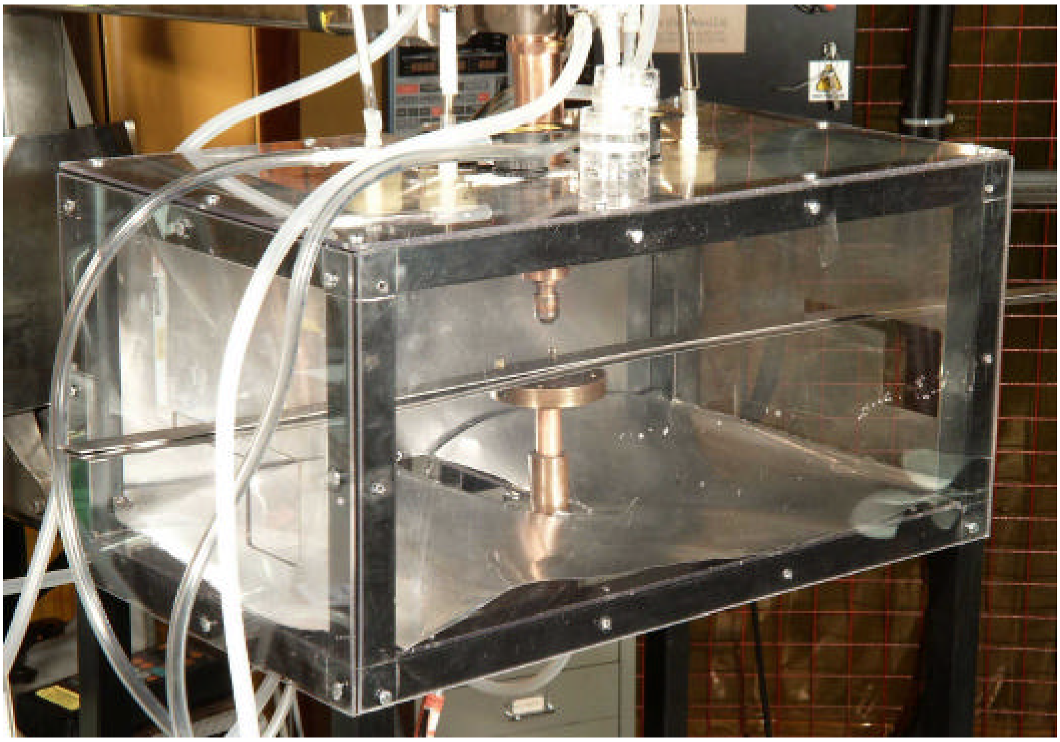

Fig.2 Sampling chamber

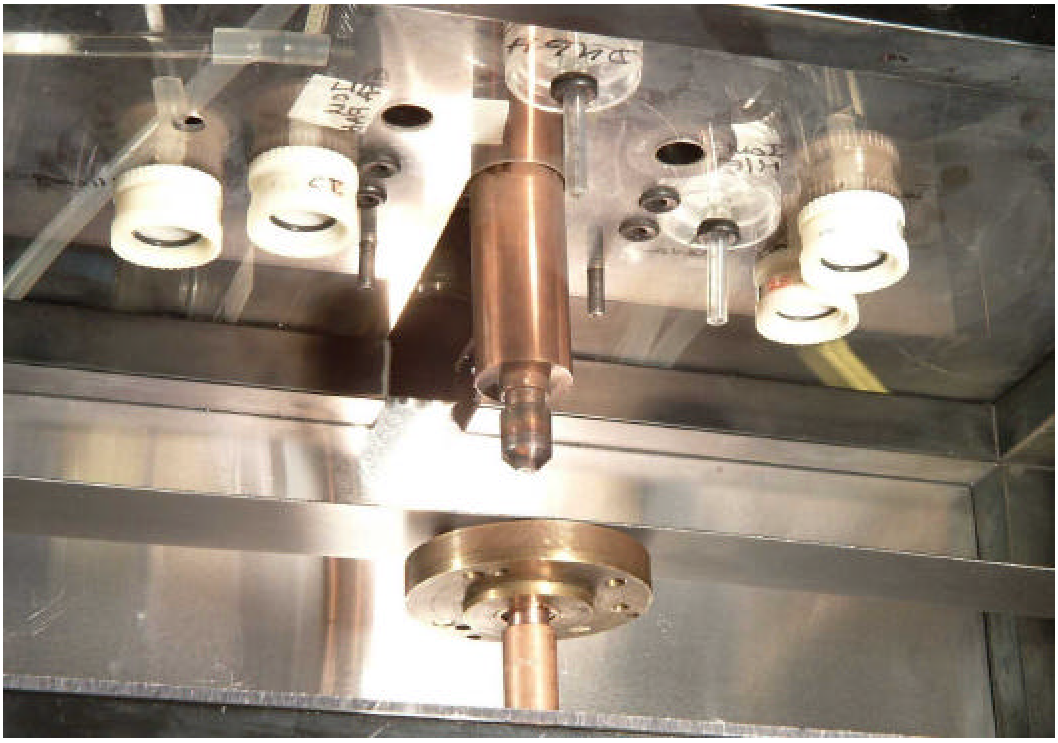

Fig.3 Samplers projecting into resistance welding chamber

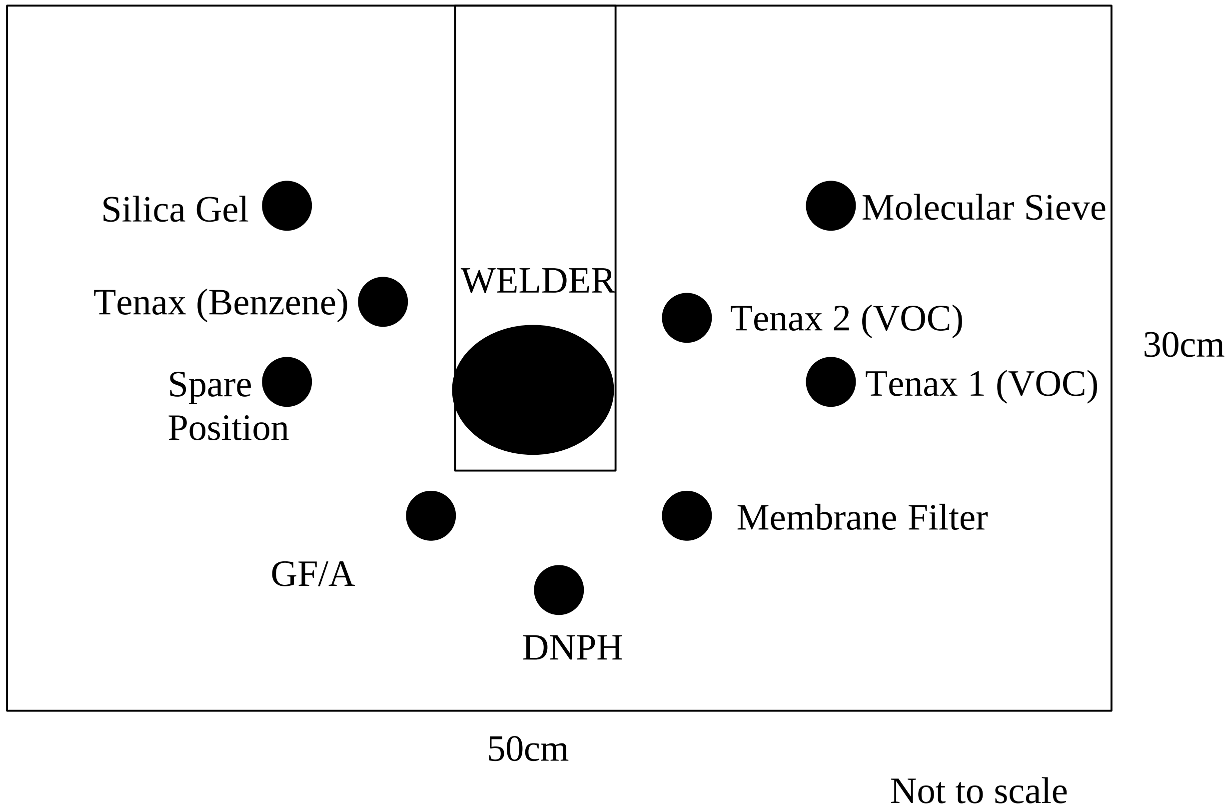

Fig.4 Location of samplers in sampling chamber

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