Biological Monitoring for Solvents and Multifunctional Acrylate Vapours in SME Printing Factories

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1. INTRODUCTION

This paper describes a section of the work carried out under the Uvitech Project [(1)], which was aimed at addressing the inequality found in the printing industry experienced by SME printers over the introduction of UV curing technology. Printers are aware of the economic and technical advantages of this technology, as well as the safety implications of using polymer systems containing acrylates. Uncured UV inks and lacquers may contain constituents which are skin irritants or sensitisers or which may be harmful to the eyes.

The objects of this project were to carry out a detailed study, using recognised methodologies, of UV printing activities in typical SME factories found in 4 European countries, in terms of the risks involved to operatives in-house, and also the environmental impact from emissions to atmosphere and paper recycling aspects. The objectives of this study were:

A Pan-European health and safety generic risk assessment for UV-curing technology.
A Pan-European environmental generic impact assessment for UV-curing technology.
Dissemination of the findings to key-players via a high-profile conference

The Pan-European health and safety generic risk and environmental impact assessments are freely available via the Radtech website [(2)]. The conference was delivered in Brussels on the 29th January 2004 to a selected audience of approximately 50 key players.

The intermediate results of the health and safety performance at the SME factories showed that inkfly (particulates) was not the major airborne hazard in the workplace compared with other potentially greater risks such as poor working practices, solvent exposure and noise. However, Inkfly vapour was detected qualitatively in significant amounts but it was not possible to determine the risks at this stage, as the analytical method used was not able to identify the multifunctional acrylate monomer-content (MuFa) of the vapour.

In order to complete the risk assessment of airborne MuFa's, an improvement in the analytical method for identifying and quantifying MuFa's was carried out. The basic laboratory work carried out at Envirocare and additional GC/ MS analysis was carried out by Gradko. The additional work was funded by the BG as a separate project for the benefit of the Uvitech project.

In addition, since working practices had been identified as high risk, biological monitoring was included in the on-site reassessments at selected SME's, along with repeat COSHH air monitoring, which is covered in this paper. The method is capable of measuring total airborne MuFa components for comparing with the recommended workplace exposure level (USA) of 1 mg/m^3 for these compounds.

2. EXPERIMENTAL

2.1 Improvement of the analytical method for identifying and quantifying multifunctional acrylates

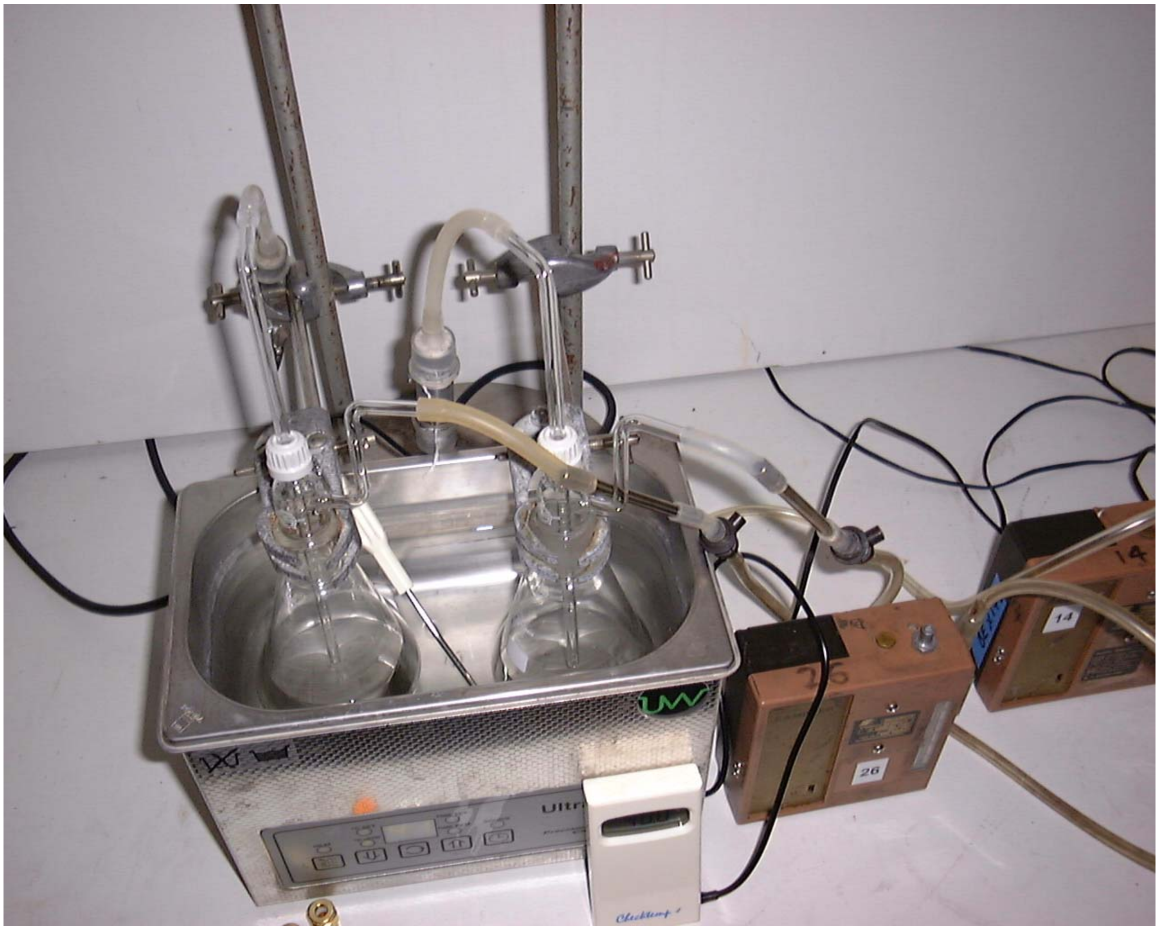
The method used to measure airborne levels of multifunctional acrylates is based on unpublished work [(3)] developed during the lifetime of the project.

In principle, the air-sampling is done by Tenax thermal desorption tubes and the analytical procedure is based on HSE methods MDHS 66 & 72 & MDHS 80. These methods provide the capability of detecting VOC's in the range C_2 – C_{18}, which effectively covers the volatile and semi-volatile range. Analysis of the multifunctional acrylate components was carried out by GC/MS, where a data-bank of multifunctional acrylate component-compositions of DPGDA, TPGDA, TMPTA, EOTMPTA & GPTA monomers, was built up from previously known analytical data [(3)]. The components were identified as acrylates, first in the bulk monomers, then by head-space-vapour analysis laboratory experiments and then by air-monitoring under workplace conditions. Commercially available acrylate monomers are known to be mixtures of several acrylate components [(4)], which are really impurities arising from the manufacturing process. The lower molecular weight components can exhibit a higher volatility in the vapour phase compared with the main acrylate component, therefore it is important to measure all acrylates present in the vapour phase to get a true indication of multifunctional acrylate exposure in the work place. It is believed that this technique has an advantage over a previously reported airborne GC/FID method [(5)], where only the main acrylate monomer component is determined.
Analysis for MuFa's was carried out by Gradko using GC/ MS using an HP 5MS (5% Phenyl) Methylpolysiloxane (30m x 0.25mm x 1um) column, which allows simultaneous analysis of MuFa's in the presence of organic solvents.

2.1.2 Head-space vapour analysis laboratory experiments

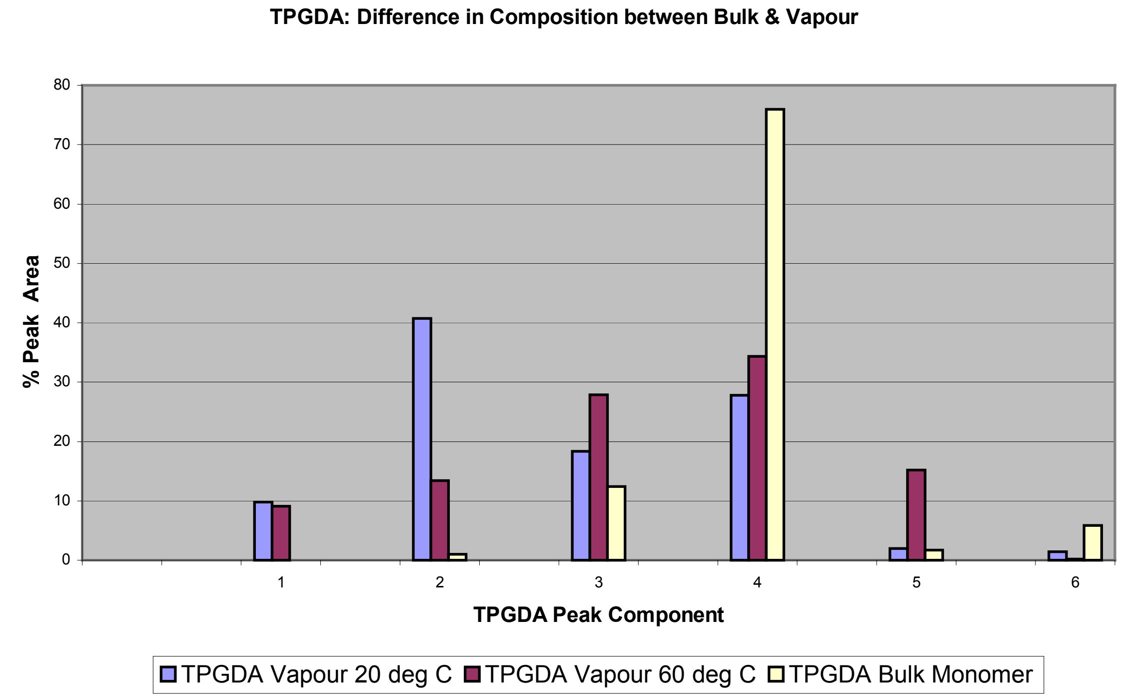
Vapour-phase sampling Apparatus

250ml Quickfit conical flasks, fitted with adjustable bottle head adaptors, were used with the inlet tube positioned so as to avoid bubbling action through the liquid. A quantity of MuFa monomer was introduced into flask so as to achieve maximum surface area of monomer in flask (approx. 50ml).
On the inlet side, silica gel/ carbon filters were fitted to remove moisture and organic impurities from the air stream. Gradko Tenax thermal desorption tubes were attached to the outlet tube coupled to pumps set to run at 100ml/ min.
The flasks were suspended in a temperature controlled water bath at a depth to ensure the monomer was submerged below the water level, at temperatures of 20^0C and 60^0C. (See below).



The results in Fig 1 for TPGDA monomer show the importance of measuring all the acrylate peak components in the vapour for occupational exposure. For example, peak 1 has a low composition in the bulk monomer of 0.03% but due to its higher volatility its composition in the vapour is almost 10% at both 20^0C & 60^0C.

Fig 1.



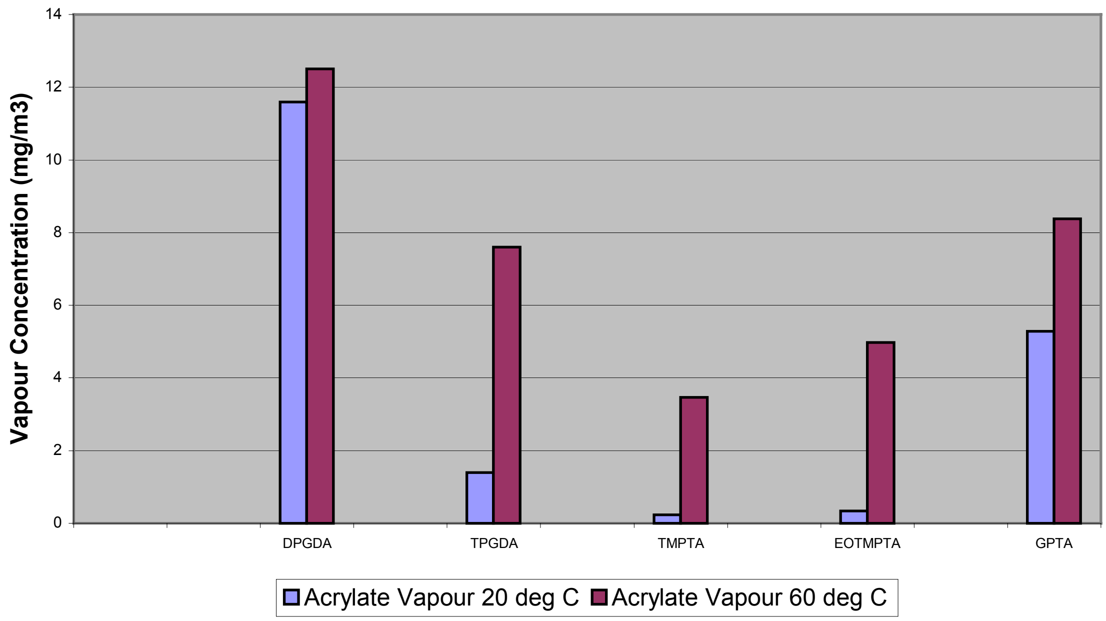
Comparison of the total components of the 5 acrylate monomers is shown in Fig 2, as expected, higher vapour concentrations of MuFa's are found at 60^0C compared to 20^0C.
The levels of total MuFa's vapours found in the laboratory experiments were generally greater than 1 mg/m^3, especially at higher temperatures. The vapour levels found in these laboratory experiments are higher than that reported (5) for TPGDA of 0.46 mg/m^3, where only the main TPGDA component was measured under similar experimental laboratory conditions.
However, these laboratory experiments do not necessarily indicate the level of MuFa vapour to be found in actual printing workplaces.

Only TMPTA & EOTMPTA monomers had consistent vapour concentrations less than 1 mg/m^3 at 20^0C but none of the monomers tested had average vapour concentration less than 1 mg/m^3 at 60^0C.

On the basis of this work it was decided to use this air-sampling and analysis method for monitoring for total MuFa vapour in printing workplaces as part of the Uvitech project to assess the MuFa vapour risks.

Fig 2

Total Acrylate Vapour Components



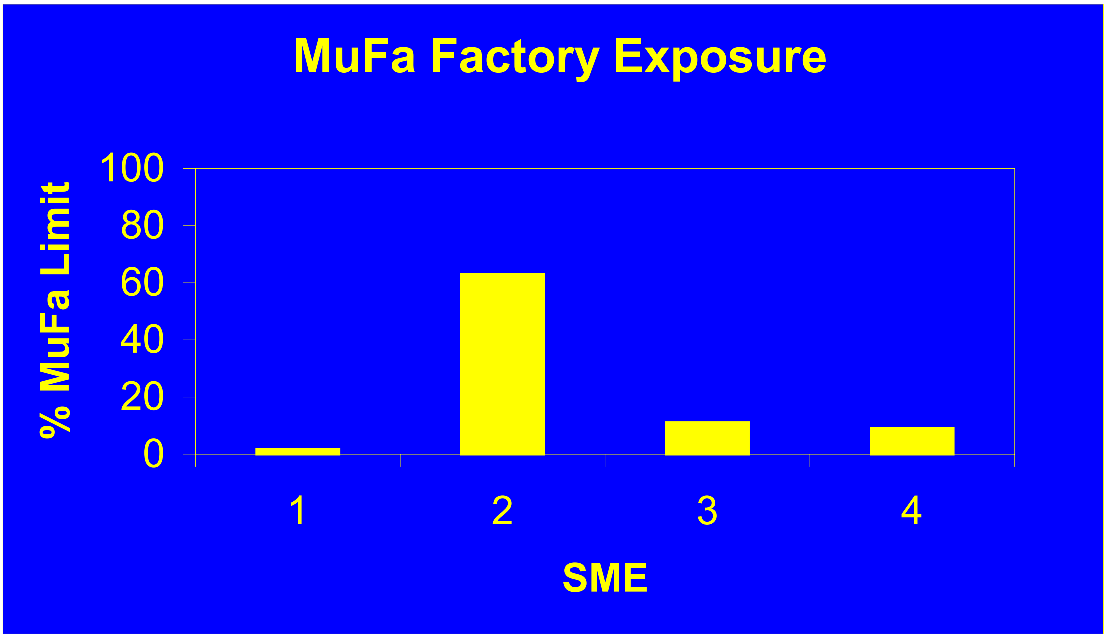
2.1.3 <u>Workplace exposure to multifunctional acrylates (MuFa's)</u>

4 SME factories were revisited to reassess their health and safety performance since the first visits. Working practices, solvent exposure, inkfly – particulates were repeated, occupational exposure to MuFa vapours was now assessed for the first time. Biological monitoring involving urine and breath tests was also included to assess the extent of entry of solvents and MuFa's in the body.

Inkfly particulate exposure was found to be at a similar level to those reported previously, i.e. 0 – 0.5 mg/m^3, and therefore a low risk. It was now possible to measure quantitatively the MuFa vapour levels in the workplace, which originated from the monomers present in the lacquer and inks.

Fig 3 shows that SME factories 1, 3 & 4 had measurable but low MuFa vapour exposures (< 10%) of the recommended exposure limit of 1 mg/m^3. These factories had UV printing machines fitted with good local exhaust ventilation, primarily to remove ozone and heat, but the extraction also removes other volatile hazardous compounds such as solvents and multifunctional acrylate monomer vapours.
SME Factory 2 carried out small hand printing proofing trials on machines not fitted with extraction. MuFa vapour exposure was found to be approximately 0.6 mg/m^3 i.e. 60% of the long-term limit, which is significant. For UV lithographic, small-scale print proofing and UV label printing processes, the risk assessed was MEDIUM.

Fig 3.



New Generation UV Lacquers

It was realised during the laboratory experiments that if MuFa vapours were detected in the workplace at significant levels, the potential existed to reduce these levels by selecting an acrylate monomer system with inherent lower volatility (e.g. using TMPTA & EOTMPTA monomers).

As a result of this work, "New Generation" lacquers were specifically developed by manufacturers and suppliers during the project to reduce the risk from MuFa vapours.

At SME factory 1, two new-generation – low MuFa-vapour lacquers were tested under commercial conditions on one day. MuFa vapours were detected by both static and personal sampling, but at significantly lower levels than when TPGDA monomer was used, under virtually the same conditions, as shown in the table below.

TPGDA Lacquer % Exposure Limit	Lacquer A % Exposure Limit	Lacquer B % Exposure Limit
2 - 5	0.4 – 0.5	0.2 - 1

2.2 **Biological Monitoring**

As a complementary exercise to the COSHH air monitoring for solvents and multifunctional acrylates, a programme of biological monitoring was carried out involving specific residual solvents (or metabolites) in urine and breath tests. Breath tests were also carried for multifunctional acrylates (post shift) on printing operators.
The urine tests for solvents are for comparison with either a UK Health Guidance Value or a German Guidance (BAT-Wert) figure, which gives a measure of whether the control of exposure, by any route, is adequate.
For breath tests, there is no published quantitative data for comparison, but the tests are intended as a fact-finding exercise to build-up information on SME printers. Qualitative conclusions may be possible where there are differences between different operators, printing machines, working practices, job functions etc. There has been no work done previously, as far as is known, on the detection of multifunctional acrylates in breath tests.

2.2.1 **Urine Tests**

Propan-2-ol (Isopropanol)
The main solvent used in sheet-fed offset lithographic printing is propan-2-ol, which is used in the fountain solution. In Germany, there is a BAT-Wert of 50mg/ l (860µmol/l) in urine taken post shift. At all the 4 SME factories propan-2-ol was used and solvent in air monitoring was carried out on the days the urine tests were taken (post shift).
At all the factories the level of propan-2-ol used in the fountain solution was typically 12% - 13%.

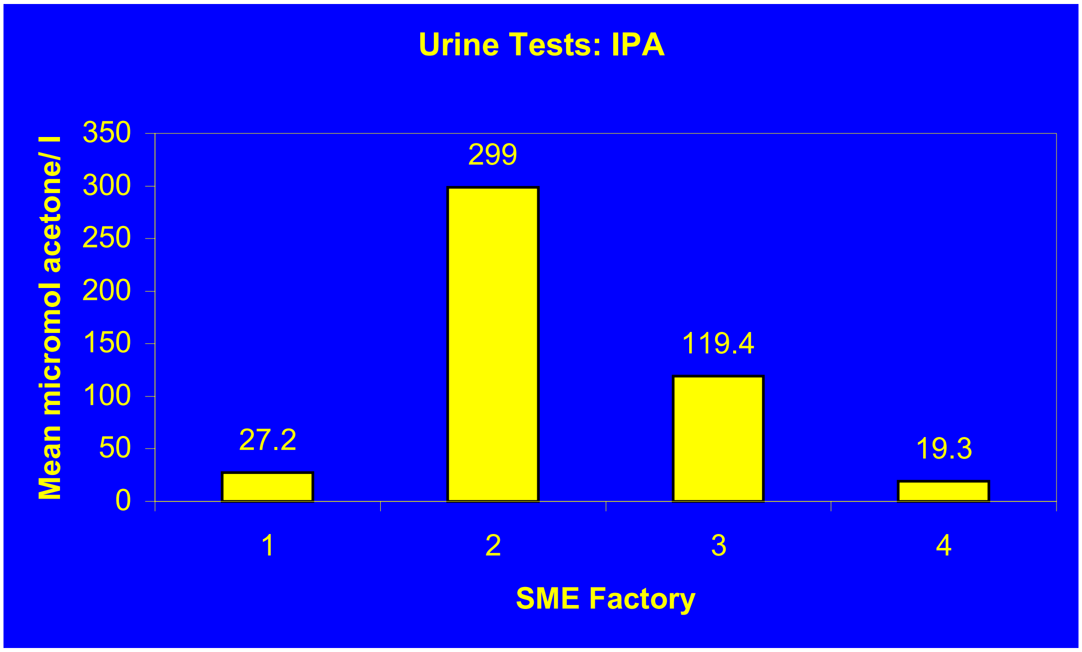
SME	Mean Post-shift acetone-in urine value* µmol/ l	% of BAT Wert Value	Wear Gloves	Eating/ drinking in workplace	Measured mean long term IPA exposure C/L
1	27.2	3.2	Yes	No**	0.013
2	299	34.8	No	Yes	0.34
3	119.4	13.9	No	Yes	0.04
4	19.3	2.2	Yes	No**	0.02

* German Guidance (BAT Wert) Value 860 µmol/l
** Some drinking of liquid observed at workstations during hot weather

All urine test results were below the German Guidance value of 860 µmol/ l.
The lowest mean results were from factories with better working practices, i.e. wearing gloves and mainly restricting eating & drinking to designated rest areas. The SME factories with better working practices had mean results 2.2% – 3.2% of the Guidance value whereas the factories with poorer working practices and poorer controls had mean results 13.9% - 34.8%.
For three out of the four SME factories the propan-2-ol airborne levels were insignificant and well controlled.
There was no significant difference between printers working on conventional and UV printing since the printing machines both use a fountain solution.

The results of the 4 SME’s can be represented graphically and are shown in Figure 4 below.

Fig. 4



2- Butoxyethanol

Only at one SME factory was a UV cleaning solvent used which contained 2-butoxyethanol, which is known to be absorbed through the skin, and has a Health Guidance Value (HGV) in the UK of 240 mmol butoxyacetic acid/ mol creatinine in urine, (taken post shift).

All urine tests were below the UK Guidance value of 240 mmol/.mol creatine, the spread of results were from 10.1 – 61.7 mmol/.mol creatine.
The mean value of all the tests was 15.1%. The range of results being between 4.2% - 25.7% of the UK Guidance value.
The higher results were associated with printers who were working the longer shift (12 hours) than the shorter shift (7,5hours).
This SME had reasonably good working practices, operators wore gloves for handling cleaning solvents and had a separate rest area for eating & drinking. A chilled-water dispenser was allowed in the main factory, which was a potential source of ingestion of chemicals in the workplace.

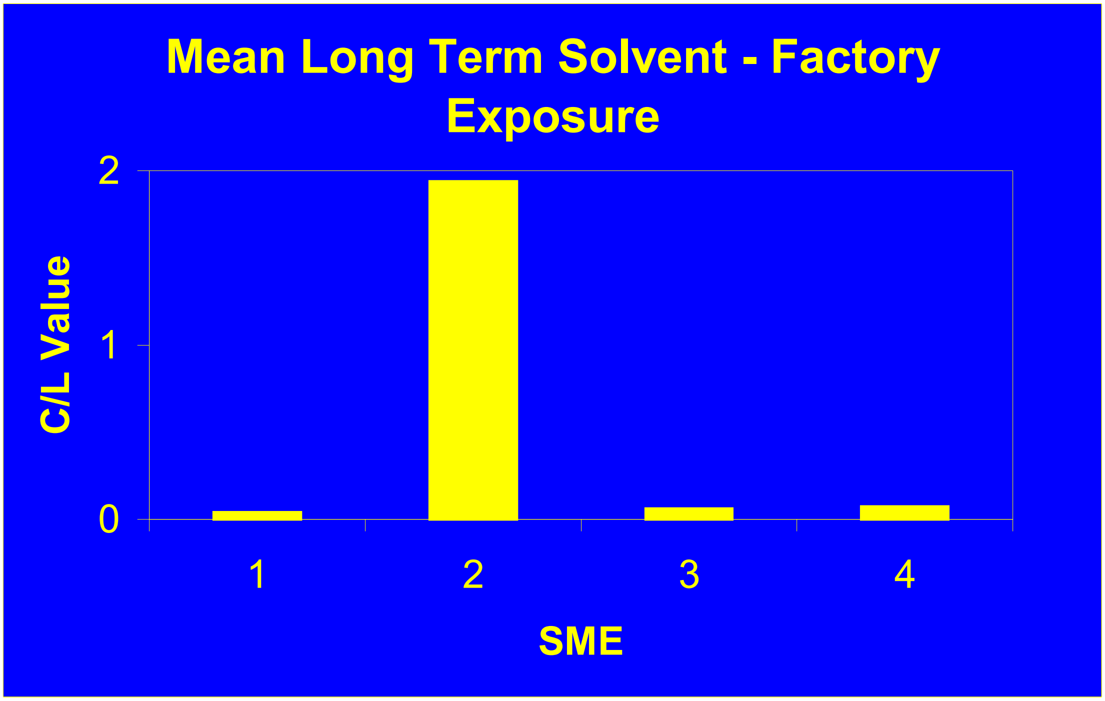
2.2.2. Breath Tests

Breath tests were carried out on the same people for analysis of solvents (VOC's) and multifunctional acrylates using the HSL BIOVOC sampler. Air exhaled from the sampler was then injected onto Tenax thermal desorption tubes for analysis by GC/MS. Due to the different analytical conditions required for VOC's & MuFa's, separate Tenax tubes were collected for analysis of these substances.

SME Factory Exposure to Solvents

SME factory 2 had a problem with poor general ventilation and did not have any local exhaust ventilation installed at the time of monitoring which resulted in the mean long- term exposure to total solvents being above the occupational exposure limit. This is graphically shown in Fig, 5.

Fig. 5

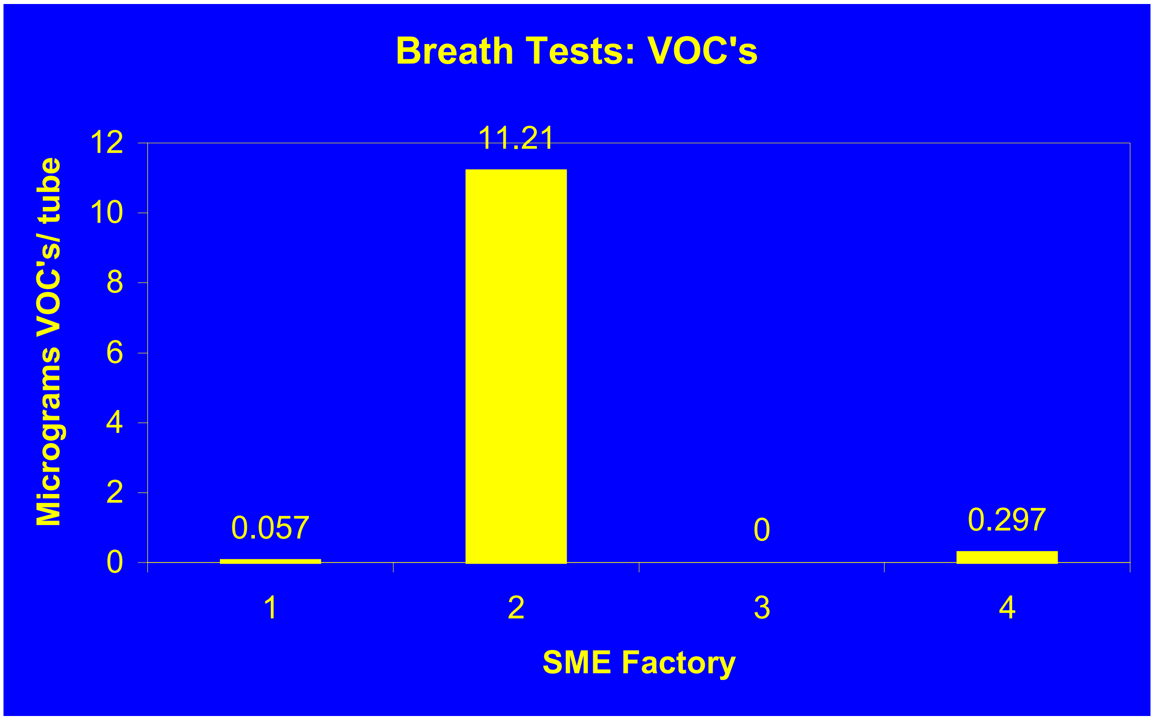


Solvent Breath Tests

There were three major solvents used during the UV printing operations at the SME factories: the fountain solution (isopropanol), cleaning solvents, which contained one of the following (2-butoxyethanol, 1-methoxy-2-propanol, diacetone alcohol and 1-butoxypropan-2-ol), & trimethyl benzenes. In addition toluene was also detected which is known to be present in small amounts in UV inks and lacquers as a bi-product of manufacture. In most cases these solvents were detected on the breath, post shift. The total sum of these solvents (in µg) detected on the breath is shown graphically in Figure 6 below. The following observations can be made: -

The lowest VOC breath-test levels were from factories with better working practices and engineering controls, i.e. wearing gloves and mainly restricting eating & drinking to designated rest areas.
The highest VOC breath levels were from SME factory 2 where the long-term C/L value was > occupational exposure limit on the day of measurement.

Fig. 6.



Influence of UV cleaning solvent

Where printing solvents were detected in the post-shift breath-tests, the percentage of the UV cleaning solvent component, shown in the table below, was determined as well as some physical properties of the main UV cleaning solvent components, which may have an influence on their potential for being breathed in and/ or absorbed through the skin.

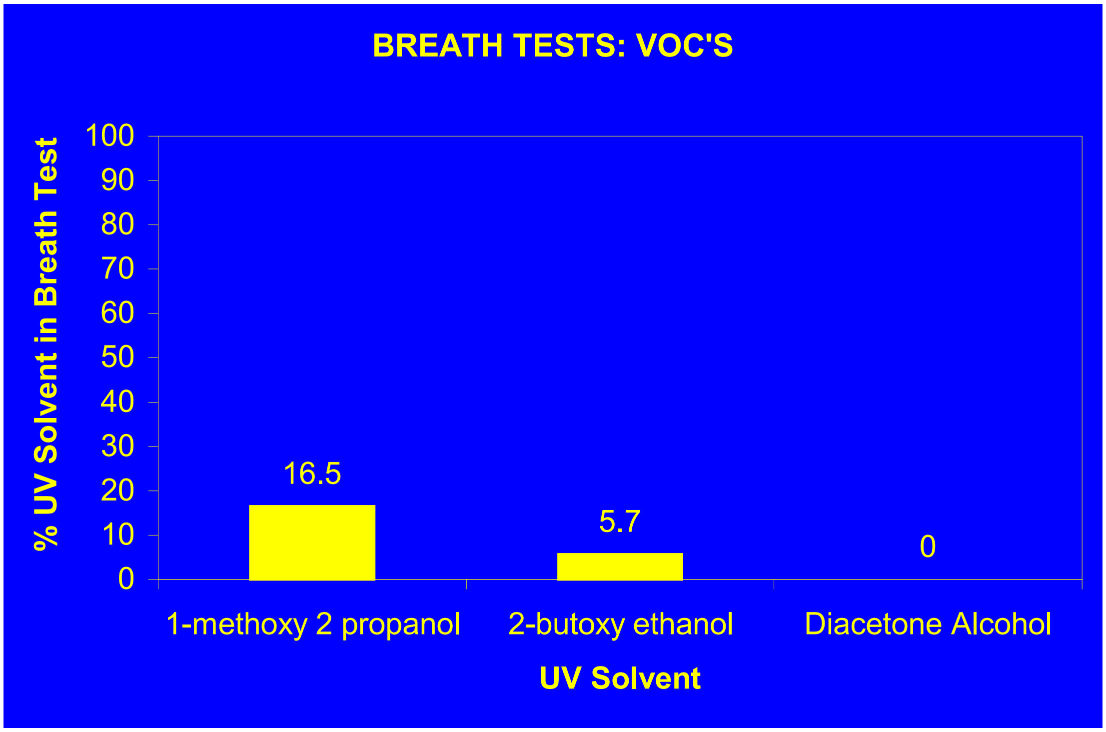
UV Solvent	Boiling point ^{0}C	Vapour Pressure mm Hg (^{0}C)	Absorbed through the skin: Yes/ No
methoxy 2-propanol	120	9.0 (20)	Yes
2- butoxyethanol	168.4	0.76 (20)	Yes
Diacetone Alcohol	167.9	1.0 (20)	No

Fig 7 shows that diacetone alcohol was not detected on the breath, whereas 2-butoxyethanol was to a minor extent 5.7% of the total main-printing solvents, and 1-methoxy propan-2-ol was detected to a larger extent of 16.5%.

Diacetone alcohol and 2-butoxyethanol have similar boiling points and vapour pressures but the latter is absorbed through the skin. 1-methoxy-2- propanol has a lower boiling point and increased vapour pressure at room temperatures making it less suitable for use as a cleaning solvent.

From a health and safety point of view only, diacetone alcohol is a more suitable solvent to be used in cleaning formulations than the other two solvents mainly due to fact that there is a reduced chance of it entering into the body by skin absorption and inhalation.

Fig.7.

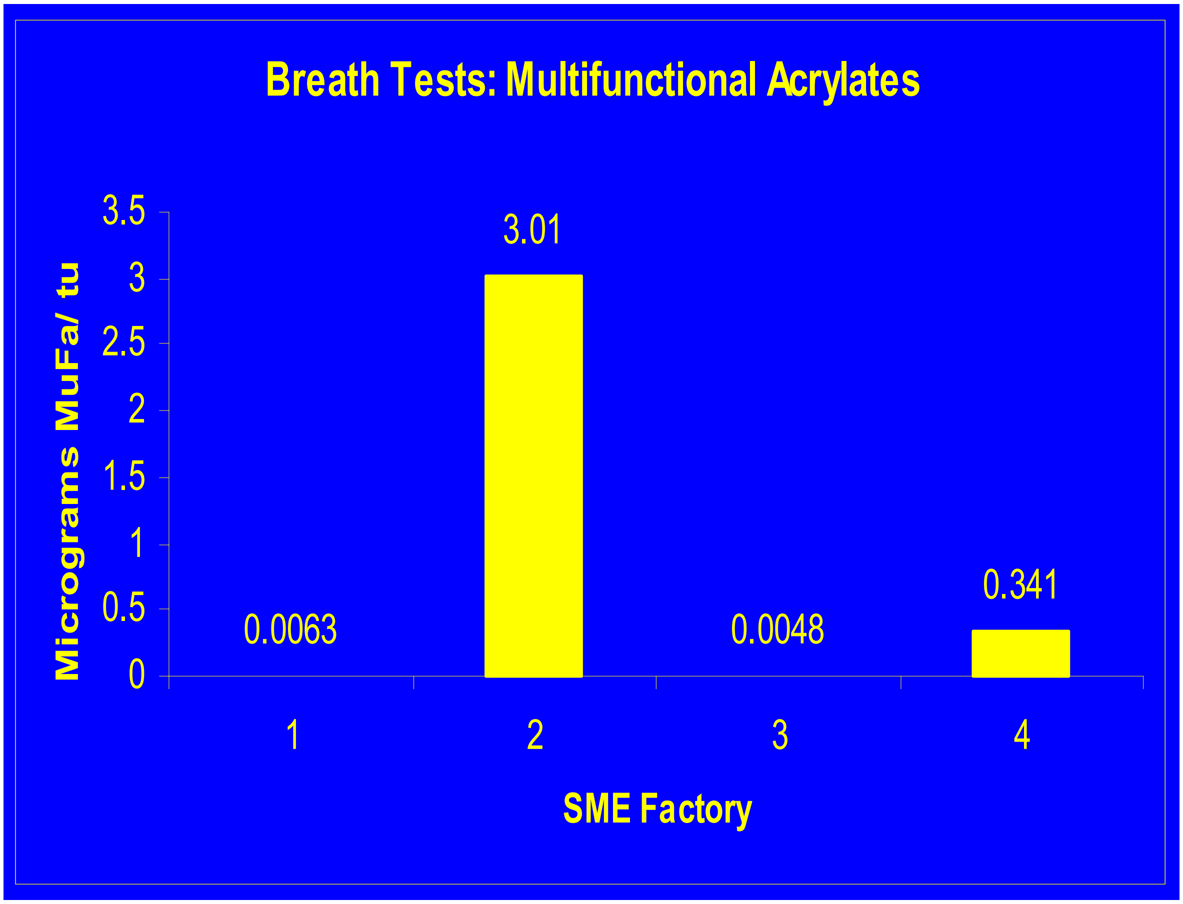


<u>Multifunctional Acrylate (MuFa) Breath Tests</u>

Workplace airborne MuFa exposure has already been discussed in Fig.3, where SME factory 2 had the highest exposure, due to poor general ventilation etc, which is in agreement with the higher solvent exposure found at this site.
Tripropylene glycol diacrylate (TPGDA) is the most commonly used monomer in lacquer and ink formulations, and this was confirmed both in the airborne monitoring and breath tests, where TPGDA and its component acrylates were detected. Lacquer formulations contain the highest concentration of TPGDA monomer (up to 30% m/m).

In most cases, MuFa's were detected on the breath, post-shift, at all the 4 SME's, and shown graphically in Fig. 8.

Fig. 8.



New-Generation UV Lacquers At SME factory 1, two low MuFa vapour lacquers were tested under commercial conditions on one day, these lacquers were formulated from acrylate monomers previously tested, under both laboratory conditions (see Fig.2.) and workplace exposure (see section 2.1.3) to have much lower MuFa vapours than TPGDA. MuFa vapours were detected close to the machine's lacquer unit, at significantly lower levels than TPGDA monomer as, but no MuFa components were detected from these monomers in breath tests.

The results of the MuFa breath tests show similar trends to the VOC breath tests namely:
The lowest MuFa breath-test levels were from factories with better working practices, i.e. wearing gloves and mainly restricting eating & drinking to designated rest areas.
The highest MuFa breath levels were from SME factory 2 where the long-term C/L value was close to the recommended occupational exposure limit.
No MuFa vapours were detected on the breath when two "new generation" low-vapour UV lacquers were used under commercial printing conditions.

As a result of this work it was possible to assess MuFa vapours as a medium risk, the full assessment of all hazards is shown in the following table.

	Risk Assessment	Comments
Total Inhalable dust	Low-Risk	Insignificant levels of Total inhalable dust found in workplace
(Inkfly – particulate)	Low-Risk	No deposits of coloured inkfly found on filters exposed in workplace by personal or static monitoring
(Inkfly – MuFa vapour)	Medium Risk	Significant levels of MuFa vapours found one workplace with poor general ventilation and high solvent vapour levels
Airborne Solvents	Medium Risk	Solvent exposure can be a problem in some factories with poor ventilation. Trichloroethylene found in one factory in general use as a cleaning solvent.
Ozone	Low-risk	Normal extraction on machines adequate to control exposure
Actinic UV	Low Risk	Most UV lamps in modern printing machines are adequately shielded.
Noise	Medium-Risk	Noise can be a problem around some machines.
Working Practices e.g. use of PPE, eating, drinking, smoking in factory workplace	High-Risk	Commercial pressures still override implementation of good health & safety working procedures at some SME's

MuFA - Multi-functional acrylate, PPE – Personal protective equipment

3. CONCLUSIONS

This work has shown the importance of using an analytical method, which is capable of identifying and measuring all multifunctional acrylate components present in the vapour arising from uncured acrylate monomers under both laboratory and workplace monitoring conditions. Under laboratory conditions, the most commonly used acrylate monomer (TPGDA), was shown to have total vapour concentrations of 1.4 mg/ m^3 and 7.6 mg/ m^3 at 20^0C & 60^0C respectively. Multifunctional acrylate vapours were detected in one workplace at significant levels (0.6 mg/ m^3), where there was inadequate general ventilation and poor working practices. Solvent vapour levels were also elevated in this factory.
As a result of this work it was possible to assess MuFa vapours as a medium risk

3.1 Biological Monitoring – Solvents

Urine analysis

At 4 SME factories, acetone residue values for isopropanol, ranged between 9 and 334μmol/l. These results were all below the German Guidance value of 860μmol/l.

At 1 SME factory, butoxyacetic acid residue values for 2-butoxy ethanol, ranged between 10.1 and 61.7 mmol/ mol creatine. These results were all below the UK Guidance value of 240 mmol/ mol creatine.

Breath Tests VOC's

VOC's were detected on the breath at the SME factories to greatly different degrees. By far the major solvent component on the breath was isopropanol, which comprised at least 70% of the major printing solvents used. There is no breath test limit to compare the results with but qualitative conclusions can be made in certain circumstances.

The highest VOC mass (mean 11.2μg/ tube), found in the breath, was for a factory where the long-term exposure limit was exceeded. At all the other factories the solvent vapour levels were well controlled (4% - 7.5%) of the long-term limit, resulting in mean breath test VOC masses of (0 – 0.3μg/ tube).
The lowest VOC breath-test levels were from factories with better working practices and engineering controls, i.e. wearing gloves and mainly restricting eating & drinking to designated rest areas.
This work showed that diacetone alcohol, was not detected on the breath, this solvent is used as a UV cleaning solvent and not absorbed through the skin and exhibits relatively low volatility. This indicates that other suitable UV cleaning solvents should demonstrate similar characteristics to diacetone alcohol from a health and safety point of view.
This work indicates that VOC breath test may form a useful role in assessing solvent risks to printers, in conjunction with normal airborne monitoring and observation of working practices.

3.2 Biological Monitoring – Multifunctional Acrylates

Breath Tests

MuFa's were detected on the breath at the SME factories to greatly different degrees. As for VOC's, there is no breath test limit to compare the results with, but qualitative conclusions can be made in certain circumstances.

This work shows that the most common acrylate monomer (TPGDA), used in UV inks and lacquers, can be detected in the breath of printing operatives.
The highest MuFa mass (mean 3µg/ tube), found in the breath, was for a factory where the long-term exposure limit was 63% of the limit. At all the other factories the MuFa vapour levels were well controlled (1.6% - 11%) of the long-term limit, resulting in mean breath test MuFa masses of (0005 – 0.34µg/ tube).
As for VOC's, The lowest MuFa breath-test levels were from factories with better working practices and engineering controls, i.e. wearing gloves and mainly restricting eating & drinking to designated rest areas.
Two "new generation" low-vapour UV lacquers, specially developed using acrylate monomers of low volatility, gave no MuFa vapours in the breath test, which originated from the monomers used. This probably indicates that inhalation is a major route of entry into the body of MuFa's, and can now be successfully controlled at the formulation stage.
Since it is believed that MuFa's have not been previously measured in the breath before, further work is necessary to assess the significance of these results. It is however, noteworthy that "new generation" low vapour MuFa lacquers and inks are technically possible, and it is hoped that this work has contributed in indicating the "way forward" to chemical manufacturers and formulators from a health and safety point of view.

4. REFERENCES

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