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To cite this version:

Emma Bradley, Malcolm Driffield, James Guthrie, Nick Harmer, Peter Kenneth Thomas Oldring, et al.. ANALYTICAL APPROACHES TO IDENTIFY POTENTIAL MIGRANTS IN POLYESTER-POLYURETHANE CAN COATINGS. Food Additives and Contaminants, 2009, 26 (12), pp.1602-1610. 10.1080/19440040903252256 . hal-00573886

HAL Id: hal-00573886

https://hal.science/hal-00573886v1

Submitted on 5 Mar 2011

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ANALYTICAL APPROACHES TO IDENTIFY POTENTIAL MIGRANTS IN POLYESTER-POLYURETHANE CAN COATINGS

Journal:	*Food Additives and Contaminants*
Manuscript ID:	TFAC-2008-400.R1
Manuscript Type:	Special Issue
Date Submitted by the Author:	25-Jun-2009
Complete List of Authors:	Bradley, Emma; The Food and Environment Research Agency Driffield, Malcolm; The Food and Environment Research Agency Guthrie, James; University of Leeds, Department of Colour Science Harmer, Nick; The Food and Environment Research Agency Oldring, Peter; Valspar Corporation Castle, Laurence; The Food and Environment Research Agency
Methods/Techniques:	Chromatographic analysis, GC/MS, LC/MS
Additives/Contaminants:	Cans, Coatings, Food contact materials
Food Types:	Canned foods

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Abstract

The safety of a polyester-polyurethane can coating has been assessed by using a suite of complementary analytical methods to identify and estimate the concentrations of potential chemical migrants. The polyester was based on phthalic acids and aliphatic diols. The polyisocyanate cross-linking agent was 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl cyclohexane homopolymer (IPDI) blocked with methylethylketone oxime (MEKO) to make a one-part formulation. The overall migrate, obtained using solvent extraction of cured films, comprised almost completely of twelve cyclic and one linear polyester oligomers up to molecular weight 800 and containing up to six monomer units. These 13 oligomers were in a total of 28 isomeric forms. Other minor components detected were plasticisers and surfactants as well as impurities present in the starting materials. There was no detectable residue of either the blocked isocyanate (< 0.01 µg/dm^2) used as the starting substance or the unblocked isocyanate (< 0.02 µg/dm^2). The level of extractable IPDI was used as an indicator of the completeness of cure in experimental coatings. These studies revealed that there was an influence of time, temperature and catalyst content. Polymerisation was also influenced by the additives used and by the ageing of the wet coating formulation over several months. These studies allow parameters to be specified to ensure that commercial production coatings receive a full cure giving low migration characteristics.

Keywords: Can coatings; migration; analysis, safety evaluation, overall migrate

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Introduction

The internal surface of metal cans used to pack foodstuffs is often coated to form a barrier between the food and the metal of the can. The most widely used coatings applied to metal substrates are epoxy resins which are based on bisphenol A diglycidyl ether (BADGE) formed by the reaction of bisphenol A with epichlorohydrin. As pressure, particularly commercial, increases to reduce exposure to bisphenol A, for which the safety evaluation is subject to frequent scrutiny and review (e.g. EFSA 2006, EFSA 2008; Health Canada, 2008) then alternative coating types are sought. Polyester-based coatings provide an alternative to epoxy-based resins. In these systems the three-dimensional coating network is built up from any combination of a number of poly-functional alcohol and carboxylic acid monomers (Deligny & Tuck 2000).

Safety and technical requirements

All food contact materials and articles, including coatings applied to metal substrates, should comply with the Framework Regulation (EC) No. 1935/2004 (EC 2004).

This Regulation allows for the introduction of implementing directives concerning specific groups of materials and articles (specific directives). For coatings one specific directive is in place for the control of BADGE as well as its hydrolysis and hydrochlorination products (EC 2005). For other coating types no specific measures have been introduced. The Council of Europe has prepared Resolutions for materials for which specific measures have not yet been introduced at EU level. One such area is coatings. The Resolution on coatings

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ResAP (2004) 1 (Council of Europe 2004) has been prepared however this Resolution has no legal status.

In addition to satisfying relevant legal safety requirements, described above, the coatings must also satisfy a number of technical requirements, namely:

- Adhesion to the metal surface
- Flexibility to withstand the deformations involved in the can-making process
- Durability to withstand the heat treatment associated with the sterilisation of food
- Inertness - so that the coatings are not affected by, or do not affect, the food itself

Migration from polyester-based coatings

As mentioned above, all materials and articles intended for contact with food should not transfer their constituents at levels that may endanger human health. How this should be demonstrated for coatings applied to metal substrates is not defined. In the absence of specific legislation for coatings the legislation for plastics food contact materials (EC 2003) is often used as a guide. The migration of known monomers and additives used to manufacture the plastic is controlled by defining the substances that can be used in a positive list. Where the toxicity of these substances has been assessed, specific migration limits and/or maximum permitted quantities in the final material or article have been assigned. In addition to the list of permitted substances in the plastics legislation, the 4th amendment to Directive 2002/72/EC (EC 2007) includes the explicit provision that there is a general requirement to assess the safety of all potential migrants, including impurities,

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reaction products and breakdown products and the onus is on the business operator to do so. Again although this Directive is applicable to plastics it can also be used as a guide for other food contact materials and articles.

There are many different monomers used to prepare polyester resins and some of the most common are given in Table 1. Using the plastics legislation as a guide then the migration of these monomers should not exceed any migration limits assigned to them.

< Insert Table 1 about here >

Combinations of the different monomers provide a large number of possible polyester oligomers that have the potential to migrate from the can coating into food. Small cyclic oligomers have been reported as by-products of the polymerisation process and have been seen to migrate into food simulants (Schaefer et al. 2004). In addition to the polyester monomers and oligomers, any other additives used should not migrate at toxicologically significant levels. Typical additives used to achieve the required technical function of the coating are: cross-linking agents, catalysts, lubricants, wetting agents and solvents.

Work to minimise the migration from polyester-based coatings led to the development of polyester-polyurethane (PEPU) coatings. These coatings are formulated using a polyisocyanate to facilitate the cross-linking of the polymer network. The high reactivity of the isocyanate moiety results in the creation of urethane linkages on curing. This results in

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a more inert coating with an extensive 3-dimensional polymer network that should have lower migration characteristics.

This paper describes an assessment of the safety of a PEPU coating taking into account the migration of both the known starting substances included in the formulation as well as any reaction and breakdown products that form during curing and storage. The analytical approaches used in this assessment are described. The work was carried out within a 3-year Defra LINK project. This project brought together academic expertise in coatings formulation, food science, and chemical analysis at the University of Leeds and the Central Science Laboratory (York), and industrial companies that develop and supply coatings (Valspar), make cans for the food industry (Impress), and are major users of food cans (Heinz). By working closely with industry partners the identities of previously unidentified coating components could be proposed, removing many of the uncertainties that present themselves in the safety assessment of such materials.

Analytical approach

A test protocol to assess the safety of food contact can coatings has been described (Bradley et al. 2008). This protocol contains a suite of analytical methods to identify and quantify chemical migrants from polymeric coatings applied to metal substrates. This includes FT-IR analysis for characterisation of coatings; the gravimetric determination of the overall migrate and the total solvent (dichloromethane and acetonitrile) extractable substances; screening analysis including gas chromatography-mass spectrometry (GC-MS)

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with headspace and liquid injection analysis to detect volatile and semi-volatile substances; and liquid chromatography-time-of-flight-mass spectrometry (LC-TOF-MS) to detect any polar and non-volatile substances. The techniques listed above facilitate the identification of unknown substances present in the coating. In addition, for any safety evaluation, the migration of any starting monomers and additives should also be determined. The test protocol is outlined below.

Test protocol

1. Confirm the coating type by FT-IR spectroscopy.
2. Assemble, if possible, the formulation details along with a description of the manufacturing process - especially with regard to the coating thickness, the time/temperature conditions of stoving, and the intended food or beverage packaging applications.
3. Determine the overall migration and total solvent extractables.
4. Determine the identities and estimated levels of any volatile potential migrants in the coated panels by headspace GC-MS.
5. Determine the identities and estimated levels of any semi-volatile potential migrants in the coated panels by solvent extraction followed by GC-MS.
6. Determine the identities and estimated levels of any polar and/or non-volatile potential migrants in the coated panels by solvent extraction followed by LC-TOF-MS
7. Based on the coating type identified in (1) an evaluation of the information in (2) above and that derived from the generic screening procedures described in (3-6),

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decide which, if any, specific chemical analyses should be performed to check these estimates. This evaluation and decision process should be documented.

Specific analyses should be carried out for those substances expected to be present from the formulation details or detected in the screening exercise which have been assigned exposure restrictions and/or specific migration limits. For example Directive 2002/72/EC, as amended, the Synoptic Document (see later) which contains the provisional list of monomers and additives notified to the European Commission as substances which may be used in the manufacture of plastics or coatings or listed in the Technical document No. 1 - List of substances to be used in the manufacture of coatings intended to come into contact with foodstuffs a supporting document to the Council of Europe Resolution). Where available standard methods (such as CEN standards or Technical Specifications) should be used to determine these substances. In cases where standard methods are not available then specific methods should be developed and validated in-house according to recognised validation protocols (e.g. Thompson et al. 2002).

Materials and methods

Chemicals

Dichloromethane, acetonitrile, methanol, ethyl acetate, ethanol, acetic acid, ammonium formate and formic acid were all obtained from Fisher (Loughborough, UK). d_{10}-Benzophenone, d_{10}-ethylbenzene and 2-ethylhexanoic acid were from Aldrich (Poole, UK). Isooctane was from BDH (Poole, UK). IPDI trimer and MEKO-blocked IPDI trimer (see later for full names) were provided by Valspar Corp. (Gruningen, Switzerland).

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Coated metal panels

Samples of PEPU coated tin plate were provided by Valspar (Witney, UK) and C. Jiang (University of Leeds, UK). The wet (uncured) coating formulation and the individual ingredients used in the formulation were also supplied by Valspar.

Formulation details

The polyester polyurethane coating was described as containing a polyester resin, a blocked polyisocyanate resin, a cellulosic resin, an organotin solution, two wax additives, aromatic solvent, glycol ether acetate and aluminium paste. The panels were industrially stoved at 190°C for 12 min. The coating thickness on the panels provided was 8 µm.

The specific identities of the monomers used to prepare the polyester were not provided therefore when establishing the identities of the migratable oligomers then all possible combination of the acids and polyols given in Table 1 were considered.

The polyisocyanate used in this coating is 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl cyclohexane homopolymer (IPDI). To make the wet coating one-pack (as opposed to 2-packs that need pre-mixing before application) the IPDI is blocked with methylethylketone oxime (MEKO). During high temperature stoving of the coating the MEKO blocking agent is released, evaporates, and leaves the isocyanate moieties free to participate in polymerisation and cross-linking reactions to form the cured film. If this process is

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incomplete then unreacted MEKO-blocked IPDI trimer or residual free IPDI trimer could remain in the cured coating and may then migrate into the packed foods.

For the other coating components only generic names were provided and therefore the identities of any specific potential migrants could not be defined from this source. As it has been reported in the scientific literature (Elss et al. 2004) that hydrolysis of organotin catalysts can yield 2-ethylhexanoic acid then the concentration of this acid in the solvent extracts was determined.

Analytical screening

The procedures to confirm coating type, overall migration, mass of the solvent extractable substances and the identities of any potential migrants in the coatings are as described elsewhere (Bradley et al. 2008).

Targeted analysis

MEKO-blocked IPDI. Triplicate portions of each panel (0.25 dm^2) were cut into 1 cm x 1 cm pieces and extracted using acetonitrile (50 ml) for 18 hours at room temperature. The acetonitrile was removed by evaporation and the residue was re-dissolved in 1 ml of acetonitrile. Blank and over-spiked samples were treated in the same way to allow recovery corrected concentrations to be calculated. Solvent standards (equivalent to 0 – 3.5 $\mu g/dm^2$) were prepared and run alongside the samples. HPLC-MS analysis was conducted using Waters Alliance 2695 HPLC apparatus and Micromass Quattro Ultima

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mass detection using electrospray ionisation and the selected ion monitoring mode with m/z 928.7 $[M+H]^+$ for quantification and m/z 950.68 $[M+Na]^+$ for confirmation.

IPDI trimer. Methodology for the determination of residual IPDI trimer in cured panels has been published elsewhere (Driffield et al. 2007). The same methodology was used here.

2-Ethylhexanoic acid. Three 1 dm^2 sections were cut from three separate panels to form the triplicate samples for analysis. The three samples were cut into 0.5 x 0.5 cm portions and were extracted with ethanol containing 2-methylpentanol as an internal standard for 4 hours at 60°C. The extracts were analysed by GC-MS using an Agilent MSD 5973 operated in selected ion monitoring mode. Ions m/z 43 and 55 were monitored for the internal standard and ions m/z 88 and 116 were monitored for the 2-ethylhexanoic acid. For quantification purposes, blanks and solvent standards (range 0 - 1.5 µg/ml) were analysed in the same batch.

Results and discussion

Analytical screening

Headspace GC-MS. No substances were detected in the headspace GC-MS analysis using a method with a detection limit equivalent to a worst case migration of 1 µg/kg. This was not unexpected since the high temperature stoving process (190°C for 12 min) is effective at driving all volatiles out of the coating. No further work was necessary to determine the specific migration of any volatile substances.

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Solvent extraction followed by GC-MS. GC-MS analysis of the solvent extracts identified seventeen potential migrants. No good library matches were obtained for fifteen of these substances. However the mass spectra obtained (e.g. Figure 1) were consistent with those expected for polyester oligomers. The polyester oligomers were also detected by LC-TOF-MS. Using this technique the identities of such substances can be proposed (see later). The best library matches for the other two solvent extractable substances were: butyl octadecanoate, and 2-[2-[4-(1,1,3,3-tetramethylbutyl)phenoxy]ethoxy]ethanol. Butyl octadecanoate is listed in the Synoptic Document. As mentioned previously the Synoptic Document contains the provisional list of monomers and additives notified to the European Commission as substances which may be used in the manufacture of plastics and coatings intended to come into contact with foodstuffs. The Synoptic document is no longer updated by the Commission and it is intended to be replaced in the future by a new database of evaluated substances. However the document was active at the time that this work was conducted and the status of the substances discussed hereafter has not changed. Therefore in the absence of any specific restrictions for the use of these substances information provided in the Synoptic Document was considered. Both butyl octadecanoate and 2-[2-[4-(1,1,3,3-tetramethylbutyl)phenoxy]ethoxy]ethanol are listed but no restrictions are given. Butyl octadecanoate has been assigned to SCF List 7 'Substances for which some toxicological data exist, but for which an ADI or a TDI could not be established. The additional data required is specified as 'hydrolysis data'. This is because being a simple ester of butanol with stearic acid, the substance can be expected to hydrolyse to innocuous substances in vivo, although the placement in List 7 means that this needs to be

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demonstrated experimentally. 2-[2-[4-(1,1,3,3-Tetramethylbutyl)phenoxy] ethoxy]ethanol, a non-ionic detergent, has been assigned to SCF List 9 'Substances and groups of substances which could not be evaluated due to lack of specifications (substances) or to lack of adequate description (groups of substances).' For both substances the levels present in the coating would result in worst case migration levels of less than 10 µg/kg therefore these were not considered further.

< Insert Figure 1 about here >

Solvent extraction followed by LC-TOF-MS. Mass spectral libraries exist for GC-MS data and therefore the identification of any volatile and semi-volatile substances can be achieved by comparison with library spectra. This is not the case for substances detected by LC-MS. However the use of the accurate mass data generated by the LC-TOF-MS instrumentation aids in the identification of the unknown compounds and those for which more than one identity is proposed.

The TOF-MS data produced was processed using Agilent Molecular Feature Editor software. This package examines the data, extracts chromatographic peaks and produces mass spectra for those peaks. Figure 2 shows the total ion chromatogram (TIC) resulting from the analysis of the acetonitrile extract of the polyester polyurethane coated panels. Analysis was carried out at two fragmentor voltages. The higher the fragmentor value the more likely it is that in-source fragmentation will occur producing accurate masses of fragment ions to aid identification. The accurate masses of both the molecular and

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fragment ions present in the extracts were located. Some of the chromatographic peaks seen in the TIC obtained from the analysis of the extracts are very small, but were pinpointed nevertheless, highlighting the power of TOF-MS.

< Insert Figure 2 about here >

A database of potential structures was prepared from the information known about the raw materials used to prepare the coating. The monomers used to form the polyester resin listed in the formulation were not specified and therefore a database was constructed. This database contained combinations of all of the different diols and diacids that may be used to make these polyester resins (Table 1). An excerpt from the database is shown in Table 2. The accurate masses of each of the potential polyester oligomers, over one thousand possible structures, were calculated. As well as the polyester oligomers, reaction products of the polyester monomers with the IPDI trimer were also included in the database. Using the software provided with the instrumentation the accurate masses of each of the peaks in the chromatogram were compared with the calculated masses of the monomers, polyester oligomers and reaction products. This database in conjunction with the TOF-MS data (accurate mass determinations of molecular ion adducts and fragment ions) of the coating extracts and the raw materials and wet coating formulations and MS data (not TOF) reported in the literature (e.g. Schaefer & Simat 2004) was used to assign the identities of the chromatographic peaks that were detected when the extracts were analysed by electrospray operated in the positive mode. Searches of scientific literature and the Internet were also carried out to propose possible identities for the substances detected in the

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extracts which could not be assigned from the knowledge of the starting materials used in the manufacture of the coating.

< Insert Table 2 about here >

The polyester oligomers identified in the coating extracts are given in Table 3. Analysis of the TOF-MS data identified 28 polyester oligomers, i.e. more than double the number listed in Table 3. This is due to isomeric forms of the oligomers that chromatograph differently. These isomers can arise from (a) using different isomers of starting substances (e.g. ortho, meta or para-phthalic acid or isomeric polyols); (b) oligomers having the same composition but different structures (e.g. linear PA-EG-PA-EG-PA-NPG versus linear PA-EG-PA-NPG-PA-EG); (c) from two or more oligomers having the same empirical formula but a different identity (e.g. 3PA+2EG+NPG and 3PA+3PG both have the formula $C_{33}H_{30}O_{12}$) and; (d) from diastereoisomers formed when incorporating the chiral 1,3-propylene glycol monomer. The confidence in the identification is good as all mass error values (difference between the experimental and theoretical masses) are less than 5 ppm. This means for example, an error of less than 3 milliDaltons on a molecular mass ion of 600 Daltons. Analysis revealed the polyester was based on phthalic acid esterified with five of the polyols listed in Table 1. Twelve of the thirteen oligomers are cyclic and only one is linear. This is because cyclic oligomers lack any free functional group, cannot be incorporated into the polymeric network of the coating, and so can accumulate as unreactive by-products in the cured coating.

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< Insert Table 3 about here >

The identity of those peaks that could not be assigned as polyester oligomers were proposed based on the knowledge of the coating manufacturer as well as the analysis of the starting materials used to make the lacquer. Identities were proposed for a plasticiser, dioctyl sebacate, a surfactant, nonylphenol(ethoxylate)$_5$ and di-(2-ethylhexyl) phthalate which was also detected as an impurity in the aluminium paste starting material. Other peaks were detected in the extracts however their identities could not be proposed from the molecular formulae generated. Therefore although LC-TOF-MS goes some way towards the identification of the otherwise unknown substances it was not possible to identify every solvent extractable substance present in the polyester polyurethane coating.

Targeted analysis

2-Ethylhexanoic acid. No 2-ethylhexanoic acid was detected in the ethanol extracts of the commercial panels (limit of detection 0.1 µg/dm^2 which is equivalent to a migration of 0.6 µg/kg assuming the conventional food contact ratio of 6 dm^2 food contact material to 1 kg food).

MEKO-blocked IPDI trimer analysis. PEPU coated tinplate prepared commercially gave no detectable migration of the MEKO-blocked IPDI trimer using a method of analysis with a detection limit of 0.01 µg/dm^2. This confirms that under the stoving conditions used the MEKO blocking agent is completely released generating the free IPDI trimer.

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IPDI trimer analysis. PEPU coated tinplate prepared commercially gave no detectable migration of IPDI trimer using a method of analysis with a detection limit of 0.02 µg/dm^2. This indicates that as the IPDI-MEKO unblocks, the free IPDI trimer liberated then reacts quantitatively to form the cross-linked polymer network. Separate studies indicated that, even if migration did occur at these low levels, the IPDI trimer would not be expected to persist in canned aqueous or fatty foodstuffs as it would hydrolyse to the corresponding aliphatic amine or react with food components to destroy the isocyanate moiety (Driffield et al. 2007).

As well as measuring the concentration of the free IPDI trimer in the commercially applied can coatings, the methodology developed by Driffield et al. (2007) was used in laboratory studies to identify those factors affecting the residual free IPDI trimer concentrations in polyester polyurethane coated metal panels. A model coating formulation was used with laboratory cure conditions to ensure some residual isocyanate in order that parameters affecting residual levels could be evaluated. In this way industry could ascertain the acceptable tolerances in the curing parameters and in the starting materials used that need to be met for a coating to be considered as suitable for food contact applications. The following were investigated:

The effect of curing time and temperature.

Figure 3 shows the effect of both the curing time and curing temperature on the free IPDI concentration detected in laboratory prepared experimental coatings. As expected the

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longer the curing time and the higher the curing temperature the greater the extent of the cure and the lower the level of residual free IPDI trimer in the coating.

< Insert Figure 3 about here >

The effect of pigment

To produce a white rather than a grey PEPU coating, a titanium dioxide pigment with and without extender was introduced. The presence of this pigment in the coating resulted in an increase in the level of the residual free IPDI trimer in laboratory prepared coated panels (Jiang et al. 2009a). This means that the pigment had interfered with (retarded) the polymerisation process somehow. The extent of the effect was grade specific and suggests that surface treatments or impurities are responsible rather than the TiO_2 itself. This should be borne in mind in setting specifications for the pigments used. Any changes in raw materials should be tested for their effects on migration and technical performance.

The effect of waxes

A higher concentration of residual free IPDI trimer was detected in the samples without the wax slip agents added – meaning less complete polymerisation. For the experimental coatings studies the concentrations of the IPDI trimer increased from 6 to 45 $\mu g/dm^2$ when the wax slip agent was excluded from the formulation. It may be that the presence of these additives causes the film to remain a little more fluid in the end stages of the polymerisation process, before the film turns into a rigid 3-dimensional network, and this fluidity allows

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the last vestiges of reactants to diffuse, meet and react. This is just conjecture however and the effect may merit further study.

The effect of catalyst level

Increasing the amount of catalyst in the formulation resulted in a reduction in the free IPDI trimer levels in laboratory prepared coatings. Although the commercially applied coatings gave no detectable migration, changes in formulation may be better controlled using a higher concentration of catalyst.

The effect of ageing the wet lacquer

Coated panels were prepared using freshly prepared wet coating and wet coating that had been allowed to stand for 1, 2, 3, 4, 5 and 6 months at room temperature prior to mixing and application (Jiang et al. 2009b). Wet coatings are routinely supplied with a six month shelf-life and therefore this was consistent with practices employed on a commercial scale. The results obtained are shown in Figure 4. The residual free IPDI trimer concentration in the coating increased to $> 300\ \mu g/6\ dm^2$ when panels were coated with the 'old' wet coating. The addition of extra catalyst to aged wet coatings prior to pre-mixing and application resulted in lower levels of free IPDI trimer in the cured coating. Possible explanations for this effect are that the organotin catalyst degrades during storage or that the free hydroxyl content of the resin decreases reducing the number of polymerisation sites. Although these findings were for laboratory prepared coated panels it was recommended that the shelf-life of the commercial coatings should be closely monitored.

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< Insert Figure 4 about here >

Conclusions

Combination of the analytical approaches described should be used by the responsible industries to demonstrate due diligence in the assessment of the food contact materials and articles that they produce/use. This is especially true when new products and new formulations are proposed for commercialisation. Testing should involve targeted analysis of known starting materials as well as screening analyses to identify any impurities, reaction products or breakdown products. Although analytical methodology continues to advance, close collaboration between analytical testing laboratories and the manufacturers is required to facilitate a more complete assessment of the potential migrants present. Even with this collaboration it is unlikely that every peak in the chromatograms will be identified and therefore other complementary approaches may also need to be considered to assess the safety of the overall migrate. These could include concepts advocated elsewhere, such as toxicological evaluation of the whole migrate (if feasible) and/or threshold concepts such as threshold of regulation or thresholds of toxicological concern.

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Acknowledgements

This work was carried out as a part of a Defra LINK project: FQS45 'New technologies and chemistries for food can coatings'. Funding by Defra and matching funds in kind from

Valspar Corporation, Impress Group and H.J. Heinz are gratefully acknowledged. We also thank Agilent Technologies for the loan of the LC-TOF-MS instrumentation. The contents of this paper are the responsibility of the authors alone and should not be taken to represent the views of the supporting organisations.

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Figure 4. Effect of wet coating age on residual free IPDI trimer concentrations in an experimental coating

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Figure 1. Typical mass spectrum of a polyester oligomer detected by GC-MS analysis of the PEPU solvent extract

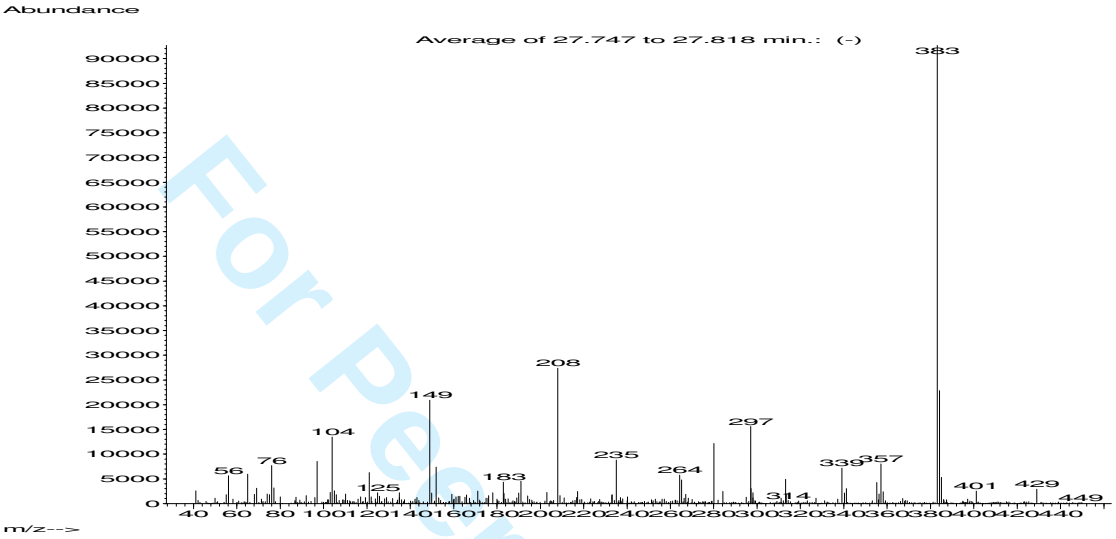

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Figure 2. Total ion chromatogram of the acetonitrile extract of a polyester-polyurethane coated tinplate

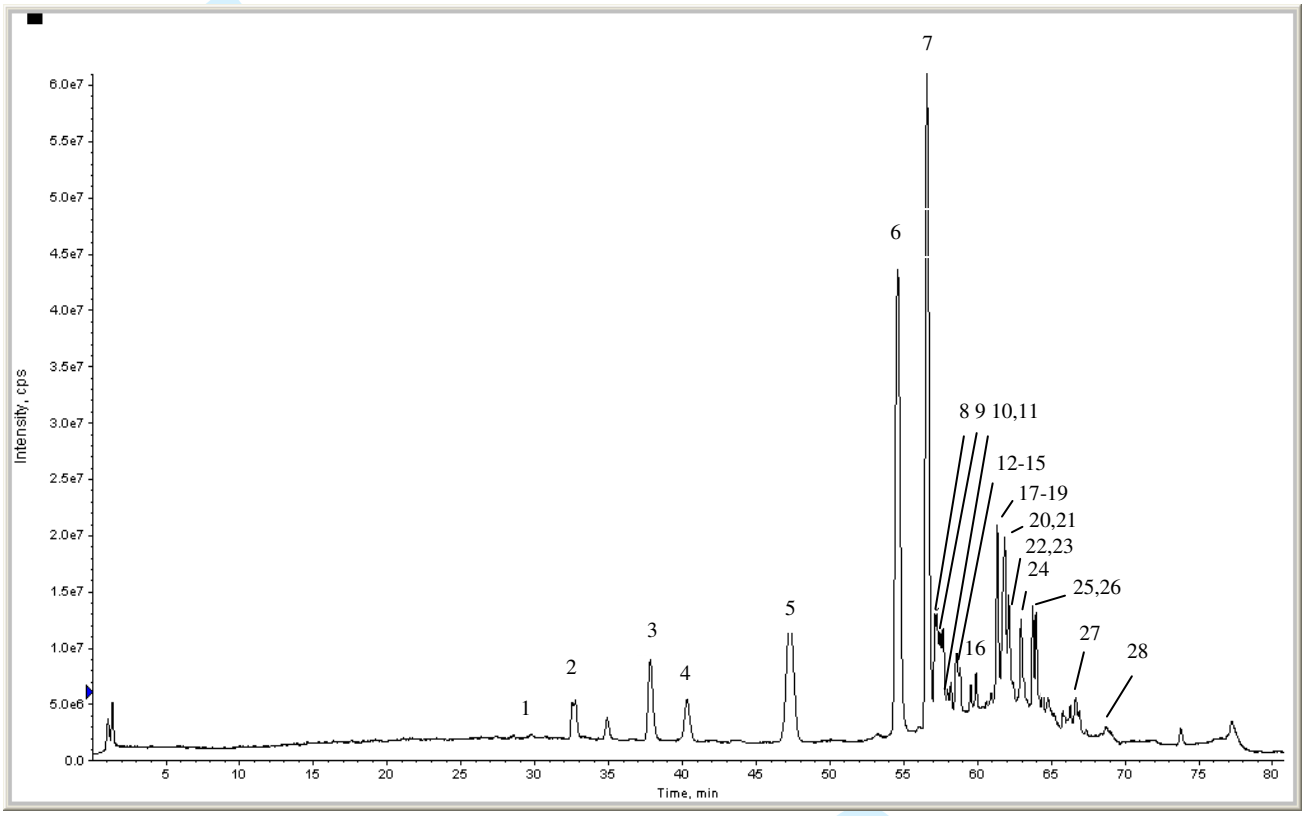

Figure 3. The effect of curing time and temperature on residual free IPDI trimer levels

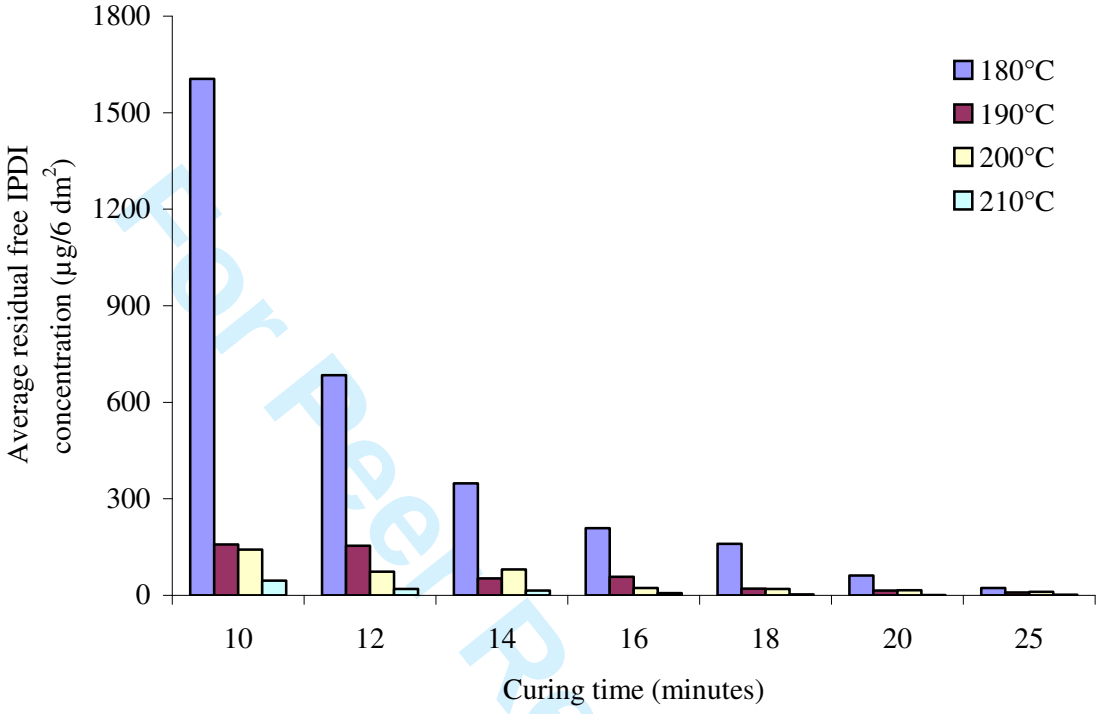

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Figure 4. Effect of wet coating age on residual free IPDI trimer concentrations in an experimental coating

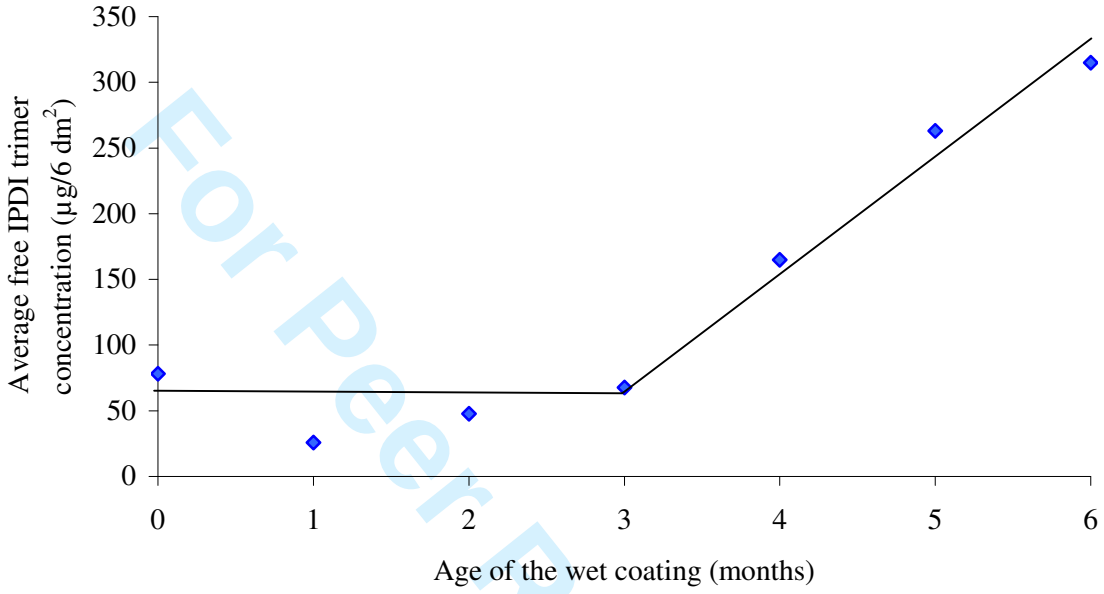

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Table 1. Commonly used monomers for polyester resins

Name	**Abbreviation**	**Formula**	**Type**
Ethylene glycol	EG	C2H6O2	Alcohol
Propanediol, 1,2- and 1,3- isomers	PG	C3H8O2	Alcohol
1,3-Butanediol (+ isomers)	BD	C4H10O2	Alcohol
Ethylene glycol dimer	EGD	C4H10O4	Alcohol
2,2-Dimethyl-1,3-propanediol	NPG	C5H12O2	Alcohol
1,6-Hexanediol	HD	C6H14O2	Alcohol
1,1,1-Tris(hydroxymethyl) propane	HMP	C6H14O3	Alcohol
1,4-Bis(hydroxyl-methyl) cyclohexane	CHDM	C8H16O2	Alcohol
2,2,4-Trimethylpentane-1,3-diol	TMP	C8H18O2	Alcohol
Adipic acid	AA	C6H10O4	Carboxylic acid
Phthalic acids (1,2-, 1,3-, 1,4-isomers)	PA	C8H6O4	Carboxylic acid
Trimellitic acid (from the anhydride)	TMA	C9H6O6	Carboxylic acid

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Table 2. Excerpt from the polyester user-prepared database (see Table 1 for abbreviations)

-	-	AA	TMA	PA	CHDM	BD	EG	DEG	PG	HD	HMP	TMP	NPG	H_2O	MW
PA+EG	linear			1			1							1	210.0528
EG+PA+EG	linear			1			2							2	254.0790
PA+EG+PA+EG	linear			2			2							3	402.0951
PA+EG+PA+EG	cyclic			2			2							4	384.0845
PA+EG+PA+EG+PA	linear			3			2							4	550.1111
PA+EG+PA+EG+PA+NPG	linear			3			2						1	5	636.1843
PA+EG+PA+NPG+PA+EG	linear			3			2						1	5	636.1843
PA+PG+PA+PG+PA+PG	linear			3					3					5	636.1843
PA+PG+PA+PG+PA+PG	cyclic			3					3					6	618.1737

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Table 3. Polyester oligomers identified using Molecular Feature Extraction and database searching

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Mass of compound	Formula predicted	Mass error (ppm)	Proposed identity	Notes	Peak numbers
384.0845	$C_{20}H_{16}O_8$	1.4	2PA+2EG	Cyclic	2
426.1315	$C_{23}H_{22}O_8$	1.4	2PA+EG+NPG	Cyclic	3,4,5
428.1107	$C_{22}H_{20}O_9$	1.1	2PA+EG+DEG	Cyclic	1
466.1630	$C_{26}H_{26}O_8$	0.36	2PA+CHDM+EG	Cyclic	13,15
468.1784	$C_{26}H_{28}O_8$	0.50	2PA+2NPG	Cyclic	6,7,10,11
508.2114	$C_{29}H_{32}O_8$	3.3	2PA+CHDM+NPG	Cyclic	19,20,23
618.1737	$C_{33}H_{30}O_{12}$	0.84	3PA+2EG+NPG or 3PA+3PG	Cyclic	8,9,12,14,16
660.2238	$C_{36}H_{36}O_{12}$	4.6	3PA+EG+2NPG	Cyclic	17,18,21
700.2520	$C_{39}H_{40}O_{12}$	0.82	3PA+CHDM+EG+NPG	Cyclic	25
702.2703	$C_{39}H_{42}O_{12}$	4.8	3PA+3NPG	Cyclic	24,26
704.2469	$C_{38}H_{40}O_{13}$	0.79	3PA+CHDM+2PG	Linear	22
742.3003	$C_{35}H_{50}O_{17}$	0.74	3PA+CHDM+2NPG	Cyclic	27
782.3330	$C_{45}H_{50}O_{12}$	4.2	3PA+2CHDM+NPG	Cyclic	28

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Mass of compound	Formula predicted	Mass error (ppm)	Proposed identity	Notes
384.0845	$C_{20}H_{16}O_8$	1.4	2PA+2EG	Cyclic
426.1315	$C_{23}H_{22}O_8$	1.4	2PA+EG+NPG	Cyclic
428.1107	$C_{22}H_{20}O_9$	1.1	2PA+EG+DEG	Cyclic
466.1630	$C_{26}H_{26}O_8$	0.36	2PA+CHDM+EG	Cyclic
468.1784	$C_{26}H_{28}O_8$	0.50	2PA+2NPG	Cyclic
508.2114	$C_{29}H_{32}O_8$	3.3	2PA+CHDM+NPG	Cyclic
618.1737	$C_{33}H_{30}O_{12}$	0.84	3PA+2EG+NPG or 3PA+3PG	Cyclic
660.2238	$C_{36}H_{36}O_{12}$	4.6	3PA+EG+2NPG	Cyclic
700.2520	$C_{39}H_{40}O_{12}$	0.82	3PA+CHDM+EG+NPG	Cyclic
702.2703	$C_{39}H_{42}O_{12}$	4.8	3PA+3NPG	Cyclic
704.2469	$C_{38}H_{40}O_{13}$	0.79	3PA+CHDM+2PG	Linear
742.3003	$C_{35}H_{50}O_{17}$	0.74	3PA+CHDM+2NPG	Cyclic
782.3330	$C_{45}H_{50}O_{12}$	4.2	3PA+2CHDM+NPG	Cyclic

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