FEICA The European voice of the **adhesive** and **sealant industry**

Brussels, 15 March 2022

FEICA recommendation to adhesive suppliers and users on the assessment of PAAs in polyurethane adhesives intended to be used in food packaging

FEICA, the Association of the European Adhesive and Sealant Industry, is a multinational association representing the European adhesive and sealant Industry. This specialty chemical sector represents more than 2 % of the total European chemical industry's turnover and contributes more than 14 billion euros to the EU economy. Our industry invests about 370 million euro yearly on R&D and employs more than 41,000 people. FEICA represents close to 800 adhesive and sealant producers in Europe. With the support of its national associations and several direct and affiliated members, FEICA coordinates, represents and advocates the common interests of our industry throughout Europe. In this regard FEICA aims to establish a constructive dialogue with legislators in order to act as a reliable partner and create a mutually beneficial economic and legislative environment.

Background

For many decades Primary Aromatic Amines (PAAs) have been under discussion due to their potential to cause cancer in humans. In food packaging materials, PAAs are not intentionally added components but may be present as Non-Intentionally Added Substances (NIAS) mainly caused by azo pigments or polyurethane adhesives used in materials for packaging. Polyurethane adhesives do not contain PAAs. However, they can be formed by the reaction of residual monomeric aromatic diisocyanates from the not fully cured adhesive layer of a laminate in contact with moisture present in the food.

As long as monomeric aromatic diisocyanates are present in the polyurethane adhesive, migration through the film separating the not fully cured adhesive from the food can happen and PAAs will be formed. Consequently, the adhesive user has to be made aware of the potential formation of PAAs.

Current legal restriction for PAAs in food contact materials

Due to the toxicological concerns about PAAs (some of them are carcinogens, while others are suspected carcinogens), legislators worldwide defined restrictions for these substances a long time ago. In Europe, the Federal Institute for Risk Assessment (BfR, Germany) has published several documents on this topic. The precursor of the Plastics Regulation, the Plastics Directive 2002/72/EC, already contained restrictions for PAAs. Currently, Annex II to the Plastics Regulation (EU) No.10/2011 states that primary aromatic amines which are not listed in the Union List 'shall not migrate or shall not otherwise be released from plastic materials and articles into food or food simulant'.

In Regulation (EU) 2020/1245 the Commission takes into consideration the experience of the EURL-FCM[1] that analytical equipment is now commonly available which allows the detection limit of individual PAAs to be lowered from 0.01 mg/kg to 0.002 mg/kg food or food simulant. Consequently, the Regulation requires the use of analytical equipment with a limit of detection of 0.002 mg/kg for each PAA listed in entry 43 to Appendix 8 of Annex XVII to Regulation (EC) No.1907/2006 (REACH) – see the listing at the end of this document.

'For PAAs not listed in entry 43 to Appendix 8 of Annex XVII to Regulation (EC) No 1907/2006, but for which no specific migration limit is specified in Annex I, compliance with Article 3 of Regulation (EC) No 1935/2004 shall be verified in accordance with Article 19. The sum of those PAAs shall however not exceed 0.01 mg/kg in food or food simulant'.

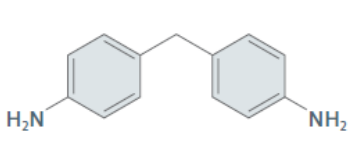
Typical PAAs occurring if polyurethane adhesives for food contact applications have not been fully cured

Polyurethane adhesives containing aromatic diisocyanates are typically based on methylene diphenyl diisocyanate (MDI) and/or toluene diisocyanate (TDI). Both substances may contain different possible isomers. The most widely used is MDI is 4,4'-MDI. This diisocyanate can contain 2,4'-MDI and lower amounts of 2,2'-MDI as isomers. Looking at the TDI isomers, 2,4-TDI as well as 2,6-TDI are commercially important. Four of the five mentioned aromatic diisocyanates are listed in the Union List of the Plastics Regulation:

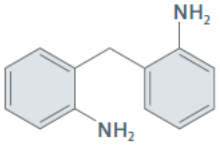
FCM 198: diphenylmethane-4,4'-diisocyanate (CAS No.101-68-8)
FCM 490: diphenylmethane-2,4'-diisocyanate (CAS No.5873-54-1)
FCM 354: 2,4-toluene diisocyanate (CAS No.584-84-9)
FCM 167: 2,6-toluene diisocyanate (CAS No.91-08-7)

Each of these has the restriction of SML[2] (T) = not detectable and the QMA[3] of 1 mg NCO/kg in the final product.

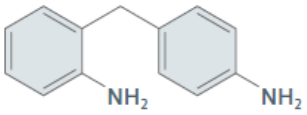
When using a polyurethane adhesive with aromatic diisocyanates, the user has to take into consideration the following possible five PAAs:



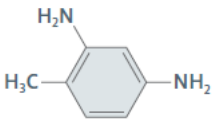
Methylenediphenyl-4,4'-diamine



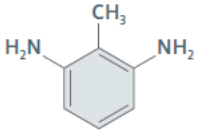
Methylenediphenyl-2,2'-diamine



Methylenediphenyl-2,4'-diamine



2,4-Diaminotoluene



2,6-Diaminotoluene

[1] European Union Reference Laboratory for Food Contact Materials (EURL-FCM)
[2] Specific Migration Limit
[3] Residual content per food contact surface area

According to the 15th amendment of the Plastics Regulation, Regulation (EU) 2020/1245, the user of the adhesive has to prove that the quantity migrating into food is below the detection limit of 0.002 mg/kg food for each of the PAAs listed in entry 43 of Annex XVII of REACH. 2,2'-MDA; 2,4' MDA and 2,6 TDA are not listed in entry 43 Appendix 8 of REACH Annex XVII, and consequently they would fall under risk assessment following Article 19 of Regulation (EU) No.10/2011.

Change in analytical method to prove compliance for PAAs in polyurethane adhesives for food contact applications

Previously, a photometric sum method was sufficient to prove compliance with legislation. In this method, the calibration function and the detection limit of 0.002 mg/kg food simulant were established using the external reference substance aniline hydrochloride as a defined primary aromatic amine.[4]

Both the diluted reference solutions with a defined aniline hydrochloride content as well as the migration solutions with unknown PAAs content – the latter obtained via migration of the packaging material – are derivatised via their amine moiety (so-called azo coupling), the result being dyes with absorption maxima to be evaluated at 550 nm.

Afterwards, enrichment of dyes from reference and migration solutions is performed via solid phase extraction. The resulting measurement solutions can easily be analysed and evaluated using standard photometer equipment. Due to the principle of the applied calibration, the detected amount of PAAs is indicated in aniline hydrochloride equivalents.

Because this method is not sensitive enough, it is no longer recommended:

- PAAs have to be evaluated specifically, not as a sum of PAAs. For that purpose, separation techniques (e.g. chromatographic techniques) need to be applied.
- Each PAA has to be quantified using the respective PAA as a reference substance. Expression of test results as aniline hydrochloride equivalents are no longer recommended under Regulation (EU) 2020/1245.

The photometric method might not be sensitive enough for the reliable evaluation of the 0.002 mg/kg limit. One of the reasons for that can be primarily explained due to the deterioration of blank value measurements: matrix compounds in the migration solution contribute to unspecific absorption, so that small differences in PAA content cannot be identified. In addition the different response factors of the dyes formed by aniline and the other PAAs influence the result. A modified version of this method can be used if you have only one diisocyanate isomer in your migration solution and you do the calibration with the corresponding primary aromatic amine. For the sensitive and specific analysis of primary aromatic amines, several methods have already been published. Partly, they cover PAA isomers from polyurethane-based adhesives. Analytical laboratories are capable of adapting these methods, proving their suitability by adequate method validation.

The basic principle of most of the methods is the liquid chromatographic separation of the PAAs in the migration solution via high-performance liquid chromatography (HPLC), followed by detection of the separated PAAs via mass spectrometry (MS) or diode array detectors (DAD) In contrast to the photometric method. Derivatisation of the migration solution is not needed; however, a

[4] The detection limit of 0.002 mg/kg food or simulant is laid down in method 00.00 6 LFGB (Germany).

concentration step, e.g. via solid phase extraction, can still be a helpful option to establish the required limit of detection.

MS detectors offer high sensitivity and specificity but are more complex to operate and more expensive to purchase. DAD detectors (using the UV absorption of the aromatic moiety) are cheaper to purchase and more robust to operate; however, sensitivity is lower so that PAA enrichment from migration solutions before performing HPLC-DAD analysis is mandatory (similar to enrichment of the dyes in the photometric method).

The following publications can serve as guidance:

- C. Simoneau ed., Technical guidelines on testing the migration of primary aromatic amines from polyamide kitchenware and of formaldehyde from melamine kitchenware, JRC 64903, EUR 24815 EN 2011
- M. Aznar, E. Canellas, C. Nerín, Quantitative determination of 22 primary aromatic amines by cation-exchange solid-phase extraction and liquid chromatography–mass spectrometry, Journal of Chromatography A, 1216 (2009) 5176–5181
- S.K. Mortensen, X. Thorsager Trier, A. Foverskov, J.H. Petersen, Specific determination of 20 primary aromatic amines in aqueous food simulants by liquid chromatography–electrospray ionization-tandem mass spectrometry, Journal of Chromatography A, 1091 (2005) 40–50

FEICA recommendation to downstream users

Considering the limits for PAAs in Regulation (EU) 2020/1245, FEICA makes the following recommendations to adhesive users:

- When using polyurethane adhesives with aromatic diisocyanates, contact your adhesive supplier and ask which possible PAAs might be formed. Also contact the supplier of the other materials used in packaging (e.g. ink producers) to determine whether other components are present which might possibly form or contain PAAs. Collect a list of all PAAs which might be present in the final packaging.
- Provide all information about possible PAAs to the laboratory that has to verify compliance of the final packaging according to the limits in the legislation

As previously explained, analytical methods can exclude migration only up to their limit of detection. For the purpose of compliance verification, and to ensure legal certainty, the migration of PAAs into food has been restricted to a specified level that is not detectable in the food or food simulant by means of commonly used analytical methods. However, according to the EURL-FCM, advances in analytical capabilities ensure that equipment is now commonly available that allows lowering the detection limit of 0.01 mg/kg food or food simulant that the Regulation presently assigns to the detection of individual PAAs to a new detection limit of 0.002 mg/kg food or food simulant. Therefore that lower detection limit should be defined in the Regulation as the detection limit for individual PAAs.

Following these considerations, FEICA recommends using the detection limit of 0.002 mg/kg food for any PAA either listed or not listed in Annex XVII to Regulation No 1907/2006 as well. Therefore please:

- Check that the migration does not exceed the specific detection limit of 0.002 mg/kg for each individual (listed and non-listed) PAA
- Check that the migration does not exceed the sum of 0.01 mg/kg for the sum of listed and non-listed PAAs
- Use analytical methods that can reach the detection limit of 0.002 mg/kg, examples of these methods being LC-MS/MS or SPE- LC/UV

Annex 1 – Appendix 8 of the Regulation (EC) No 1907/2006 (REACH) Annex XVII

Entry 43 — Azo colourants — List of aromatic amines

	CAS No	Index No	EC No	Substances
1.	92-67-1	612-072-00-6	202-177-1	biphenyl-4-ylamine 4-aminobiphenyl xenylamine
2.	92-87-5	612-042-00-2	202-199-1	benzidine
3.	95-69-2		202-441-6	4-chloro-o-toluidine
4.	91-59-8	612-022-00-3	202-080-4	2-naphthylamine
5.	97-56-3	611-006-00-3	202-591-2	o-aminoazotoluene 4-amino-2',3-dimethylazobenzene 4-o-tolylazo-o-toluidine
6.	99-55-8		202-765-8	5-nitro-o-toluidine
7.	106-47-8	612-137-00-9	203-401-0	4-chloroaniline
8.	615-05-4		210-406-1	4-methoxy-m-phenylenediamine
9.	101-77-9	612-051-00-1	202-974-4	4,4'-methylenedianiline 4,4'-diaminodiphenylmethane
10.	91-94-1	612-068-00-4	202-109-0	3,3'-dichlorobenzidine 3,3'-dichlorobiphenyl-4,4'-ylenediamine
11.	119-90-4	612-036-00-X	204-355-4	3,3'-dimethoxybenzidine o-dianisidine
12.	119-93-7	612-041-00-7	204-358-0	3,3'-dimethylbenzidine 4,4'-bi-o-toluidine
13.	838-88-0	612-085-00-7	212-658-8	4,4'-methylenedi-o-toluidine
14.	120-71-8		204-419-1	6-methoxy-m-toluidine p-cresidine
15.	101-14-4	612-078-00-9	202-918-9	4,4'-methylene-bis-(2-chloro-aniline) 2,2'-dichloro-4,4'-methylene-dianiline
16.	101-80-4		202-977-0	4,4'-oxydianiline
17.	139-65-1		205-370-9	4,4'-thiodianiline
18.	95-53-4	612-091-00-X	202-429-0	o-toluidine 2-aminotoluene
19.	95-80-7	612-099-00-3	202-453-1	4-methyl-m-phenylenediamine
20.	137-17-7		205-282-0	2,4,5-trimethylaniline
21.	90-04-0	612-035-00-4	201-963-1	o-anisidine 2-methoxyaniline
22.	60-09-3	611-008-00-4	200-453-6	4-amino azobenzene

Contact

FEICA Regulatory Affairs:
Jana Cohrs (j.cohrs@feica.eu)

FEICA is registered in the **EU Transparency Register** with ID No. **51642763262-89**

FEICA - Association of the European Adhesive & Sealant Industry
Rue Belliard 40 box 10, 1040 Brussels, Belgium
Tel: +32 (0)2 896 96 00
info@feica.eu | www.feica.eu

Publication ref.: POP-EX-L03-021