FPE Guideline on Use of Isocyanate-based Polyurethane Adhesives in Packaging Laminates (Issue 2.7)

1.0 Introduction and Scope

Flexible packaging materials used for foodstuffs frequently consist of multi-layer structures. Such materials may utilise isocyanate-based polyurethane adhesives to bond together different functional layers to give a high performance specification.

These isocyanate-based adhesives use either aromatic (e.g. MDI, TDI) or aliphatic (e.g. IPDI, HDI) systems. It has to be underlined that only the aromatic isocyanates lead to the potential formation of primary aromatic amines which are of potential toxicological concern.

The levels of isocyanates and primary aromatic amines are time dependent. They will be present in newly applied adhesive but will disappear when the adhesive is fully cured under controlled conditions. This is a fundamental aspect of their chemistry which is in contrast to other migrants of packaging which – once present in the packaging material – generally remain a potential source of migration.

The aim of this document is to provide FPE members and their customers with information on why laminates made with isocyanate-based polyurethane adhesives require a curing time prior to food contact, thus maintaining the safety and quality of the packaged food. It provides an overview of the relevant EU and US legislation, an outline of the basic chemistry and use of isocyanate- based adhesives, and it provides simple guidance that all users of such materials should follow.

Note that this document only deals with consumer safety aspects. It does not address any issues relating to the handling and use of such adhesives and safety in the workplace.

2.0 Legislative background

2.1 Regulatory status: Europe
Commission Regulation (EU) No. 10/2011, as subsequently amended[1], states in Annex II 2:
"Primary aromatic amines which are not listed in Table 1 of Annex I shall not migrate or shall not otherwise be released from plastic materials and articles into food or food simulant in accordance with Article 11(4). The detection limit referred to in the second subparagraph of Article 11(4) applies to the sum of primary aromatic amines released.".

[1] A consolidated version of the Plastics Regulation 10/2011, including all amendments to September 2016, is available at: http://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:02011R0010-20160914&from=EN

The text in the second subparagraph of Article 11(4) reads *"… unless specific detection limits have been set for particular substances or groups of substances, a detection limit of 0,01 mg/kg shall apply."*
Isocyanates are listed in Annex I of the Regulation and are subject both to a specific QM of 1 mg/kg and a group SML(T) of non-detectable.

2.2 Regulatory status: United States of America
The US Food and Drug Administration (FDA) has specified within the Code of Federal Regulation (CFR)[2] the circumstances under which adhesives may be safely used in food packaging materials and the substances that may be used[3]:

2.2.1 The adhesive is either separated from the food by a functional barrier, which serves as a non-permeable obstacle to migration or used subject to the following additional limitations:

2.2.1.1 *For dry foods*, the quantity of adhesive that contacts packaged dry food shall not exceed the limits of good manufacturing practice (GMP).

2.2.1.2 *For aqueous and fatty foods*, where the risk of migration is greatest, FDA has specified that contacts shall not exceed trace amount at the seams and at the edge exposure between packaging laminates that may occur within the limits of GMP.

2.2.2 Packaging seams or laminates must remain firmly bonded without visible separation under normal conditions of use.

FDA has also specified, within the CFR, requirements for migration of isocyanates or diisocyanates from laminate materials at high temperature[4, 5]. This reflects the potential degradation of such adhesives at high temperature and the fact that plastic laminates may not serve as a functional barrier to substances such as isocyanates or aromatic amines at high temperature.

3.0 Chemistry

3.1 Curing Process.
Isocyanate based adhesives typically consist of two pre-polymeric components (diisocyanate and diol) which, when mixed, react and cure to form a stable polyurethane polymer layer, capable of bonding together plastics films, paper, foil, metallised films and other materials. As with most chemical reactions, the rate of cure is dependent on time and temperature.

When the adhesive is fully cured, the isocyanate has completely reacted and the laminate is safe to use. The actual chemistry of adhesive reactions is complex. This paragraph just concentrates

[2] The Electronic Code of Federal Regulations (e-CFR) is a currently updated, but not an official legal, version of the CFR. It can be accessed at http://162.140.57.127/cgi-bin/ECFR?page=browse
[3] Code of Federal Regulation (CFR): Title 21- Food and Drugs; Chapter 1- Food and Drugs Administration, Department of Health and Human Services. Part 175 – Indirect food additives: Adhesives and components of coatings
[4] Code of Federal Regulation (CFR): Title 21- Food and Drugs; Chapter 1- Food and Drugs Administration, Department of Health and Human Services. Part 177 – laminate structure for use at temperatures of 250°F and above
[5] Code of Federal Regulation (CFR): Title 21- Food and Drugs; Chapter 1- Food and Drugs Administration, Department of Health and Human Services. Part 177 – laminate structure for use at temperatures between 120°F and 250°F:

on the potential formation of primary aromatic amines. Reactions also occur between the (aromatic) diisocyanate and water to form (primary aromatic) amines. During a normal cure, these amines will react further with more isocyanate and will be incorporated into the adhesive structure. However, if the laminate is brought into contact with food before curing is complete, both unreacted isocyanates and such amines may migrate into the packed food product to form additional amounts of (aromatic) amines. Detection of these PAAs in the food would be of toxicological concern.

Migration of these substances is dependent on the packaging specification being used and on the foodstuff being packed. A dry foodstuff will extract less than will a liquid, acidic food.

As a GMP measure it is necessary to make sure that the curing starts right after the lamination process – at temperature conditions described in the TDS. If the temperature is too cool, the curing will not take place leaving isocyanates and (primary aromatic) amines in the material, which pose a risk for migration. This step is irreversible. Curing will not take place later/ anymore, even at higher temperatures.

3.2 High Temperature Applications
A fully cured adhesive is stable under normal conditions of use. However, at elevated temperatures, e.g. as used for retorting packages, thermal degradation can occur. If the adhesive is based on an aromatic isocyanate, monomeric isocyanates can be generated and potentially migrate into the food forming PAAs. Such migration can be prevented by the use of a functional barrier. Alternatively, aliphatic based adhesives can be used which do not generate PAAs.

4.0 Due diligence

4.1 The flexible packaging industry has studied the subject of primary aromatic amine migration.
Curing conditions may vary according to the adhesive type, weight used, humidity, curing temperature and laminate make up. The adhesive supplier will define some basic parameters such as application temperature, mix ratio and curing time. On the basis of such information, converters will develop the precise processing and curing (time and temperature) conditions required for their individual products so as to ensure that the limits as defined in Regulation 10/2011 Annex I and II for primary aromatic amines and isocyanates are not exceeded.

In the following table, some representative examples are given for solvent-based and solvent-free adhesive systems:

	Application temp.	***Curing temp.***	***Curing time***
Adhesive 1	***Room temperature***	***40 °C***	***5 d***
Adhesive 2	***Room temperature***	***40 °C***	***10 d***
Adhesive 3	***40 °C***	***Room temperature***	***7 d***
Adhesive 4	***Room temperature***	***Room temperature***	***3 d***

By increasing the curing temperature for example it is possible to decrease the curing time dramatically. The curing time will increase with the weight of adhesive used. Very low humidity (e.g. in winter) increases the curing time.

If a packaging supplier reduces the curing times defined by the adhesive supplier, he has to justify the shorter curing time. This justification may be based on calculations / estimations, based on earlier practical measurements. Best practice is to do a control measurement on the laminate. Currently the most practical method for doing that is the acknowledged "BfR colorimetric test"[6] which currently is the only practical test available and suitable as a screening/ quality control technique. This method can demonstrate that PAA levels comply with the 10 ppb ND level specified in Regulation 10/2011. More sophisticated methods, such as HPLC, are available in specialized laboratories and must be used if it is not possible to demonstrate compliance using the BfR method.

4.2 Where laminate materials are imported from outside the EU, the packer/filler should ensure that the packaging supplier understands the issue.

4.3 Supplier GMP should include a process control procedure which manages coating weight and component mixing ratio with alarms in case of deviation from the set-point. Quality systems must ensure that significant changes to the adhesive curing time are communicated down the value chain.

4.4 The packer/filler has to remain vigilant with regard to quality problems of the laminate (odour, tackiness, failing heat seal etc.) possibly caused by the adhesive but should be aware that there is no straight-forward relationship between such quality problems and the issue of primary aromatic amines.

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[6] Amtliche Sammlung von Untersuchungsverfahren nach § 64 LFGB, Buchst. L. Nr. 00.00-6: "Untersuchung von Lebensmitteln - Bestimmung von primären aromatischen Aminen in wässrigen Prüflebensmitteln"