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Artikel: Identification of migrants from coatings of food cans and tubes : reaction products of bisphenol-A-diglycidyl ether (BADGE) with phenols and solvents

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Identification of Migrants from Coatings of Food Cans and Tubes: Reaction Products of Bisphenol-A-Diglycidyl Ether (BADGE) with Phenols and Solvents

Key words: Canned foods, Epoxy polymers, Can coatings, Bisphenol-A-diglycidyl ether (BADGE)

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Introduction

Internal coatings of food cans rather frequently released unacceptably high quantities of Bisphenol-A-diglycidyl ether (BADGE) into fat-containing foods (1). In Switzerland, this problem has largely been solved by strict control (2). Often, however, BADGE is merely a minor component in a highly complex mixture of migrants (3). Apparently little is known about the identity and safety of the latter.

A recent paper (4) reported a method for the estimation of the total amount of migrants with a bisphenol type structure to be expected in fatty or oily foods, restricting the analysis to components with a molecular weight below 1000 D, i.e. with a potential physiological effect. It is based on the following three principals. Firstly, the bisphenolic materials involved have similar response in Fluorescence Detection (FD) as Bisphenol A, BADGE or Bisphenol-F-diglycidyl ether (BFDGE). Hence, FD can be used for selective analysis of the phenolics. Secondly, migrates with a molecular weight below 1000 D are separated from higher molecular weight materials by Size Exclusion Chromatography (SEC). Finally, extraction of coatings with acetonitrile during 24 h at 25 °C well simulates fat and oil as long as only compounds with a molecular weight below 1000 D are considered.

SEC-FD analysis indicates the total amount of the material which needs to be characterized and toxicologically evaluated before can coatings can be considered as safe for food packaging. Amounts of fluorescent migrants below 1000 D released

from 13 unused cans and a tube coated by epoxy lacquers varied between 0.5 and 5 mg/dm^2. Calculated as concentrations in the packed foods (typical 100–300 g can of fish in oil, meat or sauces), this corresponds to about 5–75 mg/kg. Eating the content of one can of sardines or tuna, 1–10 mg of such migrants are ingested.

Characterization and identification of the migrants may well turn out to be a demanding and time-consuming issue. At the high temperatures used for curing the coatings, reactive chemicals used as starting point materials are converted into a large number of new compounds. Impurities may render the mixture even more complex.

This paper reports the identification of components other than the starting point materials, such as BADGE, its oligomers (4), the epoxy Novolaks (5, 6), and the reaction products of these with hydrochloric acid and water (7). The analysis was restricted to epoxy coatings and compounds accessible by GC-MS.

Experimental

Extraction of cans

Can coatings were extracted with acetonitrile during 24 h at 25 °C. Cans were opened to slightly less than half. The contents were removed and the cans washed with water. After drying, they were rinsed with pentane in order to eliminate fat or oil and filled to half with acetonitrile (HPLC, Mächler, Reinach, Switzerland). They were positioned on their side wall, such that the solvent was in contact with half of the bottom, side and lid. 10 µl of acetonitrile extract were injected into SEC.

Re-extraction for NPLC

For NPLC, a partitioning procedure was applied to transfer the extract into a solvent suitable for NPLC, but also to eliminate the bulk of the large molecular weight components (causing memory effects in NPLC). In a 20 ml measuring flask, 1 ml of extract was diluted with 18 ml of water and extracted with 1 ml of 15% dichloromethane/heptane. From most can extracts, substantial amounts of material precipitated.

Size Exclusion Chromatography (SEC)

As described in (4), two 250 × 7 mm i.d. SEC columns from Chrompack (Middelburg, The Netherlands) were coupled in series: one packed with Microgel-5 100 Å, the other with Microgel-5 50 Å. A Phoenix SFC syringe pump (CE Instruments, Milan, Italy) delivered tetrahydrofurane (THF, Fluka, for UV spec-

troscopy) at 400 µl/min. The fluorescence detector (FD) from Merck/Hitachi (F1000) was used at 275/325 nm.

Normal Phase HPLC (NPLC)

NPLC was performed on a 25 cm x 2 mm i.d. column packed with Gromsil 100 CN 2 PR 5 µm (Stagroma, Wallisellen, Switzerland). A gradient (400 µl/min) was used with 2% 1-propanol/pentane in pump A and 50% 1-propanol/methyl tert.-butyl ether (MTBE) in pump B, programming as follows: pump A, 7 min, then 1%/min pump B up to 10%, 3%/min pump B up to 22% and 5% pump B up to 60% (3 min). The injection volume was 80 µl; fluorescence was detected at 225/295 nm. Quantitative determinations were based on the external standard method using BADGE for calibration. Equal response was assumed for all components, as justified previously (4).

GC-MS

An UltraTrace gas chromatograph, equipped with an autosampler for large volume on-column injection (250 µl syringe) and a vapor exit, was coupled to a quadrupole mass spectrometer MD-800 working in the EI mode (all C.E. Instruments). Separation involved an 8 m × 0.25 mm i.d. capillary column coated in the laboratory with an 0.2 µm film of PS-255, a dimethyl polysiloxane (Fluka).

On-column injection was applied because the high molecular weight epoxides hardly survived vaporization in a hot injector. Large volumes (100–150 µl) were introduced in order to obtain sufficient sensitivity for GC-MS of SEC or LC fractions.

Injection conditions were selected to result in fully concurrent solvent evaporation (8). During solvent evaporation, the oven temperature of 80 °C substantially exceeded the dew point of the solvent/carrier gas mixture at the inlet pressure in order to result in a short flooded zone (determined by the cooling resulting from solvent evaporation (9)). This enabled to do without an uncoated precolumn, since flooded zones of up to 10–30 cm length can be tolerated (10). Uncoated precolumns caused problems concerning adsorption of the more active components.

Samples were injected into a 1.5 m × 0.53 mm i.d. retaining precolumn coated with an 0.15 µm film of OV-1701-OH (Fluka). The latter was connected to a T-piece leading to the early vapor outlet (consisting of 0.53 mm i.d. fused silica capillary tubing) and the separation column. During solvent evaporation, the inlet pressure was 30 kPa, before injection resulting in a gas (helium) flow rate of 100 ml/min through the exit. After closure of the vapor exit, pressure was increased to 80 kPa.

The injection rate by the autosampler was 1 µl/s. It was chosen that low in order to enable injection of samples in all the solvents used for the previous steps, including (as a worst case) 1-propanol. 1-propanol was left after reconcentration of LC-fractions collected at elevated retention time, i.e. with an elevated proportion

of 1-propanol in the mobile phase. The vapor exit was closed 2 min after starting injection. 1.5 min later, the column temperature was programmed at 15 °/min to 350 °C (10 min, removing triglycerides).

Acylation

Standards, extracts, or LC-fractions were acylated in order to obtain structural information (11). In a first step, acetylation was conducted under conditions derivatizing hydroxy and phenol functions, but leaving epoxy groups unaffected. From extracts or LC-fractions, the solvent was evaporated. 50 µl each of pyridine and acetic anhydride were added and the mixture kept at ambient temperature for 5 min. Then the reagent was removed by a stream of nitrogen.

In a second step, trifluoroacetylation was performed for the determination of epoxy groups. Reaction with trifluoroacetic anhydride (TFAA) opens epoxides and forms bis-trifluoroacetates. To the usually acetylated and dried sample, 50–100 µl of TFAA were added and the sample allowed to react during 15 min at ambient temperature. Then TFAA was removed on a heating plate at 40 °C. Direct trifluoroacetylation provided the sum of hydroxy and epoxy groups.

Experimental reactions

BADGE was reacted with phenols and solvents (alcohols, glycol ethers) in order to obtain retention time and MS data. Reactions were neither complete nor were the products purified.

1 g of BADGE (Araldit GY 250, Ciba, Basle, Switzerland), 9 ml of alcohol (or 2 ml each of four different solvents) and 1–3 drops or 50–70 mg of phosphoric acid were mixed and heated to 60–100 °C for 1–3 h. Reaction mixtures were diluted in THF, then in the mobile phase. They contained BADGE having reacted with one or two moles of solvent as well as some residual BADGE and unidentified substances.

10 mg of BADGE was refluxed (180 °C) with 1 g of a phenol (Phe) for 1 h without using a catalyst. The product contained mono-reaction product with phenol (BADGE.Phe) and completely reacted BADGE (BADGE.2Phe) beside little unreacted BADGE and some unidentified components.

1 g of BADGE was mixed with 200 mg of tert. butylphenol (tBuPhe), 9 ml of butoxyethanol (BuEtOH) and 3 drops of tributylamine. The mixture was refluxed (175 °C) for 3 h and then contained all reaction products of BADGE with tBuPhe and BuEtOH to be expected, including BADGE derivatized with one mole each of tBuPhe and BuEtOH (BADGE.tBuPhe.BuEtOH).

Results

Reaction products with phenols

Reaction products of BADGE with phenol are introduced into the coating through the epoxy resins. In Bisphenol A, phenol may be present as an unreacted raw material. When added to BADGE for the formation of a prepolymer, the so-called «advancement» of the epoxy resin, it reacts with the epoxy group. Phenol may also be added to the reaction mixture of BADGE and Bisphenol A for stopping the polymerization reaction. In particular, it helps preventing excessive chain elongation (gelation) by blocking a glycidyl group («chain stoppers»). It seems, however, that tert.-butylphenol (tBuPhe) is more commonly used for this purpose than phenol.

Mass spectrum of the mono-reaction product

Figure 1 shows the structure and the mass spectrum of BADGE having reacted with one mole of phenol (BADGE.Phe). It is considered as an example for all the many mono-reaction products identified (of which the data is reported below in tabulated form), since the fragmentation follows the same pathway.

In a first step, the molecular ion loses a methyl group from the bisphenol. This usually results in the base peak, in this instance at m/z 419, from which further fragmentation occurs. Loss of the complete substituents of the bisphenol provides important first information. The ion m/z 269 represents the Bisphenol-A-mono-glycidyl ether (BAMGE) after loss of the methyl group and results from cleavage of the derivatized glycidyl group. Important presence of m/z 269 is, in fact, indicative for BADGE mono-reaction products. The loss of 150 mass units corresponds to the sum of the glycidyl group and the substituent, 56 and 94 mass units, respectively, 94 mass units indicating phenol.

Loss of the other side chain, the glycidyl group, formed m/z 363. Removal of both reduces the molecule to the Bisphenol-A structure deprived of a methyl group (m/z 213) and is another characteristic signal. The difference in mass again corresponds to the 150 units of the substituted glycidyl group. The signal at m/z 325, observed in many spectra of BADGE mono-reaction products, stems from the elimination of phenol and restoration of the epoxide (it is the base peak in the spectrum of BADGE).

A fragment with m/z 191 is observed in most spectra and results from cleavage of the molecule in the center (see fig. 1). After loss of the glycidyl group, it is converted to m/z 135, which is another characteristic fragment of BADGE derivatives.

Normal versus abnormal product

As shown in figure 2 for BADGE.tBuPhe, the addition of a hydroxyl to the epoxy group may result in the normal (position 3 of the glycidyl group) or the abnormal reaction product (position 2). In extracts of can coatings as well as in

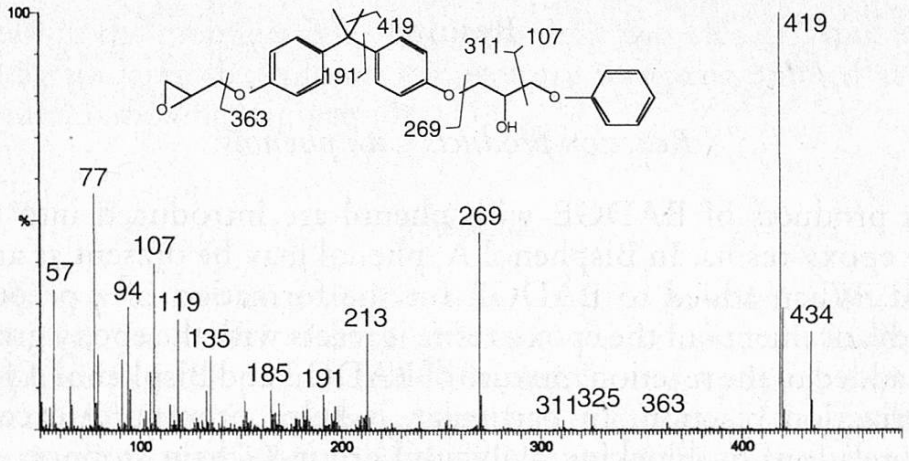

Fig. 1. Reaction product of BADGE with phenol (BADGE.Phe) and its mass spectrum

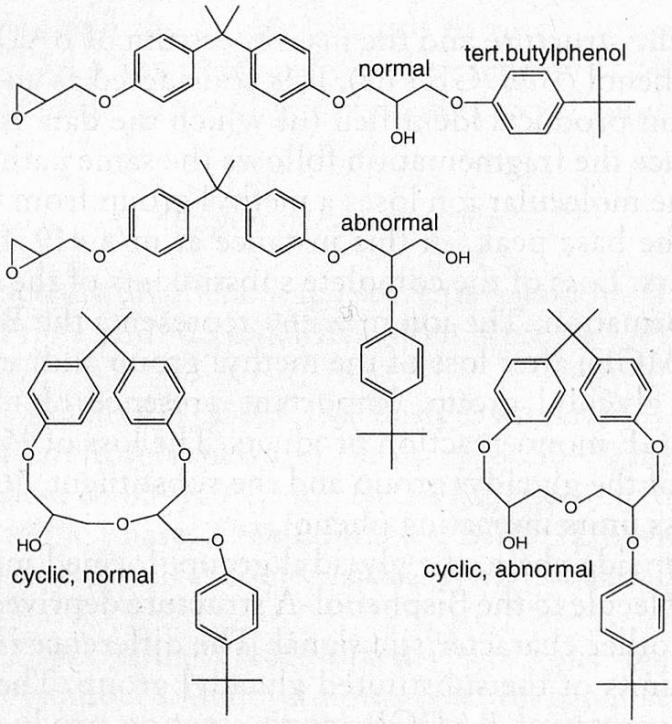

Fig. 2. Possible reaction products of tert. butylphenol with BADGE

products of experimental reactions, LC and GC-MS only showed one peak for BADGE.Phe or BADGE.tBuPhe. Since chromatography tends to well distinguish between primary and secondary alcohols, it is probable that only one product is formed. Presence of m/z 107 and 311 suggests the normal substitution; in fact, loss of C(3) with an OH group, as to be expected from the abnormal structure, is not observed. A 23% signal for m/z 163 in the mass spectrum of BADGE.tBuPhe (tert.-butylphenol with a methylene unit) confirms the normal product even more clearly.

Cyclic products

BADGE mono-reaction products may form cyclic structures through addition of the hydroxyl group to the epoxy group at the other end of the molecule (see fig. 2). Particularly the cyclic structure of the normal adduct is under considerable molecular strain, however. They have the same molecular mass as the open chain compound. Furthermore, fragmentation turned out to be almost identical: a substantially smaller signal m/z 213 for the cyclic compound seemed to be the only significant difference (table 2).

The two structures were distinguished by acylation experiments. At the bottom of figure 3, two well separated peaks of the GC-(EI)MS chromatogram from a can extract are shown, recorded at m/z 490, the molecular mass of the cyclic (c) and the linear (l) BADGE.tBuPhe. For both components, acetanhydride acetylated one hydroxyl group and caused a small increase in GC retention time (second trace at m/z 532). This conforms with both the open chain and the cyclic structure. Subsequent trifluoroacetylation had no effect on the retention time of the first peak and the molecular mass remained 532 (third chromatogram), suggesting the cyclic structure. The later eluted component, however, added two trifluoroacetyl groups: the retention time decreased and the molecular mass reached 724 (top chromatogram), which is consistent with the presence of one epoxy group, i.e. the open chain derivative.

Direct derivatization with TFAA formed a mono- and a triacylated product, confirming the conclusion that the product eluted earlier from GC is the cyclic, whereas that eluted later has the linear structure. The large signal for m/z 269 in the spectrum of the cyclic BADGE.tBuPhe (table 2) indicates that decomposition in

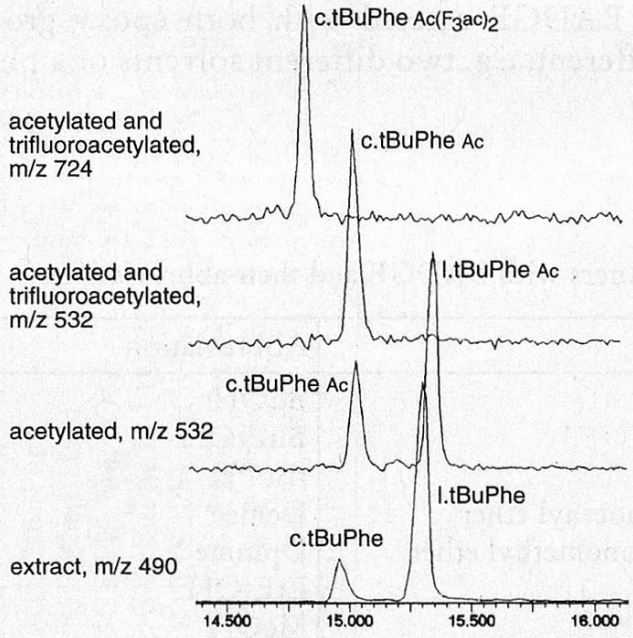

Fig. 3. Acylation experiments distinguishing between the cyclic (c.tBuPhe) and the linear (l.tBuPhe) mono-reaction product of BADGE with tert. butylphenol. GC-(EI)MS chromatograms recorded at the masses indicated

the mass spectrometer occurs through ring opening and restoration of the epoxy group.

Cyclic mono-reaction products of BADGE were observed in a few can and food extracts only, and their concentrations never exceeded 25% of those of the linear compound, presumably because of the molecular strain.

When ring closure to form the abnormal product is disregarded, still two isomers of the cyclic components should be expected, namely with the tBuPhe and the hydroxyl group being in cis or trans to each other. These isomers have not been separated, however.

Summarized spectra of derivatives with phenols

Table 1 lists the phenols and solvents identified in reaction products with BADGE as well as their abbreviations used in the tables to follow.

Table 2 lists the products of the reaction of BADGE with one or two moles of phenols or one phenol and a solvent identified in can coatings. The EI mass spectra are summarized by the predominant mass signals.

Reaction products with solvents

Solvents are added to the coating preparations. Predominantly alcohols or glycol ethers are used, at least partly because this helps to prevent gelation during storage of the ready product. Reaction of BADGE with alcohols is far slower than that with phenols, but alcohols are present in higher concentrations.

Mass spectra of the reaction products of BADGE with one mole of solvent resemble that shown in figure 1 for BADGE.Phe. Coating extracts also contained important peaks of BADGE reacted with both epoxy groups. Often the two substituents were different, e.g. two different solvents or a phenol combined with a solvent.

Table 1. Reaction partners with BADGE and their abbreviations

Compound	Abbreviation
Butanol	BuOH
Butoxyethanol	BuEtOH
tert. Butylphenol	tBuPhe
Diethyleneglycol monoethyl ether	Demee
Dipropyleneglycol monomethyl ether	Dpmme
Ethoxyethanol	EtEtOH
Methanol	MeOH
1-Methoxy-2-propanol	MePrOH
Phenol	Phe
Propanol	PrOH

Table 2. Reaction products of BADGE with phenols and their EI mass spectra (mass, abundance in percent of the base peak in brackets). MM, molecular mass; cy, cyclic compound

	Compound	MM	Mass spectrum
A	BADGE.Phe	434	419, 77 (60), 269 (50), 107 (40), 94 (30), 57 (30), 213 (25), 434 (25), 325 (5)
B	BADGE.2Phe	528	77, 513 (95), 107 (95), 213 (65), 94 (55), 135 (40), 528 (30), 363 (20), 269 (8)
C	BADGE.tBuPhe	490	475, 57 (70), 135 (60), 269 (55), 107 (30), 213 (30), 191 (25), 490 (25), 325 (10)
D	cyBADGE.tBuPhe	490	475, 269 (80), 135 (80), 57 (65), 191 (50), 107 (40), 490 (30), 325 (15), 213 (10)
E	BADGE.2tBuPhe	640	135, 57 (70), 625 (55), 107 (40), 213 (35), 305 (25), 640 (15), 419 (10), 269 (5)
F	BADGE.Phe.BuOH	508	493, 57 (59), 213 (40), 77 (30), 107 (30), 135 (30), 508 (20), 363 (15), 343 (5)
G	BADGE.Phe.MePrOH	524	509, 73 (90), 135 (50), 213 (50), 107 (40), 524 (30), 363 (25), 119 (25), 285 (20)
H	BADGE.tBuPhe.BuEtOH	608	57, 593 (70), 135 (60), 213 (40), 107 (25), 119 (25), 608 (20), 419 (10), 387 (5)
I	BADGE.tBuPhe.BuOH	564	549, 57 (60), 135 (50), 213 (40), 107 (25), 202 (20), 564 (20), 343 (10), 419 (10)
K	BADGE.tBuPhe.MePrOH	580	73, 135 (80), 565 (70), 57 (50), 163 (50), 213 (40), 107 (30), 580 (20), 419 (10)
L	BADGE.tBuPhe.PrOH	550	535, 135 (80), 57 (60), 213 (60), 75 (40), 107 (40), 119 (30), 550 (20), 419 (10)
M	BADGE.tBuPhe.HCl	526	135, 511 (80), 57 (70), 107 (60), 213 (50), 91 (40), 119 (40), 305 (30), 526 (20)
N	BADGE.tBuPhe.MeOH	522	507, 135 (70), 213 (50), 107 (40), 57 (30), 91 (30), 119 (30), 522 (25), 301 (20)

Mass spectrum of a di-reaction product

As an example, figure 4 shows the mass spectrum of BADGE reacted with butanol and 1-methoxy-2-propanol (BADGE.BuOH.MePrOH). Loss of the methyl group in the center of the molecule again produces the base peak m/z 489, from which most fragmentation starts. The signal for m/z 269 is small because it can only be formed by loss of one of the solvents and restoration of the epoxy group. There is a more important signal for m/z 213 from the loss of both side chains.

Presence of butanol is deduced from the molecular mass, as well as from m/z 343, the Bisphenol-A with the butanol-substituted glycidyl group (or loss of the methoxypropanol-substituted glycidyl from m/z 489). Losses of 74 (butanol, m/z 415) and 130 (whole side chain, m/z 359) confirm the interpretation by small signals. m/z 265 corresponds to the frequently large signal m/z 191 in BADGE mono-reaction products and is derived from cleavage in the center of the molecule. m/z 135 represents this fragment after loss of the side chain.

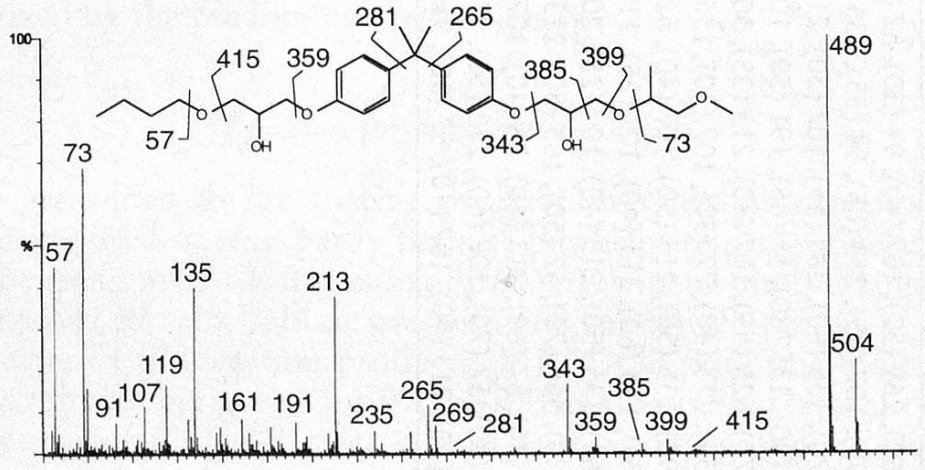

Fig. 4. Mass spectrum of BADGE reacted with butanol and 1-methoxy-2-propanol (BADGE.BuOH.MePrOH)

Summarized spectra of derivatives with solvents

The products of the reaction of BADGE with one or two moles of hydroxylic solvents so far identified in can coatings are listed in table 3 together with the predominant mass signals. The spectra of BADGE.MePrOH, BADGE.2MePrOH, BADGE.EtEtOH and BADGE.2EtEtOH are from products synthesized in the laboratory (although also found in coatings) and show the small difference in fragmentation between the compounds of equal molecular mass. In the derivatives with 1-methoxy-2-propanol, the signals for m/z 73 (methoxypropylen) are larger, suggesting that the spectrum in figure 4 is really from BADGE.BuOH.MePrOH and not from BADGE.BuOH.EtEtOH.

To obtain additional structural information (cyclic or linear molecules), a number of components were acetylated, trifluoroacetylated or both. Spectra are summarized in table 4.

Table 3. Reaction products of BADGE with solvents identified in can coatings and their EI mass spectra

	Compound	MM	Mass spectrum
a	BADGE.Me	372	357, 269 (40), 57 (20), 119 (20), 213 (20), 372 (20), 135 (10), 165 (8), 311 (5)
b	BADGE.PrOH	400	385, 269 (60), 75 (30), 400 (25), 57 (20), 119 (20), 135 (20), 191 (20), 213 (20)
c	BADGE.2PrOH	460	445, 213 (40), 75 (25), 135 (25), 117 (20), 119 (20), 319 (20), 460 (20), 371 (5)
d	BADGE.BuOH	414	399, 57 (90), 269 (50), 75 (20), 119 (20), 213 (20), 414 (20), 135 (15), 191 (15)
e	BADGE.2BuOH	488	473, 57 (95), 213 (35), 75 (30), 135 (30), 119 (20), 343 (15), 488 (15), 385 (5)
f	BADGE.MePrOH	430	415, 269 (70), 73 (70), 191 (50), 430 (30), 135 (20), 213 (15), 325 (5), 311 (5)
g	BADGE.2MePrOH	520	73, 505 (60), 135 (30), 213 (25), 520 (15), 235 (10), 191 (10), 359 (10), 269 (5)
h	BADGE.EtEtOH	430	415, 269 (70), 73 (30), 119 (20), 135 (20), 191 (20), 213 (20), 430 (20), 311 (7)
i	BADGE.2EtEtOH	520	505, 73 (50), 213 (50), 135 (45), 59 (40), 119 (30), 259 (30), 520 (30), 401 (5)
j	BADGE.BuEtOH	458	343, 57 (100), 269 (70), 191 (25), 119 (20), 135 (20), 458 (20), 213 (15), 311 (8)
k	BADGE.2BuEtOH	576	57, 561 (70), 135 (30), 101 (25), 213 (25), 119 (20), 576 (20), 387 (10), 429 (5)
l	BADGE.Demee	474	269, 459 (80), 73 (50), 191 (50), 59 (30), 117 (30), 474 (25), 135 (20), 175 (20)
m	BADGE.BuOH.HCl	450	435, 57 (90), 305 (35), 75 (30), 119 (39), 135 (30), 213 (30), 450 (20), 399 (10)
n	BADGE.PrOH.HCl	436	421, 305 (55), 135 (50), 213 (50), 75 (40), 119 (30), 436 (20), 269 (10), 385 (10)
o	BADGE.PrOH.BuEtOH	518	503, 57 (70), 135 (50), 213 (50), 75 (40), 119 (25), 329 (20), 518 (20), 387 (10)
p	BADGE.BuOH.PrOH	474	459, 57 (40), 213 (40), 75 (30), 135 (30), 119 (20), 474 (20), 329 (10), 343 (10)
q	BADGE.BuOH.MeOH	446	431, 57 (40), 213 (40), 135 (25), 75 (20), 119 (20), 301 (20), 464 (20), 343 (10)
r	BADGE.BuOH.MePrOH	504	489, 135 (40), 213 (40), 57 (30), 73 (25), 75 (25), 119 (20), 505 (20), 343 (10)
s	BADGE.BuOH.Demee	548	533, 57 (40), 135 (40), 213 (40), 73 (35), 119 (20), 343 (20), 548 (20), 403 (5)
t	BADGE.BuOH.Dpmme	562	73, 135 (40), 547 (30), 57 (25), 213 (20), 265 (20), 343 (15), 562 (10), 417 (3)
u	BADGE.MePrOH.MeOH	462	443, 73 (90), 213 (60), 127 (40), 135 (40), 301 (40), 462 (25), 59 (20), 119 (20)
v	BADGE.MePrOH.Demee	464	73, 549 (60), 135 (40), 117 (25), 213 (25), 59 (20), 564 (20), 359 (10), 403 (5)
w	BAMGE	284	269, 57 (40), 59 (40), 72 (20), 119 (20), 213 (20), 284 (20), 85 (15), 153 (10)
x	BAMGE.BuOH	358	213, 343 (90), 57 (40), 135 (30), 119 (25), 75 (20), 358 (20), 91 (10), 107 (10)
y	BAMGE.MePrOH	374	135, 213 (95), 73 (80), 359 (60), 119 (25), 374 (25), 107 (20), 255 (10), 269 (8)
z	BAMGE.Demee	418	213, 135 (60), 73 (50), 403 (50), 119 (40), 59 (25), 117 (25), 418 (20), 269 (10)

Table 4. EI mass spectra of reaction products of BADGE with phenols and solvents after acylation

Acetylated components

Compound	MM	Mass spectrum
BADGE.Phe	476	133, 193 (45), 105 (35), 77 (15), 57 (10), 269 (10), 476 (3), 213 (2), 461 (2)
BADGE.2Phe	612	133, 193 (50), 105 (45), 77 (15), 91 (5), 213 (3), 269 (2), 612 (2), 597 (1)
BADGE.tBuPhe	532	57, 133 (70), 191 (65), 189 (60), 135 (40), 249 (30), 173 (20), 269 (10), 532 (5)
cyBADGE.tBuPhe	532	191, 57 (98), 133 (75), 189 (60), 135 (35), 173 (30), 249 (30), 269 (10), 532 (5)
BADGE.2tBuPhe	724	57, 133 (85), 189 (70), 249 (40), 135 (30), 117 (25), 173 (20), 724 (5), 708 (2)
BADGE.tBuPhe.BuEtOH	692	57, 207 (75), 101 (55), 133 (45), 189 (35), 135 (20), 249 (20), 692 (5), 677 (2)
BADGE.BuEtOH	500	217, 57 (95), 101 (95), 269 (15), 191 (15), 161 (15), 309 (8), 500 (5), 485 (3)
cyBADGE.BuEtOH	500	217, 101 (95), 57 (90), 191 (20), 83 (15), 269 (10), 309 (8), 500 (5), 485 (2)
BADGE.2BuEtOH	660	57, 217 (90), 101 (70), 135 (25), 159 (25), 133 (20), 189 (15), 660 (3), 645 (2)
cyclo-diBA	652	135, 173 (50), 637 (30), 119 (30), 117 (30), 233 (20), 652 (20), 107 (20), 213 (20)

Trifluoroacetylated components

Compound	MM	Mass spectrum
BADGE	760	153, 69 (60), 745 (60), 59 (30), 125 (30), 267 (30), 401 (20), 97 (15), 760 (10)
BADGE.tBuPhe	796	57, 781 (60), 153 (50), 135 (30), 267 (20), 401 (15), 796 (15), 383 (10), 479 (10)
cyBADGE.tBuPhe	586	57, 571 (90), 191 (40), 278 (30), 135 (30), 269 (20), 586 (20), 309 (5), 421 (5)
BADGE.BuEtOH	764	57, 749 (50), 153 (40), 101 (25), 69 (15), 267 (15), 401 (15), 539 (15), 764 (10)
cyBADGE.BuEtOH	554	539, 57 (75), 191 (40), 71 (30), 69 (25), 85 (25), 111 (20), 554 (20), 269 (15)
cyclo-diBA	760	745, 119 (100), 135 (60), 365 (60), 213 (50), 173 (40), 91 (35), 760 (35), 631 (10)

Acetylated, then trifluoroacetylated components

Compound	MM	Mass spectrum
BADGE.Phe	686	133, 193 (50), 105 (35), 153 (15), 69 (10), 77 (10), 59 (5), 267 (5), 686 (1)
BADGE.BuEtOH	710	217, 101 (80), 57 (70), 153 (20), 157 (10), 161 (10), 267 (10), 401 (8), 710 (2)
BADGE.tBuPhe	742	57, 133 (80), 189 (65), 401 (55), 153 (50), 249 (40), 267 (25), 533 (20), 593 (7)

Mixed derivatives

Figure 5 shows the relevant section of a GC-(EI)MS chromatogram that demonstrates the complexity of the mixtures which may result from two compounds reacting with BADGE, i.e. tBuPhe and BuEtOH. From the total ion chromatogram (TIC) at the bottom, a chromatogram with the ions characteristic for these products (MIC) was reconstructed. BADGE.BuEtOH and BADGE.tBuPhe are present in cyclic as well as open chain structure. The three peaks eluted later represent the combinations of the two substituents in doubly reacted BADGE, i.e. BADGE.2tBuPhe, BADGE.2BuEtOH and the mixed BADGE.tBuPhe.BuEtOH.

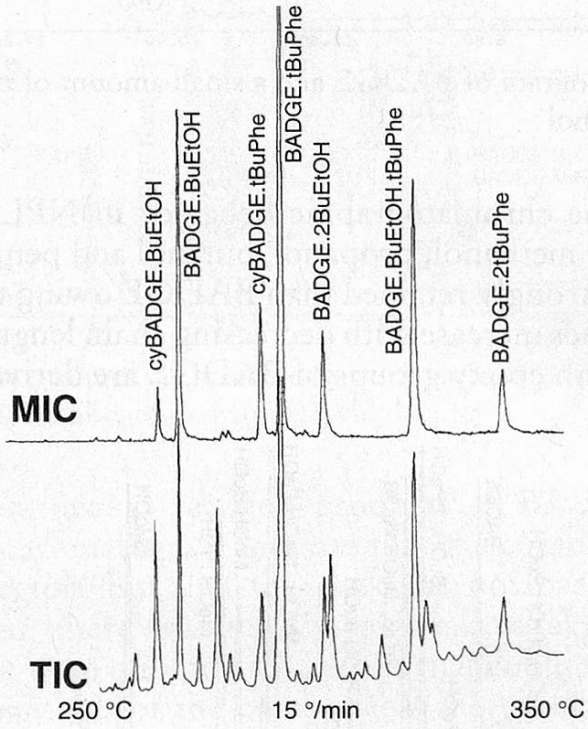

Fig. 5. GC-MS of a can extract: section of a chromatogram shown as total ion chromatogram (TIC) and as multiple ion chromatogram (MIC) from m/z 458, 490, 568, 576, 608, and 640

Experimental reactions

Figure 6 shows an LC-FD chromatogram of experimental reaction products from BADGE and butoxyethanol in presence of phosphoric acid. Reaction mixtures obtained after 2 and 3 h at 90 °C were combined in order to provide a more complete picture of the products. The educts had shown peaks for BADGE (85%) and BADGE-dimer (15%). Since the phosphoric acid contained some humidity, after a short reaction time at 25 °C a peak for the monohydrolysis product of BADGE (BADGE.H2O) appeared in the chromatogram and remained of constant size as reaction proceeded futher. After BADGE.BuEtOH and BADGE.2BuEtOH, numerous other compounds are eluted, the identity of which has not been determined.

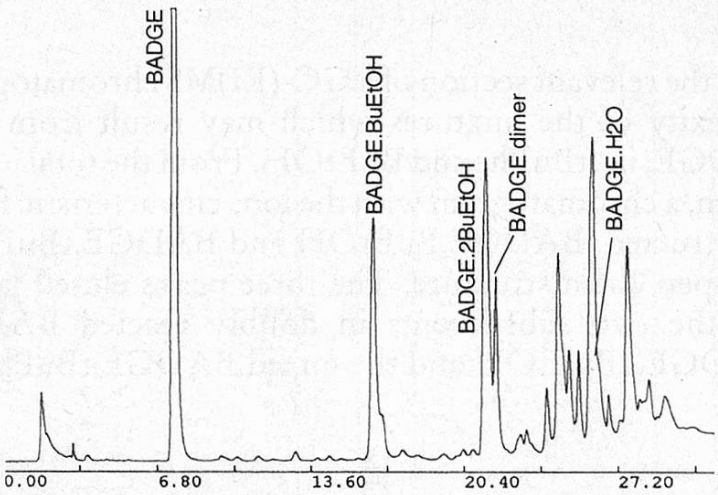

Fig. 6. LC-FD chromatogram of BADGE and a small amount of its dimer partially reacted with butoxyethanol

Figure 7 shows the chromatographic behavior in NPLC of the products of BADGE reacted with methanol, propanol, butanol and pentanol (2 h 100 °C). All derivatives are more strongly retained than BADGE owing to the hydroxyl group formed. Retention times increase with decreasing chain length of the alcohol. They also increase when both epoxy groups of BADGE are derivatized.

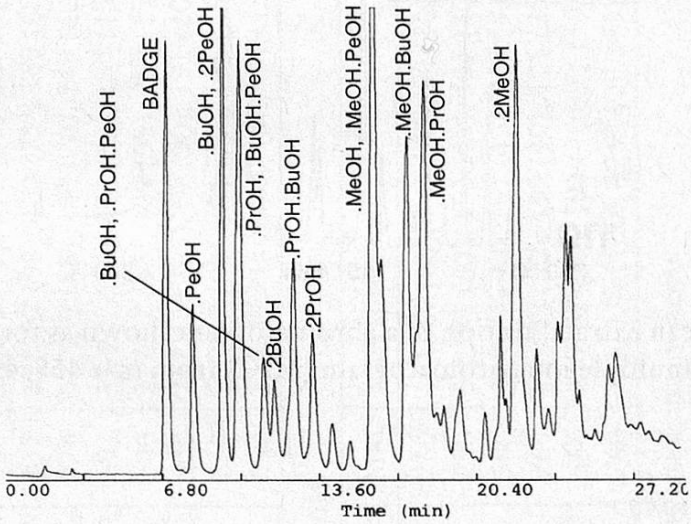

Fig. 7. LC-FD chromatogram of BADGE reacted with a mixture of methanol, propanol, butanol and pentanol

Two examples of can extracts

Figure 8 shows acetonitrile extracts from two cans with epoxy coatings after isolation of the components with less than 1000 D molecular weight through SEC. Single LC peaks or small groups were analyzed by GC-MS. The predominating peak in NPLC-FD corresponds to the cyclo-di(Bisphenol-A-monoglycidyl ether) (cyclo-diBA), as characteristic for all epoxy coatings. Some of the other important

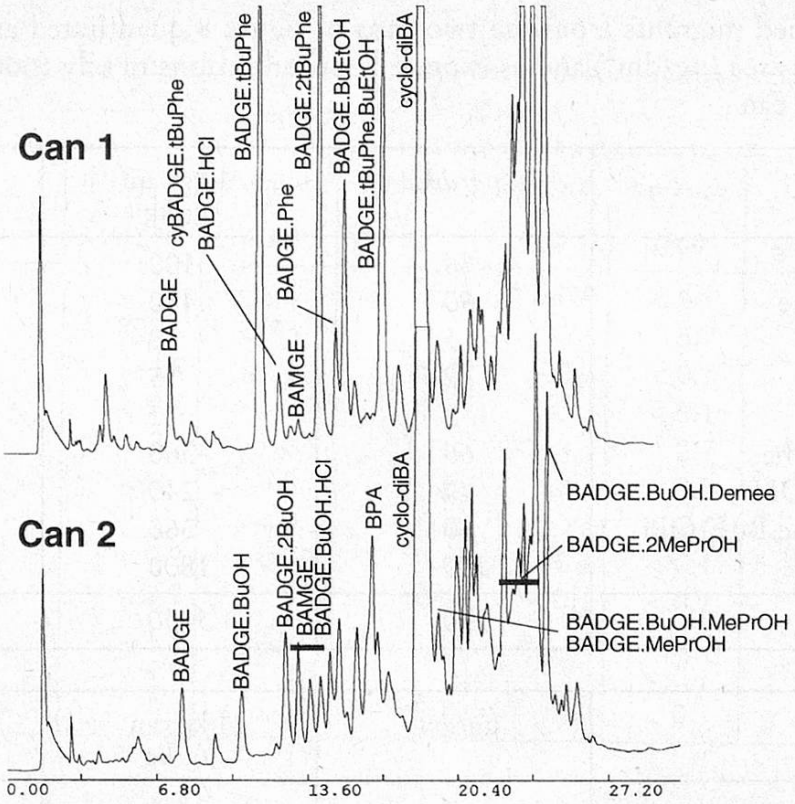

Fig. 8. LC-FD chromatogram of acetonitrile extracts from two unused cans. BPA, Bisphenol-A; BAMGE, Bisphenol-A-Monoglycidyl Ether

peaks have been identified as reaction products of BADGE with solvents or phenols. Bars in the chromatogram indicate that the compound was identified in the corresponding region, but that the peak has not been assigned. Where no identification is given, there was mostly no peak of expected size in the gas chromatogram. There were only few GC peaks that could not be identified.

Table 5 shows quantities of the components migrating from can 1 and can 2 identified in figure 8, as well as the concentrations to be expected in oily foods in a large (1 kg) and a small (30 g) can. Compared to other cans coated by epoxy lacquers, can 1 released a rather large amount of BADGE (about 200 µg/kg in a typical can of tuna in oil of 200 g content), but even more mono-epoxy compounds, such as BADGE.tBuPhe (1 mg/kg) and BADGE.BuEtOH (0.5 mg/kg). Of the 2.8 mg/dm² of migrate with less than 1000 D molecular weight determined by SEC, only 0.57 mg/dm² could be identified (20%), more than half of which was cyclo-diBA.

Can 2 released a more complex mixture of migrants, of which only a small proportion could be identified. Since GC-MS was not sufficiently quantitative, it was not confirmed that the assigned LC peaks predominantly represented the identified substances. For this reason, components eluted after cyclo-diBA were not quantitated. Of the 2.6 mg/dm² of migrate with < 1000 D determined by SEC, approximately 0.35 mg/dm² (13%) was identified. It was not even 2% when disregarding the cyclo-diBA.

Table 5. Identified migrants from the two cans of figure 8 quantitated as release per unit surface area (µg/dm²) and as expected concentrations in oily foods for a large and a small can

Can 1	*µg/dm²*	1 kg can µg/kg	30 g can µg/kg
BADGE	*16*	100	800
BADGE.tBuPhe	*80*	480	4000
BADGE.HCl	*5*	30	250
BAMGE	*2.5*	15	125
BADGE.Phe	*2*	12	100
BADGE.2tBuPhe	*60*	360	3000
BADGE.BuEtOH	*40*	240	2000
BADGE.tBuPhe.BuEtOH	*60*	360	3000
Cyclo-diBA	*300*	1800	15000
Sum	*570*	*3400*	*28000*

Can 2	*µg/dm²*	1 kg can µg/kg	30 g can µg/kg
BADGE	*4*	24	200
BADGE.BuOH	*4*	24	200
BADGE.2BuOH	*5.5*	33	275
BAMGE	*6*	36	300
BADGE.BuOH.HCl	*4*	24	200
Bisphenol A	*8*	48	400
Cyclo-diBA	*315*	1900	15800
Sum	*350*	*2100*	*17000*

Epoxy resins

Some of the components found in the migrates originate from the epoxy resins, as concluded from the results of table 6 listing the major byproducts with less than 1000 D found in epoxy resins of various suppliers and of various average molecular weight (as reflected by the varying BADGE concentrations).

Cyclo-diBA is primarily formed during advancement of the resin: BADGE and Bisphenol A react to a dimer that performs ring closure instead of reacting to the BADGE-trimer by addition of another BADGE. In the commercial epoxy resins analyzed, it is present in concentrations of around 1%. It is poorly integrated into the polymer during curing of the lacquer, probably because it exhibits two hydroxyl groups only. This explains why it is enriched in the migrates of such coatings. If 100 mg/dm² of coating is applied to the can surface, if cyclo-diBA represents 8 mg/g of the resin, and if 50% of the final coating consists of epoxy resin, there are 0.4 mg/dm² of cyclo-diBA on the can surface. Roughly 10% of it are finally encountered in oily foods (11).

Table 6. Concentrations (mg/g) of the compounds listed in some epoxy resins. Epi, epichlorohydrin

	BADGE Araldit GY 250	Araldit GT 7071	Araldit GT 7077	Epikote 1007	Epikote 1009	DER 667-20	Kukdo YD-019
Bisphenol-A		≤ 1	3	0.9	< 0.1	0.7	3
BADGE	850	155	17	50	5.2	12	7
BADGE.Epi	4.9	1.1	0.2	0.4	< 0.1	< 0.2	< 0.1
BADGE.HCl	2.4	2.3	0.9	0.2	< 0.1	0.4	≤ 0.2
cyclo-diBA	≤ 0.3	8	13	8	2.7	15	20
BADGE dimer	150	60	7.7	52	9.5	6	4
BADGE.Phe		< 0.3	< 0.2	< 0.2	≤ 0.15	1	< 0.2
BADGE.tBuPhe	< 0.2	< 0.1	3.8	< 0.1	< 0.1	< 0.1	5.1
BADGE.2tBuPhe	< 0.2	< 0.1	0.2	< 0.1	< 0.1	≤ 0.3	1.2
BADGE.MeOH	1.8	≤ 0.3					
BADGE.PrOH	4.4	2.4			< 0.1		
BADGE.BuOH		0.6	0.2		< 0.1		

The data of table 6 suggest that epoxy resins advanced in presence of phenols contain 1–5% of corresponding BADGE mono-reaction products. Owing to the remaining epoxy group, they are more efficiently bonded into the coating polymer than cyclo-diBA; depending on the curing conditions, they may be almost absent in the acetonitrile extracts. Integration into the polymer was also reflected by the finding that BADGE.2tBuPhe concentrations in the migrates often exceeded those of BADGE.tBuPhe, despite being present in the resin as a substantially smaller component. This confirms the rule that the less reactive compounds are enriched in the migrate.

In the epoxy resins, concentrations of the reaction products of BADGE with solvents were mostly small. This suggests that most of the solvent derivatives are formed during storage of the lacquers or curing of the coating.

Conclusions

Every time a person consumes a can of tuna or other oily food, he or she ingests 1–10 mg of phenolic migrants with a molecular weight below 1000 D, i.e. with potential physiological effect. This calls for an identification or at least characterization of the migrating components in order to enable a toxicological assessment.

In most European countries, the concept behind present legislation on polymers and coatings assumes that the migrates accepted within the global migration limit consist of monomers, oligomers and additives of which toxicity has been checked.

The migrates of epoxy coatings, however, often contain hardly any monomer and oligomers, but large amounts of unknown components.

GC-MS proved to be a method suitable for the identification of reaction products of BADGE with phenols or hydroxylic solvents. Many of these were found to be mono-reaction products and, hence, are still epoxides. In the few samples analyzed, their migration frequently approached 100 µg/dm², i.e. they are expected to reach or exceed 1 mg/kg in critical canned foods. If a limit of 1 mg/kg is considered for BADGE and its reaction products with water and hydrochloric acid (SCF of the EU (12)), these mono-reaction products should be included.

A majority of the components forming LC peaks did not produce a peak in GC and must be analyzed by other methods. The complexity of the chromatograms obtained by NPLC provides an idea on the amount of work required and the degree of difficulty to be expected. If the principle is taken seriously that producers are responsible for the safety of their products, it is their duty.

Summary

Some components migrating from epoxy coatings into oily foods were identified in fractions from normal phase HPLC, using large volume on-column injection and GC-MS. They consisted of reaction products of BADGE with phenols (used as chain stoppers during preparation of the epoxy resins) or solvents (alcohols and glycol ethers used for preparing the coating solutions). Mono-reaction products of BADGE still contain an epoxy group and may well reach a concentration of 1 mg/kg in oily foods. Although nearly 40 compounds have been identified, at best 20% of the migrating material with a molecular weight below 1000 D have been reached.

Zusammenfassung

Einige aus Epoxybeschichtungen in ölhaltige Lebensmittel migrierende Komponenten wurden mittels GC-MS identifiziert. Fraktionen aus Normalphasen-HPLC wurden aufgefangen und mit der on-column Technik grossvolumig eingespritzt. Es handelte sich um Reaktionsprodukte von BADGE mit Phenolen (Kettenstopper bei der Herstellung von Epoxyharzen) oder Lösungsmitteln (Alkohole, Glycolether in den Lackformulierungen). Mono-Reaktionsprodukte von BADGE enthalten immer noch eine Epoxygruppe und können in ölhaltigen Lebensmitteln leicht Konzentrationen von 1 mg/kg erreichen. Obwohl beinahe 40 Komponenten identifiziert wurden, liessen sich damit im besten Falle 20% des Migrats mit einem Molekulargewicht von unter 1000 D erfassen.

Résumé

Quelques composés migrant des vernies époxidiques aux aliments huileux ont été identifiés par GC-MS. Les fractions de HPLC en phase normale étaient récupérées et injectées par la technique «on-column» de grands volumes. Il s'agissait de produits de réaction de BADGE avec des phénoles (ajoutés pendant la production des résins époxidiques) ou des solvants (alcohols, éthers glycoliques utilisés pour préparer les vernis). Les produits d'une mono-réac-

tion contiennent toujours un groupe époxy et peuvent être présents dans les aliments huileux en concentrations au-dessus de 1 mg/kg. Presque 40 composés ont été identifiés, bien que dans le meilleur des cas 20% seulement du matériel migrant des vernis époxidiques avec un poids moléculaire au-dessous de 1000 D pouvait être identifiés.

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