**Zeitschrift:** Mitteilungen aus Lebensmitteluntersuchungen und Hygiene = Travaux de chimie alimentaire et d'hygiène

**Herausgeber:** Bundesamt für Gesundheit

**Band:** 91 (2000)

**Heft:** 3

**Artikel:** Bisphenol-A-diglycidyl ether (BADGE) and Novolak glycidyl ether (NOGE) as additives in can coatings

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**DOI:** https://doi.org/10.5169/seals-981870

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# Bisphenol-A-Diglycidyl Ether (BADGE) and Novolak Glycidyl Ether (NOGE) as Additives in Can Coatings

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Received 17 January 2000, accepted 18 April 2000

## Introduction

### Bisphenol-A-diglycidyl ether (BADGE)

The majority of food cans and metallic tubes are internally coated in order to prevent corrosion. The most frequently used coatings are prepared from epoxy resins, pre-polymerized from bisphenol A and BADGE (figure 1), and a hardener, such as a phenolic resin, an amine, or an anhydride. Epoxy coatings release highly complex mixtures of migrants into the foods, only a minority of which has been identified so far (1), such as reaction products of BADGE with phenols (used as chain stoppers) or hydroxylic solvents (e.g. butanol or butoxyethanol).

The production of deep-drawn food cans (two-piece cans) and easy open lids requires coatings of high flexibility, since the lacquers are applied before shaping the can or lid. This is an important reason for the use of organosol coatings, the backbone of which primarily consists of PVC.

### Reaction products of BADGE

Coating with organosols must be cured at temperatures of around 200 °C, at which PVC tends to decompose. Hydrochloric acid is released, which catalyzes further degradation. To stabilize the polymer, the hydrochloric acid is removed by reaction with epoxy compounds, such as BADGE, added at concentrations of several percents.

Beside unmodified BADGE, such coatings release the reaction products with HCl, i.e. BADGE.HCl and BADGE.2HCl (fig. 1). BADGE.HCl is also present as an impurity of BADGE, although at relatively low concentrations. In oily or fatty foods, the epoxy groups are protected by the hydrophobic phase,

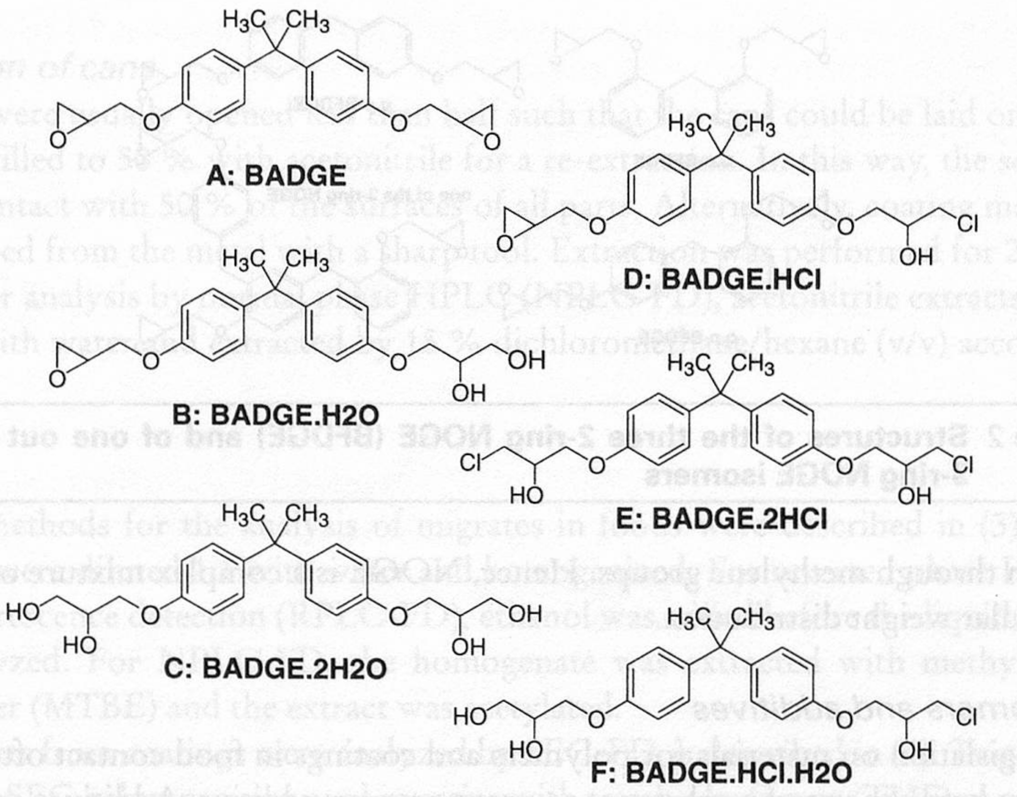


Figure 1 **Structures of BADGE and its reaction products with hydrochloric acid and water.** A, B, C..., designation used by the EU-SCF

but in aqueous foods they are hydrolyzed, resulting in BADGE.2H2O and BADGE.HCl.H2O.

When BADGE was added to foods, such as tuna in water, and heated simulating sterilization, as much as 97 % of BADGE "disappeared", i.e. did no longer show up as peaks in HPLC, neither as BADGE nor as reaction products with water or chloride (2). This indicates that most of the migrating BADGE reacts with food components; the migration may be more than 30 times higher than determined when analyzing packed foods. The identity and toxicity of the resulting products is unknown.

### *Novolak glycidyl ether (NOGE)*

Epoxy novolak (here called novolak glycidyl ether, NOGE) was introduced many years ago, but received additional attention as a potential substitute for BADGE. Novolak is the technical name for complex mixtures obtained by reaction of phenol with formaldehyde under acidic conditions. NOGE is produced by reaction of novolak with epichlorohydrin.

While acetone reacts with phenol only at the para-position (resulting in a single compound, bisphenol A), formaldehyde also attacks the two ortho sites, with the effect that, firstly, three isomers of the 2-ring compound are formed (fig. 2) and, secondly, up to three phenols can be bonded to a given phenol, enabling oligomer-

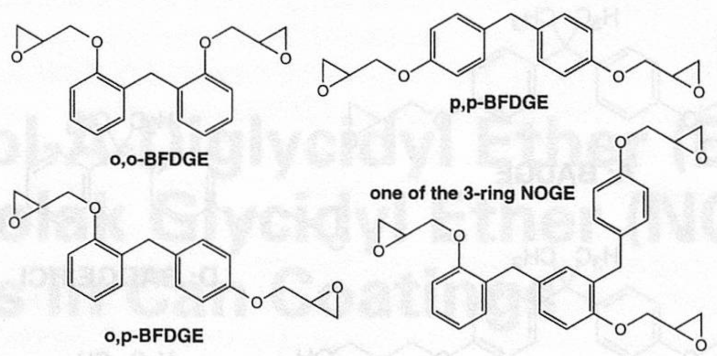


Figure 2 **Structures of the three 2-ring NOGE (BFDGE) and of one out of seven 3-ring NOGE isomers**

ization through methylene groups. Hence, NOGE is a complex mixture of variable molecular weight distribution.

### *Monomers and additives*

Legislation on materials for polymers and coatings in food contact often differentiates between use of a substance as a monomer or additive. Additives are considered more critical (and approved more restrictively) because the compounds are more likely to be extractable. In fact, the additive lists of national legislations in Europe and of the European Council (Resolution AP (96) 5) do not include BADGE, nor does the US legislation. This is in contradiction with the wide use of BADGE as a scavenger in organosols, where it is expected to have the typical characteristics of an additive. Critical evaluation is important, indeed, since a large proportion is extracted into food. Furthermore, the purpose of its use involves the conversion to chlorohydrins, the toxicity of which should have been tested before such coatings were marketed in large scale.

The use of NOGE for food contact materials is not authorized in Europe. The Swiss authorities took the position that the lack of an approval (based on toxicity data) means that its use is illegal. The replacement of the increasingly investigated and better defined BADGE by a non-investigated complex mixture is not considered meaningful.

It is argued that NOGE is an oligomer of (positive-listed) phenol, formaldehyde, and epichlorohydrin and that its use does not need to be authorized therefore. This might hold true when NOGE is an intermediate of a polymerization (an oligomer). However, when applied as an additive, NOGE is a starting point material added to another polymer (such as a PVC).

This paper focusses on the use of BADGE and NOGE in organosols, in particular on the clarification of whether they are used as additives. Analytical arguments based on whether or not they participate at a polymerization and largely remain extractable are of importance for control.

## Methods

### *Extraction of cans*

Lids were usually opened less than half such that the cans could be laid on their side and filled to 50 % with acetonitrile for a re-extraction. In this way, the solvent was in contact with 50 % of the surfaces of all parts. Alternatively, coating material was scraped from the metal with a sharp tool. Extraction was performed for 24 h at 25 °C. For analysis by normal phase HPLC (NPLC-FD), acetonitrile extracts were diluted with water and extracted by 15 % dichloromethane/hexane (v/v) according to (1).

### *Analysis*

The methods for the analysis of migrates in foods were described in (3). Can contents were diluted 1:1 with water and homogenized. For reversed phase HPLC with fluorescence detection (RPLC-FD), ethanol was added before the liquid phase was analyzed. For NPLC-FD, the homogenate was extracted with methyl tert. butyl ether (MTBE) and the extract was acetylated.

Extracts from coatings were analyzed by SEC-FD as described in (4). Two 250 × 7 mm i.d. SEC columns were used in series with tetrahydrofurane (THF) as mobile phase.

IR-spectroscopy: flat pieces of 1–3 $cm^2$ were cut from the cans or lids and analyzed by a Perkin Elmer FT-IR 1600 instrument using the attenuated total reflection (ATR) technique. Data was handled by the "Spectrum" software version 2.0 (4 scans).

Beilstein test: to check for the presence of chlorine, some lacquer was scraped from the metal. A copper wire of 1 mm o.d. was heated above a blue flame. With the hot wire, the lacquer material was picked up and brought back into the flame. A green color was interpreted as chlorine-containing material or "Beilstein-positive".

## Results regarding BADGE

### *Anchovies in oil*

As a first example, a deep-drawn two piece can with an easy open end containing 26 g of anchovies at 46 g net weight (i.e. containing 43 % oil) was analyzed. The Beilstein test indicated the presence of chlorine in the coatings of the can and the lid, i.e. suggested an organosol coating on both parts.

The lower chromatogram in figure 3 is from SEC-FD of the edible oil phase (5 µl of a 10 % solution of oil in THF). The high concentration of BADGE (see below) rendered contributions of food components to the chromatogram negligible. There is a large amount of monomeric BADGE and HCl derivatives, a small amount of dimer, but no relevant fluorescent material of higher molecular weight.

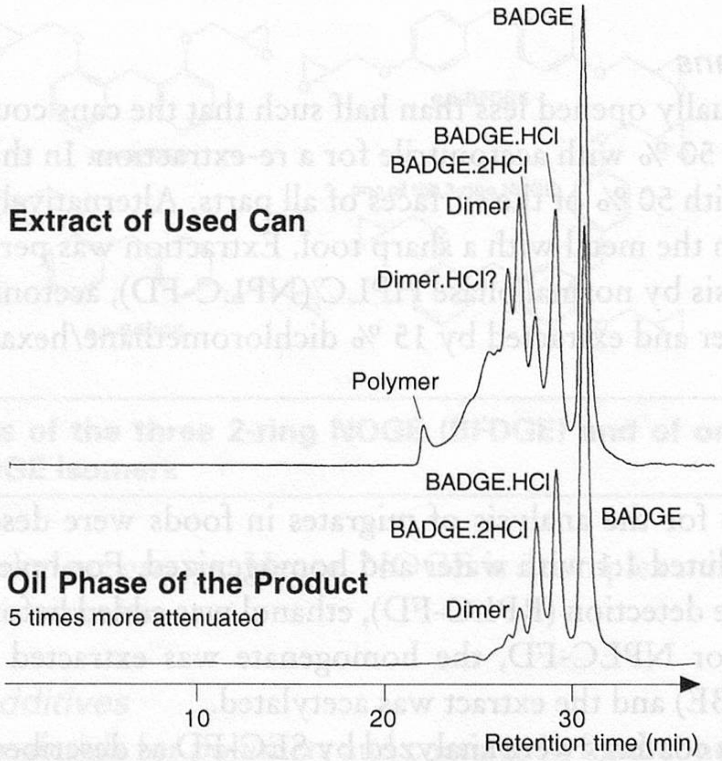


Figure 3 **Anchovies in oil: SEC-FD chromatograms of the oil phase and of the extract from the emptied can**

The partly opened and emptied can (i.e. body together with the lid) was extracted with acetonitrile (24 h/25 °C). The SEC-FD chromatogram shown in the upper part of figure 3 was recorded with a five times reduced attenuation compared to the oil phase, i.e. depicts a minor residue left in the coating after efficient extraction by the oily food. The early eluted, higher molecular weight material was present in a somewhat higher proportion than in the oil, but remained small.

Considering that about 50 % of the can content was oil (including that in the anchovies), 84 % of the BADGE accessible by acetonitrile was extracted by the oil (table 1). The proportion was similar for BADGE.HCl, higher (92 %) for BADGE.2HCl, but clearly lower (45 %) for the dimer. This confirms previous findings (3) that extraction efficiencies of oily food and acetonitrile are similar for low molecular weight material, but also that acetonitrile extracts higher molecular weight components better than a sterilized oily product.

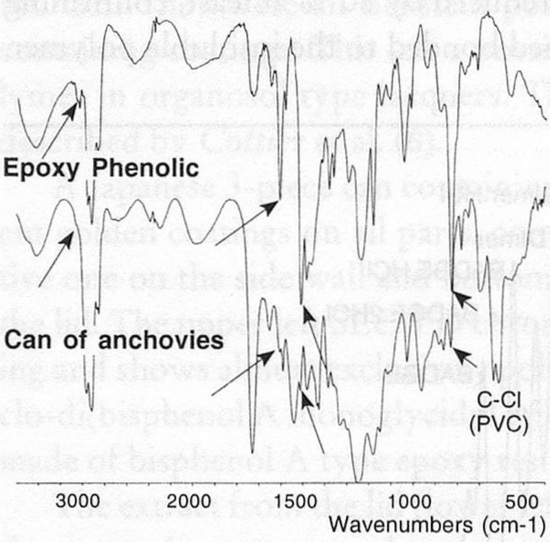
Adding up the material in the oil and the acetonitrile extract, about 75 % of the fluorescing material admixed to the coating consisted of BADGE and BADGE-HCl derivatives. The dimer made up about 5 %. The rest was not identified, but most of it was also of a molecular weight below 1000 Dalton.

Merely some 2 % of the fluorescence response belonged to polymeric material. Hence there is no indication that a relevant amount of the BADGE added to the organosol had polymerized or reacted with the backbone polymer.

Table 1
**Anchovies in oil: concentrations of BADGE-type components in the oil phase and in the acetonitrile extract of the used can (mg/kg referring to the oil phase or can content).** "> Monomer", material of a molecular weight larger than BADGE.2HCl

| | *BADGE* | *.HCl* | *.2HCl* | *Dimer* | *>Monomer* | *Total* |
|---|---|---|---|---|---|---|
| Edible oil | 73 | 26 | 17 | 5 | 16 | 152 |
| Can extract | 7.3 | 3.3 | 0.7 | 3 | 17 | 35 |
| % extracted by oil | 84 | 80 | 92 | 45 | 32 | 68 |

Figure 4 compares the IR spectrum of the can surface after acetonitrile extraction with that from a reference, a surfaces coated by an epoxy phenolic polymer. Regarding the bands of interest (arrows), the spectra of this reference and of BADGE were virtually identical. In the spectrum from the anchovy can, the bands of BADGE and related compounds are hardly visible, indicating that no important amount of BADGE had been bonded to the polymer. This completes the evidence that BADGE was admixed as an additive and did not become part of the polymer.



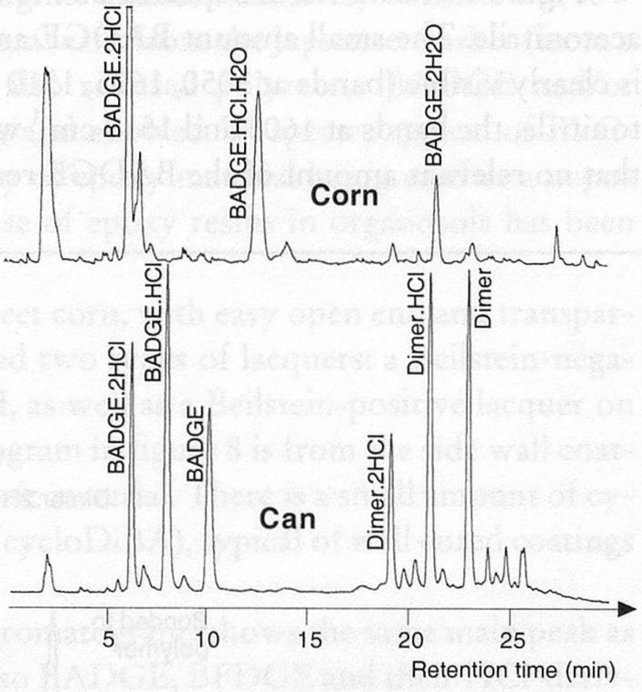


Figure 4 **IR spectra from the internal surface of the extracted anchovy can and from a surface coated with an epoxy phenolic lacquer.** Arrows point out the bands used

Figure 5 **NPLC-FD chromatograms of the acetylated extracts from the corn and the emptied can**

### *Sweet corn*

As an example of a food in water, sweet corn in a 340 g two-piece can with a normal end was chosen. Figure 5 shows the NPLC-FD chromatograms of the extract from the homogenized corn and the acetonitrile extract of the emptied can (both acetylated). As the migrating epoxy compounds were hydrolyzed, in the corn, BADGE showed up as BADGE.2H2O, BADGE.HCl as BADGE.HCl.H2O and the dimers in an analogous way (neglecting the material that "disappeared"). The corn contained monomeric BADGE derivatives almost exclusively (2.1 mg/kg for the sum of the three compounds), whereas in the coating extract, the dimers were present in almost equal quantities. The latter results from a high extraction yield for the monomeric compounds by the food, while the dimer had migrated hardly at all.

Figure 6 shows the SEC-FD chromatogram of the emptied can extracted with dioxane at 90 °C for 3 h. This dissolved most of the coating, but the acetonitrile extract obtained at 25 °C (24 h) hardly differed, suggesting that both extracts were almost complete. Primarily BADGE and its dimer together with their chlorohydrins are observed, but also a minor peak representing high molecular weight material. The absence of oligomeric material suggests that it does not originate from polymerization of BADGE, but from BADGE or its dimer bonded to the polymer of the organosol. The size of the peak indicates that only little BADGE was bonded to the polymer.

Figure 7 shows the IR spectra of the coating before and after extraction with acetonitrile. The small amount BADGE and dimer left after extraction by the food is clearly visible (bands at 3050, 1605, 1510 and 830 cm$^{-1}$). After extraction with acetonitrile, the bands at 1605 and 1510 cm$^{-1}$ were reduced by 80 % at least, confirming that no relevant amount of the BADGE remained bonded to the insoluble polymer.

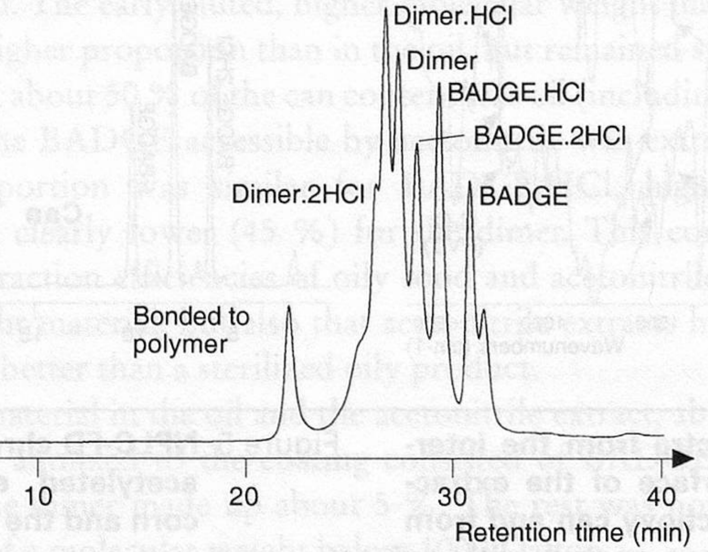


Figure 6 **SEC-FD chromatogram of a hot dioxane extract of the sweet corn can, dissolving most of the polymer**

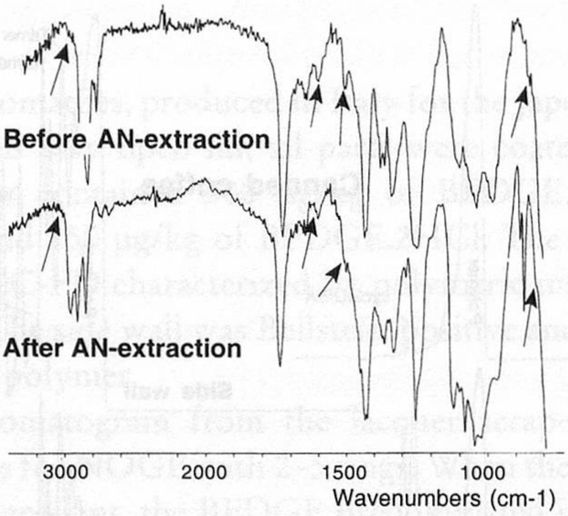


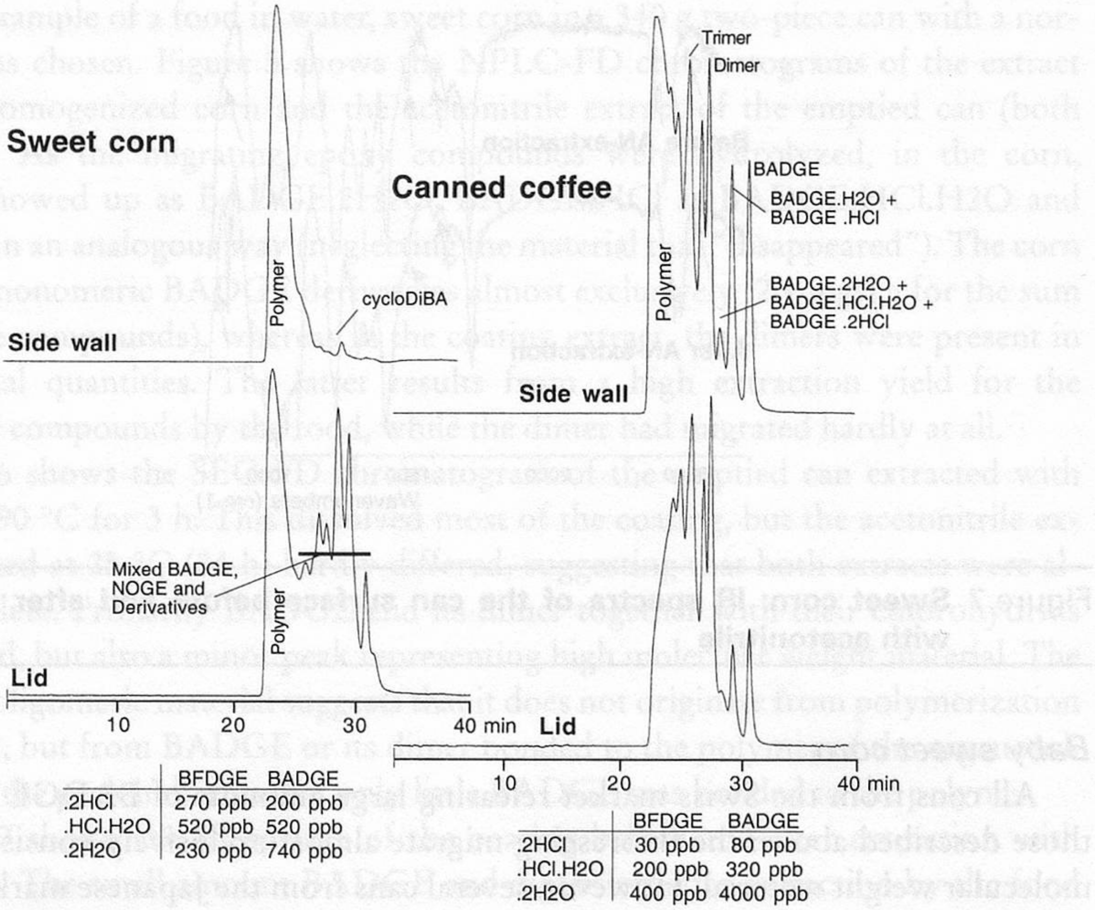
Figure 7 **Sweet corn: IR spectra of the can surface before and after extraction with acetonitrile**

### *Baby sweet corn*

All cans from the Swiss market releasing large amounts of BADGE resembled those described above: the fluorescing migrate almost exclusively consisted of low molecular weight material. However, several cans from the Japanese market (from a series analyzed by *Uematsu* et al. (5)) also released polymeric BADGE and/or NOGE. They were all Beilstein-positive and showed IR spectra typical of PVC-containing coatings. This left a possibility of epoxy material being used as a copolymer in organosol type lacquers. The use of epoxy resins in organosols has been described by *Cottier* et al. (6).

A Japanese 3-piece can containing sweet corn, with easy open end and transparent golden coatings on all parts, contained two types of lacquers: a Beilstein-negative one on the side wall and bottom end, as well as a Beilstein-positive lacquer on the lid. The upper left SEC-FD chromatogram in figure 8 is from the side wall coating and shows almost exclusively polymeric material. There is a small amount of cyclo-di(bisphenol A monoglycidyl ether) (cycloDiBA), typical of well cured coatings made of bisphenol A type epoxy resins.

The extract from the lid (lower left chromatogram) shows the same main peak as the upper chromatogram, but there are also BADGE, BFDGE and their HCl-derivatives together with a far smaller amount of BADGE dimer and 3-ring NOGE (confirmed by NPLC, RPLC, and the compounds recovered in the food extract, listed at the bottom of figure 8). The almost complete absence of higher BADGE oligomers and NOGE with more than four rings indicates that the monomers encountered are not residues from an incomplete polymerization. The monomeric and polymeric material are from different sources, for instance from an epoxy coating with an organosol containing BADGE and NOGE on top.



|  | BFDGE | BADGE |
|---|---|---|
| .2HCl | 270 ppb | 200 ppb |
| .HCl.H2O | 520 ppb | 520 ppb |
| .2H2O | 230 ppb | 740 ppb |

|  | BFDGE | BADGE |
|---|---|---|
| .2HCl | 30 ppb | 80 ppb |
| .HCl.H2O | 200 ppb | 320 ppb |
| .2H2O | 400 ppb | 4000 ppb |

Figure 8 **Japanese can of sweet corn (left) and ready coffee (right), with the SEC-FD chromatograms of the internal coatings of the side walls in the upper row and the lids in the lower.** The tables at the bottom list the concentrations of the BADGE and BFDGE derivatives in the can contents

### *Coffee*

The can with ready-to-drink coffee consisted of 3-pieces with an easy open lid and was internally coated by a transparent beige-golden lacquer, Beilstein-positive on all parts. The IR spectra contained strong bands for C-Cl bonds (600–650 cm$^{-1}$), but also clearly visible bands for aromatics (3050, 1605, 1510, and 830 cm$^{-1}$).

The SEC-FD chromatogram from the coating of the lid showed BADGE and its derivatives, slightly less dimer and trimer, but hardly any higher oligomers (figure 8, confirmed by NPLC-FD). NOGE was a minor component. Considering the large amount of BADGE extracted into the coffee, the coating obviously contained a low molecular weight epoxy resin with a large proportion of BADGE. Since the IR bands of the aromatics were still clearly visible after acetonitrile extraction, some of this resin must have been bonded to the insoluble polymer.

The side wall released the same compounds as the lid, but also polymeric material. Again, the coexistence of small molecular weight material and of polymer with little oligomeric material suggests two different sources of starting materials.

## Results regarding NOGE

### *Peeled tomatoes*

The can of peeled tomatoes, produced in Italy for the Japanese market, consisted of three pieces with an easy open lid; all parts were coated by a brownish gold lacquer. The tomatoes contained 500 µg/kg of BFDGE.2H2O, 450 µg/kg of BFDGE.HCl.H2O, and 150 µg/kg of BFDGE.2HCl. The lid carried a Beilstein-negative coating, in SEC-FD characterized by polymeric material and cycloDiBA, i.e. an epoxy lacquer. The side wall was Beilstein-positive and the IR showed strong bands for a PVC-type polymer.

The SEC-FD chromatogram from the lacquer scraped from the side wall (figure 9) shows signals for NOGE with 2–5 rings. When the material transferred to the food is taken into account, the BFDGE predominated in the NOGE added to coating. The peak of the 3-ring NOGE also contained a substantial amount of BFDGE.HCl and that of the 4-ring NOGE a minor amount of BFDGE.2HCl. In fact, addition of water or HCl to a glycidyl group decreased SEC retention times to the same extent as the addition of a glycidyl phenyl moiety. Consequently a major portion of the peak assigned as 5-ring NOGE represents 3-ring.2HCl and 4-ring.HCl. There is virtually no polymeric material.

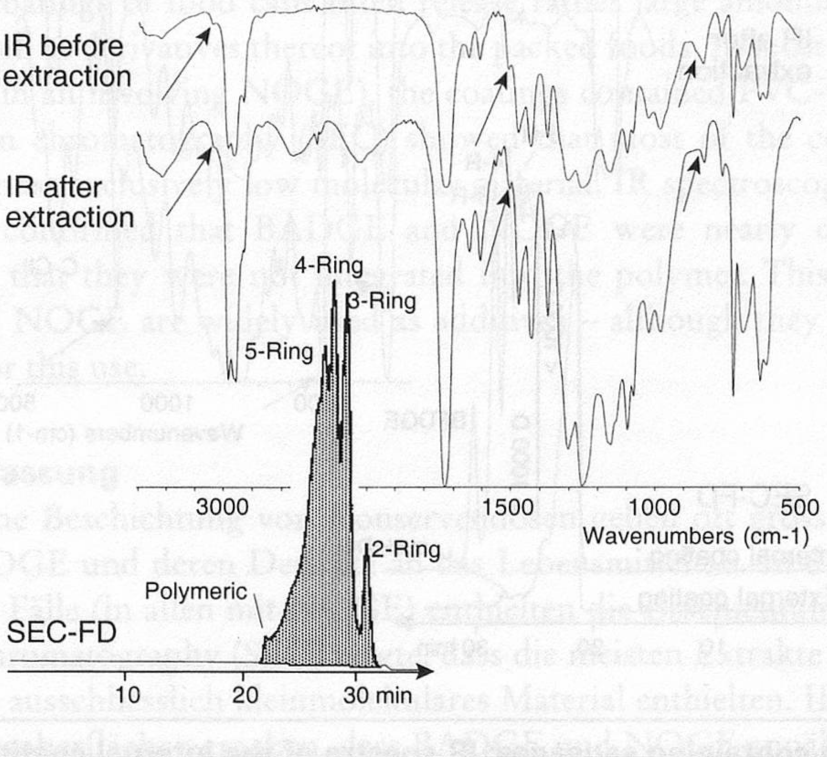


Figure 9 **Peeled tomatoes: SEC-FD chromatogram of the internal coating of the side wall; IR spectra of the surface before and after acetonitrile extraction.** Arrows: bands indicating aromatic compounds

Before acetonitrile extraction (but after extraction by the food), the presence of NOGE was visible in the IR spectrum by some minor bands. After extraction, they were clearly reduced or eliminated almost totally (840 $cm^{-1}$). It is concluded that the NOGE added to this lacquer was neither polymerized nor bonded to the polymer to a significant extent. It has the characteristics of an additive.

### *Sausages*

The 3-piece can with an easy open lid had a Beilstein-negative, white coating on the side wall and the bottom end. SEC confirmed an epoxy polymer. The internal and external surface of the lid carried gold lacquers. As shown in figure 10, the Beilstein-negative external coating consisted of an epoxy polymer, some cyclo-DiBA being the only small molecular weight material of some importance. The internal coating released material producing clear signals for the 2–5 ring NOGE, but also for material of molecular weight exceeding 1000 D.

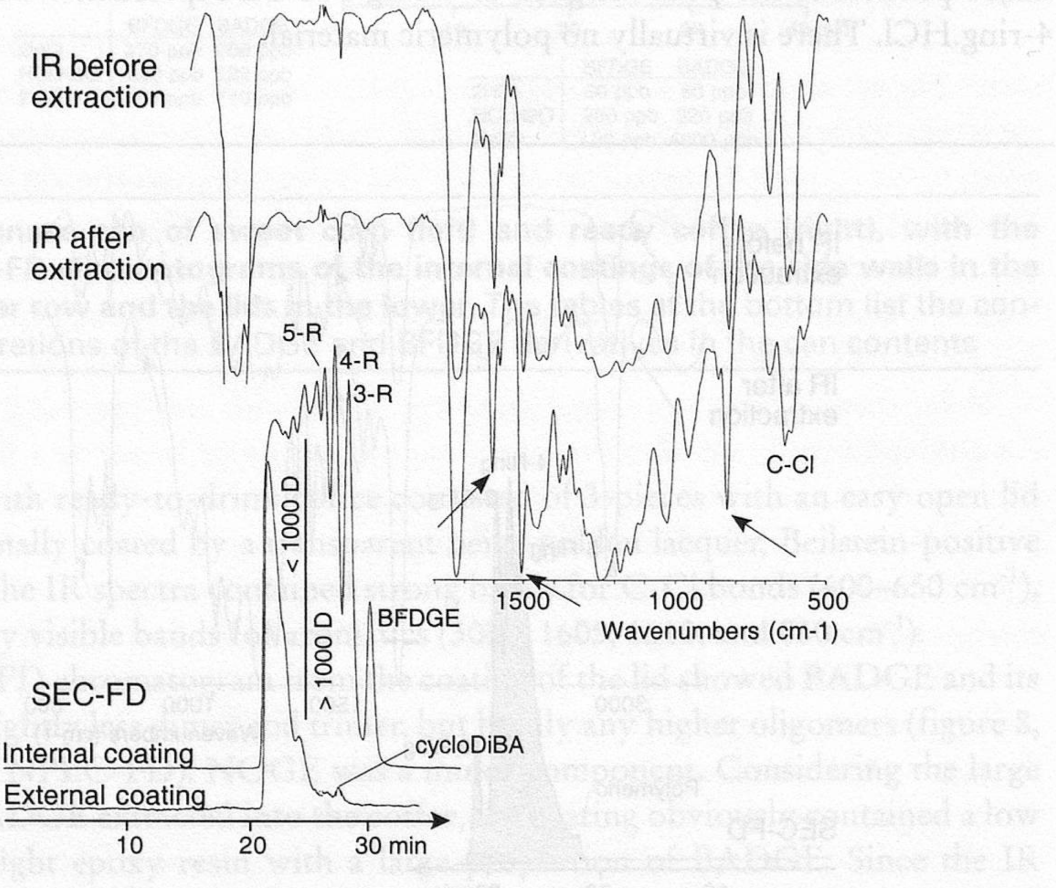


Figure 10 **Can containing sausages: IR spectra of the internal coating of the easy open lid before and after extraction with acetonitrile (arrows on bands suggesting epoxy components). SEC-FD chromatograms of the lacquers from the internal and external lid surface**

The IR spectrum obtained before acetonitrile extraction showed rather intense bands for aromatics, suggesting the presence of more than a few percent of an epoxy material. Acetonitrile extraction did not significantly reduce these bands, indicating that this material was polymeric or bonded to the polymeric backbone.

There is the same kind of co-existence of low and high molecular weight material without oligomers in between as shown in figure 8, again suggesting an epoxy polymer and an organosol containing NOGE as additive.

## Discussion

Analytical methods are described for determining whether or not BADGE and NOGE should be considered as additives to a coating.

Among the more than 500 cans analyzed, all releasing detectable amounts of NOGE and most with large amounts of BADGE contained Beilstein-positive coatings and the IR spectra showed C-Cl bands typical of PVC polymers (organosols). Hence organosols were the source of problems regarding this type of migration. From most of the coatings, BADGE and NOGE were largely extractable, and there were no signs of a polymerization or substantial integration into the backbone of the polymer, which proves that BADGE and NOGE were used as additives – without the required approval.

## Summary

Internal coatings of food cans often release rather large amounts of BADGE, NOGE, as well as derivatives thereof into the packed foods. In most of the samples investigated (in all involving NOGE), the coatings contained PVC-type materials. Size exclusion chromatography (SEC) showed that most of the coating extracts contained almost exclusively low molecular material. IR spectroscopy of the coating surfaces confirmed that BADGE and NOGE were nearly completely extractable, i.e. that they were not integrated into the polymer. This indicates that BADGE and NOGE are widely used as additives – although they have not been authorized for this use.

## Zusammenfassung

Die interne Beschichtung von Konservendosen geben oft grosse Mengen von BADGE, NOGE und deren Derivate an das Lebensmittel ab. In den meisten der untersuchten Fälle (in allen mit NOGE) enthielten die Beschichtungen PVC. Size Exclusion Chromatography (SEC) zeigte, dass die meisten Extrakte aus diesen Beschichtungen ausschliesslich kleinmolekulares Material enthielten. IR-Spektren der Beschichtungsoberflächen ergaben, dass BADGE und NOGE annähernd vollständig extrahierbar, also nicht ins Polymere eingebunden waren. Dies erlaubt die Folgerung, dass BADGE und NOGE in diesen Beschichtungen als Additiv verwendet wurden – obwohl sie für diesen Zweck nicht bewilligt sind.

## Résumé

Le revêtement interne des boîtes de conserve laisse souvent migrer dans les aliments des quantités importantes de BADGE, NOGE et de leurs dérivés. La plupart des échantillons analysés (tous avec du NOGE) comportaient des enduits PVC. Les analyses par «size exclusion chromatography» (SEC) ont montré que la plupart des extraits de laque contenaient essentiellement du matériel de faible masse moléculaire. Les spectres IR de surface des revêtements ont montré que le BADGE et le NOGE sont presque complètement extractibles et donc pas retenus dans le polymère. Cela permet de conclure que le BADGE et le NOGE ont été utilisés comme additifs, bien que cet usage ne soit pas autorisé.

## Key words

Bisphenol-A-diglycidyl ether (BADGE), Novolak glycidyl ether (NOGE), Additives to can coatings, Organosol coatings, Size exclusion chromatography (SEC)

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