

Dossier – Can coatings

December 2016

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1 Introduction

Canning of food and beverages allows their preservation for months to years while maintaining taste and nutritional values. Metal cans are generally coated with an organic layer protecting the integrity of food cans from effects of the food. For example, highly acidic foods and some food ingredients promote corrosion of metal leading to leakage of the can and spoilage of the food. In addition, coatings prevent reactions between the can's metals and the food which could e.g. result in unwanted cloudiness of beverages or staining of food. Can coatings have to fulfill a variety of different technical and legal requirements (Figure 1) [1, 2].

Ideally, can coatings should...

- ... be flexible enough to withstand forming of the cans.
- ... be universally applicable to all different food types.
- ... resist a wide temperature range, because food may be processed in the cans at high temperatures and under pressure.
- ... not transfer constituents to food in quantities that endanger human health.
- ... not peel off during can production, shelf-life and after non-intentional deformation of the cans.
- ... withstand the chemistry of aggressive food types (e.g. acidic foods) and protect the metal of the can from corrosion.
- ... preserve the flavor and appearance of food and maintain its organoleptic properties.
- ... be stable over several years.

2 Can production

2.1 Can body

Food and beverage cans are made of three different materials [3, 4]. Firstly, aluminum which is light and ductile, but relatively weak and which cannot be soldered. Aluminum cans have a wall thickness of about 0.1 mm. Secondly, tin-coated steel (tinplate) which is usually less than 0.5 mm thick and covered on both sides with a tin layer of approximately 1 μm . Thirdly, electrolytic chromium coated steel (ECCS) which is typically 0.2 mm thick and has a layer of chromium that is in the low nanometer range. Tinplate and ECCS can be soldered.

Cans are formed from two or three pieces of metal according to three main procedures:

- **3-Piece welded cans (3PC):** For three-piece cans, a rectangular piece of coated tinplate is rolled into a cylinder and closed with a seam, which is subsequently coated from the inside. The bottom piece and the can body are joined by a process called double seaming. After filling, a lid is also seamed on the top of the can body.
- **2-Piece drawn and redrawn (DRD) cans:** Two-piece cans are made from a coated aluminum or steel disk, which is first drawn into the shape of a shallow cup. Several redrawing steps can be performed progressively reducing the diameter and increasing the height of the can. The surface area and the thickness of the material remain constant during the process.
- **2-Piece drawn and ironed (D&I) cans:** Alternatively, two-piece cans are formed by drawing an uncoated tinplate or aluminum disk into the shape of a cup, followed by stretching and ironing steps. The ironing steps typically reduce the wall thickness of the can. These cans are coated on the exterior and interior after production.

2.2 Can coating

Organic coatings are routinely applied onto the inside and outside of food and beverage cans made of aluminum, tinplate, and ECCS. Most coatings form thin films of 1 to 10 μm [5]. As an exception, tin cans without internal coatings are used for light colored, acidic juices and fruits (e.g. pineapple, pears, peaches). Under these conditions, tin is more easily oxidized than the food, thus preventing darkening and flavor changes caused by oxidation of the food.

For the majority of food and beverage cans, coatings are applied to both sides of planar metal sheets or coils by roller coating before the cans are formed [6]. This process is also used to coat the outside of cylindrical can bodies. Alternatively, spray coatings are applied on the interior of preformed 2-piece D&I cans and sometimes for 2-piece DRD cans [4]. Can coatings often also serve as lubricants during the production process.

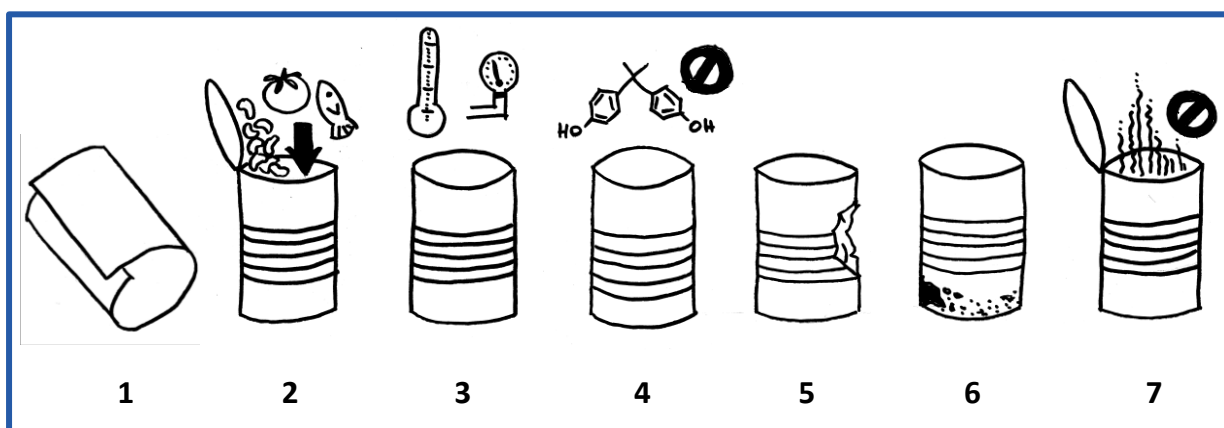


Figure 1. Can coatings should - 1 withstand the can manufacturing process, 2 be universally applicable to different food types and withstand aggressive food types, 3 withstand the food sterilization process, 4 minimize the release of their constituents into food, 5 adhere to the metal, even after mechanical deformation of the can, 6 prevent corrosion processes, and 7 not change the organoleptic properties of the food.

Coatings are generally spread as suspensions in organic or aqueous solvents. They are dried by solvent removal, oxidation or heat polymerization, which is usually achieved by heating and/or UV radiation. During this process (known as “curing”) cross-linking reactions take place forming a three-dimensional network and giving the coating the final properties [4]. In some cases, e.g. for sealing the side seams of 3PCs, powder coatings are applied under the direction of an electrostatic field and cured by heat.

Depending on the material and application, it is sometimes necessary to use several layers of coatings, e.g. to overcome low adhesion to the metal, secure high protection or introduce a functional barrier preventing migration from the base coat.

Interior coatings are typically colored gold, white, gray or they appear aluminized. Exterior coatings often have a clear or gold appearance. Beverage cans are usually printed on their outside, whereas most food cans have a printed label which is glued on using adhesives.

2.3 Canned foods and beverages

Canned foods include a large variety of vegetables, fruits, meat, and fish, but also dairy products and ready meals. For sterilization, the cans are filled, sealed and then heated under pressure for a certain time whereas the exact conditions depend on the food type. Heating up to 100°C without pressure is only sufficient for highly acidic foods with a pH value below 4.5

Beverage cans are used for carbonated soft drinks, beer, juices, teas, coffee, energy drinks, and others. Beverages may be pasteurized or sterilized in the sealed cans or filled under aseptic conditions.

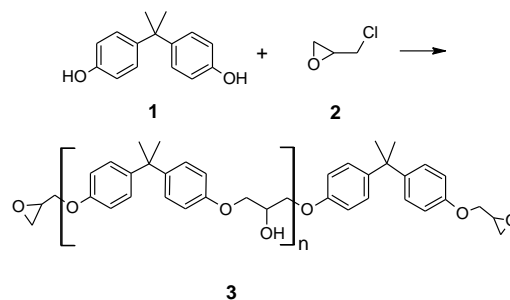
3 Coating materials

A large variety of can coatings are commercially available. They differ in the main chemical compositions, production processes, costs, and technical properties [3, 4, 7]. However, only a limited number of chemical functionalities is used to produce these resins. The high diversity of coatings is caused by variations and combinations of the resins and further increased by the number of possible cross-linking agents and additives [5]. The main types of resins are detailed in the following sections and the cited information was retrieved from references [3-5, 7-9], if not stated otherwise.

3.1 Epoxy

Since the 1950s, epoxy-based resins became the most commonly used class of coatings for aluminum and steel cans. In 2013, their market share was estimated to be 95%. Epoxy coatings protect the metal from corrosion, withstand a wide range of foods and resist heat and acidic conditions. Additionally, they adhere well to different metal surfaces and exhibit sufficient flexibility during most production processes.

The most common epoxy coatings are synthesized from bisphenol A (BPA, **1**) and epichlorohydrin (**2**), forming bisphenol A-diglycidyl ether epoxy resins (**3**).



Many different blends of epoxy coatings have been developed with epoxy-phenolic coatings being the most important subgroup. Other blended resins are e.g. epoxy amines, acrylates, and anhydrides.

3.2 Oleoresin

First can coatings were made of oleoresins, which are mixtures of oil and resin extracted from plants. Their use largely stopped with the invention of epoxy coatings in the middle of the last century, but oleoresins were rediscovered as BPA-free alternatives. Oleoresins are rather flexible, but do not adhere well to metal surfaces. They are easily applied, but need long curing times. The corrosion resistance of oleoresin-coated cans is limited, which restricts their use to mild foods e.g. different kinds of beans. Oleoresins have been reported to change the organoleptic properties of food.

Box 1: History

- In the beginning of the 19th century, food canning methods were developed with the aim to preserve large amounts of food. A first tin can process was patented in 1810. The cans of the first generation were hand-made and needed to cook for up to 6 hours.
- By the 1860s it was possible to manufacture smaller machine-made steel cans. The time to cook food in such sealed cans was reduced to thirty minutes.
- In the 19th century, tin cans were usually sealed with solder containing high levels of lead. In the years 1845-48 and 1872-73, two arctic expeditions ended dramatically with the deaths of the entire crews. It was hypothesized that lead poisoning caused by the consumption of canned food contributed to the failure of these two expeditions [10, 11].
- Beer was successfully canned for the first time in the year 1933 [4].
- In the 1940s, synthetic coatings were developed and started to be used in cans [3]. The use of epoxy coatings began in the 1950s [3].
- In the late 1950s, aluminum beverage cans were introduced to the market followed by 2-piece D&I cans in the late 1960s [6].
- Around 1960, epoxy-phenolic resins were invented that prevented the migration of metal into sensitive beverages such as beer [4].
- In the 1970s, polyester-based can coatings became commercially available. They were mainly combined with phenolic resins [12].
- In 1978, the use of polyester-urethanes for internal coatings started [12].
- In 1995, the U.S. Food and Drug Administration (FDA) issued a final rule prohibiting the use of lead-tin solder in food containers ([21 CFR 189](#)).
- In the late 1990s, oleoresin can coatings were re-introduced for certain vegetables in the U.S. and Japanese companies started to apply polyester-based alternative can coatings (including PET laminates) on top or instead of epoxy coatings.
- In 2015, the use of bisphenol A (BPA)-based coatings in food and beverage cans was banned in France (LOI [n° 2010-729](#)).
- In 2016, the U.S. food companies Del Monte and Campbell announced the phase-out of BPA-based coatings by 2016 and 2017 at the latest, respectively.

3.3 Vinyl

Vinyl coatings are synthesized using the monomers vinyl chloride and vinyl acetate. They exhibit excellent flexibility and are commonly applied as a second coating layer ("top coat"), because they do not adhere well on metal. The addition of stabilizers and plasticizers is generally needed and vinyl coatings are often blended with other resins to optimize their properties. Vinyl coatings are stable under acidic and alkaline conditions, but do not withstand high temperatures. These properties make them suitable for cans which need completely unbroken films and are not sterilized after filling (e.g. soft drinks).

Vinyl organosols are prepared from suspensions of resin in organic solvent. They also require plasticizers and stabilizers. Organosols offer comparably higher chemical resistance, thermal stability, and adhesion properties than vinyl coatings.

3.4 Phenolic

Phenolic resins are generally composed of phenols and aldehydes. They are highly corrosion resistant and protect cans from sulfide staining. Phenolics have low flexibility, do not adhere well to metal, and may change the odor and flavor of some foods. They find application as coatings for drums and pails, but unblended phenolic resins are not used in food and beverage cans. However, phenolics are common crosslinkers (e.g. in epoxide resins) and increase their resistance against corrosion and sulfide stains.

3.5 Acrylic

Ethylacrylate is the most commonly used monomer to synthesize acrylic coatings. Acrylic resins display corrosion and sulfide stain resistance, but they are rather brittle which is a disadvantage during production and processing. They have a clean appearance when pigmented with titanium dioxide, but may change the organoleptic properties of food. Because of these properties, they are commonly used as external coatings. Acrylics and their blends are currently under investigation as replacements for BPA-based epoxy coatings [1].

3.6 Polyester

A wide variety of polyester resins can be synthesized by condensation reactions between a polyvalent acid and polyalcohol(s) or epoxide(s) [13]. Isophthalic acid (IPA) and terephthalic acid (TPA) are the main carboxylic acids used in polyester coatings [12]. Polyester resins are easy to handle during the production process and adhere well to the metal surface. However, they are usually not stable under acidic conditions and have a poor corrosion resistance. Therefore, they cannot be used for acidic food types.

Alternatively, polyethylene terephthalate (PET) coatings are laminated onto the inside and sometimes also the outside surface of non-welded food and beverage cans (tradename aTULC) [14]. In these cases, adhesives are needed to bind the PET laminate onto the metal. Polyester-coated laminated cans were developed in Japan and labeled "BPA-reduced cans" [15].

3.7 Polyolefins

Coatings that are based on dispersions of polyolefins have recently entered the market and are sold under the tradename Canvera™. The development of a new technology allows the dispersion of high molecular polyolefins in aqueous systems without the addition of surfactants or emulsifiers. The final polyolefin coating exhibits corrosion protection, adhesion, and flexibility without impacting the flavor of the food, the manufacturer states.

3.8 Additives

Additives include agents to increase surface slipping as well as abrasion and scratch resistance. Further additives are used to prevent foam formation during production and to improve the adhesion of the coating on the metal surface. Scavengers for hydrochloric acid are especially added to vinyl-based coatings.

Lubricants are used to enable the can forming process, minimize adhesion of food to the packaging and to enhance the elasticity of the coating [16]. Waxes, paraffins, fats and oils, partial acyl glycerols or fatty acid amides are commonly used for these purposes.

Protein-rich foods contain sulfur that may be released in the form of free sulfide, hydrosulfide ions, and hydrogen sulfide gas during processing and lead to unwanted organoleptic properties [4]. Additionally, sulfide may react with tin and/or iron leading to dark stains inside the can. The addition of zinc oxide or aluminum pigment helps to prevent such stains due to the formation of almost invisible white metal sulfides. Titanium dioxide is another common additive providing a clean white appearance of the coating and masking sulfide stains because of its good hiding power [17].

4 Alternatives to epoxy coatings

Epoxy coatings combine several advantages such as universal applicability, high stability, good processability, and low cost [6]. Nevertheless, food companies have started to replace BPA-based epoxy coatings by alternatives in response to toxicological evidence, public discussions, and recent regulatory decisions.

Already in 2013, patent filings and regulatory approvals by paint and chemical firms showed that many new coatings were under development [1]. Acrylic and polyester coatings are currently used as first generation alternatives and, more recently, polyolefin and non-BPA epoxy coatings have been developed with the aim to replace traditional epoxy coatings [18, 19]. Other inventions developed to reduce BPA migration include BPA capturing systems [20] and top coatings [21]. Instead of replacing epoxy coatings, food manufacturers may also decide to change completely to other types of packaging (e.g. from cans to plastic bottles or composite cartons) [22].

Manufacturers introduced the term "bisphenol A non-intent" (BPA-NI) for coatings that are based on other monomers than BPA [6]. With this practice, they avoid labelling their products as BPA free, which would be an ambitious aim due to the ubiquitous presence of BPA, but instead claim that they do not intentionally add BPA.

Although several alternative coatings already exist, none of them fulfills all the above-mentioned requirements of an 'ideal' can coating. Therefore, alternative coatings can presently only be used with certain limitations. Most of them are more expensive than epoxy coatings. Furthermore, their use may reduce the storage time of foods because the stability is not sufficient or it has not been adequately tested before bringing onto the market. The latter shows an important difficulty in the search for alternative coatings: Not only the research and development, but also the testing phase of novel coatings contribute to the long periods of time until a new material can be introduced into the market. Additionally, suitable alternatives should be compatible with many different food types, which extends the effort during the testing phase even more [23] and lead to typical development times of approximately ten years [24].

However, first evidence for the toxicological properties of BPA has been published in the 1990s and the debate on the safety of BPA intensified in the beginning of the 2000s [25]. The time elapsed indicates that coating manufacturers may have missed an opportunity to react faster and start to work on safer alternatives earlier.

5 Market data

5.1 Cans

Global estimates of recent years showed that more than 300 billion beverage cans were produced each year and that the trend is continuously increasing [6, 26, 27]. Furthermore, it was estimated that approximately 75 billion food cans were produced globally in 2011 [26]. In 2014, 90% of the beverage cans were made of aluminum; the remaining 10% consisted of steel [27]. Major global players of the beverage can market are Ball (who acquired can manufacturer Rexam in June 2016), Crown, MCC, and Can Pack [27]. The preferences for beverage packaging strongly differed by region: Whereas more than 40% of beverages were sold in cans in the U.S. and Canada, this value was between 10-20% in the rest of the world [6]. In 2013, 350 cans per capita were consumed in North America, followed by 80, 70, 17, and 2 cans per capita in Latin America, Europe, China, and India, respectively [6].

In 2013, about US \$30 billion and US \$9 billion were globally earned with beverage and food cans, respectively [6]. The global metal food packaging market was estimated to be US \$64 billion in 2014 and rise to US \$75 in 2019 [27].

5.2 Can coatings

In 2011, the global production capacity of can coatings was estimated to be 800'000 metric tons, which corresponds to a market value of €2.8 billion [28]. In 2013, another study assumed a global market value of approximately \$3 billion dollar for packaging coatings [6]. The end-uses of coatings in the packaging market were beverage can bodies (20-25%) and ends (10-15%), food cans (25-30%), and caps and closures (5-10%) [6]. Approximately one third of the coatings were used in non-food packaging. Global market leaders were Valspar, PPG, and AkzoNobel who shared two third of the market for packaging coatings [6]. Due to increased pressure to substitute BPA-based epoxy coatings, many new substances are under investigations by paint and chemical firms [1]. This development may significantly change the coating market in future.

6 Regulation

6.1 Europe

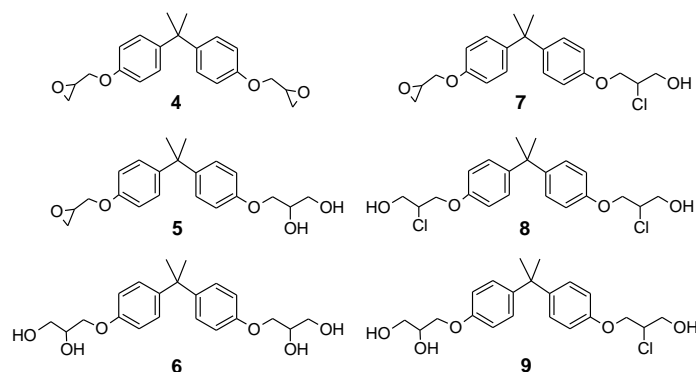
In Europe, can coatings generally have to fulfill the requirements of the European Framework Regulation [EC 1935/2004](#) on food contact materials (FCMs) [2]. In article 3, the regulation defines that FCMs shall be manufactured "so that [...] they do not transfer their constituents to food in quantities which could endanger human health or bring about an unacceptable change in the composition of the food or [...] deterioration in the organoleptic characteristics."

Can coatings are not regulated by an EU-wide legislation, but specific measures exist in several Member States. In the Netherlands, coatings of FCMs are covered under the Dutch Packaging and Food Utensils legislation. Chapter X includes nine different types of FCM coatings, but various other chapters also comprise coatings. A revision of all chapters dealing with coatings is currently in progress and may lead to three new parts concerning (1) general provisions, (2) general-purpose coatings, and (3) coatings for specified applications. In the Netherlands, can coatings continue to be regulated based on a positive list of substances in future. They will belong to the general-purpose coatings. Other Member States with national regulation on can coatings in place are Belgium [29], Czech Republic, Greece, Italy, Slovakia, France and Spain [30-32].

Few chemicals that are known to have the potential to migrate from cans and coatings into food are specifically regulated in the EU:

- Specific migration limits for bisphenol A diglycidyl ether (BADGE, **4**) and its derivatives were defined in Commission Regulation [EC](#)

[1895/2005](#) [33]. BADGE and its hydrolysis products BADGE·H₂O (**5**) and BADGE·2H₂O (**6**) shall not exceed a group specific migration limit (SML) of 9 mg/kg food. The SML is based on a tolerable daily intake (TDI) of 0.15 mg/kg. A second group SML of 1 mg/kg food was assigned to the three chlorohydrins of BADGE (BADGE·HCl (**7**), BADGE·2HCl (**8**), BADGE·H₂O·HCl (**9**)). The use of bisphenol F diglycidyl ether (BFDGE) and novolac glycidyl ether (NOGE) in FCMs was not authorized due to the lack of toxicological data. However, BFDGE and NOGE were permitted in the coating of large containers intended for repeated use. For such applications, no migration limits were set.



- Regulation [EC 466/2001](#) on setting maximum levels for certain contaminants in foodstuffs was amended by Commission Regulation [EC 242/2004](#) regarding inorganic tin in foods. Accordingly, tin concentrations of 200, 100, and 50 mg/kg food shall not be exceeded in canned food, canned beverages, and products for infants and young children, respectively.
- In the beginning of 2016, the European Commission (EC) published a draft regulation on the use of BPA in varnishes and coatings as well as an amendment of the plastics regulation (Commission Regulation [EU 10/2011](#)). An SML of 0.05 mg/kg food is proposed for coatings and varnishes. The current SML of 0.6 mg/kg food as defined for plastic FCMs shall be reduced to 0.05 mg/kg food, too.
- In January 2015, France banned the use of BPA in FCMs including all packaging, containers and utensils intended to come into direct contact with food (LOI [n° 2010-729](#)). In September 2015, the French Constitutional Council decided to partially lift the ban on the manufacture and export of BPA-containing FCMs, while the ban remains valid at national level.

6.2 United States

In the U.S., polymeric and resinous coatings are generally covered under [21 CFR 175.300](#). This code lists permitted starting substances and specifies test conditions and migration limits. Can coatings meeting these specifications are compliant with the law.

A specific legal measure concerning can coatings exists in California [34]. In May 2015, California's Office of Environmental Health Hazard Assessment (OEHHA) added BPA to the [list of chemicals](#) known to cause reproductive harm under [Proposition 65](#). As a consequence, manufacturers, distributors, and retailers have to inform the consumers of BPA-containing products with a clear and reasonable warning regarding the chemical hazards. In May 2016, OEHHA proposed a temporary point-of-sale [warning label](#) for canned and bottled food and beverages. By the end of 2017, products containing BPA are required to be directly labelled.

7 Migration

The majority of studies about chemical migration from food cans focused on epoxy coatings and the migration of BPA, BADGE and their derivatives. However, many other substances may migrate from all different types of can coatings, e.g. oligomers, catalysts, reaction accelerators, epoxidized edible oils, amino resins, acrylic resins, various esters, waxes, and lubricants [35].

7.1 Test conditions

In Europe, no harmonized legislation regulates the use and testing of coated metal cans. Standardized test conditions were published in the standard CEN/TS 14235:2002 ("Polymeric coatings on metal substrates - Guide to the selection of conditions and test methods for overall migration"). Due to the lack of further legal guidelines, companies also apply the testing guidelines for plastics, although the typical filling, processing, and storage conditions strongly vary between plastic food packaging and food and beverage cans. Whereas cans are often hot-filled or even sterilized, plastic packaging materials are generally not heated during packaging. Also, the storage times may differ significantly: food cans have typical shelf-lives of 2-5 years leading to very long contact times between the packaging and the food.

The FDA currently recommends migration test conditions including a retorting step at 121°C for 2 hours followed by storage for 10 days at 40°C to evaluate the safety of cans. In a recent study, the migration from polyester can coatings was measured up to 515 days [36]. Based on the results, the authors suggested to modify FDA's test protocols for new can coatings to be able to adequately address long-term storage and monitor ongoing hydrolysis and interactions between the coating and the filling of the can. Migration studies from vinyl coatings supported this proposal to modify the current test conditions [37]. The finding of appropriate food simulants and the measurement of migrants directly in the food were identified as further challenges [36].

7.2 Overall migration

In the 1990, the values for overall migration from food cans were typically in the range of 1-5 mg/dm², but sometimes even exceeded 10 mg/dm² [35, 38]. As a consequence, Grob et al. proposed an overall migration limit of 0.3 mg/kg food for the sum of unknown/untested migrants below 1000 Da [39]. Many migrants from all different can coatings belong to the group of non-intentionally added substances (NIAS), which may be structurally and toxicologically characterized or even completely unknown [40].

7.3 Specific migration

Bisphenol A (BPA) from epoxy coatings

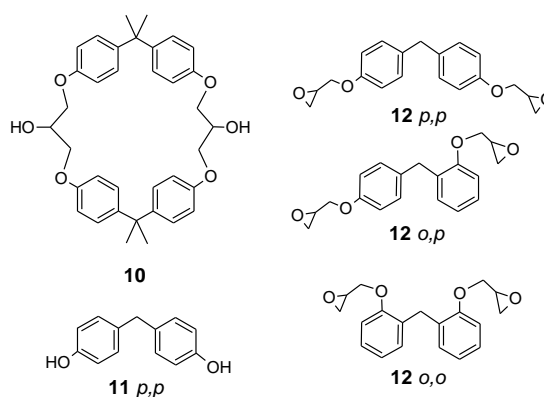
Since the late 1990s, numerous studies from all over the world demonstrated that the occurrence of BPA in epoxy can coatings and its migration from such coatings into food and beverages are common phenomena (e.g. [21, 41-61]). Migration of BPA mainly occurred during can processing, sealing and sterilization, and less during storage or after can damage [62].

Bisphenol A diglycidyl ether (BADGE) and its derivatives

BADGE is used as intermediate during the production of epoxy coatings [38]. Furthermore, BADGE has commonly been added to organosol coatings as scavenger for hydrochloric acid which is formed as unwanted by-product after exposure to heat [63-65]. In the late 1990s, first studies were published showing the migration of BADGE into canned fish, regularly exceeding levels of 1 mg/kg food [35, 38, 66-68]. Since then BADGE has continuously been measured in canned food and beverages [50, 61, 69].

Depending on the intended function of BADGE and the production and storage conditions of the can, different reaction products are formed [70]. The epoxy groups of BADGE can hydrolyze in the presence of water to BADGE·H₂O (5) and BADGE·2H₂O (6). When BADGE is used as scavenger for hydrochloric acid or in the presence of salty food, BADGE·Cl (7), BADGE·HCl·H₂O (9) and BADGE·Cl₂ (8) are formed. Furthermore, a cyclic product (cyclo-diBA, 10) is a common by-product from BPA and BADGE during the production of epoxy resins [35, 71]. The migration of many different BADGE derivatives was described in various publications, e.g. [49, 70, 72-74]. In general, the total migration of BADGE and its derivatives was higher from organosols than from epoxy coatings because of its different functions in the two materials [72].

In 2010, more complex reaction products of BADGE with food ingredients such as sugars and peptides were identified [75]. The high reactivity of BADGE's epoxy group explains the commonly observed decrease of BADGE during storage and leads to increased diversity of unknown molecules in the food [75].



Novolac glycidyl ether (NOGE) from organosol coatings

In the U.S., NOGE has commonly been used as scavenger for hydrochloric acid in organosols; in the EU, it has replaced BADGE for certain years until regulatory action banned the use of NOGE in can coatings [64]. NOGE is a complex mixture of epoxidized molecules based on the three isomers of bisphenol F (*p,p*-BPF (11), *o,p*-BPF, *o,o*-BPF) and its 3- to 8-ring derivatives [33, 64]. NOGE typically contains 30-40% BFDGE. In 2001, 5.6 mg/kg NOGE was measured in stuffed peppers packaged in food cans [64]. Migration of BFDGE, which is usually present in three isomeric forms (*p,p*-, *o,p*- and *o,o*-BFDGE (12)), and further NOGE-related compounds was measured in various other studies [49, 69, 74, 76]. In some cases, concentrations of BFDGE and its derivatives reached levels above 1 mg/kg food [68, 77].

BPF is also formed from white and yellow mustard seeds under certain production conditions and was detected in 48 of 61 samples of mainly mild mustard from the Swiss market [78].

Oligoesters

Linear and cyclic oligoesters belong to the common non-intentional by-products of polyesters [13]. Analyses of total migrates showed that up to 50% of the migrate consisted of such oligoesters, typically at concentrations below 1 mg/dm² [12]. The variety of monomers used in coating polyesters makes the prediction, analysis and quantification of oligomers very challenging and analytical standards are generally not available yet [79]. Hydrolysis of some high molecular weight polyester compounds after long-term storage was demonstrated and may complicate the analysis even more [36].

Attempts to minimize the migration from polyester coatings led to the development of polyester-polyurethane coatings. However, a broad

variety of different oligomers, plasticizers, surfactants and impurities were identified in the migrate of these materials [80].

Crosslinkers

Trimellitic acid (TMA), melamine and benzoguanamine (BGA) are used as cross-linkers in e.g. epoxy- and PVC-based coatings. In 2004, migration of more than 1 mg TMA and its possible derivatives per kg food was reported from cans purchases at the Swiss and Austrian market [81]. Under standard retorting conditions, melamine migration up to 0.4 mg/kg food was measured from epoxy-based coatings [82]. BGA migrated from PVC-coated food cans and reached levels up to 84 µg/dm² after 1.5 years of storage at 40°C [37].

Lubricants

The sum of migrating lubricants was reported to be 0.3 mg/dm² and 5.5 mg/dm² from epoxy-anhydride coatings and polypropylene films, respectively [16].

Metals

Metals are common migrants from non-coated and/or dented cans. Steadily increasing migration of iron into pineapple juice was reported for dented cans reaching maximum iron levels of 14.4 mg/L after one year of storage at room temperature [83]. Other exemplary studies reported migration of e.g. lead and iron into chickpeas [84], aluminum into tea and beer [85], and tin into different food types [86].

8 Exposure and biomonitoring

8.1 BPA

Exposure studies from all over the world showed the contribution of canned food and beverages to BPA exposure, e.g. [15, 21, 48, 51, 53, 54, 58, 87]. Two review articles from 2007 and 2011 judged that BPA migration from cans strongly contributed to human BPA exposure [88, 89]. In 2015, the European Food Safety Authority (EFSA) concluded in its most recent scientific opinion on BPA that a large majority of food categories contained higher levels of BPA in canned than in non-canned food [90]. Seven out of 17 canned food categories exceeded average BPA levels of 30 µg/kg (grain and grain-based products, legumes, nuts and oilseeds, meat and meat products, fish and other seafood, herbs, spices and condiments, composite food, and snacks, desserts, and other foods), whereas average BPA concentrations in canned beverages remained below 3 µg/kg [90]. In 2016, biomonitoring data confirmed this observation: According to an analysis based on the National Health and Nutrition Examination Survey (NHANES), urinary BPA levels were increased for people who regularly consumed canned food, whereas the consumption of canned beverages did not show a correlation with urinary BPA levels [91]. Another comparison of general BPA exposure with biomonitoring data led to the identification of canned foods as potentially important BPA exposure source for children [92].

8.2 BADGEs and BFDGEs

A second, common group of migrants from can coatings are BADGE, BFDGE and their derivatives. In 1999, exposure to BADGE was estimated to be 0.7 mg per person and year based on concentrations

measured in canned fish [93]. In 2013, the exposure to cyclo-diBA from food cans was assessed [71]. Based on Swiss consumption data and the maximum concentrations measured in canned fish, it was concluded that high consumers of canned fish could easily exceed safe cyclo-diBA levels. In 2012, first biomonitoring data for BADGE and its derivatives (BADGEs) showed that the urinary concentrations of BADGEs in the U.S. population exceeded those of BPA by 3 to 4 times [94]. The occurrence of BADGE was also reported in Indian children [95] and in the Greek population [96]. In 2015, first results were published on the occurrence of BFDGE and its derivatives (BFDGEs) in human blood and adipose fat [97]. BFDGEs concentrations were generally higher than the total concentration of BADGEs. However, a positive correlation was seen between the concentrations of BFDGEs and BADGEs. BADGE and BFDGE are designated chemicals for the California Environmental Contaminant Biomonitoring Program [98].

9 Toxicity

9.1 Bisphenols and derivatives

Toxicity data for BPA are extensive and cover many different endpoints such as reproductive and developmental effects as well as neurological, immune-modulatory, cardiovascular and metabolic effects [25, 90, 99-105]. Although there are ongoing controversies on the interpretation of this information, BPA's toxicity, especially its reprotoxic properties, are widely recognized by different authorities ([106], Annex VI of [107], [108]).

In 2004, the toxicity of BADGE was reviewed and it was concluded that it neither affects reproduction and developmental endpoints nor acts as endocrine toxicant [109]. In the same year, EFSA concluded in a scientific opinion that BADGE and its derivatives do not raise concern for genotoxicity and carcinogenicity *in vivo* [110]. However, more recent studies showed effects of BADGE e.g. on the testes of rats [111], on adipocytes *in vitro* [112], and on the development of amphibians [113]. The lack of toxicity data for NOGE and BFDGE led to the prohibition of their use and presence in FCMs in Europe [33]. In 2016, an epoxy coating based on tetramethylbisphenol F (TMBPF, CAS 5384-21-4) was introduced to the market. Toxicity tests which were published by the manufacturer did not show any evidence for endocrine activity and genotoxicity [114].

9.2 Total migrates/extracts

Besides the well-known migrants BPA and BADGEs from epoxy-coatings, can coatings generally release a far more complex mixture of substances into the food [39, 71]. Many of these substances are neither structurally identified, nor toxicologically tested, nor routinely analyzed. However, they may strongly contribute to the total toxicity of the migrate. In 2006, cytotoxic effects of migrates from epoxy- and polyester-based coatings were tested using a series of assays [115]. The results of one of these assays showed that only about 0.5% of the cytotoxic effects measured in the migrate from epoxy coatings could be traced back to the amount of BPA, BADGE and BADGE·H₂O. This example illustrates the importance of tests targeting the final migrate and not only single substances during risk assessment.

Abbreviations

3PC	3-Piece welded cans
BADGE	2,2-Bis(4-hydroxyphenyl)propane bis(2,3-epoxypropyl) ether
BADGEs	BADGE and its derivatives
BFDGE	Bisphenol F diglycidyl ether
BFDGEs	BFDGE and its derivatives
BGA	Benzoguanamine
BPA	Bisphenol A
BPA-NI	Bisphenol A non-intent
cyclo-diBA	Cyclic product formed from BPA and BADGE
D&I	Drawn and ironed
DRD	Drawn and redrawn
EC	European Commission
ECCS	Electrolytic chromium coated steel
EFSA	European Food Safety Authority
FCMs	Food contact materials
FDA	U.S. Food and Drug Administration
IPA	Isophthalic acid
NHANES	National Health and Nutrition Examination Survey
NOGE	Novolac glycidyl ether
OEHHA	Office of Environmental Health Hazard Assessment
PET	Polyethylene terephthalate
PVC	Polyvinylchloride
SML	Specific migration limit
TMA	Trimellitic acid
TMBPF	Tetramethylbisphenol F
TPA	Terephthalic acid

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