Safety assessment of tetra-methyl bisphenol F diglycidyl ether (TMBPF-DGE) for use in coating in canned food packaging materials

Assessment of non-toxicological data

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Identity of substance

11. The substance is a non-defined liquid mixture, with oligomeric and monomeric units, and the chemical name phenol, 4,4’methylene bis-2,6-dimethyl-, polymer with 2-(chloromethyl)oxirane. The trade name is reported as diglycidyl ether of tetramethyl-bisphenol F – aromatic diglycidyl ether (TMBPF-DGE).

12. TMBPF-DGE is produced by the reaction of tetramethyl bisphenol F (TMBPF) with epichlorohydrin, which results in a mixture of bis(3,5-dimethyl-4-hydroxyphenyl)methane bis(2,3-epoxypropyl)ether, the major component, oligomers (due to the reaction of one or both of the epoxy groups), the dimer, trimer and tetramer (all bi-functional epoxy) of TMBPF-DGE and minor quantities of other reaction products. Hydrolysis of the epoxy group during an aqueous washing step in the reaction may occur.

13. The water content of TMBPF-DGE was 0.05% and the residual content of epichlorohydrin and sodium were 0.79 mg/kg and 3.6 mg/kg, respectively.

14. The residual content of TMBPF was 0.77 µg/kg.

15. Formation of a TMBPF-DGE containing oligomer may occur during the synthesis of the resin or during the migration process if an oxirane/epoxide functional group on a linear oligomer reacts with a free hydroxyl group. It is possible that the cyclic oligomers are not incorporated into the cured polymer structure and hence migrate more readily. The reaction does not involve a loss or addition of mass; therefore, the linear and cyclic forms will have the same mass.

16. The submitted information considered that 93% of the resin and components cannot form a cyclic structure due to the length of the molecules. TMBPF-DGE by itself is too short, even if one of the epoxy groups is hydrolysed. A linear dimer of TMBPF-DGE with at least one epoxy group and one diol end group could theoretically form a cyclic dimer. The data provided showed that any cyclic substances were present at low (non-detectable) levels.

Physical and chemical properties

17. TMBPF-DGE is liquid at room temperature (RT). No melting point was cited.

18. No data were available on a boiling point or decomposition temperature.

19. TMBPF-DGE is soluble in water at 1.26 ± 0.1 mg/L at 20°C. The octanol/water partition coefficient (Log Po/w) is 4.47 at 25°C. As demonstrated by the Log Po/w TMBPF-DGE would also be expected to be soluble in organic solvents, such as ketones, glycols, alcohols and aromatics.

20. TMBPF-DGE contains epoxy groups and as such is intended to be reactive. However, reactivity is negligible in the finished (cured) coating where it is incorporated into the polymer backbone. Hence, the submitted documentation considered the substance to be stable under the final conditions of use. While epoxy groups of any remaining TMBPF-DGE may react with food constituents no interactions with food substances are anticipated after polymerisation.

21. Epoxy groups are known to be hydrolysed into the diol components when reacted with water. No test on hydrolysis was performed but TMBPF-DGE was assumed to produce the same hydrolysis and diol components as listed under Annex I of Regulation (EC) No 1895/2005 for bisphenol A diglycidyl ether (BADGE).

Characterisation of substance after incorporation in FCM

22. TMBPF-DGE is a mixture of the mono- and diglycidyl ethers and TMBPF-DGE oligomers which are then processed to form an epoxy resin, copolymerised with acrylic-based monomers in water, forming a polymer dispersion. The epoxy resin/polymer dispersion then forms part of the final can coating material intended for food contact applications.

23. The final coating is meant as an internal protection coating in food can bodies and can end coatings (e.g., aluminium) in contact with all types of food, including beverages.

24. As a worst case the coated cans and can ends are intended for sterilisation at a maximum temperature of 130°C for 1 hour, followed by long term storage (> 6 months) at room temperature (RT).

25. The surface to volume (S/V) ratio would vary from article to article. In general, the conventional S/V ratio of 6 dm^2/kg would be applicable to small cans, for larger cans this would represent a worst-case scenario. For can ends, the actual S/V ratio would be less than the conventional 6 dm^2/kg. Coating on metal used for can ends would not be likely to exceed 12.4 g/m^2.

Migration

26. A worst-case approach was applied using, as a proxy for overall migration, extraction into olive oil and acetonitrile, and quantification of TMBPF-DGE, its hydrolysis products and the total number of epoxy groups.

27. The sum of all compounds migrating out of the coating (overall migration) into olive oil was 2.0 mg/dm^2 or 12 mg/6 dm^2.

28. The sum of all compounds migrating out of the coating (overall migration) into acetonitrile was 4.9 mg/dm^2 or 29.4 mg/6 dm^2.

29. The overall migration into acetonitrile was greater than the overall migration into olive oil and both the FCMJEG and COT agreed that acetonitrile provided the worst-case extraction of TMBPF-DGE and hence would provide the worst-case migration, with a degree of conservativism of at least 2.5-fold.

Quantification and identification of migrating oligomers and reaction products

30. The final coating, while in contact with food, may release residual monomers or additives, but also non-intentionally added substances (NIAS) such as

oligomers and reaction products of ingredients or impurities.

31. Thus, the substances in the acetonitrile extract were further examined by liquid chromatography time of flight mass spectrometry (LC-ToF-MS) and, according to the documentation provided, the majority were found to be associated with components of the manufacturing process or the final coating. Only three were directly associated with TMBPF-DGE. The total amount of TMBPF-DGE related oligomers plus substances not identified amounted to 2.1 mg/6 dm^2. This includes substances that were present at a low level (50 µg/6 dm^2).

32. The sum of all compounds migrating from the coating (overall migration) showed that extraction in acetonitrile represented a worst-case scenario and is approximately 2.5-fold greater than extraction in olive oil under worst-case conditions. If this factor were applied to the specific extraction value for TMBPF-DGE and related substances of 2.1 mg/6 dm^2, then the migration of TMBPF-DGE and related substances from the coating would be approximately 1 mg/6 dm^2.

33. The submitted documents further provided an analysis of potential cyclic oligomers in the final can coating, with substances that may contribute to the quantity of cyclic oligomers. Substances that had a database match for an oligomer with a free oxirane group and/or masses with more than one peak in the extracted ion chromatograms would have the potential to have linear and/or cyclic isomeric structures. No substances (with a molecular weight 1000 Dalton) were detected, other than those identified and quantified previously.

Residual content

34. The toxicologically active part of TMBPF-DGE is the oxirane ring (C2H3O) and as part of the curing process these groups are meant to react and hence would be inactivated. However, as residual amounts may remain, the final coating may contain free TMBPF-DGE with the oxirane ring intact or a range of oligomers that may contain one or more oxirane rings.

35. The residual oxirane functionality in acetonitrile extracts was 29 µg/6 dm^2, determined by nuclear magnetic resonance (NMR) spectroscopy. The submitted documentation assumed that the worst-case migration would be identical to the extracted quantity. If the surface/volume (S/V) ratio was reduced, then the worst-case migration would decrease proportionally. This would be the case for many can-end applications.

36. The total residual content of TMBPF-DGE and its hydrolysis and chlorinated products (TMBPF-DGE.H2O, TMBPF-DGE.2H2O), TMBPF-DGE.HCl, TMBPF-DGE.2HCl and TMBPF-DGE.H2O.HCl) in the final cured coating was 92.8 µg/6 dm^2 (sum of all compounds), TMBPF was detected at 0.77 µg/6 dm^2. Analysis was by liquid chromatography coupled to mass spectrometry (LC-MS/MS). The potential hazard of TMBPF-DGE stems from the oxirane/epoxy function. Neither TMBPF nor TMBPF-DGE.2H2O have an epoxide functional group and are therefore considered less reactive and not of toxicological concern.

37. The assessment focuses on TMBPF-DGE alone and substances associated with components of the manufacturing process, or the final coating are not directly relevant. To produce the epoxy resin TMBPF-DGE can be reacted with any authorised monomer. The final product/can coating must therefore comply with the specific migration limits (SMLs) for the respective compounds.

38. Thus, the total residual content of TMBPF-DGE, including all monomer derivatives (92.8 µg/6 dm^2) was used in the submitted documents as a worst-case dietary concentration for human exposure considerations.