German Federal Institute for Risk Assessment

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LI. Temperature Resistant Polymer Coating Systems for Frying, Cooking and Baking Utensils

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Contents

1. Preamble

Coating systems in the sense of this Recommendation are dispersions or solutions of artificial organic resins[1] in water or organic solvents for producing slippery, non-stick coatings on kitchen utensils and other articles that come into contact with foodstuffs. As a rule, thickness of the coating does not exceed 60 µm. Usually, the coating consist of combinations of fine-grain homo- or copolymers of tetrafluoroethylene with solutions or dispersions of film-forming artificial organic resins. Coatings of fluoropolymers and fluoropolymer-free coatings of artificial resins are also covered by this Recommendation. There are no objections to the use of temperature resistant polymer coating systems in the manufacture of commodities in the sense of § 2, Para. 6, No. 1 of the Food and Feed Code (Lebensmittel- und Futtermittelgesetzbuch), provided they are suitable for their intended purpose and comply with the following conditions:

[1] Artificial resins in the sense of this Recommendation are polymers obtained through modifying natural products, polymerisation, polycondensation or polyaddition, e.g. thermoplastics, thermosetting plastics and elastomers.

2. Substances for producing temperature resistant coatings

2.1 Systems for producing coatings on kitchen utensils for frying and cooking (e.g. frying pans, saucepans etc.)[2]

2.1.1 Fluoropolymers:

2.1.1.1 Polytetrafluoroethylene,
provided its melting viscosity[3] at 380 °C is greater than 50 Pa · s and its melting point[4] higher than 320 °C.

2.1.1.2 Copolymers of tetrafluoroethylene with the following comonomers:
Perfluoroalkyl vinyl ether with 1 - 3 C-atoms in the alkyl group
Hexafluoropropylene, max. 5 %, based on the weight of tetrafluoroethylene copolymers.
The melting viscosity[3] of these copolymers at 372 °C, must be greater than 10^3 Pa · s; their melting point[4] must be no less than 305 °C.

2.1.2 Binding resins:

2.1.2.1 Polyamide-imides:
Polyamide-imide 1 (PAI-1) =
poly-N-(4,4'-diphenylmethane trimellitamide imide), produced by reaction of 4,4'-diisocyanatodiphenylmethane with trimellitic acid anhydride and, as necessary, ethyleneglycol monomethyl ether[5]
Polyamide-imide 2 (PAI-2) =
poly-N-(4,4'-diphenylmethane trimellitamide imide), produced by reaction of 4,4'-diaminodiphenylmethane with benzoyl chloride-3,4-dicarboxylic anhydride
Polyamide imide 3 (trione resin) =
poly-(2,4,5-triketoimidazolidino-diphenylmethano-N,N'-diphenylmethano-bis-imino-trimellitamide), produce by reaction of the reaction product of trimellitic acid anhydride and 4,4'-diaminodiphenylmethane with 4,4'-bis-ethoxalylaminodiphenylmethane and diphenylmethane-4,4'-diisocyanate

2.1.2.2 Polyphenylene sulfide (PPS),
produce from the conversion of equimolar parts of p-dichlorobenzene and sodium sulfide[6]

2.1.2.3 Polyether sulfone (PES) =
poly(oxy-p-phenylene-sulfonyl-p-phenylene), produced through polycondensation of equimolar parts of the di-potassium salt of 4,4'-dihydroxy-diphenylsulfone with 4,4'-dichloro-diphenylsulfone.

2.1.2.4 Silicone resins, provided they comply with Section II of amended Recommendation XV[7].

2.1.2.5 Polyaryl sulfone, produced by reaction of 4,4'-dihydroxy-diphenyl sulfone with 1,4-dihydroxybenzene

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[2] This includes coatings whose intended use involves them being heated to temperatures of up to 230 °C, or for short periods - max. 15 min - up to 250 °C.

[3] Determination after ASTM D 1238 "Flow Rates of Thermoplastics by Extrusion Plastometer", obtainable from American Technical Publishers Ltd., 68 a Wilbury Way, Hitchin, Herts. SG4 OTP/England.

[4] Ke, B.: Newer Methods of Polymer Characterization, London: Interscience Publishers, 1964.

[5] The nitrogen content of polyamide-imide-1 is 7.8 to 8.2 %.

[6] The sulfur content of polyphenylene sulfide is 28.2 to 29.1 %.

[7] Compare Recommendation XV. "Silicones"

2.1.3 Adhesion promoters:
Lithium polysilicate[8] (lithium oxide content, max. 2.1 %)
Mixture of aluminium phosphate and phosphoric acid[9]

2.1.4 Additives:
In further processing of the polymers listed under 2.1.1 and 2.1.2 the following production aids may be used:

2.1.4.1 Emulsifying agents:
Alkyl(C_5-C_{15})phenol oxyethylates with 5 - 15 ethylene oxide groups
Fatty alcohol (C_{10}-C_{20}) oxyethylates with 5 - 15 ethylene oxide groups
Sodium alkyl sulfates(C_{10}-C_{20})
Ammonium lauryl sulfate
Copolymers of ethylene oxide and propylene oxide; ethylene oxide content, min. 10 % Monoethanol ammonium lauryl sulfate
Triethanolamine oleate
Sodium, potassium and ammonium salts of the condensation product of naphthalene sulfonic acid and formaldehyde
Sodium, potassium, ammonium and bis-(2-hydroxy-ethyl)-ammonium salts of mono- and diesters of phosphoric acid with monohydric primary straight-chain saturated fatty alcohols of chain length C_{12}-C_{18}
Soybean lecithin
Ammonium 2,2,3-trifluoro-3-[1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propoxy]propanoate, max. 0.01 % in the dispersion.
Perfluoro[(2-ethyloxy-ethoxy)acetic acid], ammonium salt, max. 0.83 % of the polymer. The substance may only be used in fluoropolymers that are processed at temperatures higher than 300 °C for at least 10 min.

2.1.4.2 Other processing aids:
Organopolysiloxanes (silicone oil) after Section I of Recommendation XV[7]
Copolymers of acrylic acid ethyl ester after Recommendation XXII[10]
Methyl cellulose
Ethyl cellulose
Hydroxyethyl cellulose
Triethylamine
Triethanol phosphate
Diethyl ethanolamine
Cerium(III)-2-ethyl-hexanoate
Ammonium peroxydisulfate
Ethylenediamine
Dimethylbenzyl-octadecyl ammonium hectorite

2.1.4.3 Colorants[11] and fillers[12]

[8] For the transfer of lithium into food or food simulant the provisions of Commission Regulation (EU) No 10/2011 apply.
[9] Coupling agents produced using chromic acid are only met occasionally nowadays; about the requirements for such coatings, see 3.3.6.
[10] Recommendation XXII. “Polymers based on esters of acrylic and methacrylic acids, their copolymers, and mixtures of these with other polymers”
[11] Recommendation IX. "Colorants for plastics and other polymers used in commodities"

2.2 Systems for producing coatings on baking utensils, kitchen aids, small thermostatically controlled electrical appliances (up to 140 °C) and covers for frying and cooking utensils[13]

In addition to those listed under 2.1, the following substances may be used:

2.2.1 Copolymers of tetrafluoroethylene:
Copolymers of tetrafluoroethylene with hexafluoropropylene, provided their melting viscosity[3] at 380 °C is at least 10^3 Pa · s and their melting point[4] no less than 225 °C.

2.2.2 Binding resins:

2.2.2.1 Polysulfone =
poly-(oxy-p-phenylenesulfonyl-p-phenylenoxy-p-phenylene-isopropylidene-p-phenylene), produced through conversion of the di-sodium salt of 2,2-bis-(4-hydroxyphenyl)propane (bisphenol A) and 4,4'-dichlorodiphenyl sulfone.

2.2.2.2 Epoxy resins,
produced through the conversion of glycidyl ether from 2,2-bis-(4-hydroxyphenyl)-propane (bisphenol A) and epichlorohydrin with the following cross-linking agents:
melamine-formaldehyde resins, phenol-formaldehyde resins, urea-formaldehyde resins and benzoguanamine-formaldehyde resins.

2.2.2.3 Polyarylsulfone, produced by reaction of 4,4'-dihydroxy-diphenyl sulfone and 1,4-dihydroxy benzene.

2.2.3 Other auxiliary agents:
In further processing of the copolymers and binding resins listed under 2.2.1 and 2.2.2, apart from the adhesion promoters listed under 2.1.3, the following substances may also be used:
Potassium citrate
Copolymer of methylmethacrylate and 3-(2-methacryloxyethyl)-2,2-spirocyclohexyloxazolidine.

3. Requirements for the finished products

3.1 Specific migration[14] and determination of overall migration

3.1.1 Test conditions for
coated utensils for frying and cooking, after 2.1
coated baking utensils, after 2.2

The specific migration test(s) shall be carried out three times on a single sample using another portion of food simulant on each occasion.
The fulfillment of the requirements shall be checked on the basis of the level of the migration found in the third test.
The material or article shall respect the specific migration limit already in the first test for substances for which the specific migration limit is set as non-detectable.

[12] Recommendation LII. "Fillers"

[13] This includes coatings whose intended use involves them being heated to temperatures of up to 140 °C, or for short periods - max. 15 min - up to 180 °C.

[14] Methods for determining specific migration of the substances listed under 3.1.2 and 3.2 as well as the low-molecular components after 3.2, see Part B.II.LI. „Untersuchung von temperaturbeständigen Beschichtungssystemen aus Polymeren für Brat-, Koch- und Backgeräte“. In: Kunststoffe im Lebensmittelverkehr. Carl-Heymanns-Verlag. Losebl.-Ausg.

The food simulants used should be selected according to current scientific knowledge and reflect the worst-case scenario of actual use, whereby the physicochemical properties of the respective analyte must also be taken into account.

The test conditions can be found in the Technical Report of the Joint Research Center of the EU Commission on test conditions for kitchen articles[15]. The conditions for food preparation utensils of classes FPU/H2, FPU/H3 and FPU/H4 for plastic articles are applied. An exception is the testing of items in category FPU/H4. Instead of the specified test time of 8 hours, the contact time is reduced to 4 hours because an 8-hour migration with 3 % acetic acid leads to corrosion of the objects that is not typical for the application.
The test with modified polyphenylene oxides (MPPO) as a simulant is carried out for 2 h at 175 °C in accordance with DIN EN 14338.

The element permeability test is carried out in accordance with the current version of the EDQM Technical Guideline for Metals and Alloys.[16]

If the conditions of intended use deviate significantly from the test conditions described above, these are to be adapted correspondingly.[17]

The overall migration is determined in the third migration and in/under the following simulants and test conditions:

95 % ethanol	6 h bei 60 °C
Isooctane	4 h bei 60 °C

The total migration must not exceed the guideline value of 10 mg/dm^2.

3.1.2 Limits of specific migration

In determining specific migration the following limits must not be exceeded:

Total fluorine:	0.05 mg/dm^2
Phenolic substances:	0.05 mg/dm^2
Organic nitrogen:	0.02 mg/dm^2
Primary aromatic amines:	not detectable[18,19]
Formaldehyde:	in compliance with the limit stipulated in the Commission Regulation (EU) No 10/2011
Emulsifiers:	in total, 0.05 mg/dm^2
1,4-Dihydroxybenzene:	in compliance with the limit stipulated in the Commission Regulation (EU) No 10/2011
Sodium salt of perfluoro-alkenyl-oxybenzene sulfonic acid:	max. 0.005 mg/dm^2

[15] https://publications.jrc.ec.europa.eu/repository/handle/JRC134290

[16] https://www.edqm.eu/en/metals-and-alloys-used-in-food-contact-materials-and-articles

[17] Commercial deep-fry equipment or food-processing machinery, for example, may be subjected to conditions of use not covered by the test conditions given.

[18] For the release of primary aromatic amines a detection limit of 0.01 mg/kg applies to the sum of the released primary aromatic amines. Additionally, primary aromatic amines classified as carcinogens in classes 1A and 1B of the CLP Regulation (EC) 1272/2008 may not be released referred to the single substance with a detection limit of 0.002 mg/kg food or food simulant. For primary aromatic amines that are listed in Annex I, Table 1 of Regulation (EU) No. 10/2011, the limit set out there applies.

[19] This limit refers to the migration of primary aromatic amines from the monomers and to the migration of primary aromatic amines that are formed by hydrolysis of isocyanates from polyamid-imides.

Ammonium 2,2,3-trifluoro-3-[1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propoxy]propanoate: 0.0002 mg/dm^2

Coatings of polyamide imides with and without the use of polytetrafluoroethylene:
Trimellitic acid anhydride: in compliance with the limit stipulated in the Commission Regulation (EU) No 10/2011

Coatings of polyphenylene sulfide:
p-Dichlorobenzene: in compliance with the limit stipulated in the Commission Regulation (EU) No 10/2011

Coatings of polyethersulfone:
4,4'-Dihydroxy-diphenyl-sulfone:
Diphenylsulfone:
4,4'-Dichloro-diphenylsulfone:
} in compliance with the limit stipulated in the Commission Regulation (EU) No 10/2011

Coatings of polysulfone:
4,4'-Dichloro-diphenylsulfone: in compliance with the limit stipulated in the Commission Regulation (EU) No 10/2011

2,2-Bis-(4-hydroxyphenyl)-propane (Bisphenol A): 0.05 mg/6 dm^2

3.2 Limits of low-molecular components in the finished coatings[14]

3.2.1 Coatings of polyethersulfone:
4-Chloro-4'-hydroxy-diphenyl-sulfone: content in the finished coating: 0.05 mg/dm^2

3.2.2 Coatings of polysulfone:
Monochlorobenzene: content in the finished coating: 0.08 mg/dm^2

3.2.3 Coatings produced using adhesion promoters must not test positively to chromium VI. Extract from the coatings must contain no more than 0.02 mg/dm^2 chromium III.