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4MSI Common Approach: ACCEPTANCE OF ENAMELS AND CERAMIC MATERIALS USED FOR PRODUCTS IN CONTACT WITH DRINKING WATER

Part A – Methodologies for testing and accepting compositions to be included in the 4MSI Positive List of compositions for enamels and ceramic materials

Part B – 4MSI Positive List of compositions for enamels and ceramic materials

Part C – Procedure and methods for testing and accepting products or components made of enamels or ceramic materials

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France, Germany, the Netherlands, the United Kingdom and Denmark (4MSI) work together in the framework of the 4MS Common Approach as laid down in the Declaration of Intent (January 2011). This common approach aims for convergence of the respective national approval schemes for materials and products in contact with drinking water. It might also be used as a starting point for harmonized European requirements, which will have to be implemented under the revised Drinking Water Directive (DWD).

Part A of this document includes a common basis for accepting enamel and ceramic compositions as prerequisite for testing products.

Part B of this document includes a Positive List of enamel and ceramic compositions accepted in all of the 4MSI following the procedure described in Part A and a corresponding list of parameters to be investigated when products are tested according to Part C.

Part C includes a procedure and methods for testing and accepting products or components made of enamels or ceramics in a certifying or approval process.

Further information may be obtained from any of the competent authorities of the 4MSI.

Bundesministerium für Gesundheit (Deutschland)

Ministère du Travail, de l'Emploi et de la Santé (France)

Ministerie van Infrastructuur en Milieu (Nederland)

Department for Environment, Food and Rural Affairs (United Kingdom)

Miljøministeriet, and Trafik-, Bygge- og Boligstyrelsen (Denmark)

Part B – 4MSI Positive List of Compositions for Enamels and Ceramic Materials

1 Structure of the 4MSI Positive List

The 4MSI Positive List of compositions for enamels and ceramic materials contains specific material types. For each type a description is given and the accepted constituents are specified. The compositions of products and components made of enamels and ceramics have to be in line with this Positive List. For the certification or approval of products or components additional migration tests (product tests) might be required (see Part C).

2 Enamel

2.1 Description of the material

Enamel is a vitreous material produced by melting at 1200 °C – 1300 °C and quenching (fritting) with inorganic, mostly oxidic composition (see Table 1).

The ground enamel frit is applied to iron-containing metallic materials by melting at above 480 °C. The enamel layer produced in this way combines the strength and elasticity of metals with the hardness and chemical resistance of glass. In the enamelling process, the enamel and the metal undergo an electrochemical reaction to form a composite material. This causes the enamel to bind to the metal surface with a force of up to 100 N/mm². The enamel layer cannot be infiltrated, it is non-diffusible and thermally stable up to 300 °C.

Enamels used in drinking water applications should have a high level of resistance to water.

The appearance or taste of drinking water is not affected by enamels, such that respective testing is not required. Testing of microbial growth is also not required, since the smoothness of the surface and the absence of digestible organic constituents in the material do not allow any such growth to develop.

2.2 Accepted Compositions

Table 1: Accepted constituents of enamel

Constituent	Content in %		Constituent	Content in %		Constituent	Content in %	
	Min.	Max.		Min.	Max.		Min.	Max.
SiO_2	25	80	**MgO**	0	5.0	**Fe_2O_3**	0	5.0
B_2O_3	0	20	**CeO_2**	0	15	**MoO_3**	0	5.0
Na_2O	0	30	**ZnO**	0	10	**P_2O_5**	0	5.0
K_2O	0	10	**Al_2O_3**	0	5.0	**SnO_2**	0	5.0
Li_2O	0	10	**CoO**	0	5.0	**TiO_2**	0	16
CaO	0	10	**NiO**	0	3.0	**ZrO_2**	0	30
BaO	0	15	**CuO**	0	3.0	**F**	0	10
SrO	0	5.0	**MnO_2**	0	5.0	**Cr_2O_3**	0	3.0
Sb_2O_3	0	1.0						

Elements for consideration in the migration water:
Al, B, Ba, Cd, Ce, Co, Cu, Cr, Ni, Mn, Mo, Pb, Sr, Sb, Ti, Zr

Reference concentrations:
Table 9

3 Ceramic materials

3.1 Description of the material

Ceramics are an inorganic, non-metallic material. Ceramic products are commonly shaped at room temperature from a ceramic base material (such as kaolin or clay) available in either granulate form for dry pressing or in plastic form. The subsequent sintering process then leads to the typical characteristics such as diffusion resistance or chemical stability. Sintering temperatures are between 1250 °C and 2500 °C depending on the material. Crystalline structures are formed, which also contain some proportion of a vitreous phase. Ceramics exhibit high strength and hardness, are corrosion-resistant, and can generally be used at temperatures up to near the sintering temperature. Ceramics are also very resistant to water. Neither appearance nor taste of drinking water is affected by ceramics, such that respective testing is not required. Testing of microbial growth is also not required, since the smoothness of the surface (typically produced by grinding and polishing) and the absence of digestible organic constituents in the material do not allow any such growth to develop.

3.2 Accepted compositions

3.2.1 Oxide ceramics

Oxide ceramics are ceramics made of Al_2O_3 and SiO_2 (see Table 2), ZrO_2 (see Table 3) or hard ferrites (see Table 4).

Table 2: Accepted constituents of Al_2O_3 and SiO_2 ceramics

Constituent	Content in %		Constituent	Content in %	
	Min.	Max.		Min.	Max.
Al_2O_3	0	99.99	**MgO**	0	3.0
SiO_2	0	92	**MnO_2**	0	3.5
B_2O_3	0	2.0	**Na_2O**	0	3.0
BaO	0	0.2	**P_2O_5**	0	0.1
CaO	0	8.0	**SrO**	0	0.5
Cr_2O_3	0	2.0	**TiO_2**	0	2.5
Fe_2O_3	0	4.0	**ZrO_2**	0	3.0
K_2O	0	3.0	**Y_2O_3**	0	0.4

Elements for consideration in the migration water:
Al, B, Ba, Cr, Mn, Sr, Ti, Zr, Y

Reference concentrations:

Table 9

Inorganic sulphur species as contaminants with total content up to 0.5 % may be disregarded.

Table 3: Accepted constituents of ZrO_2 ceramics

Constituent	**Content in %**		**Constituent**	**Content in %**	
	Min.	**Max.**		**Min.**	**Max.**
Al_2O_3	0	95	**SiO_2**	0	5.0
ZrO_2	5	99	**TiO_2**	0	0.5
HfO_2	0	2.0	**Y_2O_3**	0	8.5
MgO	0	4.0	**Pr_2O_5**	0	0.2
CaO	0	0.1	**Na_2O**	0	0.1
Fe_2O_3	0	0.1	**K_2O**	0	0.1

Elements for consideration in the migration water:
Al, Hf, Pr, Ti, Y, Zr

Reference concentrations:
Table 9

Hard ferrites are compounds of an iron oxide with other metallic oxides of the general form: MexFeyOz. They are the basis of oxide-ceramic materials with magnetic properties, which are therefore used for specific products in contact with drinking water.

Table 4: Accepted constituents of hard ferrite ceramics

Constituent	**Content in %**		**Constituent**	**Content in %**	
	Min.	**Max.**		**Min.**	**Max.**
FeO/Fe_2O_3	85	95	**MnO**	0	3.0
Al_2O_3	0	3.0	**Ni**	0	0.1
BaO	0	12	**P_2O_5**	0	0.1
CaO	0	3.0	**SiO_2**	0	3.0
Cr_2O_3	0	0.1	**SrO**	0	12
Bi_2O_3	0	0.4			

Elements for consideration in the migration water:
Al, Ba, Bi, Cr, Mn, Ni, Sr

Reference concentrations:
Table 9

Inorganic sulphur species as contaminants with total content up to 0.5% may be disregarded. Chloride as impurity with a content up to 0.5% may be disregarded.

3.2.2 Non-oxide ceramics

Non-oxide ceramics are silicon carbides (see Table 5 and Table 6), tungsten carbides (see Table 7) and silicon nitrides (see Table 8)

Table 5: Accepted constituents of silicon carbide (SiC) ceramics

Constituent	Content in %		Constituent	Content in %	
	Min.	Max.		Min.	Max.
SiC	78	100	**Fe_2O_3**	0	3.0
Si	0	22	**Na**	0	0.1
Al	0	2.0	**Ni**	0	0.1
Al_2O_3	0	5.0	**SiO_2**	0	3.0
B	0	3.0	**Ti**	0	0.2
C	0	5.0	**Y_2O_3**	0	3.0
Ca	0	0.1	**ZrB_2**	0	11
Fe	0	0.2			

Elements for consideration in the migration water:
Al, B, Ni, Ti, Y, Zr

Reference concentrations:
Table 9
And additionally, to be considered in the migration water:
Benzo-(a)-pyrene and as sum Benzo[b]fluoranthene; Benzo[k]fluoranthene; Benzo[ghi]perylene; Indeno[1,2,3-cd]pyrene

Reference concentrations:
Table 10

Table 6: Accepted constituents of silicon carbide with free carbon (SISIC-C) ceramics

Constituent	Content in %		Constituent	Content in %	
	Min.	Max.		Min.	Max.
SiC	55	90	**Fe**	0	0.2
C	5.0	40	**Ni**	0	0.1
Al	0	0.2	**Si**	2.0	15
B	0	0.5	**SiO_2**	0	2.5
Ca	0	0.1	**Ti**	0	0.2

Elements for consideration in the migration water:
Al, B, Ni, Ti

Reference concentrations:
Table 9

And additionally, to be considered in the migration water:
Benzo-(a)-pyrene and as sum Benzo[b]fluoranthene; Benzo[k]fluoranthene; Benzo[ghi]perylene; Indeno[1,2,3-cd]pyrene

Reference concentrations:
Table 10

Table 7: Accepted constituents of tungsten carbide (WC) ceramics

Constituent	Content in %		Substance	Content in %	
	Min.	Max.		Min.	Max.
WC	90	100	**Mo**	0	1.0
Cr_3C_2	0	1.0	**Ni**	0	8.0

Elements for consideration in the migration water:
Cr, Mo, Ni, W

Reference concentrations:
Table 9

And additionally, to be considered in the migration water:
Benzo-(a)-pyrene and as sum Benzo[b]fluoranthene; Benzo[k]fluoranthene; Benzo[ghi]perylene; Indeno[1,2,3-cd]pyrene

Reference concentrations:
Table 10

Table 8: Accepted constituents of silicon nitride (SN) ceramics

Constituent	Content in %		Constituent	Content in %	
	Min.	Max.		Min.	Max.
Si_3N_4	78	97	**MgO**	0	4.0
Al_2O_3	0	7.0	**SiO_2**	0	7.0
CaO	0	2.0	**TiO_2**	0	5.0
Fe_2O_3	0	1.0	**Y_2O_3**	0	3.0
La_2O_3	0	6.0	**ZrO_2**	0	3.0

Elements for consideration in the migration water:
Al, La, Ti, Y, Zr

Reference concentrations:
Table 9

4 Ceramic materials made of carbon

4.1 Graphite

Graphite has specific technical properties. The starting materials include lignite, coal or petrol coke, which are mixed with a binding agent such as tar or a plastic resin, and then annealed at 600 °C to 1000 °C. The produced substances are known as carbon graphite and are used for applications such as slide bearings, sealing rings or pump components. In another optional manufacturing step, referred to as graphitisation, this carbon graphite is annealed once again at up to 3000 °C. This causes the individual graphite crystals to enlarge, causing an increase in density. Contaminants are burned off to improve purity. This electro-graphite exhibits good sliding properties and improved thermal and electrical conductivity. For graphite that have been impregnated with an organic resin, the resin has to be assessed separately based on 4MSI common approach on organic materials.

4.2 Amorphous Carbon layer

Ceramic or metallic materials may be covered with a carbon coating to achieve good sliding properties. These coatings may be produced using a number of different methods. This leads to the formation of crystalline layers of graphite and diamond.

4.3 Carbon fibres

In order to improve the strength of ceramic materials, carbon fibres may be used. These are made of organic fibres, such as viscose or polyacrylonitrile fibres, that are transformed into carbon by pyrolysis.

For ceramic materials made of carbon, there are no specific composition requirements provided that the manufacturing methods meet the requirements listed under 4.

5 Reference concentrations

For the evaluation of the test results the following reference concentrations in Table 9 and Table 10 have to be applied:

Table 9: Reference concentrations for the evaluation of enamels and ceramic materials

Element	Basis of reference concentration	Proportion of the limit value/ guideline value	Reference concentration in µg/l
Aluminium	DWD	50%	**100**
Antimony	DWD	10%	**0.5**
Barium	UBA	10%	**70**
Bismuth	UBA		**0.1**
Lead	DWD	5%	**0.5**
Boron	DWD	10%	**100**
Cadmium	DWD	5%	**0.15**
Chromium	DWD	10%	**5**
Cerium	UBA	50%	**20**
Hafnium	UBA		**0.1**
Cobalt	UBA	90%	**9**
Copper	DWD	10%	**200**
Lanthanum	UBA	90%	**2.7**
Manganese	DWD	50%	**25**
Molybdenum	WHO	10%	**7**
Nickel	DWD	10%	**2**
Praseodymium	UBA		**0.1**
Strontium	UBA	10%	**210**
Titanium	UBA	50%	**70**
Tungsten	UBA		**0.1**
Yttrium	UBA	10%	**3.5**
Zirconium	UBA	50 %	**5.0**

Carbon-containing ceramics (all ceramics that contain carbon, including carbides) must be examined for the release of benzo-(a)-pyrene as well as polycyclic aromatic hydrocarbons (PAHs). This should be subject to the criteria of the Table 10.

Table 10: Reference concentrations for PAH

Polycyclic aromatic hydrocarbon	Basis of reference concentration	Proportion of the limit value/ guideline value	Reference concentration in µg/l
Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[ghi]perylene Indeno[1,2,3-cd]pyrene	DWD	10 %	**0.01 for the sum of 4 PAH.**
Benzo[a]pyrene	DWD	10 %	**0.001**