

AEROSIL[®] R 104 and AEROSIL[®] R 106 for silicone rubber applications

Technical Information 1148



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1 Introduction

Synthetic silica has been used as a reinforcing filler in the silicone industry almost since the initial development of polysiloxane systems by Rochow (1) in the 1940s. In particular, the fumed silica manufactured by the AEROSIL® process is a constant companion for silicone rubber and have been making a valuable contribution to the success of this elastomer to this day.

Since then, in addition to the hydrophilic reinforcing silica, a large number of hydrophobic products have been specifically developed for this application, in which various silicone compounds commonly used in this industry are chemically bound to the surface of AEROSIL® fumed silica. With AEROSIL® R 104 and AEROSIL® R 106, both products rendered hydrophobic by octamethylcyclotetrasiloxane (D4), Evonik Industries is now introducing additionally products tailor-made for this industry, thereby expanding its already wide range of reinforcing silica for silicone rubber.

This Technical Information provides an overview of the properties of the new commercial products AEROSIL® R 104 and AEROSIL® R 106 in comparison with other AEROSIL® grades. In research, particular emphasis has been placed on their application in peroxide cross-linked HTV-silicone rubber and in 1K-silicone sealants.

2 Synthetic silica for silicone rubber

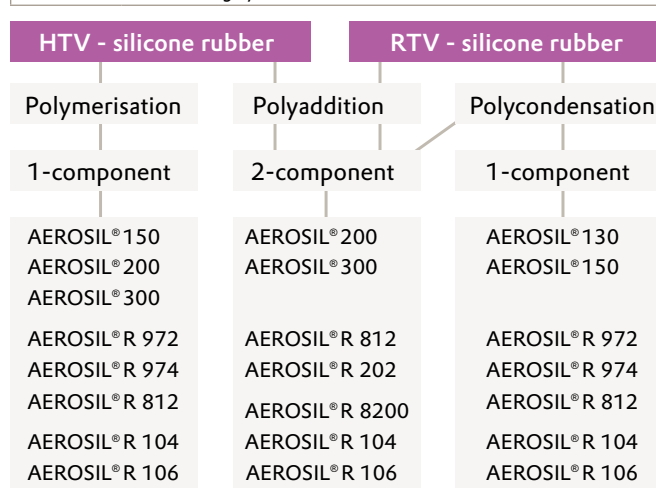
The reinforcing properties of synthetic silica are well known and are described in detail in the mentioned literature (items 2–6). In addition to their importance for the mechanical strength of silicone-vulcanizates they affect other properties, both of the non-cross-linked compound and of the silicone rubber. These cannot however be viewed in isolation from the reinforcing effect. Their thickening and thixotropic properties are often at their greatest when their reinforcing effect achieves optimum values.

The first-mentioned properties are however for the most part undesirable: for example, non-cross-linked HTV-silicone compounds become so hard and inelastic within a few days that they are completely unusable for any further processing.

This effect, known as “crepe hardening”, is due to the formation of a three-dimensional silica network structure which obtains its stability from hydrogen bonding via the silanol groups of the silica particles. If these functional groups of silica are largely eliminated, the “crepe hardening” described above is avoided. The compounds are then processable for a long time. The silicone industry has therefore developed special in-situ hydrophobizing processes in which the reinforcing silica is chemically aftertreated at temperatures above 100 °C with selected hydrophobizing agents during compounding in the kneader, which takes several hours. Very early on, Evonik adopted an alternative approach to the abovementioned in-situ hydrophobizing process and developed AEROSIL® R 972 specifically for this industry. This product, which is rendered hydrophobic by dimethyldichlorosilane (DDS), was introduced to the market 1962.

In addition to dimethyldichlorosilane, other silanes or siloxanes can be used as hydrophobizing agents for silica, some of which are intermediates from polysiloxane synthesis. In this connection dihydroxypolysiloxane (silicone oil) and octamethylcyclotetrasiloxane (D4) are of particular importance. Monomethyltrichlorosilane and hexamethyldisilazane (HMDS), a highly reactive silicone compound, are also used on an industrial scale by silica manufacturers as aftertreating agents for fumed silica. **Figure 1** lists all AEROSIL® grades for silicone applications and allocates them to the appropriate types of silicone cross-link.

Figure 1 Use of AEROSIL® grades in the different silicone crosslinking systems



All "R Types" of AEROSIL® fumed silica are hydrophobic: AEROSIL® R 972 and R 974 are rendered hydrophobic by DDS, AEROSIL® R 812 and R 812 S by HMDS and AEROSIL® R 202 by silicone oil.

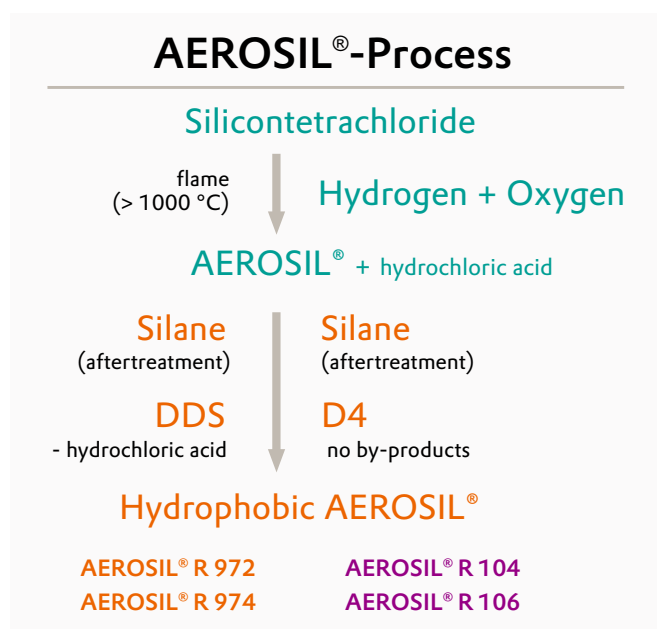
The new silica AEROSIL® R 104 and AEROSIL® R 106 rendered hydrophobic by D4 thus expand the range of reinforcing fillers, the properties of which are described in detail below.

3 Manufacture and properties of AEROSIL® R 104 and AEROSIL® R 106

3.1 Manufacture

Fumed silica is manufactured by continuous flame hydrolysis of silicon-tetrachloride (7). This process produces considerable quantities of by-product in the form of hydrochloric acid which is separated from the fumed silica by special processes. The products are hydrophilic and can be chemically aftertreated in a second reaction stage immediately after the formation of the fine silica particles. As shown schematically in Figure 2, silica manufacturers use the available degrees of freedom-range of the specific surface area of the initial hydrophilic silica and variation in the type of hydrophobizing agent-purposely to formulate the properties of the product.

Figure 2 Manufacturing scheme of hydrophobic fumed silica according to the AEROSIL®-process



Especially for the manufacture of AEROSIL® R 104 and AEROSIL® R 106 the aftertreating process was adjusted to the needs of the D4-aftertreating agent to hydrophobize AEROSIL® 200 and AEROSIL® 300. Additionally the deacidification process was further improved to receive very hydrophobic products with very few residual chloride content.

3.2 Physico-chemical properties

If octamethyl-cyclotetrasiloxane (D4) is used as an after-treating agent for synthetic AEROSIL® grades, such fumed silica generally exhibits the typical advantages of hydrophobic silica due to their water-repellent properties. Compared with hydrophilic grades of AEROSIL® they also absorb little water from atmospheric humidity and therefore contribute to uniform, trouble-free processability. Furthermore, hydrophobic products in general are distinctly better dispersible than the corresponding hydrophilic silica, as agglomeration by means of hydrogen bonding via the silanol groups has been largely prevented.

It can however be regarded as a peculiarity of these products that no additional hydrochloric acid is formed as a by-product when D4 is used as a hydrophobizing agent.

With an initial surface area of 200 m²/g AEROSIL® R 104 is characterised by a particularly low residual chloride content and, compared with AEROSIL® R 974, by a much higher degree of hydrophobicity (Figure 2). This also applies to AEROSIL® R 106 which like AEROSIL® R 812, is manufactured on the basis of AEROSIL® 300. Compared with AEROSIL® R 812, AEROSIL® R 106 has a similar low residual chloride content. Furthermore as this new silica grade approaches even the high level of hydrophobicity of this HMDS aftertreated product, AEROSIL® R 106 can be regarded as an economic alternative to AEROSIL® R 812.

For further details see Tables 1 and 2.

Table 1 Physico-chemical characteristics of AEROSIL® R 104 compared with AEROSIL® R 974 and AEROSIL® 200

Properties		AEROSIL® 200	AEROSIL® R 974	AEROSIL® R 104
Behavior towards water		hydrophilic		hydrophobic
BET surface area	m ² /g	200±25	170±20	150±25
Tamped density	g/l	approx. 50	approx. 50	approx. 50
Loss on drying (2 h at 105 °C)	wt. %	≤1.5	≤0.5	–
pH value (4% aqueous dispersion)		3.7–4.7	3.7–4.7	≥4.0
C-content	wt. %	–	0.7–1.3	1.0–2.0
SiO ₂	wt. %	≥99.8	≥99.8	≥99.8
Al ₂ O ₃	wt. %	≤0.05	≤0.05	≤0.05
Fe ₂ O ₃	wt. %	≤0.003	≤0.01	≤0.01
TiO ₂	wt. %	≤0.03	≤0.03	≤0.03
HCl	wt. %	≤0.025	≤0.1	≤0.02

These data represent typical values.

Table 2 Physico-chemical characteristics of AEROSIL® R 106 compared with AEROSIL® 300 and AEROSIL® R 812

Properties		AEROSIL® 300	AEROSIL® R 106	AEROSIL® R 812
Behavior towards water		hydrophilic		hydrophobic
BET surface area	m ² /g	300±30	250±30	260±30
Tamped density	g/l	approx. 50	approx. 50	approx. 50
Loss on drying (2 h at 105 °C)	wt. %	≤1.5	–	≤0.5
pH value (4% aqueous dispersion)		3.7–4.7	≥3.7	5.5–7.5
C-content	wt. %	–	1.5–3.0	2.0–3.0
SiO ₂	wt. %	≥99.8	≥99.8	≥99.8
Al ₂ O ₃	wt. %	≤0.05	≤0.05	≤0.05
Fe ₂ O ₃	wt. %	≤0.003	≤0.01	≤0.01
TiO ₂	wt. %	≤0.03	≤0.03	≤0.03
HCl	wt. %	≤0.025	≤0.025	≤0.025

These data represent typical values.

3.3 Properties in HTV-silicone rubber

The basic properties both of hydrophilic and hydrophobic AEROSIL® grades in peroxide cross-linked HTV-silicone rubber are described in detail in Number 12 of our Technical Bulletins. Here too, very simple formulations have been used, each with 40 parts of silica, in order to compare the properties of the products rendered hydrophobic by D4 (AEROSIL® R 104 and AEROSIL® R 106) with other AEROSIL® grades. Details of the testing method are described in Section 4.

At this point it should be remembered that the mechanical strength of silicone rubber is considerably affected by the specific surface area of the AEROSIL® grades used as a reinforcing filler. Furthermore, as shown in (2), the amount of processing agents used should be matched to the specific requirements of the silica. In this case, two simple formulations have been used, one without any processing aid (PA) and the other with 6 parts. The rheological, mechanical and optical properties measured are summarised in Tables 3 and 4.

Table 3 Properties of silicone rubbers containing AEROSIL® R 104 and AEROSIL® R 106 compared with AEROSIL® R 974 and AEROSIL® 200 (formulation without processing agent)

Properties		AEROSIL® 200	AEROSIL® R 974	AEROSIL® R 104	AEROSIL® R 106
Williams plasticity (after compounding)		942	302	305	392
Williams plasticity (replasticised after 7 days)		904	280	248	238
Hardness, Shore-A		74	57	55	57
Tensile strength	N/mm ²	7.0	8.2	8.6	9.3
Elongation at break	%	270	350	420	480
Tear strength	N/mm	29	28	26	29
Resilience	%	56	50	49	47
Transparency		33	30	28	40

Table 4 Properties of silicone rubbers containing AEROSIL® R 104 and AEROSIL® R 106 compared with AEROSIL® R 974 and AEROSIL® 200 (formulation with processing agent)

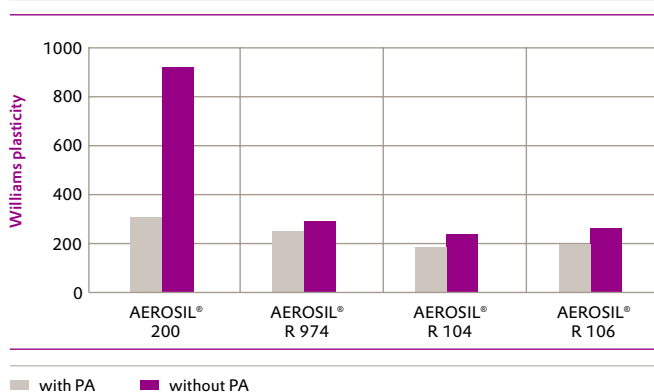
Properties		AEROSIL® 200	AEROSIL® R 974	AEROSIL® R 104	AEROSIL® R 106
Williams plasticity (after compounding)		855	245	203	233
Williams plasticity (replasticised after 7 days)		220	193	199	207
Hardness, Shore-A		57	55	49	52
Tensile strength	N/mm ²	7.5	9.2	7.3	8.3
Elongation at break	%	380	380	530	560
Tear strength	N/mm	26	29	28	31
Resilience	%	51	50	41	41
Transparency		35	31	31	35

The test results obtained with AEROSIL® R 104 and AEROSIL® R 974 are comparable, as these products all have an initial surface area of approx. 200 m²/g.

Considerable differences exist in the rheological behaviour of non-cross-linked compounds. The formulation without PA has an extremely high thickening effect for the hydrophilic AEROSIL® 200. In both cases AEROSIL® R 104 and AEROSIL® R 106 show low WP values and, as expected, provided readily processable compounds (Figure 3). When we consider that in industrial-scale compounding, hydrophilic AEROSIL® types are dispersed and undergo an in-situ hydrophobizing process for several hours at over 100 °C, AEROSIL® R 104 and AEROSIL® R 106 can contribute towards shortening this costly process. This can mean that it is not necessary to remove and dispose hydrochloric acid, ammonia or other by-products resulting from in-situ aftertreating reaction using DDS or HMDS.

The interpretation of the properties of AEROSIL® R 104 applies in the same way to AEROSIL® R 106. As this silica is manufactured on the basis of AEROSIL® 300, its overall reinforcing properties are greater. As expected AEROSIL® R 106 was particularly suitable for the manufacture of high-transparency rubbers.

Figure 3 Williams plasticity of silicone compounds with different AEROSIL® grades



3.4 Properties in RTV-1K-silicone sealants

The basic properties of AEROSIL® grades in silicone sealants are described in detail in No. 63 of our Technical Bulletin Pigments series. In contrast to HTV-silicone rubber the reinforcing effect of hydrophilic silica cannot be increased by rendering them hydrophobic. This is due to the vulcanising agents normally used in this case, which react with the silanol groups both of the polymer and of the silica.

In this instance, the hydrophobicity of the reinforcing filler must be adjusted to ensure that the vulcanised rubber retains sufficient strength, which was done in the case of both AEROSIL® R 104 and AEROSIL® R 106.

In an equally simple acetate-cross-linking formulation containing 8 % silica (for details see 4. “Details of testing method”), the reinforcing properties of these two products were compared with other AEROSIL® grades commonly used for this application. The tensile strength of all the specimens tested (Table 5) shows no significant differences at all. To a great extent the other mechanical properties tested were also on a comparable level.

In addition to the mechanical stability of the sealant, its other major quality characteristics are ease of processability, low surface roughness and satisfactory durability.

Additionally hydrophobized silica with low surface area, such as AEROSIL® R 972 (initial surface area: 130 m²/g), fulfills these quality criteria to the maximum. In comparison, AEROSIL® 150 thickens somewhat more, which means that slightly more force is required to squeeze the sealant out of the cartridge.

In general, it can be said that the dispersibility of AEROSIL® fumed silica decreases as the surface area increases. It is thanks to the hydrophobic properties of AEROSIL® R 104 and AEROSIL® R 106 that these products display properties very similar to AEROSIL® 150.

Owing to the good dispersibility of AEROSIL® R 104, this silica is very suitable for the manufacture of especially transparent sealants (Figure 4). This is not possible with low-surface area silica such as AEROSIL® 150 or AEROSIL® R 972. A further quality improvement in this regard can be achieved by using AEROSIL® R 106. However, the transparency does not increase as much as one would expect from a rise in the specific surface area of a silica from 200 to 300 m²/g. As a result of the comparatively low viscosity in the sealant, the shearing forces are no longer transmitted well enough to break down the silica agglomerates. Transparency does not therefore increase in proportion.

Figure 4 Transparency of silicone sealants containing different AEROSIL®-grades

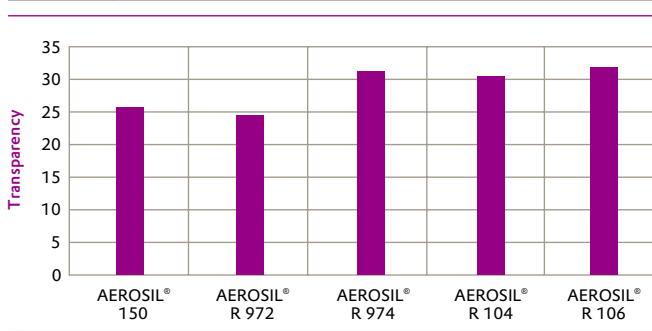


Table 5 Properties of 1K-RTV-silicone sealants containing AEROSIL® R 104 and AEROSIL® R 106 compared with AEROSIL® 150, AEROSIL® R 972, AEROSIL® R 974 and AEROSIL® R 812 S

Properties		AEROSIL® 150	AEROSIL® R 972	AEROSIL® R 974	AEROSIL® R 104	AEROSIL® R 106	AEROSIL® R 812 S
Viscosity at D=10s ⁻¹	Pa · s	126	98	137	121	120	57
Yield point	Pa	320	168	251	217	172	13
Spots *	ratings	1.5	2.0	2.5	2.0	2.0	1.5
Hardness, Shore-A		19	17	16	16	17	13
Tensile strength	N/mm ²	1.6	1.5	1.3	1.9	1.5	1.1
Elongation at break	%	610	660	510	470	410	890
Resilience	%	53	49	49	45	51	53

* Grade 1 = excellent
Grade 5 = insufficient

4 Details of testing method

However, sealants are not only formulated, as here, as acetate-cross-linking systems, but also as “neutral-cross-linking”. The reason for this is that some materials which are sensitive to acid must be combined or, as in the case of electronic circuits, protected e. g. against contamination.

Owing to their low hydrochloric acid content it should also be possible to use AEROSIL® R 104 or AEROSIL® R 106 to manufacture these types of sealants. However, it is strongly advised that appropriate tests be carried out to laboratory standard before they are transferred to production.

HTV-silicone rubber

In the comparative tests on fumed silica with different tamped densities as described below a simple test formulation was selected:

100 pts. silicone polymer
40 pts. silica
0 or 6 pts. processing agent
0.5 % bis-(2,4-dichlorobenzoyl)-peroxide

Vulcanisation conditions:

8 min at 140°C in a press
6 h post-cure at 200°C in a forced-air oven

The silicone polymer used was Silopren® VS, a dimethyl polysiloxane containing few vinyl groups, manufactured by Momentive Performance Materials. A low-viscosity dihydroxypolysiloxane was used as the processing agent. All the formulation ingredients were mixed and dispersed on a two-roller mill at room temperature.

RTV-silicone rubber

The 1K-silicone sealants investigated in the present test were manufactured with the aid of a planetary dissolver in which the following formulation ingredients were well mixed. The dispersion of the silica used occurred under vacuum:

62.6 % Silicone polymer
(α , ω -hydroxydimethylsiloxypolydimethyl siloxane)
24.4 % Silicone oil
(α , ω -trimethyl siloxypolydimethyl siloxane)
4.0 % Crosslinker (ethyltriacetoxysilane)
1.0 % Adhesion agent (alcoxyacetoxysilane)
0.01 % Catalyst (dibutyltin diacetate)
8.0 % Silica

All tests were carried out in accordance with the appropriate DIN, ISO or ASTM standards.

5 Literature

- 1 E. G. ROCHOW, CHEMTEC 1980, Sept. 532-538
- 2 Company brochure "Technical Bulletin Pigments series, No. 12", Degussa, 1995
- 3 Company brochure "Technical Bulletin Pigments series, No. 63", Degussa, 1995
- 4 R. BODE, Kautschuk+Gummi, Kunststoffe 32, 89 (1979)
- 5 B. B. BOONSTRA, H. COCHRANE, E. H. DANNENBERG, Kautschuk + Gummi, Kunststoffe 29, 29 (1976)
- 6 H. COCHRANE, C. S. LIN, RUBBER CHEM. TECHNOL. 66, 48 (1993)
- 7 DE-PS 870242 Degussa (1941)
- 8 Company Publication "Technical Information No. 1253: AEROSIL® and AEROXIDE® for liquid silicone rubber"

6 Physical-chemical data of AEROSIL® fumed silica

Test methods	AEROSIL®						
	90	130	150	200	300	380	
Behavior towards water	hydrophilic						
Appearance	-fluffy white powder -						
BET surface area BET ¹	m ² /g	90±15	130±25	150±15	200±25	300±30	380±30
Tamped density ² approx. value							
Standard material	g/l	80	50	50	50	50	50
Densified material (suffix „V“)	g/l	–	120	120	120	120	120
Loss on drying ³ (2 h at 105°C) when leaving the plant	wt. %	≤1.0	≤1.5	≤1.5	≤1.5	≤1.5	≤2.0
C-content	wt. %	–	–	–	–	–	–
pH-value ⁴ (4% aqueous dispersion)		3.7–4.7	3.7–4.7	3.7–4.7	3.7–4.7	3.7–4.7	3.7–4.7
SiO ₂ ⁵	wt. %	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8
Al ₂ O ₃ ⁵	wt. %	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05
Fe ₂ O ₃ ⁵	wt. %	≤0.003	≤0.003	≤0.003	≤0.003	≤0.003	≤0.003
TiO ₂ ⁵	wt. %	≤0.03	≤0.03	≤0.03	≤0.03	≤0.03	≤0.03
HCl ⁵	wt. %	≤0.025	≤0.025	≤0.025	≤0.025	≤0.025	≤0.025

¹ in acc. to DIN 9277

² in acc. to DIN EN ISO 787/11, JIS K 5101/20 (not sieved)

³ in acc. to DIN EN ISO 787/2, ASTM D 280, JIS K 5101/23

⁴ in acc. to DIN EN ISO 3262-20, ASTM D 1208, JIS K 5101/26

⁵ based on material ignited for 2 hours at 1000°C

The data have no binding force.

		AEROSIL®								
Test methods		R 104	R 106	R 202	R 805	R 812	R 812 S	R 972	R 974	
Behavior towards water		hydrophobic								
Appearance		-fluffy white powder -								
BET surface area BET¹	m ² /g	150±25	250±30	100±20	150±25	260±30	220±25	110±20	170±20	
Tamped density² approx. value										
Standard material	g/l	50	50	60	60	60	60	50	50	
Densified material (suffix „V“)	g/l	90	-	90	90	90	90	90	90	
Loss on drying³ (2 h at 105 °C) when leaving the plant		wt. %	-	-	≤0.5	≤0.5	≤0.5	≤0,5	≤0.5	≤0.5
C-content		wt. %	1.0–2.0	1.5–3.0	3.5–5.0	4.5–6.5	2.0–3.0	3.0–4.0	0.6–1.2	0.7–1.3
pH-value⁴ (4% aqueous dispersion)			≥4.0 ⁶	≥3.7 ⁶	≥4–6 ⁶	3.5–5.5 ⁶	5.5–7.5 ⁶	5.5–7.5 ⁶	3.6–4.4 ⁶	3.7–4.7 ⁶
SiO₂⁵		wt. %	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8
Al₂O₃⁵		wt. %	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05
Fe₂O₃⁵		wt. %	≤0.01	≤0.01	≤0.01	≤0.01	≤0.01	≤0.01	≤0.01	≤0.01
TiO₂⁵		wt. %	≤0.03	≤0.03	≤0.03	≤0.03	≤0.03	≤0.03	≤0.03	≤0.03
HCl⁵		wt. %	≤0.02	≤0.025	≤0.025	≤0.025	≤0.025	≤0.025	≤0.05	≤0.1

¹ in acc. to DIN 9277

The data have no binding force.

² in acc. to DIN EN ISO 787/11, JIS K 5101/20 (not sieved)

³ in acc. to DIN EN ISO787/2, ASTM D 280, JIS K 5101/23

⁴ in acc. to DIN EN ISO 3262-20, ASTM D 1208, JIS K 5101/26

⁵ based on material ignited for 2 hours at 1000 °C

⁶ in water : methanol 1:1

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