

Table 1 Important characteristics of industrially manufactured silicic acids (from [1])

Preparation by	Flame	Arc	Precipitation	Gel	Hydrothermal
	hydrolysis				
Spec. BET surface area (m ² g ⁻¹)	50–600	25–300	30–800	250–1000	250–400
Primary particles (nm)	5– 61	5–500	5–100	3– 20	3– 20
Annealing loss (%)	1– 3	1	3– 7	3– 15	3– 5
Technical product names					
Untreated	Aerosil 200	TK 900	Suprasil BW5	Syloid 244	HK 125
Organically treated products	Aerosil R972		Sipernat D17	Syloid 161	

On the basis of previous results [5, 6], this paper demonstrates that simultaneous TG–DTA is an adequate investigation technique for determination of the amounts of bound water and for study of the decomposition of organic coating layers.

Experimental conditions

For the thermoanalytical studies, a Thermoanalyser TA 1 (Mettler/Switzerland) was used under the following constant conditions:

Sample mass: 50 mg, reference: 50 mg Al₂O₃. Heating rate in the temperature range 25–1000°; 10 deg min⁻¹. Macro-crucible support with Pt/PtRh thermocouples and Pt crucibles. Measuring ranges: TGI = 10 mg, DTG = 1 mg min⁻¹, DTA = 100 μV. Atmosphere: dried current of air at 5 l h⁻¹.

Results and discussion

In agreement with Refs [2–4], silicic acids release the adsorbed water up to 200°. In the upper temperature range, in parallel with this, condensation of surface silanol groups begins. This process proceeds reversibly up to about 400°, since the Si–O–Si bonds are still unstable.

With increasing temperature, the dehydration process becomes increasingly irreversible; it is usually completed only at 1000°. The thermogravimetric results obtained for the 5 typical silicic acid products are shown in Table 2.

Table 2 reveals that the silicic acids prepared by the wet process exhibit an

Table 2 Thermogravimetrically determined percentages of mass loss for 5 typical uncharged silicic acids

Sample	Total mass loss at 25–1000 °C, abs. %	Mass loss in the temperature range				
		25–200	200–350	350–500	500–700	700–1000 °C rel. %
Aerosil 200	2.2	55.4	17.1	5.9	15.3	6.3
TK 900	2.3	55.7	16.1	10.4	5.7	12.2
Suprasil BW5	9.8	69.4	9.2	10.2	6.1	5.1
Syloid 244	8.6	65.0	5.8	12.1	10.1	7.1
HK 125	8.2	60.7	4.8	14.3	8.3	9.5

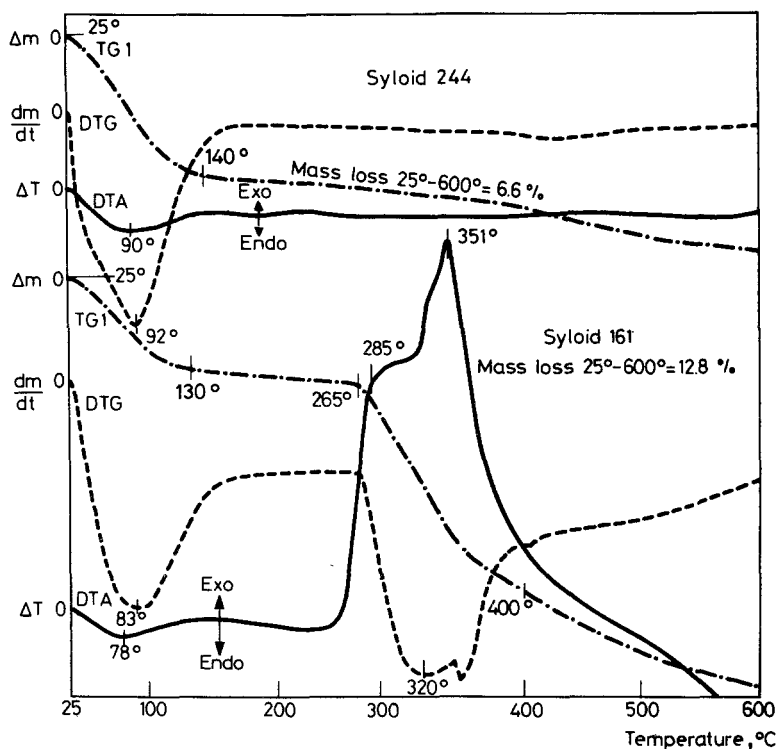


Fig. 1 TG–DTG–DTA diagrams of the two Syloid flattening agents (Grace): type 244 (untreated) and type 161 (organically coated)

annealing loss 4 times as high as those prepared thermally. About half of the mass loss is due to the water bound in the silanol groups. There is a remarkably high percentage mass loss in the upper temperature range, from 700° to 1000°. The fact that no defined degradation stages can be detected for any sample, even under quasi-isothermal conditions, may be regarded as indirect confirmation of the absence of definite arrangements of the silanol groups. This finding was verified by the relatively wide OH absorption band on IR and NIR spectroscopy [7]. Besides the untreated silicic acids, the aftertreated products are gaining more and more in significance. In the case of the coating process, a wax dispersion, preferentially of polyethylene wax, is added during silicic acid synthesis after a wet process. The silicic acid—wax product formed is separated from the aqueous medium and dried in the known manner, ground and, if necessary, air-classified. If one compares the TG–DTG–DTA diagrams (Fig. 1) of flattening agents of the type Syloid 244 (untreated) and Syloid 161 (organically aftertreated), both prepared by the gel process, clear differences are evident. At first the two products each display a mass

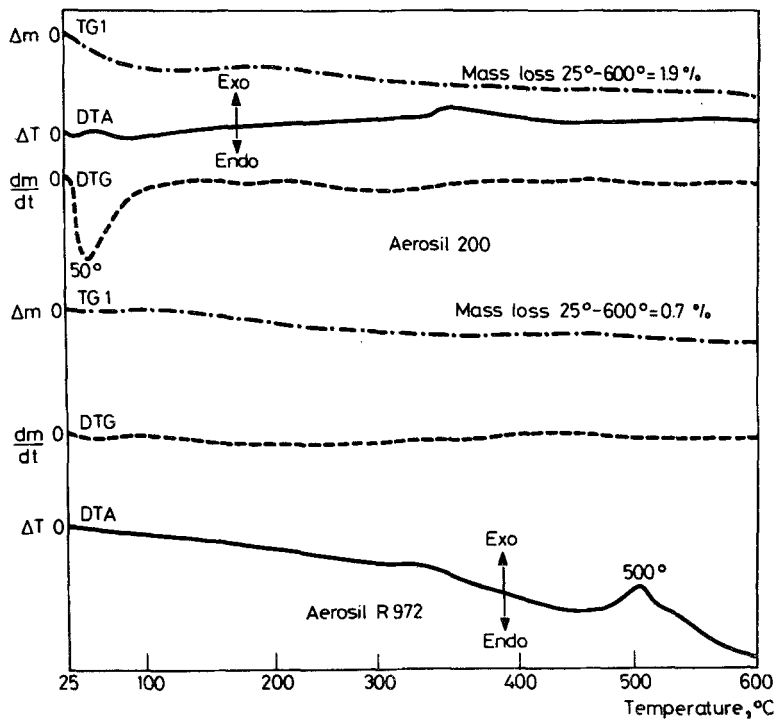


Fig. 2 TG–DTG–DTA diagrams of untreated and of hydrophobized silicic acids of the Aerosil type, prepared by flame hydrolysis

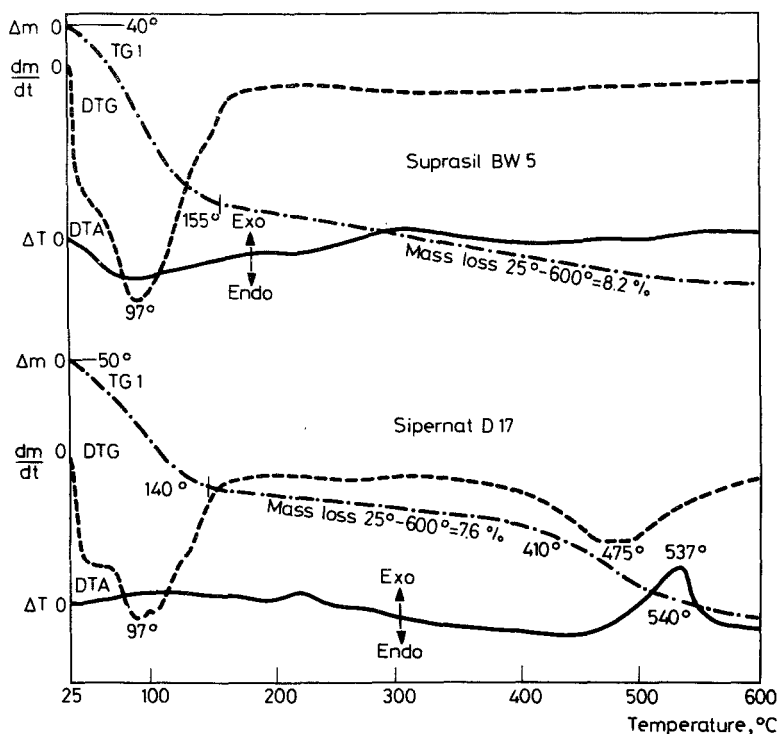


Fig. 3 TG-DTG-DTA diagrams of untreated precipitated silicic acid and of precipitated silicic acid aftertreated by surface reaction with organohalogenosilane

loss caused by adhering moisture, due to the preparation process. After this the untreated product shows a low regular mass loss, resulting from the successive degradation of the silanol groups.

For the hydrophobized organically aftertreated silicic acid, the oxidative decomposition of the wax coating predominates in the further course, accompanied by a considerable mass loss from 265° onward and a wide structured exothermic DTA effect. A second group of aftertreated silicic acids is prepared by reactions on the surface. For silicic acids of the Aerosil type, which are produced by flame hydrolysis, the silanol groups present after the thermal preparation are converted by the following treatment with an organohalogenosilane compound. As an example of such a hydrophobized silicic acid, results on Aerosil R 972 are presented in Fig. 2. The oxidative decomposition of the silane bound to the surface is expressed in the DTA curve by an exothermic peak at 500°.

In an analogous way, silicic acids prepared by the precipitation process can also be hydrophobized by conversion with organohalogenosilanes. Figure 3 compares

results on the untreated precipitated silicic acid Suprasil BW5, with an aftertreated product of the type Sipernat D17, shown in the lower part. Besides the generally high content of adhering moisture of precipitated silicic acids, a second step of mass loss between 410° and 540° and a wide exothermic decomposition peak at 537° are characteristic of silicic acid hydrophobized with silane.

References

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Zusammenfassung — Nach unterschiedlichen Verfahren hergestellte Kieselsäuren zeigen verschiedene Dispersitäten, Morphologien und strukturelle Charakteristika. Simultane TG–DTA ist gut geeignet zur Bestimmung von adsorptiv oder chemisch — in Form von Silanolgruppen — gebundenem Wasser sowie zur Charakterisierung nachbehandelter Kieselsäuren. Eine Klassifikation der verschiedenen Kieselsäure-Typen ist auf der Grundlage thermoanalytischer Ergebnisse möglich.

Резюме — Синтетические кремневые кислоты, в зависимости от способа получения, обладают разной дисперсностью и различными морфологическими и структурными характеристиками. Совмещенный метод ДТА и ТГ является пригодным для отдельного определения адсорбционной и химически связанной воды, а также для характеристики кремневых кислот после их обработки. На основе термоаналитических данных представилось возможным провести классификацию различных кремневых кислот.