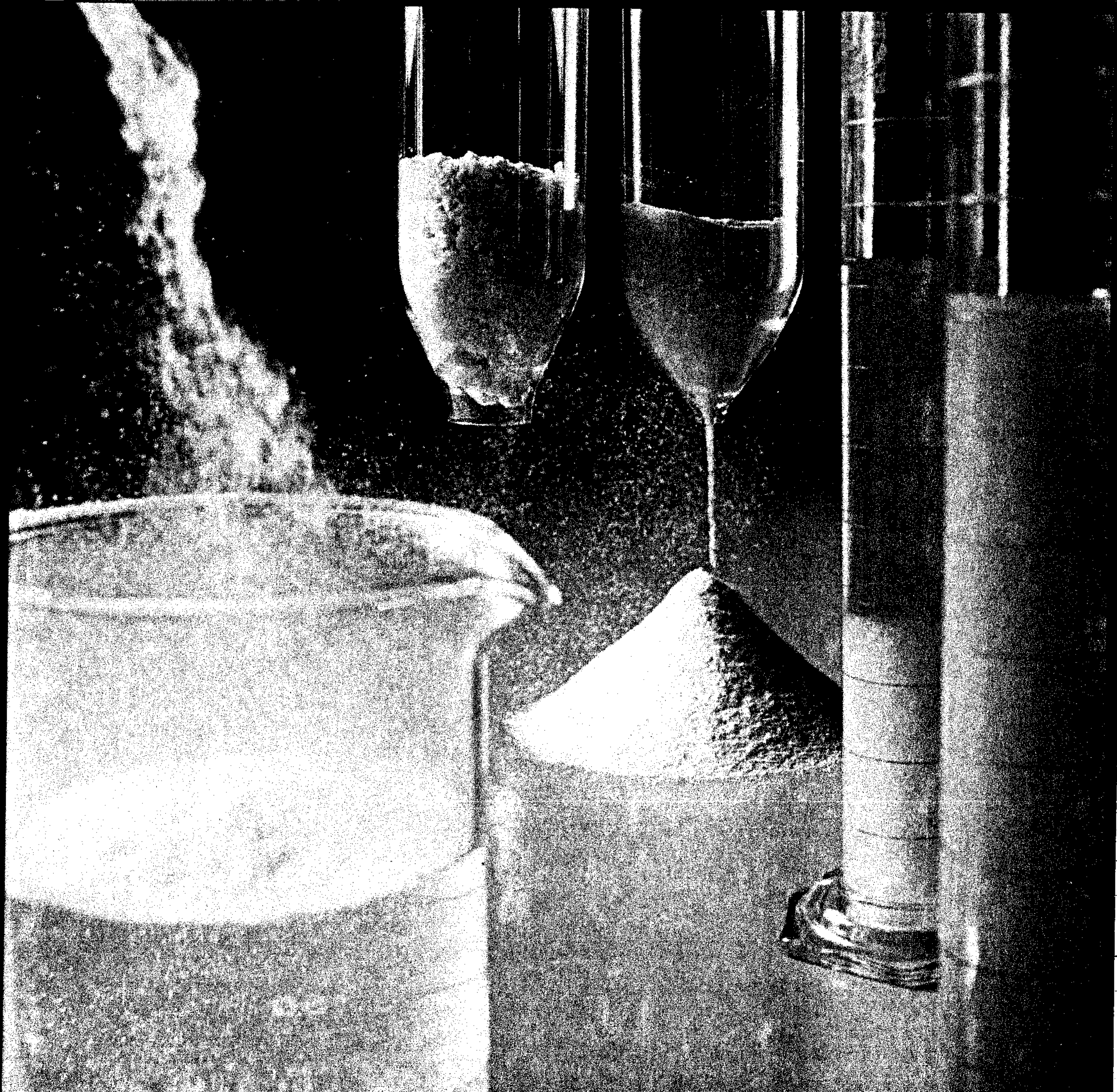
TECHNICAL BULLETIN PIGMENTS

The Use of Hydrophobic AEROSIL® in the Coatings Industry

~~P 04324~~
28310
PDF

No. 18

Degussa



The series of Technical Bulletin Pigments issued by the Inorganic Chemical Products Division discusses fields of application in the lacquer and paint industry in the following editions:

No. 3
Degussa Pigments for the Coatings Industry*)

No. 15
Carbon Blacks for Coatings and Printing Inks – A Survey

No. 17
Degussa Pigment Blacks and Pigment Black Preparations for Coating Materials

No. 21
Degussa Flatting Agents for the Coatings Industry

No. 22
Basic Characteristics and Applications of Colour Black Part 14,
Florida Test Results of Coatings Coloured with Pigment Blacks

No. 34
Aluminium Silicate P 820
for Emulsion and Decorative Paints

No. 36
Differences between Natural Fillers and Synthetic Micro-Extenders in Emulsion Paints*)

No. 37
Basic Characteristics and Applications of Colour Black Parts 10 and 16,
Coloristic Measurements of Jet-Black and Grey Coatings

No. 39
Basic Characteristics and Applications of AEROSIL® Part 17,
Reflection Measurements on Synthetic Silica Products

No. 68
AEROSIL® for Lacquers and Paints

Our cover shows:
demonstration of typical effects attainable with AEROSIL R 972: hydrophobic behaviour, effectiveness as a free-flow additive, application as an anti-settling agent.

*) not yet published in English

Basic Characteristics and Applications of AEROSIL®

FMP 1972

Part 32:
The Use of Hydrophobic AEROSIL® in the Coatings Industry

Dr. Horst Ferch
Department of Applied Research and Technical Services, Silicas and Pigments,
Degussa AG

Following a brief description of how the hydrophobic grades of AEROSIL® are produced, the author goes into some detail to describe ways of measuring this state of hydrophobicity. Possible applications in which hydrophobic AEROSIL is used in the coatings industry are then described and a brief mention is made of further uses in other branches of industry.

Based on lectures held by the author at the 47th Convention of the specialist group "API" of the Gesellschaft Deutscher Chemiker held in Hannover in 1979 and on the occasion of the 13th EUROCOAT Congress of AFTPV in Nice in 1987.

This edition of the Technical Bulletin Pigments issued by the Inorganic Chemical Products Division is printed using the Degussa carbon black PRINTEX® 55.

Table of Contents

1
Introduction

Over the past 25 years synthetic hydrophobic silicas have come to be used in numerous branches of industry. This new class of products offered the solution to problems which could not be solved by using the hydrophilic products, for example

- in the production of free-flowing powders for fire extinguishers (1);
- in the development of highly-active defoamers (2);
- in the reinforcement of special fluoroelastomers (3);
- to achieve special effects in coating systems (4);
- to regulate the water balance of offset printing inks (5).

Additional hydrophobic silicas have been developed in order to increase the possibilities of application and to open up new markets.

In this brochure, these newer products are compared with the oldest of the hydrophobic silicas, AEROSIL R 972, which was introduced in 1962 and is now produced on an industrial scale. The manufacturing process was described in 1965 (6). Technical Bulletin Pigments No. 6 in this series deals with this product in more detail.

2
Production and Properties of Hydrophobic AEROSIL

As mentioned before, the first industrially-manufactured hydrophobic silica was brought onto the market in 1962 and was known as "Filler R 972". After reports by KLOSTERKÖTTER in 1965 (7), based on a one-year long-term inhalation test carried out with laboratory animals, showed that this new material did not cause silicosis, the name was changed to "AEROSIL R 972". This hydrophobic special product is converted with dimethyl dichlorosilane in a fluid-bed reactor which is heated to approximately 400° C. As a result of this, around 70% of the previously existing silanol groups react with the silane and form Si-O-Si $(CH_3)_2$ groups (6); the material acquires a hydrophobic character, see **Figure 1**. When analysed, AEROSIL R 972 differs from the basic product as a result of its carbon content of approximately 1%. However, no difference can be observed as regards the average primary particle size when AEROSIL R 972 is compared with its hydrophilic counterpart in electron micrographs.

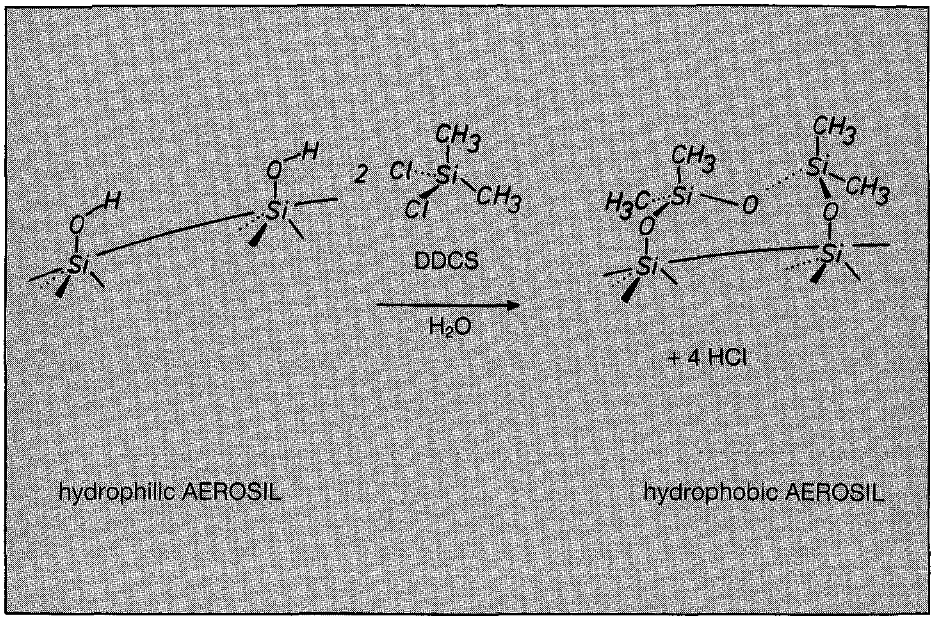


Figure 1: Schematic representation of the reaction of dimethyl dichlorosilane with the silica surface: conversion of "hydrophilic" to "hydrophobic"

Figures 2 and **3** show a transmission electron micrograph (TEM) and a scanning electron micrograph (SEM) of this product. These pictures illustrate the tendency of AEROSIL R 972 to aggregate and agglomerate, as is the case with the basic product AEROSIL 130. This statement is also valid for all of the other hydrophobic grades of AEROSIL dealt with in this edition of Technical Bulletin Pigments. The question regarding the existence of primary particles in AEROSIL, as defined in DIN 53206, was treated back in 1984 (10). Technical Bulletin Pigments No. 60 is dedicated to this subject.

The properties of and special effects to be attained with AEROSIL R 972 when applied in coating systems were described in 1979 (4) and further applicational possibilities of this special silica were reported on in 1980 (11).

Over the years it became apparent that AEROSIL R 972 was unable to fulfil all of the demands placed on it by various aspects of the different applications. What was wanted above all was a low-priced hydrophobic version.

Due to the fact that all of the hydrophilic grades of AEROSIL must be classified as high-quality products from a point of view of price, it was necessary to fall back on a less expensive starting product as a basis. For obvious reasons, the choice fell on a precipitated silica. An appropriate product was brought onto the market in 1964 (12) and is now known as SIPERNAT® D 17.

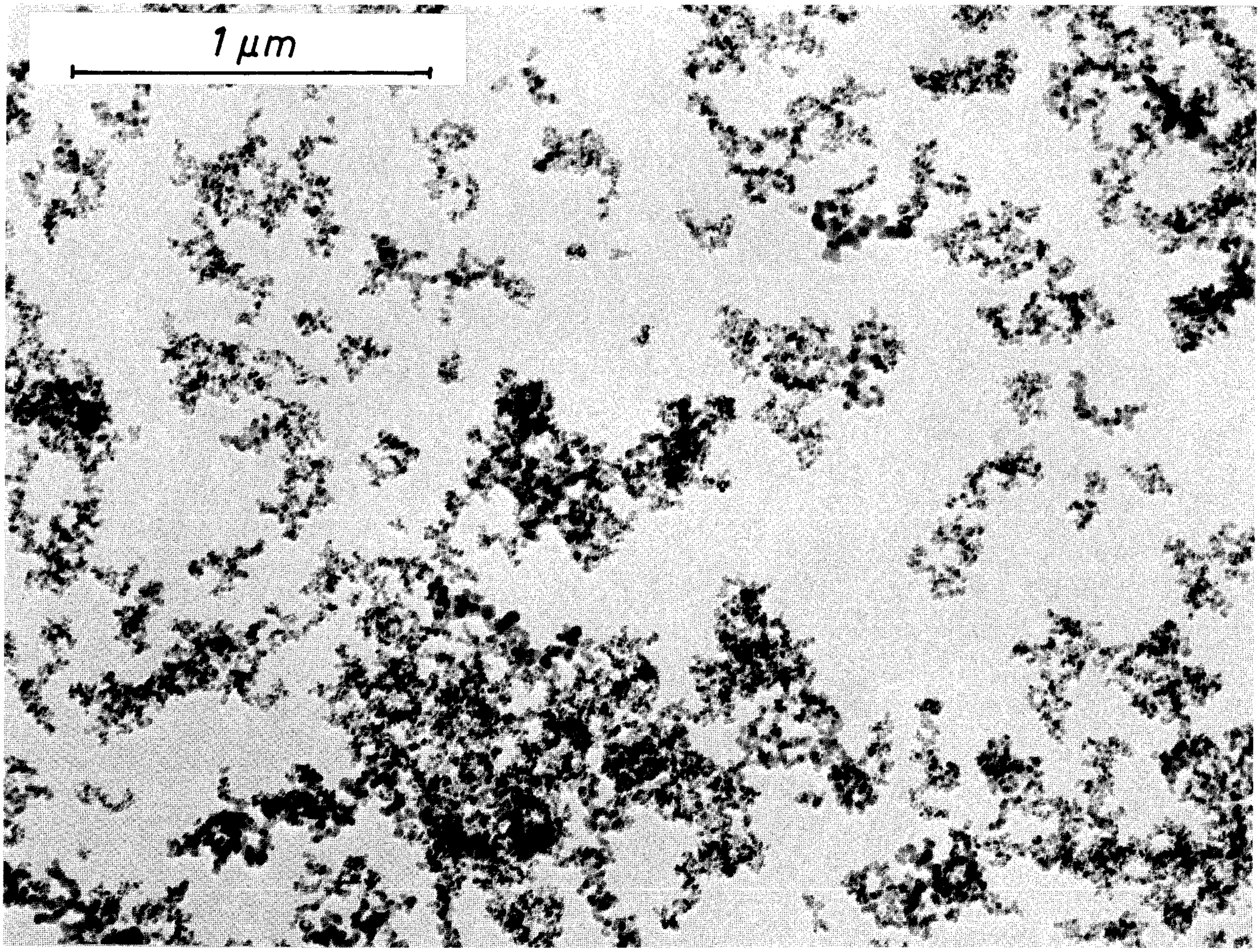


Figure 2: TEM of AEROSIL R 972

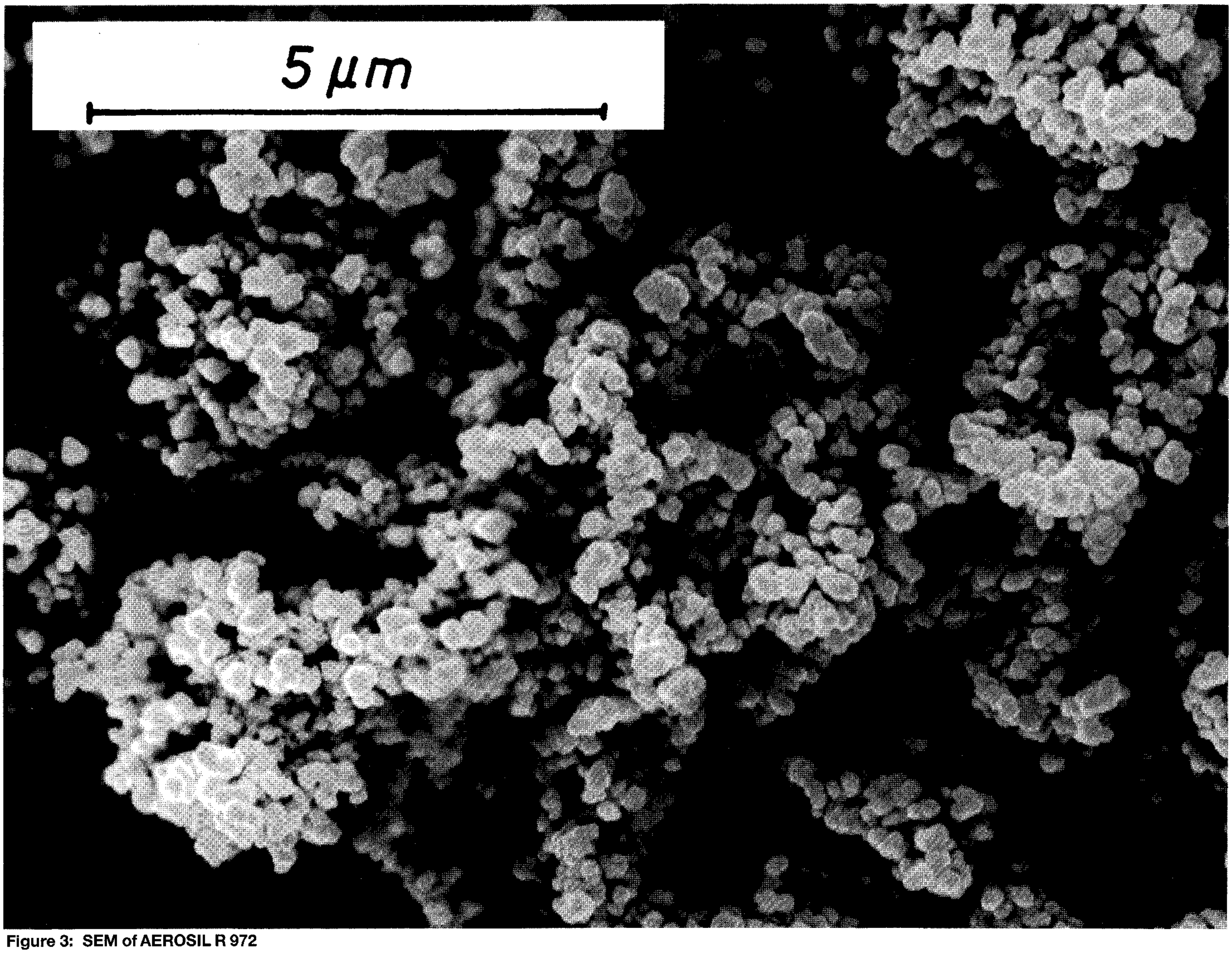


Figure 3: SEM of AEROSIL R 972

This hydrophobic special silica is used in particular to improve the free flow behaviour of substances in powder form, e.g. fire extinguishing powder based on sodium bicarbonate (1). The commercial products AEROSIL R 972 and SIPERNAT D 17 were able to satisfy virtually all the market demands for a period of nearly fifteen years. SIPERNAT D 17 was unable to find access to the coatings sector.

However, there are now several new commercial products available on the market which can be used for further applications, and whose data are compiled in **Table 1**. All of these hydrophobic grades of AEROSIL are characterized by the additional letter "R" in their name, which serves as a reference to the location of the German production plant in Rheinfelden/Baden. Similar to the production of AEROSIL R 972, the new AEROSIL grades are also manufactured according to a technical process. The nature of the chemical aftertreatment is shown in **Table 1** in the form of the chemical residues situated on the surface of the silica; these can be easily detected by means of infra-red spectroscopy, e.g. (4, 13), as demonstrated in **Figure 4**. The left-hand side of this figure depicts the range of the OH stretching vibration bands for the untreated basic product

- at 3750 cm^{-1} (free SiOH groups)
- between 3800 and 2800 cm^{-1} (bridged silanol groups);

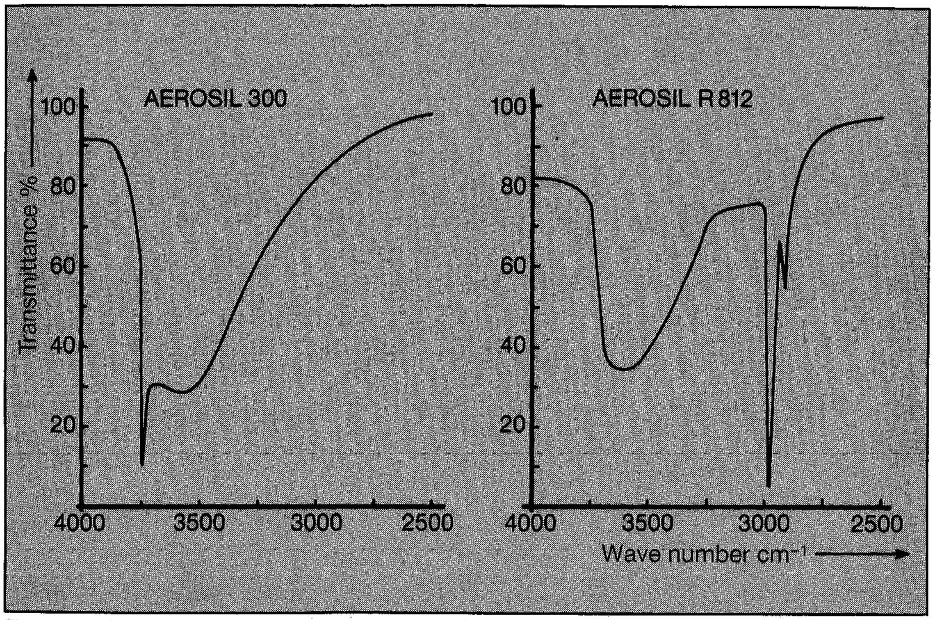


Figure 4: Infra-red spectra of hydrophilic AEROSIL 300 and hydrophobic AEROSIL R 812 (13)

the same frequency range of this sample is shown on the right-hand side following an in situ treatment of the silica with the corresponding silane. A reduction in the number of both isolated and bridged silanol groups can be observed here in the right-hand diagram, and at the same time, the CH stretching vibration bands of the newly-anchored methyl groups become apparent at 2970 cm^{-1}.

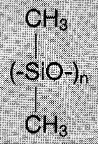
		AEROSIL grades					
		R 972	R 974	R 805	R 812	R 812 S	R 202
Specifications							
Primary particle size	nm	16	12	12	7	7	14
Specific surface area	m^2/g	110 ± 20	170 ± 20	150 ± 25	260 ± 30	220 ± 25	100 ± 20
pH value		3.6–4.3	3.4–4.2	3.5–5.5	5.5–7.5	6.0–8.0	4.0–6.0
C content	approx. %	0.6–1.2	0.7–1.3	4.5–6.5	2.0–3.0	5.5–7.5	3.5–5.0
Tapped density	approx. g/l	50	50	50	50	60	50
Further data							
Surface group		$(CH_3)_2$		C_8H_{17}	$(CH_3)_3$		 $(\text{-}\overset{CH_3}{\underset{CH_3}{SiO}}\text{-})_n$
Methanol wettability		> 40	> 35	> 40	> 50	> 60	> 60
C content per m^2 SiO_2 basis	% C/m^2	0.008	0.005	0.035	0.009	0.011	0.033
Residual surface area related to SiO_2 basis	%	85	69	79	81	67	47
Remaining silanol group density	$1/nm^2$	0.60	0.39	1.66	0.44	0.68	0.29
Remaining silanol group density	$mol/g \cdot 10^4$	1.3	1.3	5.5	2.2	3.4	0.72
Methyl groups/nm^2		2.7	2.8	–	3.5	3.9	–
Functionalized $SiOH/nm^2$		1.35	1.4	–	1.17	1.3	–
Methyl groups	$mol/g \cdot 10^4$	5.8	9.3	–	17.4	19.4	–

Table 1: Specifications and further data on the hydrophobic AEROSIL grades. AEROSIL R 812 S differs from AEROSIL R 812 as a result of having a higher degree of hydrophobicity which is achieved by means of an additional processing step

All of the hydrophobic grades of AEROSIL listed in **Table 1** are thermally stable as far as applications in the coatings industry are concerned, as **Figures 5** and **6** confirm. **Figure 5** shows the weight loss of the undried hydrophobic AEROSIL grades, which was determined by means of thermogravimetric analysis, as a function of the temperature. On the basis of infra-red measurements, **Figure 6** confirms the fact that both AEROSIL R 972 and AEROSIL R 812 only undergo changes as a result of oxidation at temperatures exceeding 400°C.

A suggestion put forward in 1976 (15) serves to classify the hydrophobic grades of AEROSIL in the wide range of synthetic silicas currently available on the market.

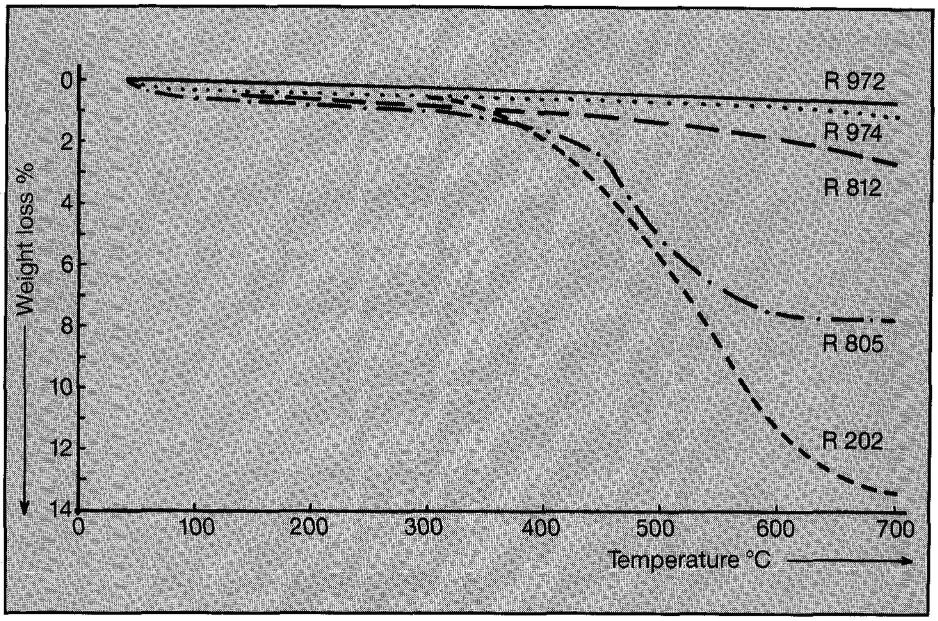


Figure 5: Weight loss of hydrophobic AEROSIL grades which were slowly heated in a nitrogen atmosphere (14). (PERKIN-ELMER thermo-balance, model TGS-2)

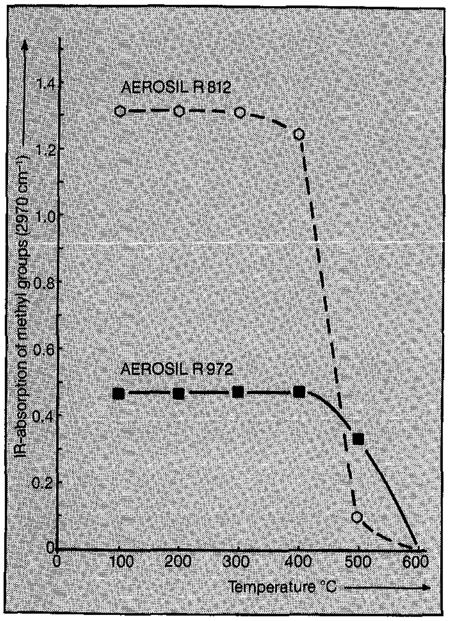


Figure 6: Reduction in the IR absorption of the methyl groups as a measure of the thermal stability of AEROSIL R 972 and AEROSIL R 812 (13). Measurements were carried out on self-supporting discs with a diameter of 13 mm and 6 mg/cm² in weight

3
How to Measure Hydrophobicity

3.1
General Information

What exactly does the term "hydrophobic" mean? Expressed simply, hydrophobic means water-repellent. The plumage of aquatic birds or the cuticles of leaves on the plants are well-known natural examples of this. Further examples of hydrophobicity in daily use come from the technical field: TEFLON®-coated frying pans and top coats for automobiles. The opposite of hydrophobic is "hydrophilic". In technology, use is often made of a combination of hydrophobic and hydrophilic properties. In the molecular range, the surfactants in household detergents should be mentioned; the increasingly important offset printing process operates with larger particles, and coarse pieces are used in the flotation of ore.

The use of hydrophobic substances in powder form has proved successful in numerous applications, with synthetic silicas playing a particularly important role here. Products of this nature attain their hydrophobic characteristics as a result of many different methods of surface treatment, such as coating with wax or chemical reaction of the surface groups with appropriate silanes. It should be repeated at this point, however, that all of the hydrophobic grades of AEROSIL mentioned in this brochure are rendered hydrophobic by means of a chemical reaction on the surface of the solid. The hydrophilic or hydrophobic character of an amorphous silica can be easily judged by shaking it together with water in a test tube; hydrophobic AEROSIL floats to the surface. All of the hydrophobic AEROSIL grades react in the same way during this test, i.e. it is not possible to differentiate between them.

Although the term "hydrophobic" appears to be easy to understand when taken to mean water-repellent, it is nevertheless difficult to accurately define or to quantitatively determine this property. It is often the case that the different methods do not lead to the same conclusions (14). A selection of methods of determination are given below.

3.2
Measuring Methods

3.2.1
Water Vapour Adsorption

A method which is somewhat time-consuming, but definitely related to practice is the intake of the water vapour adsorption isotherms measured at varying levels of relative moisture. Corresponding measurements are generally made at room temperature, e.g. in the case of AEROSIL R 972 (4). **Figures 7–10** depict the corresponding curves for the products AEROSIL R 202, R 812, R 805, R 972 and R 974, each in comparison with the respective hydrophilic base silica.

It is understandable that the adsorption of the latter is always higher. The numerical values which are obtained with AEROSIL R 972 (**Figure 10**) demonstrate an even lower adsorption than that shown in **Figure 7** for AEROSIL R 202. If the shapes of the curves shown in the four diagrams are compared, it is possible to observe definite and also characteristic differences which occur independent of the size of the specific surface area. When measured according to this method, the hydrophobic character of the individual grades declines in the following order: AEROSIL R 972 > R 202 > R 812 > R 805 > R 974.

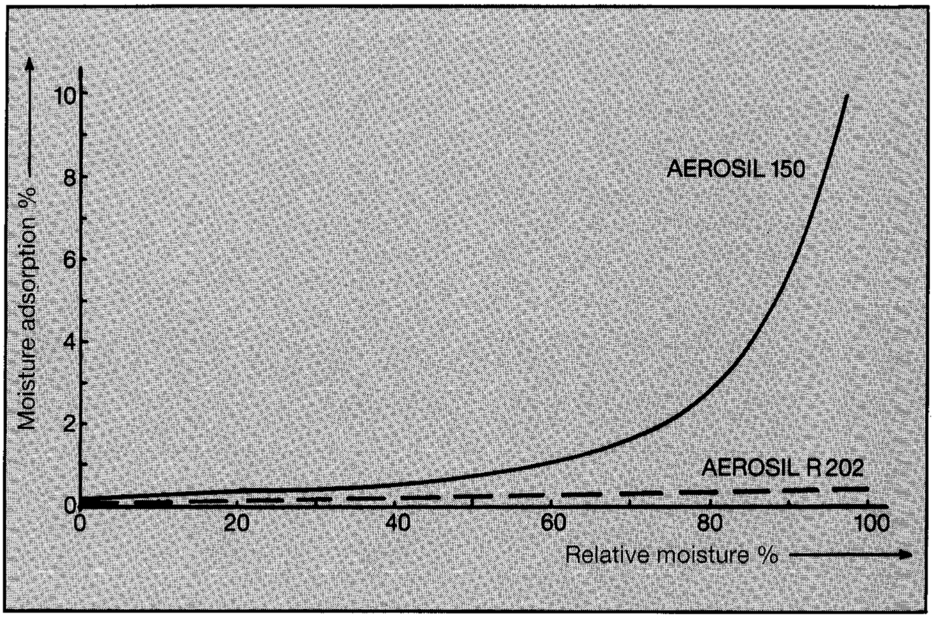


Figure 7: Water vapour adsorption isotherms at room temperature of AEROSIL 150 (basic hydrophilic substance) and the hydrophobic grade AEROSIL R 202, measured using small samples

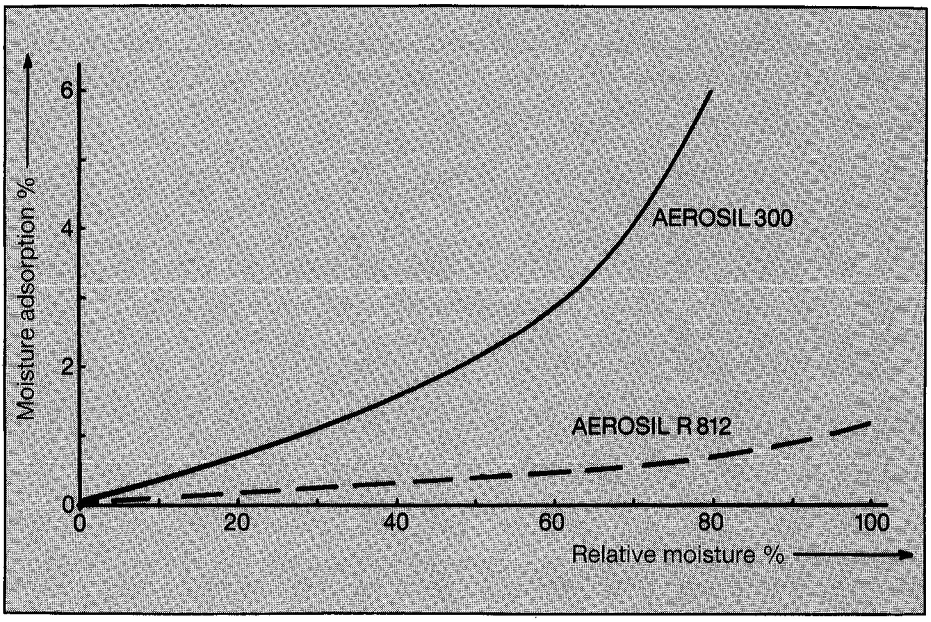


Figure 8: Water vapour adsorption isotherms at room temperature of AEROSIL 300 (basic hydrophilic substance) and the hydrophobic grade AEROSIL R 812, measured using small samples

3.2.2
Contact Angle

The so-called **contact angle method** can be used to determine the hydrophobicity or "wettability" of smooth surfaces (16). This method involves placing a droplet of water of a certain volume under specified conditions onto the surface to be examined. The contact angle is then measured with the aid of a horizontally-positioned microscope with a graduated scale. If the drop is predominantly spherical in shape, the contact angle is θ > 90° and, according to YOUNG's equation, the interfacial energy is $E_{water/solid} > E_{water/air}$. Wetting does not take place, or only to a limited extent. If the drop resembles more of a hemisphere or even spreads out (θ < 90°), the expression $E_{water/solid} < E_{water/air}$ applies and wetting takes place. This behaviour is illustrated in **Figure 11**. Difficulties arising from the production of suitable moulded tablets with "smooth" surfaces are experienced when the contact angle method is used to determine the wettability of hydrophobic powder (17).

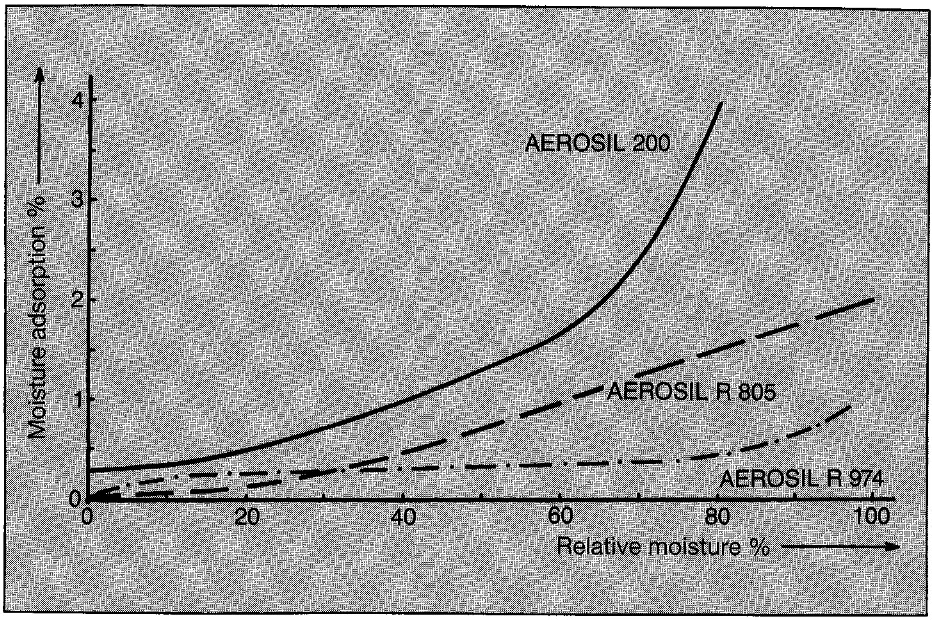


Figure 9: Water vapour adsorption isotherms at room temperature of AEROSIL 200 (basic hydrophilic substance) and the hydrophobic grades AEROSIL R 805 and AEROSIL R 974, measured using small samples

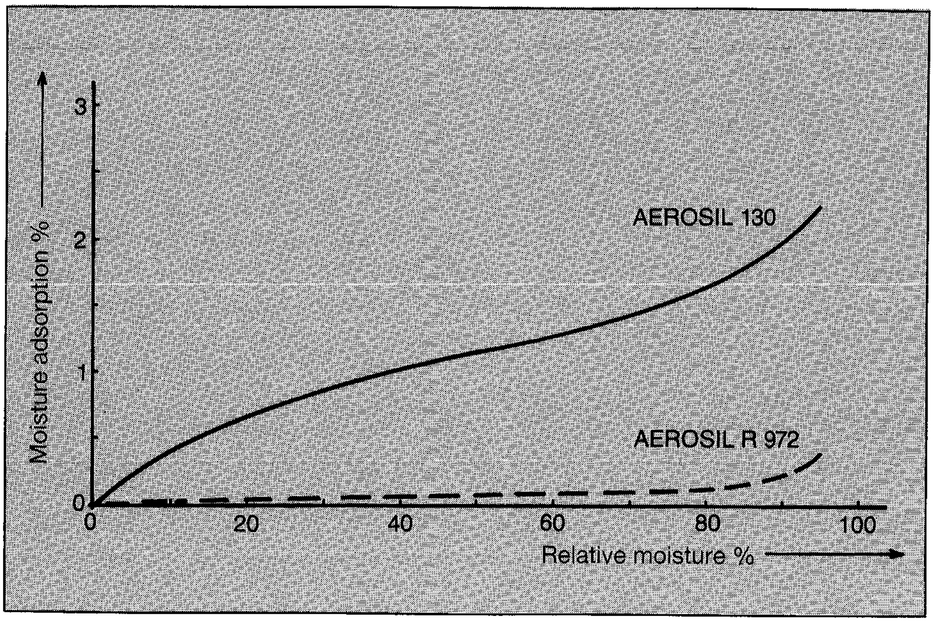


Figure 10: Water vapour adsorption isotherms at room temperature of AEROSIL 130 (basic hydrophilic substance) and the hydrophobic grade AEROSIL R 972, measured using small samples

Of all the silica grades tested here, it is only possible to produce a suitable moulded disc with AEROSIL R 972. The other hydrophobic AEROSIL grades can be compressed to moulded discs under high pressure, but these crumble on release without the application of any external force. For this reason, it is only possible to give contact angles for the Degussa silicas listed in **Table 2**. Hence the contact angle method is not suitable for the characterization of hydrophobic silicas.

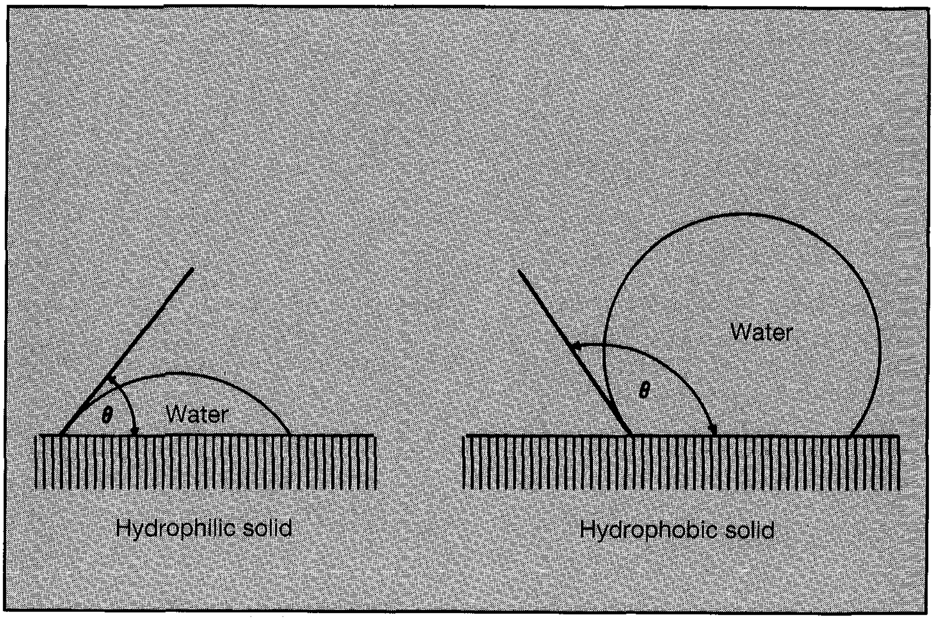


Figure 11: Illustration of the contact angle method

	Contact angle given in degrees of			
	Water	Glycerine	Silicone oil	Mineral oil
hydrophilic silica	< 20*	< 20*	< 20*	< 20*
SIPERNAT D 17	144	113	< 20*	< 20*
AEROSIL R 972	124	78	< 20*	< 20*

* soaks into the moulded tablet after a short time

Table 2: Contact angles of different liquids on moulded discs (2 mm thick, 28 mm in diameter) made of some Degussa silicas

3.2.3
Methanol Wettability

A suitable way of determining the wettability of hydrophobic powders appears to be with the aid of alcohol/water mixtures. The higher the proportion of alcohol in the liquid mixture in which wetting is taking place, – i.e. the immersion of the powder into the liquid –, the "greater" the degree of hydrophobicity (18). In principle, this method can also be used to test the homogeneity of the hydrophobicity. For this purpose, samples are shaken with various mixtures of methanol and water and are then centrifuged.

If the height of the sediment is plotted against the proportion of alcohol in the liquid, an ascending curve results. A gradual rise denotes that the powder particles are not uniformly hydrophobic.

On the other hand, a steep rise indicates a uniform surface modification, see **Figure 12**.

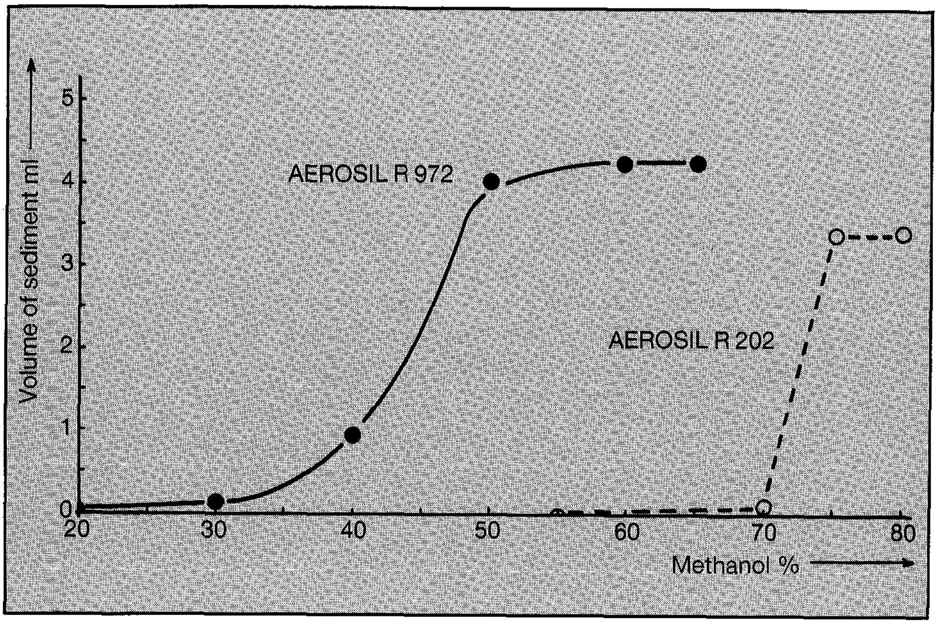


Figure 12: Characterization of the hydrophobicity by means of the methanol wettability. When measured according to this method of sediment volume, AEROSIL R 972 is less hydrohobic than AEROSIL R 202

Furthermore, it seems justified to infer that an increased methanol requirement signifies a higher degree of hydrophobicity.
A relatively simple method, which is attributed to K. KLEIN (19), has proven effective in practice with hydrophobic silicas.
200 mg of the substance are added to 50 ml water in a separating funnel. As the mixture is shaken, a burette – which is immersed to the bottom of the water – is then used to slowly add methanol until all of the silica has been wetted. The portion by weight of the methanol in the mixture needed for this purpose is a measure for the hydrophobicity of the silica. The values attained in this way are recorded in **Table 1**.
However, it should be pointed out that, within the meaning of an exact analysis, this method yields very fluctuating values. For comparative purposes, a measurement of this nature must be carried out by the same tester and if possible in the same laboratory.

3.2.4
Infra-Red Spectroscopy

Two methods of characterizing synthetic hydrophobic silicas are available when using infra-red spectroscopy:

- determination of the remaining silanol groups situated on the surface in isolated state,
- determination of the relative methyl group density on the surface.

Numerical values for the relative methyl group density are given in **Table 1**. According to both of these criteria, AEROSIL R 812 is more hydrophobic than, for instance, AEROSIL R 972.

The infra-red test method is time-consuming and a spectrometer with good resolving power (e.g. 2.5 cm^{-1}) is needed. However, once this method has been "mastered", it provides accurate comparative values for characterization purposes.

3.2.5
Total Silanol Group Density

The $LiAlH_4$ method can be employed to determine the total silanol group density of synthetic silicas (9, 13). In accordance with **Table 1**, the increasing hydrophobicity is given in the following order:

AEROSIL R 805 < R 812 S < R 972 < R 812 < R 202.

This method is not suitable for testing on an occasional basis, as especially the drying of the synthetic silica is of great significance here.

3.2.6
Carbon Content

An obvious way of characterizing a hydrophobic AEROSIL grade is to determine the C content. This is the first step towards giving an impression of the amount of organic groups that are present on the silica surface. However, this value does not seem to tell us very much because

- the size of the specific surface area of the basic silica is not taken into account,
- in addition to a chemical fixing of the organic groups, a further adsorption of organic substances can also take place on the silica.

Both the analytically-determined total carbon content and the C content related to the surface are included in **Table 1**. When the specific carbon distribution is taken as a basis, the following sequence is obtained in view of the increasing hydrophobicity:

AEROSIL R 974 < R 972 < R 812 or R 812 S < R 202 or R 805.

AEROSIL R 812 and AEROSIL R 812 S are silicas which are also capable of firmly adsorbing organic substances by physical means. This is not the case with AEROSIL R 972, R 974 and R 805.

3.2.7
Water-Soluble Part

The proportion of hydrophobic synthetic silica which is wetted by water is determined analytically. The lower this value is, the higher the degree of hydrophobicity. However, this method is relatively inaccurate and can only provide values which enable a differentiation of hydrophobic silicas in truly routine studies.

3.2.8
Calorific Quantities

Another process which can be used to characterize hydrophobic grades of AEROSIL is the determination of the heats of wetting in various liquids. The extent to which a method of this nature can be used to explain the gradual applicational differences of finely-divided hydrophobic materials is uncertain at present. The method appears to be too expensive for purposes of quality control (20, 21, 22).

3.2.9
"Residual Surface Area"

A special feature of the pyrogenic silica AEROSIL is that the N_2 adsorption according to BET (23) reflects the surface chemistry in the form of the concentration of isolated silanol groups (24). It seems logical, therefore, to use this specific surface area, determined with N_2 according to the BET method, and the "reduced" specific surface following the chemical aftertreatment as a criterion for the surface coverage (13). Numerical values for the "residual surface area" related to the basic silica are given in **Table 1**. The following order is obtained when this method is applied:

AEROSIL R 972 < R 812 < R 805 < R 812 S < R 202.

Nevertheless, it should be pointed out here that this "residual surface area" method is somewhat inaccurate. This is due in particular to the altered form of the BET adsorption isotherms which arises during the chemical surface modification. This makes it difficult to evaluate the curves and reduces the value of the statement regarding the degree of coverage.

3.2.10
SAPPOK's Degree of Hydrophilicity

The expression "degree of hydrophilicity according to SAPPOK" may also be found in certain literature (53–55). This is the quotient of the specific surface area according to BET measured with H_2O, and the same value measured with N_2. This degree of hydrophilicity according to SAPPOK is supposed to give indications as to the wettability, dispersion and stability behaviour of pigments.

On the basis of the BET theory, it should not be possible to use this quotient to characterize hydrophobic silicas, because this theory works on the principle that all the values which are obtained are independent of the properties of the solid surface. However, this is not the case.

3.3 Evaluation

Following a brief description of the various ways of characterizing hydrophobicity, an attempt will now be made to list the AEROSIL R grades in the order of their hydrophobicity. This is done in **Table 3** by compiling an "order of rank" based on the methods permitting such statements to be made; the smaller values signify the highest degree of hydrophobicity. Once the mean value has been calculated, the grade with the lowest value must represent the product with the most pronounced hydrophobic properties overall. This results in the following order:

AEROSIL R 202 > R 812 > R 805 > R 972 > R 974.

A certain degree of randomness is also present in this list, due to the fact that a comparison of the individual methods does not always result in the same order. Hence it is not easy to give a clear-cut definition of the term "hydrophobicity" (14).

Methods		R 972	R 974	R 805	R 812	R 202
3.2.1	Water vapour adsorption	1	5	4	3	2
3.2.3	Methanol wettability	4	5	3	1	2
3.2.3	(dito) "Volume of sediment"	4	5	3	1	2
3.2.4	Methyl group density	3	4	–	2	1
3.2.5	Remaining silanol groups	4	5	3	2	1
3.2.6	Rel. C content	4	5	1	3	1
3.2.9	Residual surface area	4	5	2	3	1
		24	34	16	15	10
Relative evaluation:		3.43	4.86	2.67	2.14	1.43
Result:		R 202 > R 812 > R 805 > R 972 > R 974				

Table 3: Procedure for drawing up a "hydrophobic order of rank" with the hydrophobic grades of AEROSIL

4
Applications in the Coatings Industry

Hydrophobic grades of AEROSIL may be used in numerous ways to improve the applicational properties of paints and other coatings, and to reduce the added amount of silica in certain formulations. Effects of this nature were compiled in a report back in 1979 (4). Recently-acquired knowledge relating to these new special products will be included in the familiar applications dealt with in this section.

Now and again objections are raised to the effect that the addition of AEROSIL reduces the gloss of top coats to such an extent that practical application is rendered impossible. Using as an example a black and a white stoving enamel based on a water-thinnable binder, **Table 4** illustrates that this argument is not valid if the AEROSIL is sufficiently dispersed. Only very slight reductions in gloss occur, see **Table 4**.

4.1
Rheology

The influence on the rheological behaviour of liquid systems exerted by hydrophilic AEROSIL was described way back in 1969 (25). A company publication issued in 1986 also discusses the possible interaction mechanisms of hydrophobic grades of AEROSIL (26).

	Addition of AEROSIL R 972 %	Film thickness µm	Angle of observation 45°	60°	85°
			Scale divisions		
black	0	10	52	91	100
	0.5	10	52	90	100
	0.8	12	52	90	100
	1.0	12	52	89	100
	1.5	14	51	87	100
white	0	14	48	82	99
	0.5	14	47	80	98
	0.8	15	47	80	98
	1.0	15	46	79	98
	1.5	16	46	78	97

Table 4: Effects on the gloss of water-thinnable stoving enamels caused by additions of AEROSIL R 972 (4).
Composition: RESIMENE 5.5; CHEMPOL 10-0500 – solution 65.0; TiO_2 RKB 2 27.8; 2-ethyl hexanol 1.0; defoamer TROY 999 0.3; *Fluorchemical FCI-430 0.4*

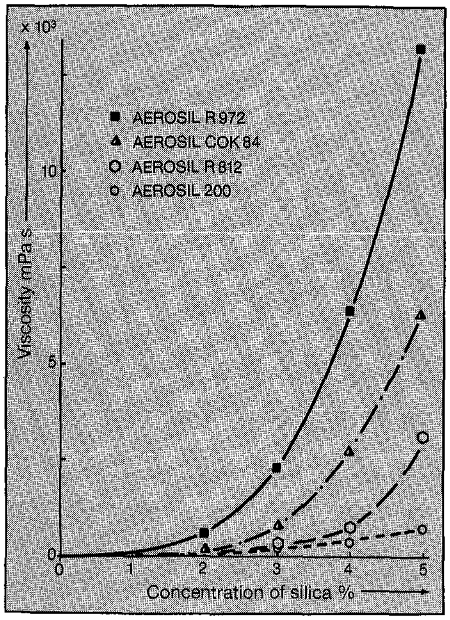


Figure 13: Viscosity behaviour of an ethanol-water mixture 1:1 following the addition of different AEROSIL grades (14)

4.1.1
Thickening Behaviour and Thixotropy

In a large number of systems, higher increases in viscosity can be attained with hydrophobic silicas than with the same added amount of hydrophilic silicas.

This is the case, for instance, in a 1:1 ethanol-water mixture, as illustrated in **Figure 13**, where AEROSIL R 972 serves as an example. It is also possible to recognize from this example how the likewise hydrophobic AEROSIL R 812 does not display this behaviour to anywhere near such an extent. It is not possible to predict which hydrophobic silica will demonstrate the best behaviour in a particular case, and for this reason, practical tests are unavoidable. This statement is valid for pure solvents and mixtures of such as well as for binder systems.

Three epoxy esters of the same composition but from different manufacturers are shown in **Figure 14**, which depicts the increases in the viscosity and the corresponding thixotropic index values of these three systems, induced by the addition of hydrophobic silicas. The thixotropic index was calculated from the viscosity values attained at a shear rate ratio of 1:10.

Figure 14 shows that

- the three binders used display different behaviour although the initial viscosity was comparable;
- AEROSIL R 812 provides the best result in each of the cases;
- the difference in the thixotropy is greater than that of the viscosity.

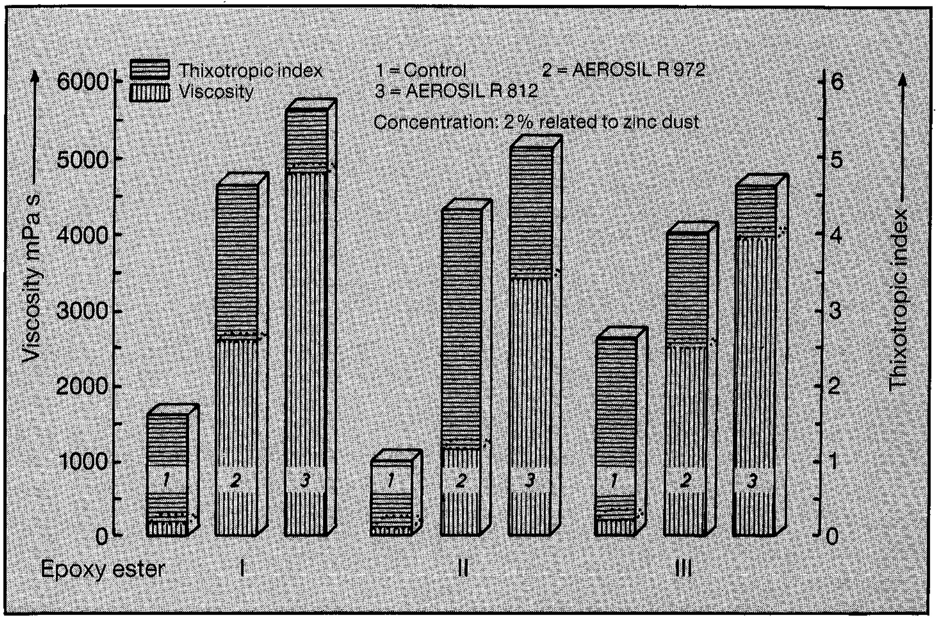


Figure 14: Increase in the viscosity and thixotropy of epoxy ester-based zinc dust paints from different manufacturers after the addition of hydrophobic AEROSIL (14). Dissolver dispersion at 4000 r.p.m. Peripheral velocity = 8.4 m/s

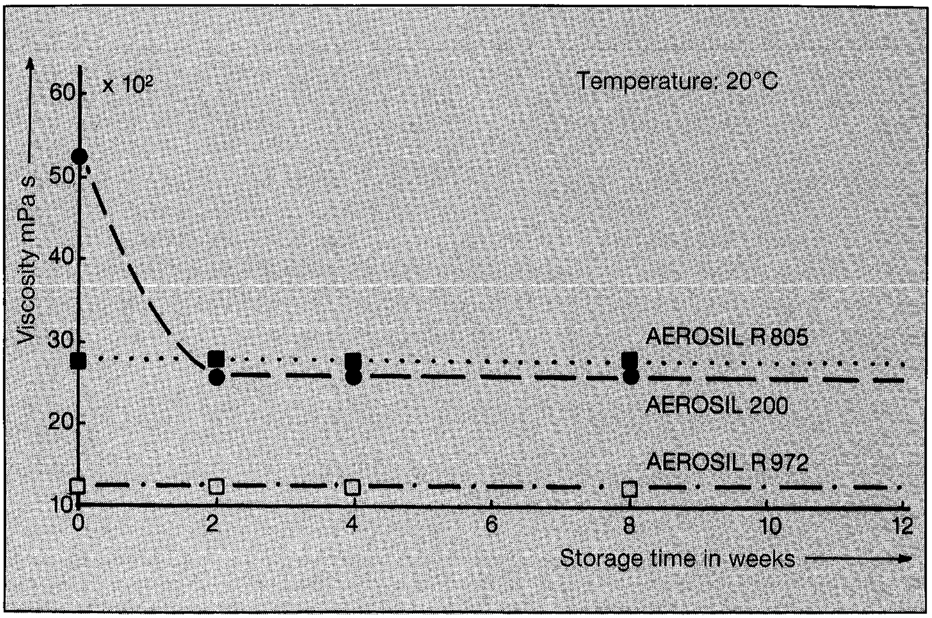


Figure 15: Viscosity behaviour of epoxy resin solutions thickened with 3% by weight of AEROSIL during 12 weeks of storage at room temperature (14)

A further example will be used to demonstrate how, in addition to the level of viscosity and a possible thixotropic effect, the time-dependent viscosity behaviour can also be changed to advantage.

Figure 15 illustrates the viscosity behaviour of 50% epoxy resin solutions containing different grades of AEROSIL.

3% by weight of silica was added in each case. The thickening effect of AEROSIL R 972 is very slight; the hydrophilic grade AEROSIL 200 only demonstrates a high initial viscosity; good long-term viscosity behaviour is attained solely with AEROSIL R 805.

Some results in a white high solids coating will now be discussed. **Figure 16** illustrates the increases in viscosity attainable with additions of 0.3% of hydrophobic silica and also the calculated thixotropic index. AEROSIL R 805 also provided the most favourable result as regards the gloss attained (87%) and the sagging behaviour. The latter was measured by coating plates of glass with a 150 μm film applicator over a length of 16 cm and then placing the plates in a vertical position. The only system which demonstrated no sagging was that containing AEROSIL R 805.

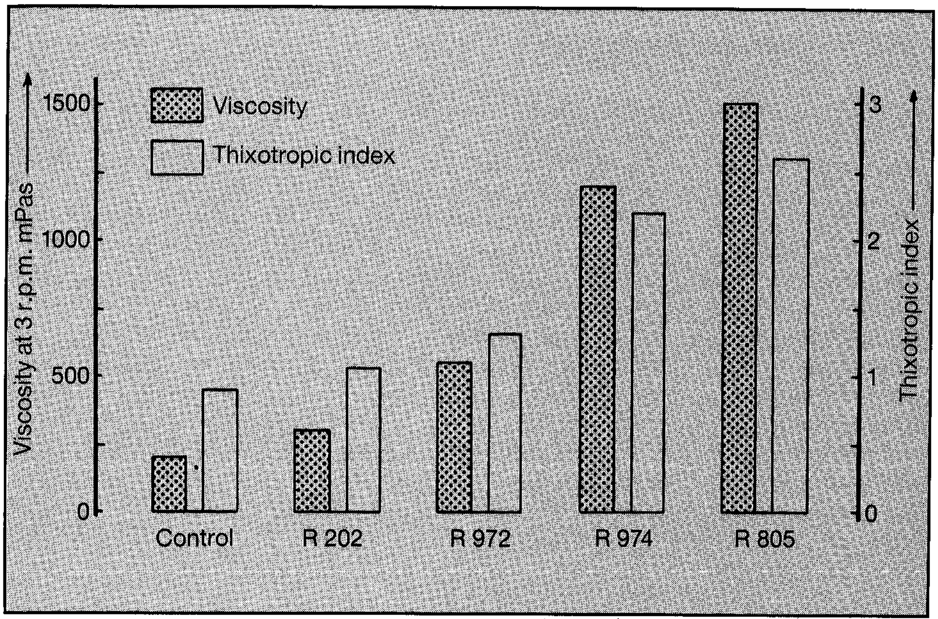


Figure 16: Rheological behaviour of a white high solids coating based on alkyd-melamine resin with and without the addition of AEROSIL at room temperature (14). Composition: BAYER-TITAN RKB 3 28.00; AEROSIL in each case 0.28; ALKYDAL F 261 hs 43.90; RESIMENE 740 13.00; ethyl glycol acetate 5.22; ethyl glycol 5.00; butyl glycol 2.30; xylene 2.50. 48 hours in the ball mill KU 1 using porcelain balls

Special mention should be made at this point about the orange peel effect which occurred on the surface of the coatings containing AEROSIL R 202. This effect can only occur with AEROSIL R 202 and not with any other grades of AEROSIL referred to in this publication. AEROSIL R 202 is produced with the aid of polydimethyl siloxanes, which are known to cause such an effect.

In a company publication issued back in 1986 (27), it was pointed out that AEROSIL R 202 can cause:

- levelling problems, e.g. the orange peel effect,
- adhesion problems, e.g. with multi-layer systems, etc.

If the best rheological results are obtained with AEROSIL R 202, tests must be carried out prior to application in practice in order to determine whether or not side-effects occur.

4.1.2
Use as an Anti-Settling Agent

The use of AEROSIL as a suspending agent for pigments and fillers in the coatings industry is the oldest field of application for this class of products (29). In general, the addition of small amounts is sufficient to obtain the desired anti-settling effect which is accompanied, as a rule, by a certain increase in the viscosity.

It is important to establish that the improvement in the suspension behaviour cannot be explained entirely by the increase in the viscosity. Parallel tests served to demonstrate how a subsequent adjustment of the viscosity up to the same level of the samples in the control test only produced a gradual improvement and not the positive effect of improving the suspension behaviour, such as is shown in **Figure 17**.

The advantage of all of the hydrophobic grades over AEROSIL 200 is that – due to their having a lower silanol group density (see **Table 1**) – agglomeration is not so great and they may therefore be dispersed more easily, see **Figure 23**. If the cost-benefit ratio is considered, all of the arguments speak in favour of the use of AEROSIL R 972.

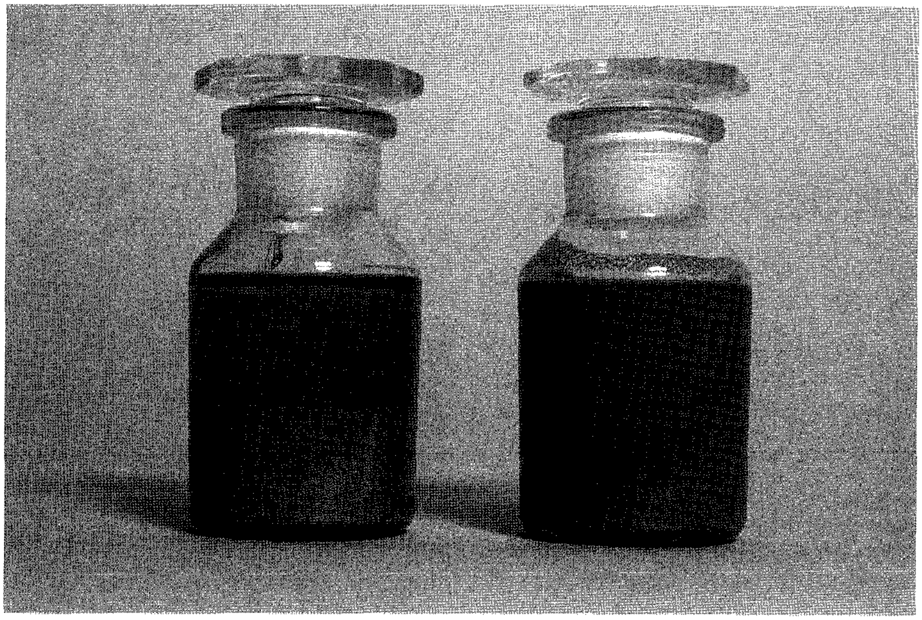


Figure 17: Comparison of the sedimentation tendency of epoxy ester-based zinc dust paints after four weeks of storage at room temperature. Left: control paint, right: paint produced with an addition of 2% of AEROSIL R 972 (4).
Composition: JÄGALYD ED 4, 50% in xylene 19.6; zinc dust super-fine 72.5; butanol 1.0; SHELLSOL A 9.4; Co octoate, 6% Co 0.2

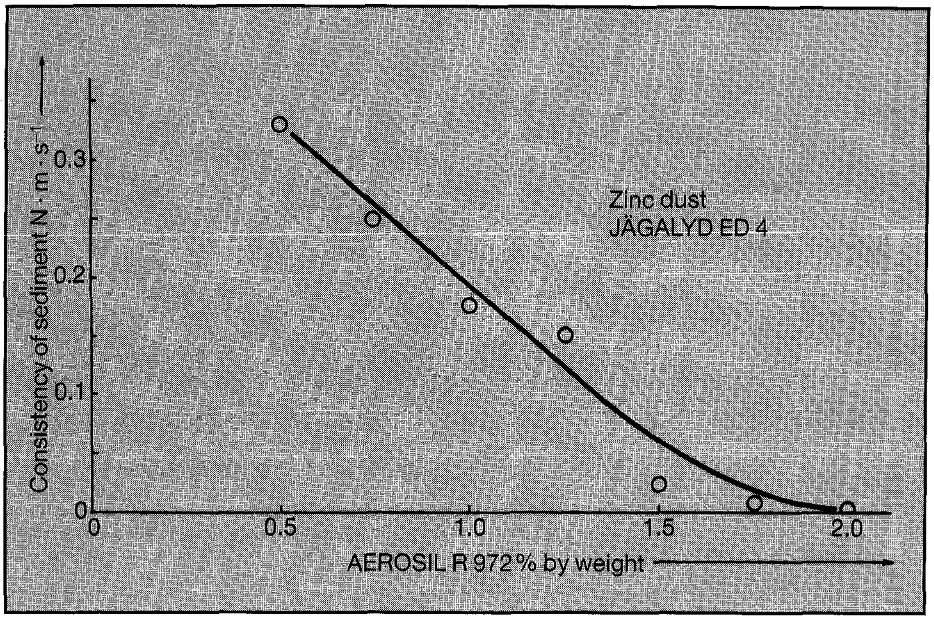


Figure 18: Sediment consistency measurements carried out on zinc dust paints (composition see sub-title to Figure 17) after three months of storage at room temperature (4)

The optimum addition of AEROSIL can be readily determined in practice with the aid of a DYNOMETER (30, 31). Using zinc dust paints as an example, **Figure 18** demonstrates the effect which may be obtained with AEROSIL R 972.

It is of significance that the control sample, which contained no addition of AEROSIL, had become so hard after only four weeks of storage that it was no longer possible to carry out a measurement with the DYNOMETER. – If 2% by weight of AEROSIL R 972 is added to these paints, the power input in the DYNOMETER required to reach the bottom of the test apparatus is nil. This value corresponds to the added amount of AEROSIL R 972 determined in practice (4).

Like AEROSIL 200, AEROSIL R 972 has also been used as a thixotrope in special effect coatings for many years (28). This statement is still valid today. By preventing the occurrence of sagging, it is possible to produce a well-defined special effect in this application, which is naturally based on the use of an appropriate silicone oil.

This statement is illustrated clearly in **Figure 19**. Finally, special mention should be made of the fact that hammer finish coatings containing AEROSIL show no sign of greying even after storage.

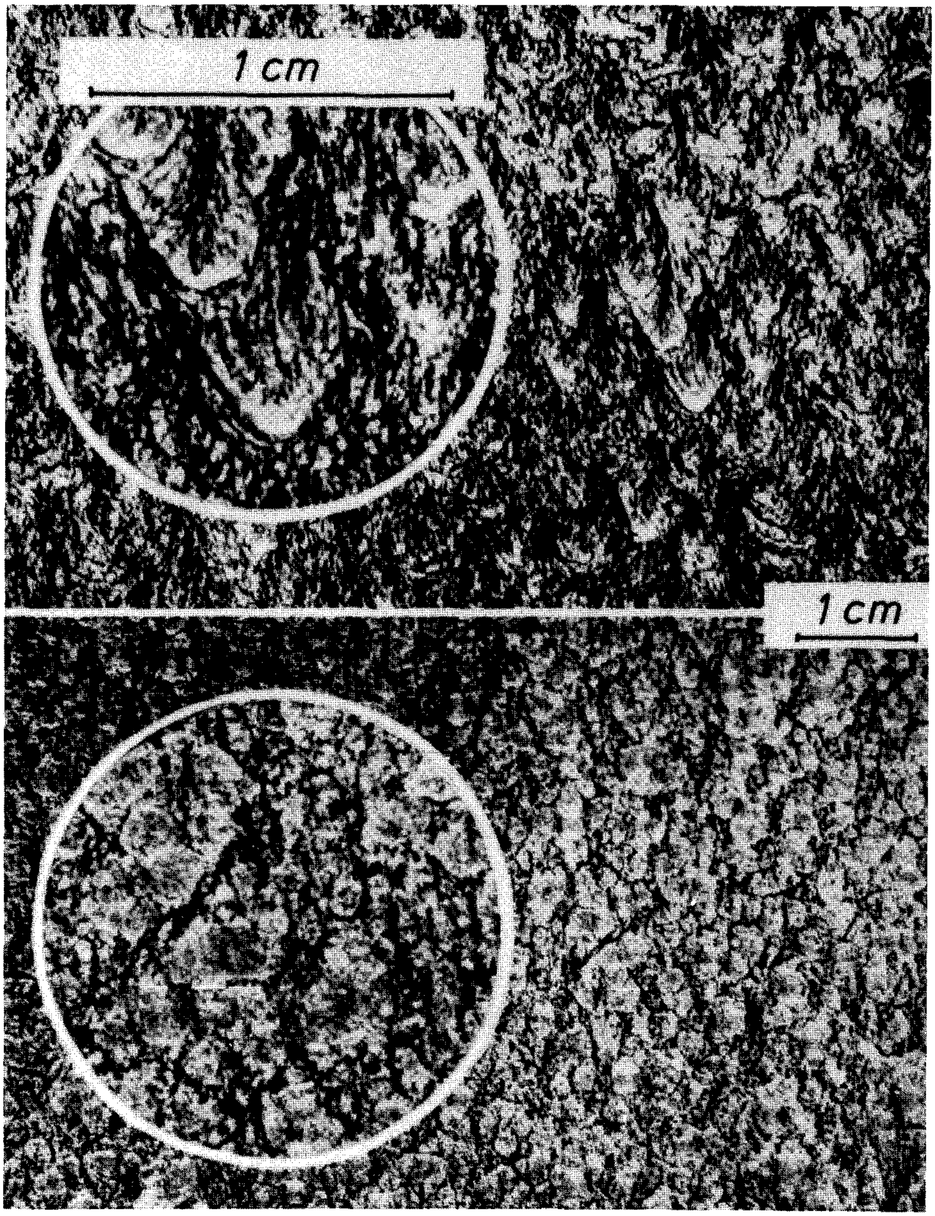


Figure 19: Sagging behaviour of hammer finish coatings. Above: control coating, below: containing 0.8% of AEROSIL R 972 (4). Composition: ALKYDAL R 40 50.0; PLASTOPAL EBS 200, 60% in butanol 3.6; MAPRENAL MF 750, 55% in isobutanol 18.0; EFWEKO NC 18/2, 20% in ethyl acetate 5.0; butanol 13.5; SHELLSOL A 4.0; ethyl glycol acetate 2.0; STAPA POLYCHROM 3 3.6; silicone hammer finish solution TRS 0.3

An improvement in the long-term suspension behaviour cannot only be achieved with specifically heavy pigments. Products with a low specific density, such as SiO_2-based flatting agents with a density of 1.9 g/cm^3, can also be held effectively in suspension, as demonstrated in **Figure 20**.

The results shown in **Figures 17** and **20** are representative of the findings of numerous other tests, in which AEROSIL grades lead to the real solution of problems in other systems.

AEROSIL R 972, for example, is effective as an anti-settling agent, improving important properties, even after application of a coating onto the respective substrate, see **Figures 34** and **35**.

4.2
Dispersion Additive

The state of dispersion of mainly high quality pigments can be greatly improved by slight additions of hydrophobic AEROSIL. This is demonstrated with a pigment black in **Figure 21** where the jetness and blue undertone attainable serve as an example.

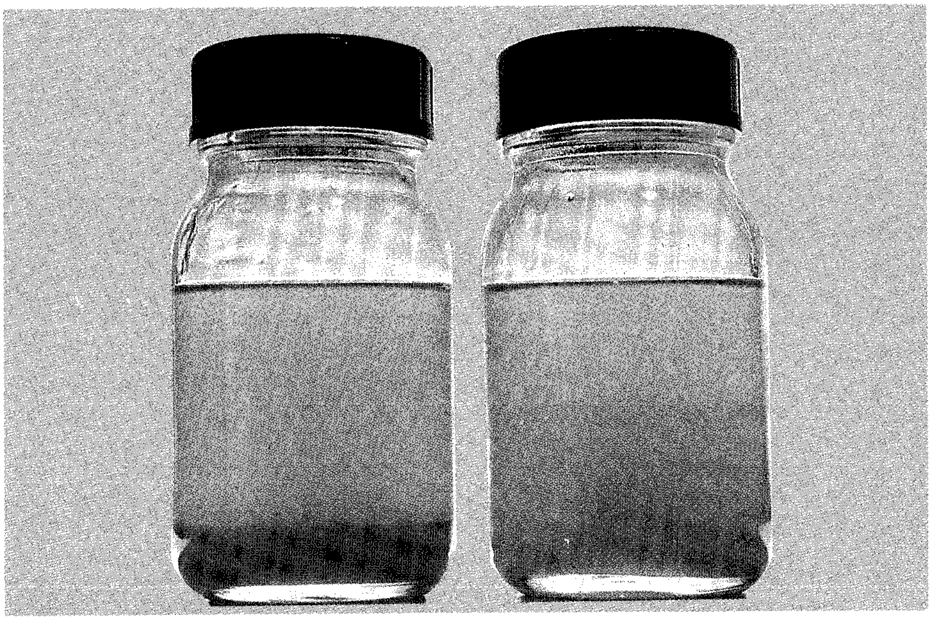


Figure 20: Improvement in the suspension behaviour of Flatting Agent TS 100 in a coating resulting from the addition of 0.5% of AEROSIL R 972

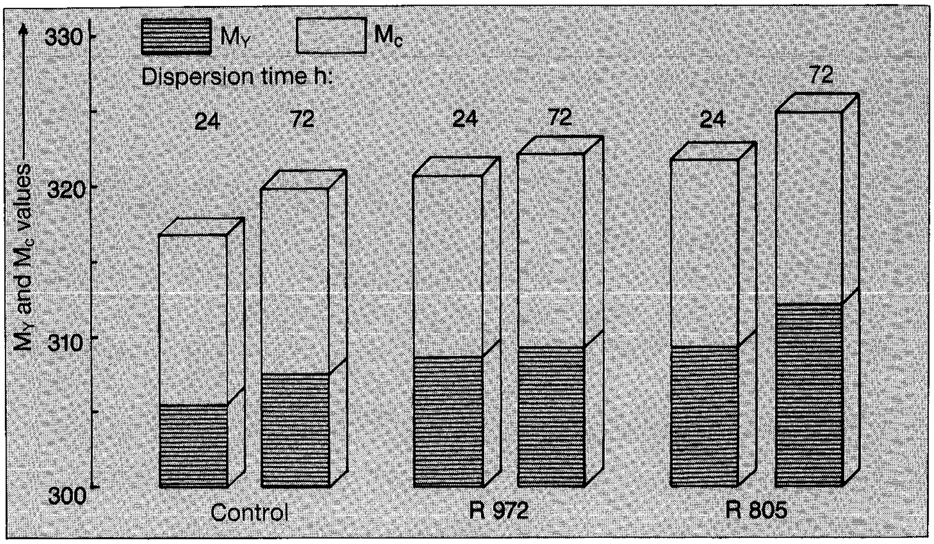


Figure 21: Black value M_Y and blue component M_c of stoving enamels containing 5% of Pigment Black FW 200 and 0.6% of AEROSIL as a function of the dispersion time in the ball mill (14).
Composition: MAPRENAL MF 800, 55% in isobutanol 13.3; butanol 0.6; Colour Black FW 200 2.2; AEROSIL 0.264; ALKYDAL F 310, 60% in MAPRENAL MF 800, 55% in isobutanol 10.7; solvent mixture RL 938/9 21.9

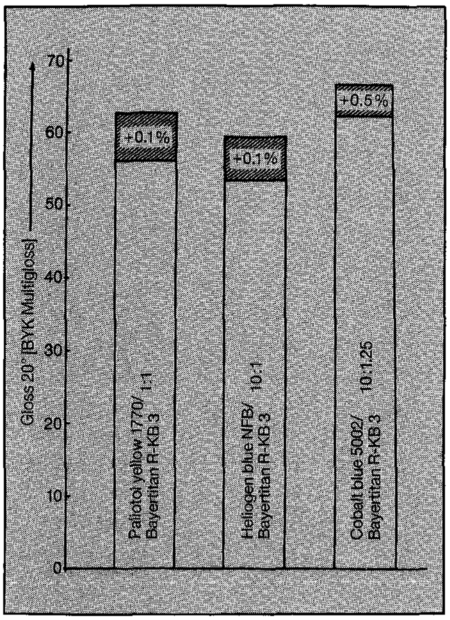


Figure 22: Increase in the degree of gloss of alkyd/melamine-based stoving enamels containing coloured pigments resulting from the addition of 0.1% and 0.5% of AEROSIL R 972 (14).
Composition: ALFTALAT AS 502, 60% in xylene 46.6; MAPRENAL MF 800, 55% in isobutanol 21.8; diluent 15.8; Paliotol yellow 1770 or Heliogen blue NFB or cobalt blue 5002 12.0; Bayertitan R-KB 3 10.0 with Paliotol yellow, otherwise 1.5

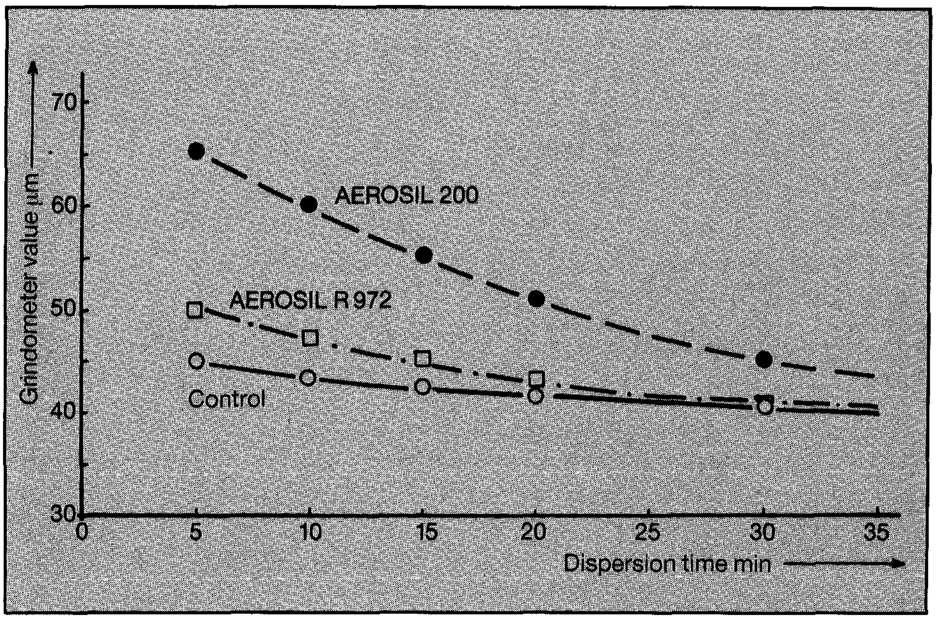


Figure 23: Degree of dispersion of a zinc dust paint based on epoxy ester as a function of the dispersion time. Peripheral velocity of the stirrer: 8.4 m/s. Both grades of AEROSIL had already been predispersed. Composition: see sub-title to Figure 17

This mode of action is demonstrated in **Figure 22** by an increase in gloss with tints of inorganic and organic coloured pigments.

The grindometer values of zinc dust paints which may be obtained as a function of the dispersion time are recorded in **Figure 23**. This diagram illustrates how much more easily hydrophobic silica may be dispersed. For practical purposes, no more differences can be detected between the hydrophobic grade and the control sample after 20 minutes of dispersion.

All of the findings discussed in this section are always dependent on the dispersing conditions. It is by no means the case that the presence of one of the AEROSIL grades necessarily leads to an increase in gloss or improvement in the optimum efficiency in every application, see **Table 4**.

4.3
Coating Effect

If zinc dust is mixed in a household blender with 0.5% of AEROSIL R 972 in the dry stage, the hydrophobic silica completely envelops the Zn particles, as demonstrated in **Figure 24.** The same effect is also observed in the corresponding zinc dust paints (4), see **Figure 25.** This coating effect of solids has been known for quite a long time (32), and is also used as a basis for the prevention of the "gassing" of zinc dust paints during storage, which is shown in **Figure 26.** The envelopment of zinc dust with AEROSIL R 972 can possibly be attributed to purely electrical interactions, because synthetic silicas are always negatively charged (33) and metals are always charged positively.

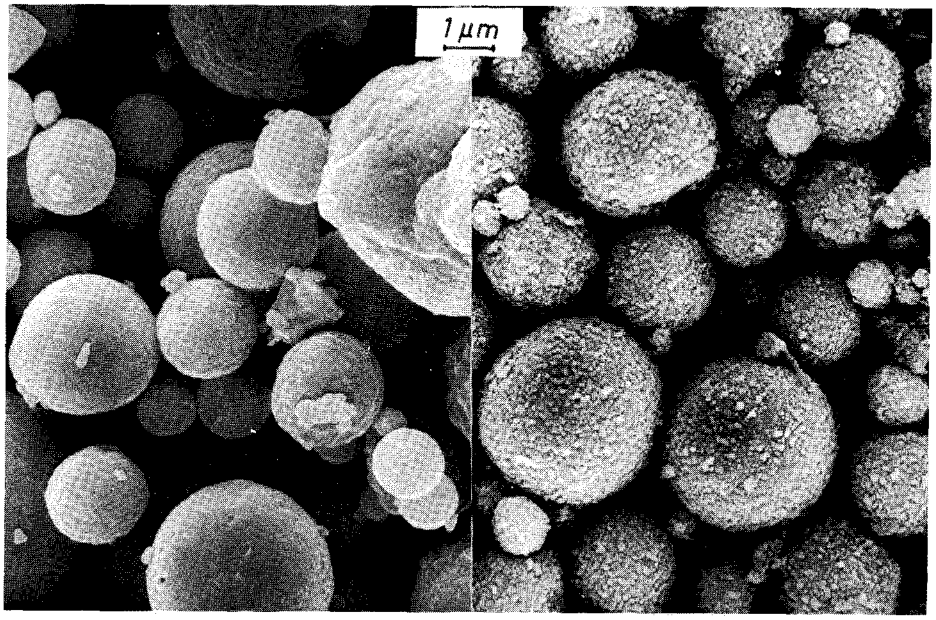


Figure 24: Scanning electron micrographs of zinc dust (left) and of zinc dust together with 0.5% of AEROSIL R 972 (right) (4)

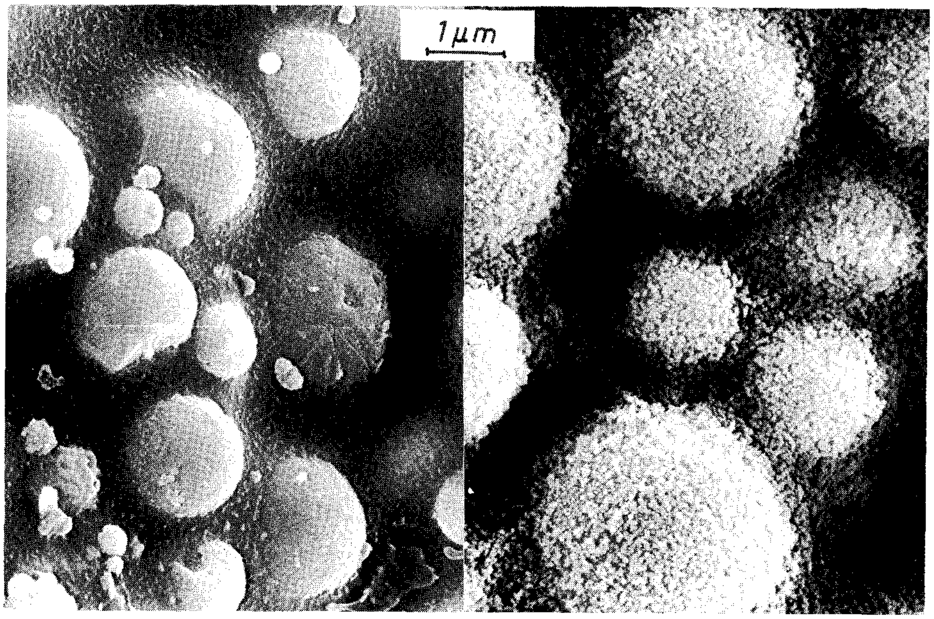


Figure 25: SEMs of etched zinc dust paints, left: control, right: containing 2% of AEROSIL R 972 related to zinc dust (4).
Composition: JÄGALYD ED 4, 50% in xylene 19.6; zinc dust super-fine 72.5; butanol 1.0; SHELLSOL A 9.4; Co-octoate, 6% Co 0.2

However, non-metallic anti-corrosive pigments can also be coated, as illustrated in **Figure 27** by using zinc phosphate as an example. The theory of electrostatic interactions cannot be used to explain this particular phenomenon. It is also possible to attribute this coating effect to the better dispersibility, discussed in 4.2, which brings about an improvement in the optical effectiveness of the different pigments.

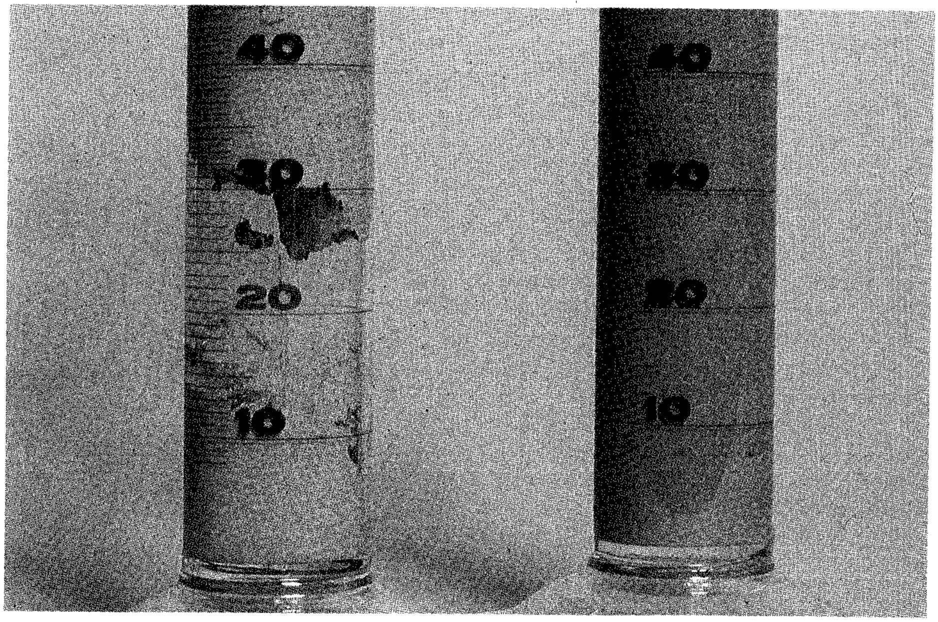


Figure 26: Prevention of gassing of a zinc dust paint on a basis of epoxy ester following storage at room temperature for four weeks. Left: no addition; right: containing 2% of AEROSIL R 972 related to zinc dust (14).
Composition: JÄGALYD ED 4, 50% in xylene 19.6; zinc dust super-fine 72.5; butanol 1.0; SHELLSOL A 9.4; Co-octoate, 6% Co 0.2

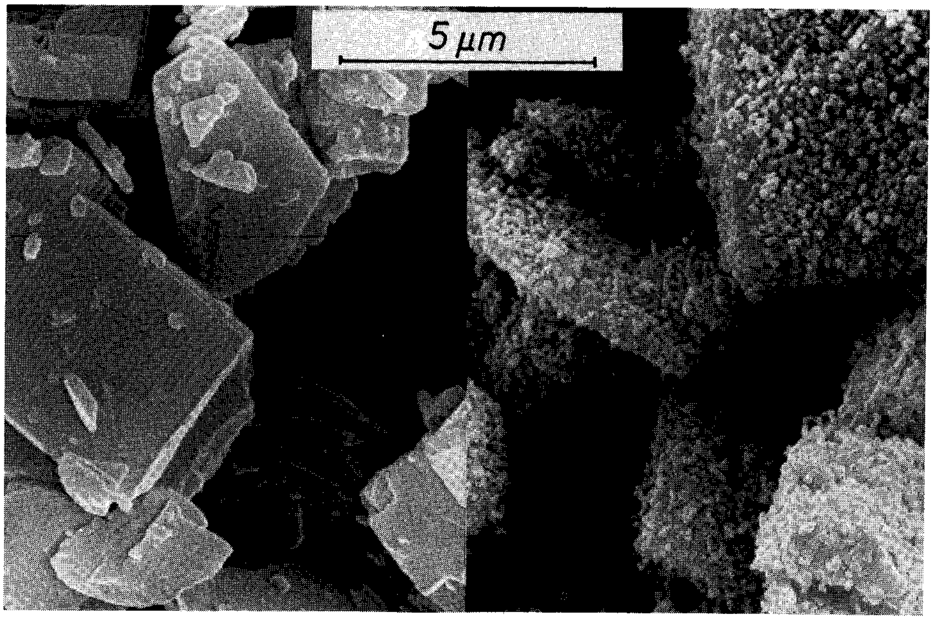


Figure 27: SEMs of zinc phosphate (left) and zinc phosphate together with 1% of AEROSIL R 972 (right) (14)

Hydrophobic silica may also be used to stabilize a particular state reached during *dispersion*. ***Table 5** gives evidence of a* more stable distribution of the red pigment frequently used in top coats for automobiles after 48 hours of dispersion in a laboratory ball mill. In addition to the transparency, which is higher than that of the control sample, and which indicates a better pigment distribution, **Table 5** also includes the changed rheological measuring data of the mill base brought about by the addition of AEROSIL.

	Paliogen red L 3885	AEROSIL R 972	AEROSIL R 805
Viscosity of mill base mPas at D= 48 s^{-1}	3711	8834	8162
(Haake RV 11, SV I) mPas at D=433 s^{-1}	1352	1785	1406
Thixotropic index	2.9	5.4	6.3
Transparency (red high solids stoving enamel) (Lange KME/Lt 12 / grey filter 2)	105.6	141.5	140

Table 5: Increase in the viscosity and thixotropic index of a mill base based on Paliogen red® L 3885 and in the transparency of a high solids stoving enamel following the addition of AEROSIL (14)

Not only solids can be coated with AEROSIL. The use of hydrophobic silicas also enables water to be enveloped. News about this world sensation was published in 1966 under the motto "Degussa chemists invent dry water" (34). Attempts were made at this time to mix 10% of AEROSIL R 972 into water with the aid of a high-shear powder mixer.

This resulted in a free-flowing white powder. Whilst 10% of AEROSIL R 972 were required in those days, smaller quantities are now sufficient to produce "dry water". The results compiled in **Table 6** are obtained with 5% of hydrophobic AEROSIL.

If this test had been included in the evaluation described in 3.3, the order of hydrophobicity determined would not have been changed, but there would have been less difference between AEROSIL R 202 and AEROSIL R 812.

	AEROSIL				
	R 202	R 805	R 812	R 812 S	R 972
Formulation possible	no	no	yes	yes	no
Shearing stability in min	–	–	0.5	5	–

Table 6: Practical test to determine which hydrohobic grades of AEROSIL are suitable for producing "dry water" using 5% by weight (35). The shearing stability was tested in a household blender. The formation of a clearly compacted, "smearable" mass was considered as signifying a collapse of the formulation

4.4
Corrosion Protection

The use of AEROSIL R 972 as an additive to increase the resistance to corrosion was described in 1974 (29). The positive effects which may be obtained with AEROSIL R 972 are illustrated in **Figures 28** and **29** using zinc dust paints and zinc chromate priming coats as examples.

However, AEROSIL R 972 can also improve formulations which do not contain anti-corrosive pigments. For example, **Figure 30** depicts an industrial coating based on a water-thinnable, oil-free alkyd resin (s. **Table 4** for formulation), which demonstrated a greatly improved resistance following stresses imposed during the accelerated durability test (dew cycle) according to DIN 50018. – Results of this nature are confirmed by independent laboratories, such as the Transportation Laboratory of the Californian Department of Transportation (38). –

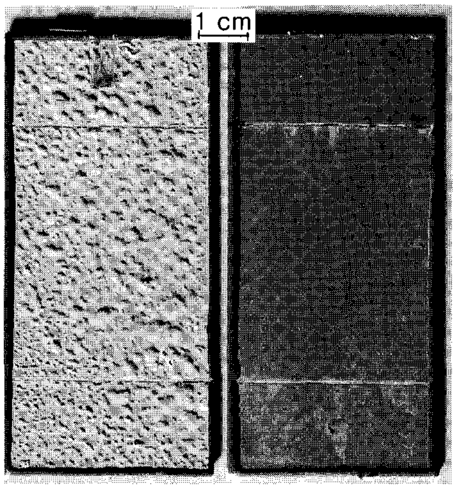


Figure 28: Zinc dust paints based on an epoxy ester after a 168-hour salt spray test in accordance with DIN 50021 and ASTM B 117-64. Left: control paint, right: containing 2% of AEROSIL R 972 related to zinc dust (14).
Composition: JÄGALYD 4, 50% in xylene 19.6; zinc dust super-fine 72.5; butanol 1.0; SHELLSOL A 9.4; Co-octoate, 6% Co 0.2. Compare Figure 31

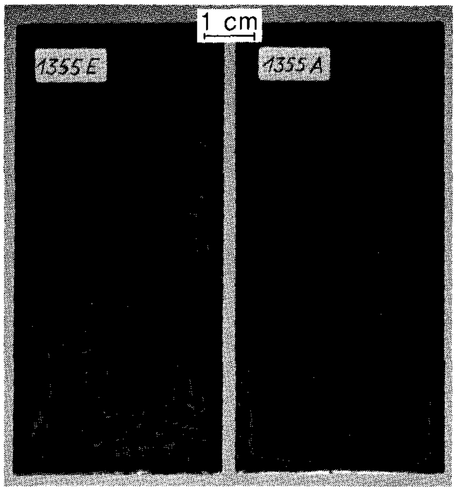


Figure 29: Zinc chromate primers after a 168-hour salt spray test in accordance with DIN 50021 and ASTM B 117-64. Left: control paint, right: containing 1.3% of AEROSIL R 972 related to pigment (14).
Composition: LAROFLEX MP 35 19.5; zinc white, red seal 2.9; zinc phosphate ZIN P 1.4; zinc chromate 1 W 6.8; iron oxide red 130 M 6.8; talc AT 1 13.5; SHELLSOL A 11.6; xylene 32.6; ethyl glycol acetate 2.4; chlorinated paraffin 40 2.0; castor oil derivate 0.6. Compare Figure 32

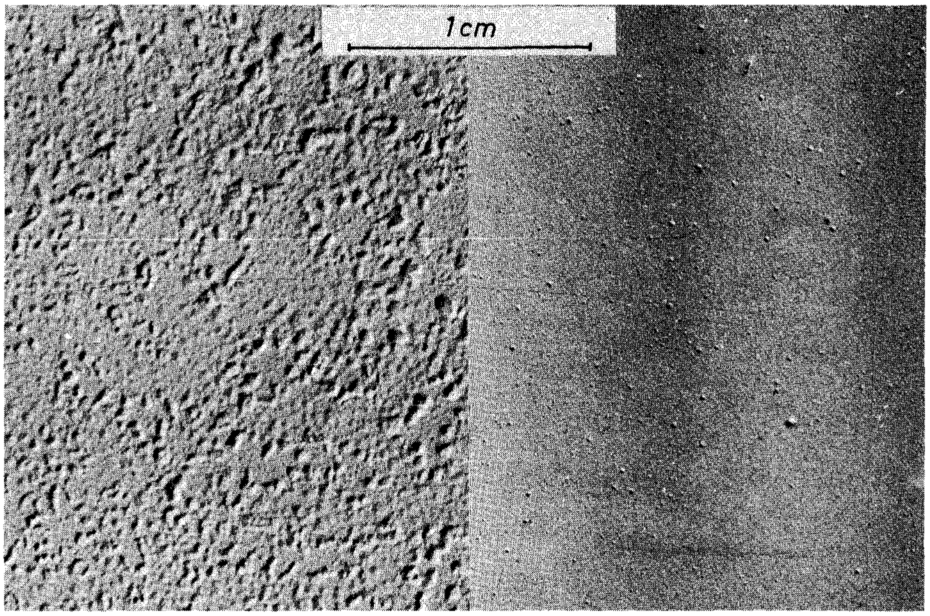


Figure 30: Stoving enamel based on a water-thinnable binder following 7 dew cycles, to conform with DIN 50018 (14). Left: control sample, right: containing 0.5% of AEROSIL R 972 related to the total formulation

4.5 Adhesion

An addition of AEROSIL is known to improve the applicational properties of stoving enamels, e.g. during the performance of the mandrel bend test, as defined in DIN 53152 (36). **Figure 31** demonstrates the improved adhesion of epoxy ester which was applied onto a steel plate. It is interesting to note that the hydrophobic grades of AEROSIL bring about an improvement in the adhesion of the epoxy resins by an average of 13%.

4.6 Uniformity

The results of numerous tests have demonstrated a tremendous improvement in the uniformity or homogeneity of coating systems that include hydrophilic or hydrophobic grades of AEROSIL. This section includes several representative examples of applications containing hydrophobic AEROSIL grades.

To begin with, these claims are supported by surface representations of priming coats depicted in **Figures 32** and **33**. For this purpose, we returned to examples which were already used for a different representation in section 4.4.

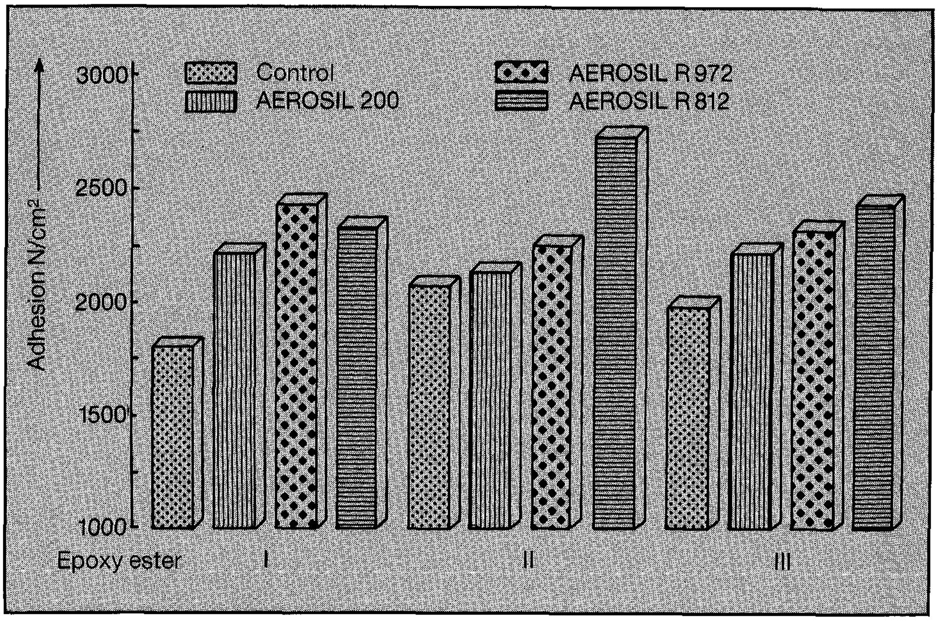


Figure 31: Increase in the adhesive strength of epoxy esters on steel plates by the addition of 1.5% of hydrophobic silica. Measured following two days of storage at room temperature (14). See Figure 28

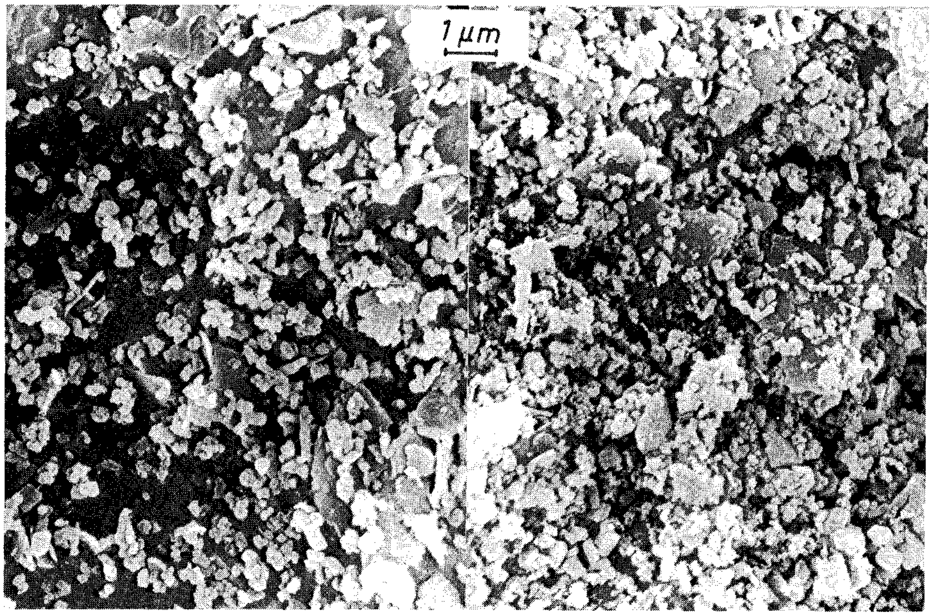


Figure 32: Scanning electron micrographs of an etched zinc chromate primer (4). Left: control paint, right: containing 1.3% of AEROSIL R 972 related to pigment content. See Figure 29

Figure 32 depicts a zinc chromate primer and **Figure 33** a zinc dust paint. The left-hand side of this picture is not out of focus; the blurred effect is due to the fact that the upper layers of the control paint not containing AEROSIL are virtually free from zinc dust, see **Figure 34**. The depth of focus of the scanning electron microscope is not sufficient to obtain a more sharply defined photograph, such as the one shown on the right-hand side of **Figure 33**. Even a top view of this sample, which contains 2 % of AEROSIL R 972, shows the completely uniform distribution in the zinc dust coating film. This fact is clearly confirmed in **Figure 34** which depicts photographs of microtome sections. The upper half of **Figure 34** also illustrates clearly how sedimentation has occurred in the relatively short time between application of the coating and drying. This can be prevented by an addition of 2 % of AEROSIL R 972.

The more uniform distribution of the zinc dust can definitely be used to explain the improvement in the anti-corrosive effect (4). This statement is valid regardless of which theories are drawn upon as a basis to explain the protection mechanism of zinc dust paints.

This goes for both the "sealing theory" and the "cathodic protection mechanism theory" which were compared in 1964 (40).

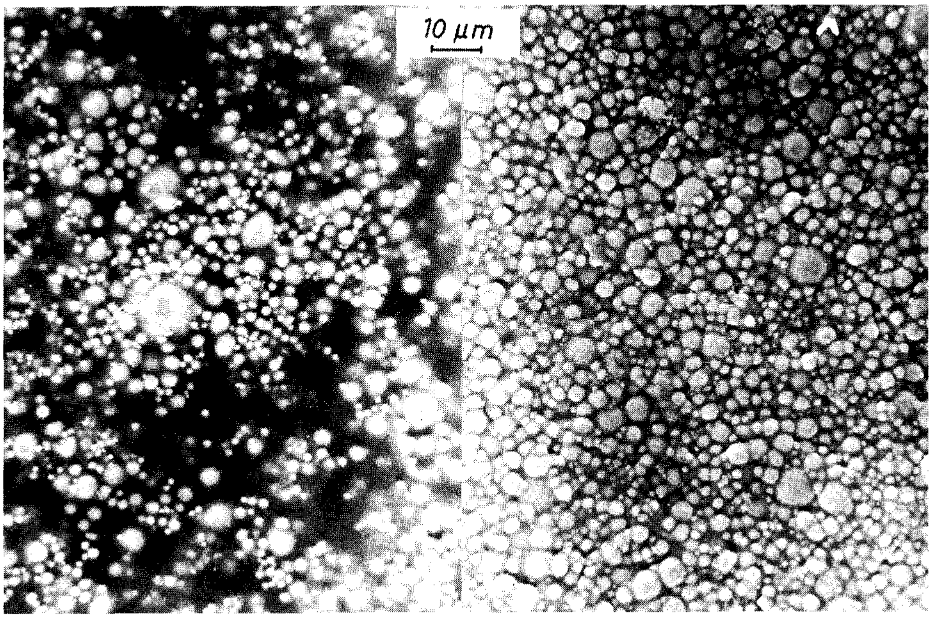


Figure 33: SEMs of etched zinc dust paints (4). Left: control paint, right: containing 2 % of AEROSIL R 972 related to zinc dust. See Figure 26

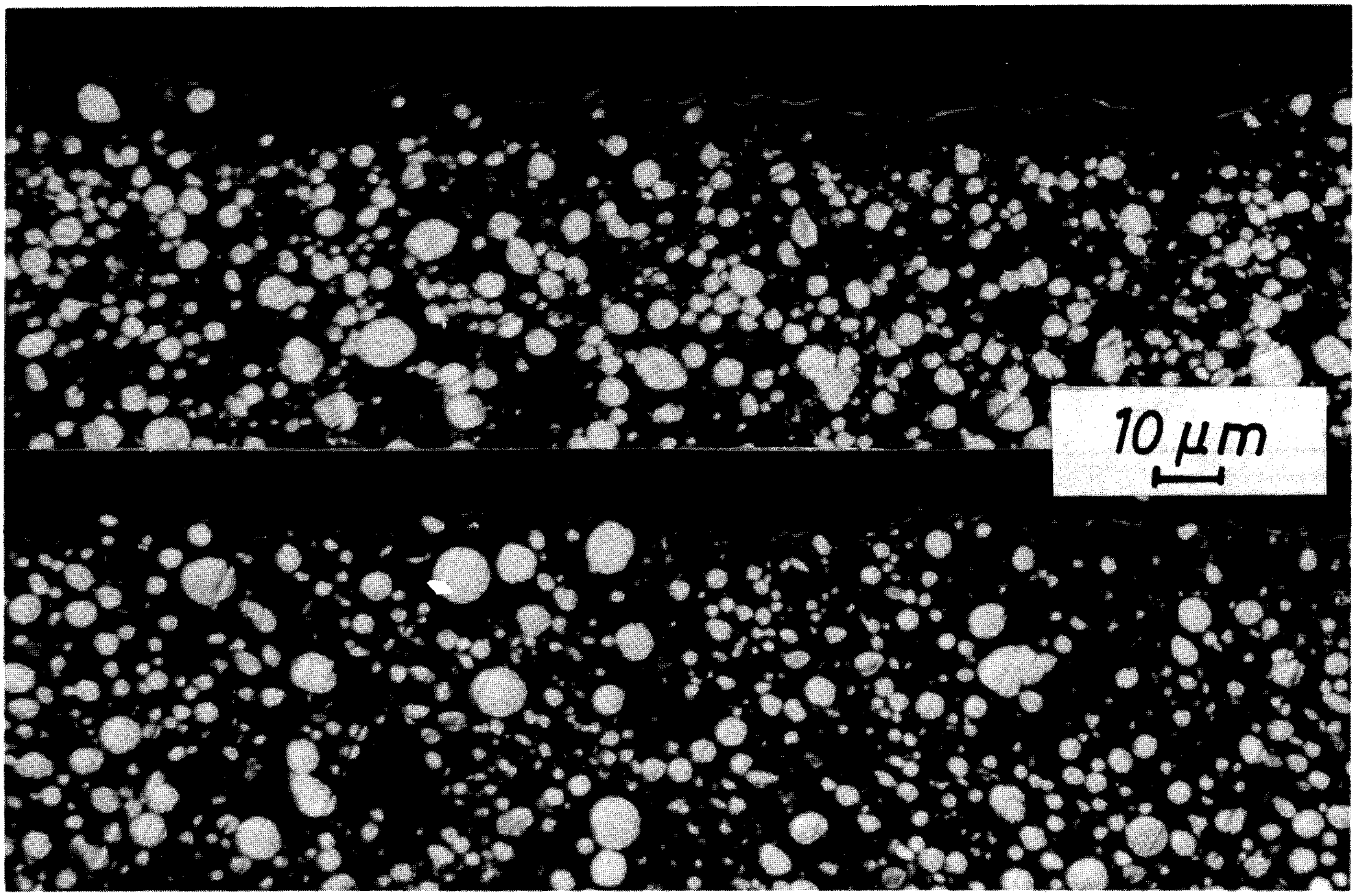


Figure 34: Optical micrographs of cryo microtome sections of zinc dust paint samples (14). Paint was applied to a PVC film, the surface was vapour-blasted with gold. Above: control paint, below: containing 2% of AEROSIL R 972 related to zinc dust

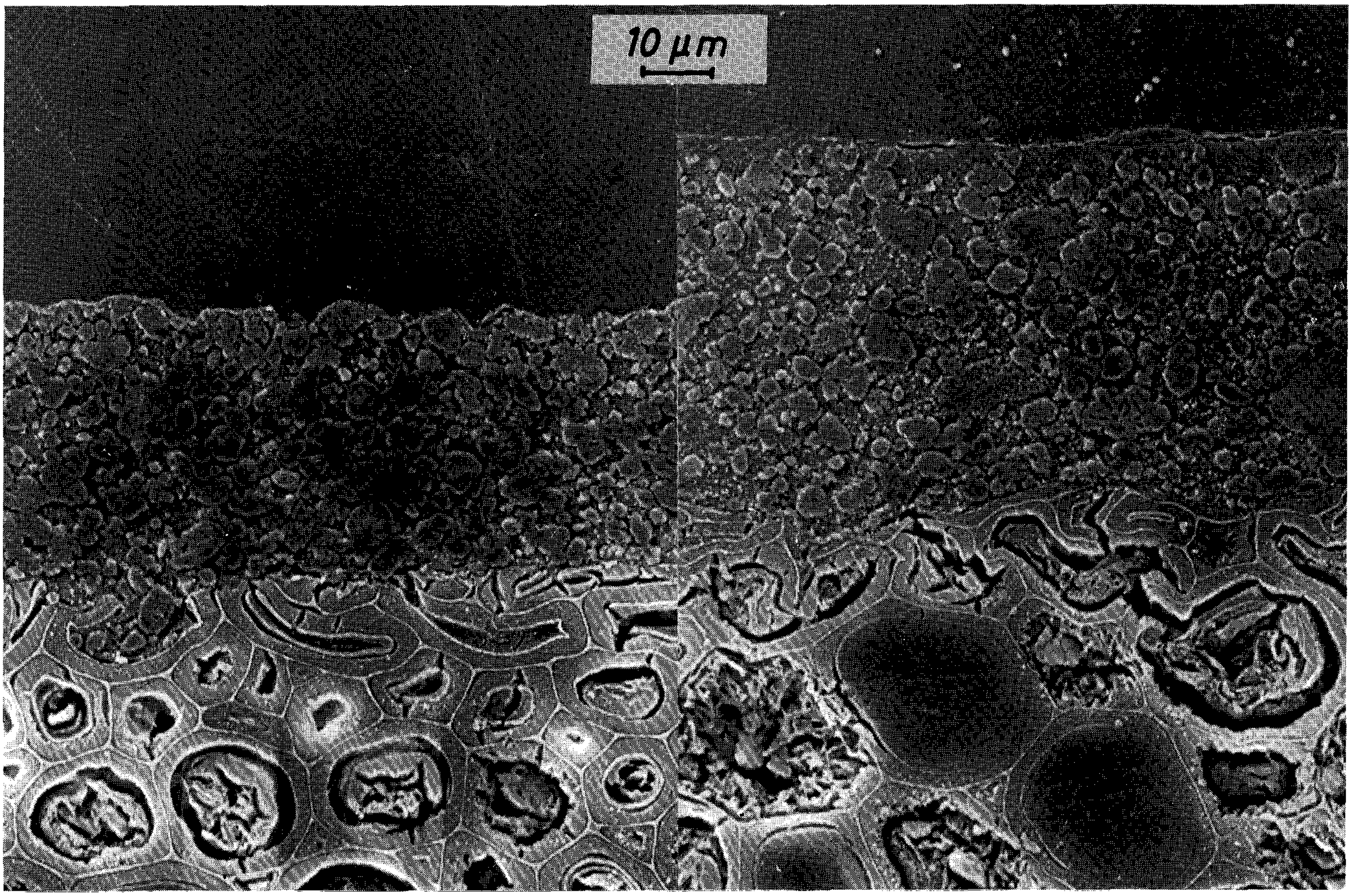


Figure 35: SEMs depicting microtome sections of wood glazes on absorbent wood. Left: control paint, right: containing 1.5% of AEROSIL R 972 related to the total coating (37). Basis: 8% of ALFTALAT AF 641 and 9% of Flatting Agent OK 412

A more uniform distribution can also bring about definite improvements in the case of applications containing flatting agents (37). **Figure 35** likewise depicts microtome sections of wood glazes on a porous wooden substrate. The coating on the left-hand side of the picture has penetrated into the substrate to such an extent that the SiO_2-based flatting agent particles are now lying on the coating surface without any binder to envelop them. This produces an extremely poor optical effect, compare the left-hand side of **Figure 36.**

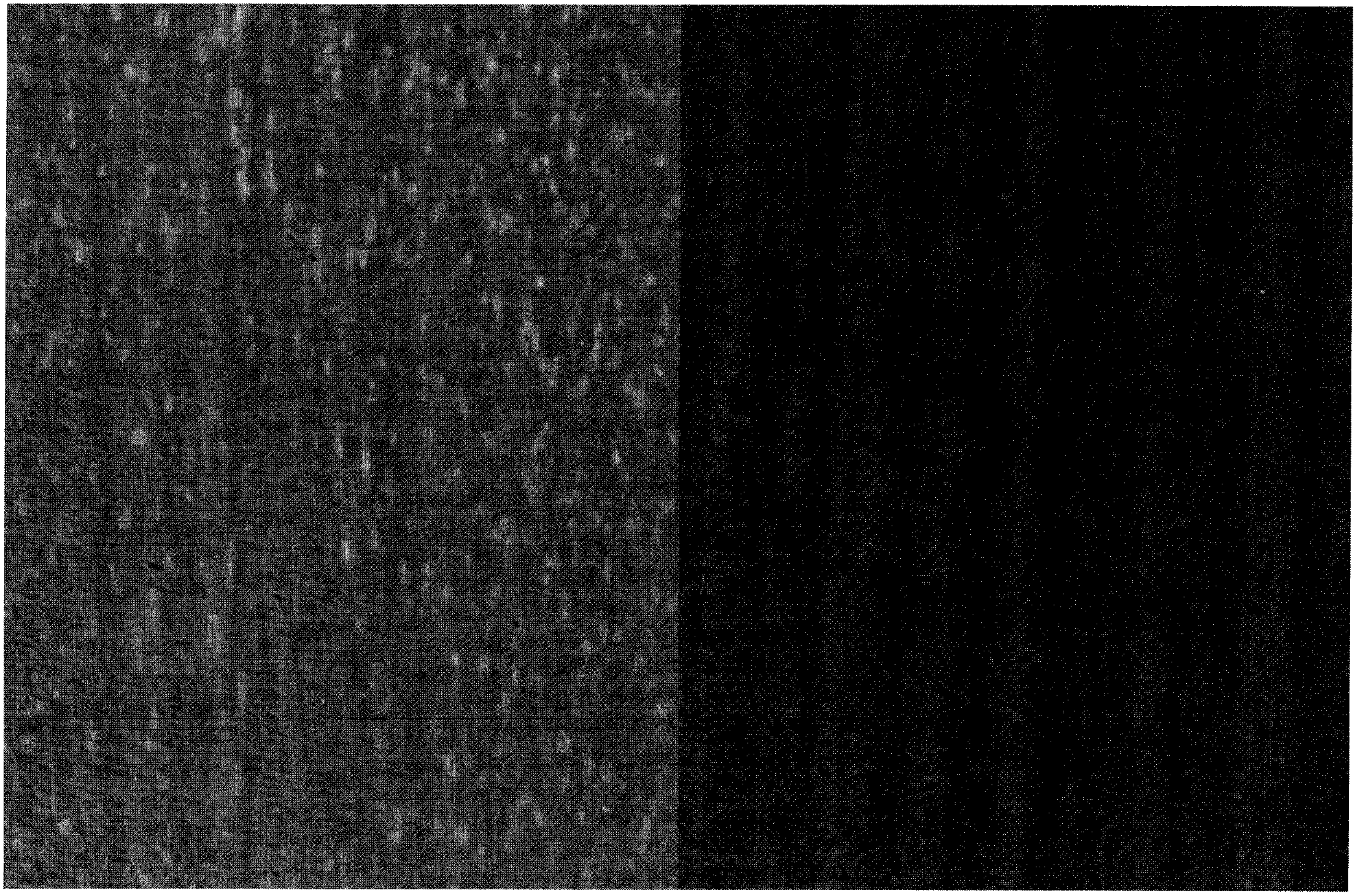


Figure 36: Photographs of the wood finishes shown in Figure 35

The addition of AEROSIL R 972 prevents an excessive penetration of the binder solution into the surface of the wood. This means that adequate binder remains in the coating to completely embed even the flatting agent particles lying on the surface. A perfect optical effect is obtained, compare the right-hand side of **Figure 36.**

4.7
Free-Flow Properties

Synthetic silicas, especially the various AEROSIL grades, are used in many branches of industry to improve the free-flow behaviour of substances in powder form (32, 39). Hydrophobic silicas are particularly effective here (4). The free-flow properties of powder coatings can also be considerably improved, as shown in **Table 7.** In addition to this, small amounts of AEROSIL R 972 can also be used to reduce the unwanted electrostatic charge of coating materials in powder form. This occurs regardless of whether the basic substance has a positive or a negative charge. The very slight additions of AEROSIL R 972 used to improve the flow properties of ready-ground powder coatings have little or no effect on the levelling properties of the powder coating during the film forming and curing processes.

	Powder coating			
	R 2433		R 2519	
AEROSIL R 972 Addition %	Cone height mm	Electrostatic charge V/cm	Cone height mm	Electrostatic charge V/cm
0	38	+460	26	–40
0.1	32	+120	18	–40
0.2	24	+ 50	18	–30
0.3	22	+ 40	–	–
0.4	22	+ 50	18	–20
0.5	24	+ 90	–	–
0.6	–	–	18	–20

Table 7: **Free-flow cone height and electrostatic charge of commercial powder coatings before and after the addition of AEROSIL R 972 (4). The measurement of the electrostatic charge is described in (33)**

5
Further Applications

Hydrophobic AEROSIL grades are also used in numerous other applications, for example outside the coatings sector in:

- toners, to stabilize the triboelectric characteristics (41, 42)
- deodorants (43), to convert the aqueous phase containing the active substances into a loose, sprayable powder;
- silicone-based sealing compounds;
- protective cable fillers for light-conductive cables as a water-repellent thickening agent (44) (so-called “cable gels”);
- waterproof gel greases;
- special greases for packaging machines used in the food industry.

The application of hydrophobic silicas in the production of powdered rubber mixtures (45) is also conceivable. This possible application and the above-mentioned use in deodorants are based on the conception of “dry water” which was published in (46).

This list is by no means complete and is intended to give some examples which could encourage ideas for further applications.

6
Practical Advice

Which grades of AEROSIL should the paint chemist use in practice? It is easy to answer this question (14):

- The most significant product is AEROSIL 200.
- If the results obtained with this standard grade are not satisfactory, AEROSIL R 972 should be applied, particularly for anti-corrosion purposes.
- Only in cases where even AEROSIL R 972 is unable to produce the desired effect should one resort to other grades of AEROSIL, e.g. in the following order:
  - AEROSIL R 805
  - AEROSIL R 812.

  For example, these grades may be used to advantage in certain vinyl ester resins for casting resins or adhesives.
- AEROSIL R 202 should only be used in the coatings industry if extensive tests by the consumer have proved that no applicational problems occur as regards levelling, recoating or adhesion. AEROSIL R 202 is recommended for use in epoxy systems (27), and especially for casting resins.

7
Toxicological Information

All of the hydrophobic silicas mentioned in this brochure are X-ray amorphous. Like the basic hydrophilic products, they do not cause silicosis (47–49). AEROSIL R 972 and AEROSIL R 974 are known to be expelled from the lungs of rats soon after intake (7, 50). The occurrence of fibrosis in animal experiments was only observed following high doses of the substance. This cannot occur if a low dust concentration at the place of work is ensured. The general dust limit value of 4 mg/m^3 has been valid in the Federal Republic of Germany since 1989. Similar values are also in force in other western industrial states.

Up until now there has been no evidence to show that hydrophobic silicas damage the skin in any way. Due to a certain water adsorption capacity, hydrophobic silicas can withdraw water from the human skin. The “dry feeling” which is experienced during direct contact with the product is based on this effect. The normal state can be restored by simply washing one’s hands.

Known data are compiled in **Table 8**. The “Patch Test” and the test for irritating effects on the mucous membranes proved negative in all cases, i.e. were without findings. It should be pointed out that the numerical values given for the acute oral LD$_{50}$ depend to a large extent on the bulk density of the material being examined and on the testing laboratory. It was not possible under the test conditions to apply more silica in any of the cases.

All of the recommended hydrophobic silicas are delivered in paper sacks. Intensive handling tests have been carried out with synthetic silicas in order to avoid any in-plant dust problems that a customer might experience. Most of these results have been published (51, 52) and include:

- the manual or fully-automatic emptying of sacks;
- the transportation of the hydrophobic silicas within the works, which is easiest in this case by means of a suction conveyor;
- the automatic weighing and dosing;
- the dust-free transfer of the silica to mixing and dispersing appliances.

		AEROSIL R 972	AEROSIL R 974	AEROSIL R 812	AEROSIL R 202	AEROSIL R 805
Acute toxicity Oral	Date	28. 12. 77	–	1984	1985	1985
	Rat mg/kg	> 500	–	> 2000	> 1000	> 5340
Inhalation	Date	–	May 83			
	Rat mg/kg	–	477			
Skin Patch test Rabbit	Date	1. 3. 78	–	1984	1985	1985
	Findings	i. O.	–	i. O.	i. O.	i. O.
Mucous membrane Eye of rabbit	Date	20. 6. 79	–	1984	1985	1985
	Findings	i. O.	–	i. O.	i. O.	i. O.
Testing laboratory		F. Leuschner, Hamburg	CIVO, TNO; Rep. V. 83.112/ 221 216	Proj. 032128 Proj. 029531 Proj. 029542 RCC, Itlingen, Schweiz	Proj. 046787 Proj. 046800 Proj. 046811 RCC, Itlingen, Schweiz	Ind. Tox. 599-84/85 Ind. Tox. 590-84/85 Ind. Tox. 591-84/85

Table 8: Toxicological data of hydrophobic grades of AEROSIL according to (49)

8
Literature

1) Technical Bulletin Pigments No. 31, Degussa AG, Frankfurt/M., 4th edition (1981)

2) H. FERCH, M. LAMBERMONT, R. OELMÜLLER, Adhäsion **29**, 21 (1985)

3) H. FERCH, A. REISERT, R. BODE, Kautsch. + Gummi · Kunststoffe **39**, 1084 (1986)

4) H. FERCH, farbe + lack **85**, 651 (1979)

5) Technical Bulletin Pigments No. 26, Degussa AG, Frankfurt/M., 3rd edition (1980)

6) H. BRÜNNER, D. SCHUTTE, Chem.-Z. **89**, 437 (1965)

7) W. KLOSTERKÖTTER, Arch. Hyg. Bakt. **149**, 577 (1965)

8) E. WAGNER, H. BRÜNNER, Angew. Chem. **72**, 744 (1960)

9) R. BODE, H. FERCH, H. FRATZSCHER, Kautsch. + Gummi · Kunststoffe **20**, 578 (1967)

10) H. FERCH, K. SEIBOLD, farbe + lack **90**, 88 (1984)

11) Technical Bulletin Pigments No. 6, Degussa AG, Frankfurt/M., 3rd edition (1981)

12) G. KALLRATH: DE-PS 1.229.504 (1962), DE-PS 1.172.245 (1963), both Degussa AG, Frankfurt/M.

13) J. MATHIAS, G. WANNEMACHER, J. Coll. Interf. Sci. **125**, 61 (1988)

14) H. FERCH, 17. AFTPV Congress Book p. 128 (1987)

15) H. FERCH, Chem. Ing. Techn. **48**, 11 (1976)

16) I. A. LICHTMAN, J. V. SINKA, D. W. EVANS, Ass. Mex. Tec. Ind. Cell. Paper (Bol) **15**, 26 (1975)

17) W. T. YENI, R. S. CHAHAL, T. SALMAN, Canad. Met. Quart. **12**, 231 (1973)

18) S. GARHSVA, S. CONTRERAS, J. GOLDFARB, Coll. Polym. Sci. **256**, 241 (1978)

19) K. KLEIN, Degussa AG, personal report (1970)

20) J. J. CHESSICK, A. C. ZETTLEMOYER, Adv. Cat. **11**, 263 (1959)

21) B. MARCINIEC, A. KRYSTAFKIEWIECZ, L. DOMKA, Coll. Polym. Sci. **261**, 366 (1983)

22) O. J. SCHMITZ, F. J. SELL, K. HAMANN, farbe + lack **79**, 1049 (1979)

23) S. BRUNAUER, P. H. EMMETT, E. TELLER, J. Am. Chem. Soc. **60**, 309 (1938)

24) E. KOBERSTEIN, M. VOLL, Z. Physik. Chem. NF **71**, 275 (1970)

25) H. FRATZSCHER, farbe + lack **75**, 6 (1969)

26) M. ETTLINGER, H. FERCH, J. MATHIAS in Technical Bulletin Pigments No. 23, Degussa AG, Frankfurt/M., 5th edition (1986)

27) Technical Bulletin Pigments No. 27, Degussa AG, Frankfurt/M., 4th edition (1989)

28) Technical Bulletin Pigments No. 42, Degussa AG, Frankfurt/M. (1968)

29) H. FERCH in H. KITTEL: Lehrbuch der Lacke und Beschichtungen, Bd. 2, Verlag W. A. Colomb, Schwandorf (1974)

30) U. VEIEL, W. PAPENROTH, IX. FATIPEC Congress Book, Sect. 3, 19 (1968)

31) W. PAPENROTH, XI. FATIPEC Congress Book 595 (1972)

32) Technical Bulletin Pigments No. 31, Degussa AG, Frankfurt/M., 1st edition (1969), 2nd edition (1978)

33) H. FERCH, Seifen, Öle, Fette, Wachse **101**, 17 (1975) and **101**, 51 (1975)

34) Frankfurter Rundschau from 8. 10. 1966, p. 8; e.g. Süddeutsche Z. from 12. 10. 1966, p. 33; Abendpost-Nachtausgabe from 12. 10. 1966, p. 3; Hanauer Anzeiger from 8. 10. 1966, p. 19

35) J. Mathias, lecture held at Colloid Chemistry Symposium VCV-STI, Antwerpen, Sept. 1987

36) Technical Bulletin Pigments No. 68, Degussa AG, Frankfurt/M., 2nd edition (1985)

37) H. FERCH, 25th Meeting OCCA New Zealand, Rotorua, (1987), Congress Book.

38) Report FHWA-CA-TL-78-21, obtainable from US-National Technical Information Service, Springfield, VA 22 161

39) K. KLEIN, Seifen, Öle, Fette, Wachse **94**, 12 (1968)

40) K. M. OESTERLE, Deutsche Farben Z. **18**, 151 (1964)

41) Xerox Corp. US-PS 3.819.367 (1974)

42) Kodak DE-PS 2.821.565 A 1 (1978)

43) S. PRUSSIN, EU-PS 18.137 (1980)

44) Raychem Corp. EU-PS 67.009 (1981)

45) R. CASPARY, I. HESKE, J. Appl. Polym. Sci. **24**, 345 (1979)

46) H. FERCH, Pharm. Ind. **32**, 478 (1970)

47) O. ISAAC, H. FERCH, Dtsch. Apoth. Z. **116**, 1867 (1976)

48) H. FERCH, S. HABERSANG, Seifen, Öle, Fette, Wachse **108**, 487 (1982)

49) H. FERCH, H. GEROFKE, H. ITZEL, H. KLEBE, Sozialmed. Präventivmed. Arbeitsmed. **22**, 6 and 33 (1987)

50) P. I. REUZEL, CIVO Inst. TNO, NL-ZEIST, pers. Mitt. (1985)

51) Technical Bulletin Pigments No. 70 Degussa AG, Frankfurt/M. (1978)

52) H. FERCH, W. SCHMITZ, J. Chem. Techn. Biotechn. **30**, 699 (1980)

53) „Einfluß physikalischer Eigenschaften organischer Pigmente auf ihr anwendungstechnisches Verhalten". BASF AG, Ludwigshafen/Rh.

54) O. J. SCHMITZ, defazet **26**, 422 (1972)

55) G. R. JOPPIEN, farbe + lack **81**, 1102 (1975)

Brief List of Technical Terms

AEROSIL®

Trade mark used by Degussa AG, Frankfurt/M. for a → submicron synthetic silica which is produced according to the process of high-temperature hydrolysis.

Agglomerates

Are defined in DIN 53206 as loose clusters of → aggregates which may be broken down during dispersion.

Aggregates

Interwoven union of particles joined at the interfaces whose surface area is less than the sum of the surface areas of the → primary particles (DIN 53206). As a rule, aggregates are not broken down during the → dispersion of → pigments.

Anti-Settling Agent

Product designed to keep → pigments which are prone to settling in suspension in a coating system.

Application

Here → coating.

ASTM

Abbreviation for the **A**merican **S**ociety for **T**esting and **M**aterials.

Binder

is the non-volatile part of a coating material excluding → pigment and → filler, but including plasticizers, → surface driers and other non-volatile additives. The binder connects the individual pigment particles and the substrate thus combining to make up the finished coating (DIN 55945).

Bridged Silanol Groups

Here: shorter expression used for → silanol groups which have entered into a hydrogen bridge linkage.

BS

Abbreviation for **B**ritish **S**tandard.

Coating

Collective term for one or more connecting layers on a substrate, which are manufactured from coating materials.

Corrosion Protection

Measures taken in order to prevent corrosive damage.

Cryo Microtome Section

is made using a piece of equipment called a microtome. The sample is cooled and then cut with a diamond knife.

Defoamers

Name given to substances which are added to frothy liquid systems in order to reduce or inhibit the formation of foam.

Dispersion

is the uniform distribution of → pigments in → binders or powdered formulation components with the aid of dispersing equipment.

Drying Agents, better: **Surface Driers**

are organic, soluble metallic compounds which are added to oils in order to considerably shorten the drying time.

Dynometer

Combined measuring apparatus which can be used to determine the surface tension of liquid systems and the depth and consistency of sediment. Manufacturer: Byk Labotron Meßtechnik AG, D-8192 Geretsried.

Elastomers

are wide-meshed, cross-linked macromolecular substances with reversible expansibility.

Electron Microscope

Microscope using electron beams to depict very small objects.

Epoxy Resins

are reaction resins with an adequate number of epoxy groups for curing purposes.

Fibrosis

Increase in connective tissue.

Filler

is a substance which is practically insoluble in the applied medium. The refractive index of white fillers is generally < 1.7.
In certain media, a filler can also serve as a → pigment (DIN 55943).

Film Formation

is the transition of an applied coating material from liquid to solid state. The film formation results from drying or curing. Both processes can take place simultaneously or one after another (DIN 55945).

Gas Black

Carbon black whose manufacture is characterized by the evaporation by heating of the hydrocarbons serving as raw materials, followed by combustion of the gas with the aid of a burnable carrier gas.

Gassing

Term used to describe the development of hydrogen occurring in zinc dust paints, which is caused by the reaction of water with the zinc dust.

General Dust Limit Value

is the maximum permissible dust concentration for "non-hazardous substances" at the place of work, valid in the Federal Republic of Germany.

Gloss

is the sensory impression for the more or less directed reflection of beams of light on a surface.

Hammer Finish Coating

is one of the special effect coatings, which can be used to achieve intentional, visible and uniformly-distributed irregularities on the surface of a coating film.

Highly Dispersed

Finely divided.

Hydrophilic

Having an affinity to water; wettable by water.

Hydrophobic

Water-repellent; not wettable by water.

Ignition Loss

is the term given in DIN 55921 for the difference in weight between the dry weight and the weight of the ignition residue. Values given as a percentage.

Infra-Red Spectroscopy

Modern optical process in which the infrared range of absorption spectra of mainly organic compounds in solid, liquid or gaseous form are used for qualitative and quantitative analysis and for determining the structure.

in situ

means the formation of a substance at the time when it is required.

JIS

Abbreviation for
Japanese **I**ndustrial **S**tandard.

LD 50

Lethal **D**ose = dose leading to death.
In experiments on animals, this is usually fixed at LD 50, which is the dose that leads to the death of 50% of the animals within a certain period of time.

Levelling

The term denotes the ability of a coating that is still in the liquid state, to self-regulate the irregularities which occurred during application (DIN 55945).

MAK Value

(German: **M**aximale **A**rbeitsplatz-**K**onzentration) is the highest permissible concentration in the air of a material being used at the place of work which, according to the present level of knowledge, must not be exceeded even as a result of repeated or long-term effects. → General Dust Limit Value.

Mill Base

Concentrated mixture of → pigments, → fillers (and dispersion additives) in a → binder: solvent ratio chosen to suit the respective method of dispersion.

Monomolecular

Monomolecular layers are made up of a single molecule thickness of the substance concerned; they play a significant role in corrosion and in many interfacial phenomena.

Offset Printing Inks

or flat-bed printing inks, are paste-like systems which dry as a result of oxidative and/or physical processes. The water stability of these systems is particularly good as a result of the printing process, which is based on an interaction between the water and the ink.

Orange Peel Effects

is a term used in ISO 4618 to describe irregularities in the surface of a coating film which give the latter the crinkled appearance of orange peel.

Patch Test

Tolerance test carried out by observing the local effect of substances on the conjunctival sac of New Zealand White rabbits.

Pigment

is defined in DIN 55945, BS 2015 and ASTM D 16 as an organic or inorganic colourant which can be chromatic or achromatic and is insoluble in solvents.

Powder Coatings

are paints in powder form which produce a coating on a substrate following application and melting.

Precipitated Silicas

are virtually non-porous synthetic silicas which are formed during the conversion of water glass and sulphuric acid.

Primary Particles

according to DIN 53206, are the smallest particles which make up powdered solids. Recognizable as individual particles by means of electron microscopy.

Priming Coat (Primer)

The primer is made up of coating layers designed to connect the substrate and the coating layers applied to the priming coat. It may also fulfil other special functions, e.g. → corrosion protection.

Residual Surface Area

Mathematical quantity which is determined as the difference between the → specific surface of the basic hydrophilic silica and that of the hydrophobic (= aftertreated) silica.

Scanning Electron Microscope

Analytical appliance which scans an object line for line with an electron beam, resulting in impulses which are converted into scanner dots to give the finished picture.

Sediment

Matter that settles to the bottom of a liquid system if not held in suspension.

SEM

Scanning **E**lectron **M**icroscopy.

Silanol Group Density

Density of the → silanol groups situated on the silica surface.

Silanol Groups

≡ Si-OH groups situated on the silica surface.

Silicosis

Progressive pneumoconiosis as a result of inhaling dust containing quartz: occupational disease.

SIPERNAT®

Registered trade mark used by Degussa AG, Frankfurt/Main for → precipitated silicas and silicates.

Specific Surface

is the surface area of a solid, relative to its mass, given in m^2/g. Generally determined according to the BET method (DIN 66131).

Substrate

is an insoluble, generally achromatic substance which is involved in the composition of certain coloured coatings (DIN 55945).

Suspending Agent

→ Anti-Settling Agent.

TEM

Transmission **E**lectron **M**icroscopy.

Thermogravimetric Analysis

Term used to describe a thermoanalytical process which makes use of the changes in weight that occur as a result of the conversion of substances caused by heating.

Thixotropic Index

Viscosity quotient established by using the measuring equipment at two different shear rates and rotational speeds.
If possible, the rotational speeds should be in a ratio of 1:10.

Thixotropy

Time-dependent gel-sol-gel conversion which is reversible under isothermal conditions.

Toner

Pigmented resin powder. The particle size is approximately 10–20 µm. Toner is the colouring substance used in photocopying processes.

Toxicology

The science of harmful, in some cases fatal, effects of substances in excessive amounts.

Triboelectric Effect

occurs when different materials are brought into contact with one another (non-conductors e.g. polymer glass). Friction causes electrons to be removed from or conveyed to the surface.

Physico-Chemical Data of Hydrophobic AEROSIL

		AEROSIL					
		R 202	R 805	R 812	R 812 S	R 972	R 974
Appearance		– fluffy white powder –					
BET surface area 1)	m^2/g	100 ± 20	150 ± 25	260 ± 30	220 ± 25	110 ± 20	170 ± 20
Average primary particle size	nm	14	12	7	7	16	12
Tapped density 2) standard product compacted product ("V")	 g/l g/l	 approx. 50 approx. 90	 approx. 50 approx. 90	 approx. 50 approx. 80	 approx. 50 –	 approx. 50 approx. 90	 approx. 50 approx. 90
Moisture 3) (2 hours at 105 °C) on leaving plant site	%	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Ignition loss 4) 8) (2 hours at 1000 °C)	%	4–6 11)	5–7 12)	1.0–2.5 13)	1.5–3.0 14)	< 2 15)	< 2 16)
pH value 5) (4 % in water : ethanol 1 : 3)		4–6	3.5–5.5	5.5–7.5	5.5–7.5	3.6–4.3	3.4–4.2
SiO_2 7)	%	> 99.8	>99.8	>99.8	>99.8	>99.8	>99.8
Al_2O_3 7)	%	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Fe_2O_3 7)	%	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
TiO_2 7)	%	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
HCl 7) 9)	%	<0.025	<0.025	<0.025	<0.025	<0.05	<0.1
Sieve residue 6) (by Mocker, 45 µm)	%						

1) acc. to DIN 66131
2) acc. to DIN ISO 787/XI oder JIS K 5101/18 (not sieved)
3) acc. to DIN ISO 787/II, ASTM D 280, JIS K 5101/21
4) acc. to DIN 55921, ASTM D 1208, JIS K 5101/23
5) acc. to DIN ISO 787/IX, ASTM D 1208, JIS K 5101/24
6) acc. to DIN ISO 787/XVIII, JIS K 5101/20
The sieve residue acc. to Mocker cannot be determined with water in the case of hydrophobic AEROSIL grades
7) related to material ignited for 2 hours at 1000 °C
8) related to material dried for 2 hours at 105 °C
9) HCl content is a part of the ignition loss
10) contains approx. 1 % of chemically bound carbon
11) contains approx. 3.5–5.0 % of chemically bound carbon
12) contains approx. 4.5–6.5 % of chemically bound carbon
13) contains approx. 2.0–3.0 % of chemically bound carbon
14) contains approx. 3.0–4.0 % of chemically bound carbon
15) contains approx. 0.6–1.2 % of chemically bound carbon
16) contains approx. 0.7–1.3 % of chemically bound carbon

Additional Degussa Products

Active oxygen compounds
Adhesives
Barium compounds
Blue pigments
Carbon blacks and pigment black preparations
Catalysts
Ceramic colours
Coloured pigments
Copper compounds
Flatting agents
Highly dispersed metallic oxides
Hydrocyanic acid and its derivatives
Lead compounds
Methacrylic acid and its derivatives
Powder cellulose
Precipitated silicas
Selenium compounds
Semi-finished plastic products
Silanes
Silica dispersions
Silicates
Strontium compounds
Titanium compounds
Toner resins
Zeolites
Zinc compounds

The Industrial and Fine Chemical Products Division of Degussa AG supplies the Coatings Industry with:

DEGALAN® LP
Thermoplastic methacrylic resin in solid form used in the manufacture of protective coatings for concrete, road marking paint and marine paint; heat-seal coatings for aluminium foils, imitation leather top coatings, etc.

DEGADUR®
Cold curing, low-viscosity methacrylic-resin for floor and wall coatings.

DEGAROUTE®
Cold curing, low-viscosity methacrylic resin used in the manufacture of 2-component cold plastics for lane markings on city streets and country roads, and for coloured markings on cycle paths.

DEGACURE®
Cyclo-aliphatic epoxides and Photoinitiator KJ 85 for use in cationic radiation curing.

The product range of Degussa AG's Inorganic Chemical Products Division includes the following registered trademarks:

ACETOCAUSTIN
AEROSIL
CALSIL
COFILL
CORASOL
CORAX
COUPSIL
DELOXAN
DERUSSOL
DUREX

DUROSIL
EFWEKO
ELCEMA
EXTRUSIL
LEPANDIN
MANOX
PASILEX
PRINTEX
PROTECTOSIL
SATESSA

SIDENT
SILTEG
SIMACOLL
SIPERNAT
TACK
TRANSPAFILL
ULTRASIL
VOSSEN-Blau
WESSALITH
WESSALON

The information and statements contained herein are provided free of charge.
They are believed to be accurate at the time of publication, but Degussa makes no warranty with respect thereto, including but not limited to any results to be obtained or the infringement of any proprietary rights. Use or application of such information or statements is at user's sole discretion, without any liability on the part of Degussa. Nothing herein shall be construed as a license of or recommendation for use which infringes upon any proprietary rights. All sales are subject to Degussa's General Conditions of Sale and Delivery.

Degussa AG
Geschäftsbereich Anorganische Chemieprodukte
Postfach 110533
D-6000 Frankfurt 11
Federal Republic of Germany
Phone (069) 218-01
Telex 41222-0 dg d
Telefax (069) 2183218

New postal code per 01.07.93:
D-60287 Frankfurt am Main

Degussa

A part of the central research, product development and technical service laboratories maintained by Degussa in the Degussa Industrial Complex at Wolfgang, Hanau-Wolfgang. Released by the president of government in Darmstadt by No. 1098/86.

Pig. 18-12-105-593 DD Printed in Germany 4th edition: May 1993