

## The Stability of Silica Hydrosols Under the Influence of Polymer Adsorption\*

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The stability of standardized, well dispersed silica (Aerosil) hydrosols at different pH has been studied using a self-constructed laser photosedimentometer. Ultrasonication was proved most suitable for providing reproducible standardized hydrosols, which were characterized by determining the viscosity/concentration dependence in a cylinder viscosimeter, the sedimentation coefficient in an analytical ultracentrifuge, the partial specific volume in an oscillating U-tube of a high precision density meter, the translational diffusion coefficient with a photon correlation spectrometer and the dimension and shape of the silica particles by transmission electron microscopy.

The Aerosil hydrosols can be reproducibly flocculated with polyethyleneglycols of molar mass 6000 and 40 000, even in the absence of electrolyte at high pH, when the sol concentration is sufficiently high. Reproducibility necessitates standardized mixing procedures of sol and polymer.

The laser-photosedimentometer provides suitable parameters for the characterization of the turbidity- and sedimentation behaviour of the flocculated sols.

The effects of different mixing procedures have been tested and the influence of titration and mixing time, intensity and time of stirring can be analyzed quantitatively as well, as the relationships of the characterizing parameters on polymer coverage, molecular weight and silica concentration.

From these dependences and by using additional rheological measurements it was possible to identify the classical model of polymer bridging as the most likely mechanism for the destabilization.

### INTRODUCTION

The practical application of polymer adsorption for controlling the stability of colloidal dispersions is becoming increasingly important. In the presence of polymers colloidal dispersions exhibit three basic phenomena: charge stabilization, steric stabilization, or flocculation.<sup>1</sup> Flocculation may

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occur even when a polymer is added to an intrinsically stable (charge-stabilized) dispersion. This phenomenon is usually described as bridging flocculation.

The identification of the exact mechanism governing the adsorption and flocculation by polymers in the, well characterized, model system Silica-Hydrosol/Polyethyleneglycol (PEG) was the purpose of the investigation described. Flame hydrolyzed and precipitated silica have been used in our laboratories for many years as adsorbents to elucidate the conformation of adsorbed macromolecules at the interface.<sup>2,3</sup> Different dispersion methods have been attempted and ultrasonication was shown to be the most suitable for producing reproducible, standardized and stable silica hydrosols.<sup>4,5</sup>

#### PREPARATION AND PROPERTIES OF THE SILICA HYDROSOLS

Adequate amounts of silica powder were weighed into cylindrical dispersion vessels and doubly distilled water was added. The powder was then dispersed, using a shaking machine, which operates by three-dimensional staggering movements or an ultrasonicator. In order to obtain reproducible sols for reliable stability studies, the efficiency of the different dispersion methods was investigated using rheological measurements.

Immediately after dispersion, 20 cm<sup>3</sup> of the sol was transferred onto a double slit concentric cylinder viscosimeter (Contraves AG, Rheomat 30 with MS-O double slit system).

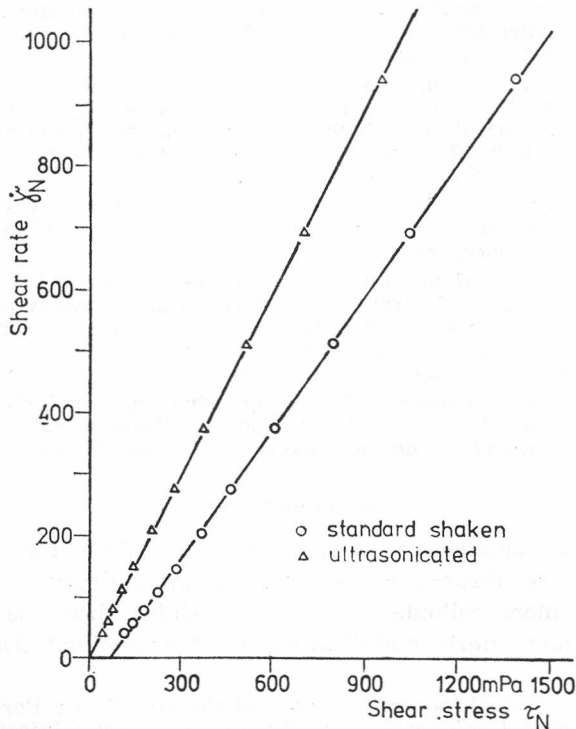


Figure 1. Shear rate  $\dot{\gamma}_N$  versus shear stress  $\tau_N$ ; Aerosil 200, H<sub>2</sub>O,  $c_s = 0,01 \text{ g cm}^{-3}$ , pH 4.7, 25 °C

After dispersion by 6000 shaking impulses (30 min. shaking time), the flow behavior of an Aerosil-hydrosol at pH 4.7 with a disperse phase concentration,  $c_s$ , of  $0.01 \text{ g cm}^{-3}$  demonstrates a Bingham flow with a yield value (Figure 1),

$$\dot{\gamma}_B = \frac{1}{1.41} (\tau_B - 70.6) \tag{1}$$

where  $\dot{\gamma}_B$  is the rate in  $\text{sec}^{-1}$  ( $43.7 \leq \dot{\gamma}_B \leq 941 \text{ sec}^{-1}$ ), and  $\tau_B$  is the shear stress in Pa.

After dispersion by ultrasonication the same sol shows genuine Newtonian flow behavior with a viscosity,  $\eta_{N\infty}$ , of  $1.01 \text{ m Pa sec}$ , Figure 1. With time of ultrasonication causes the sols to steadily move from Bingham to Newtonian flow behavior for  $c_s \leq 0.03 \text{ g cm}^{-3}$ .

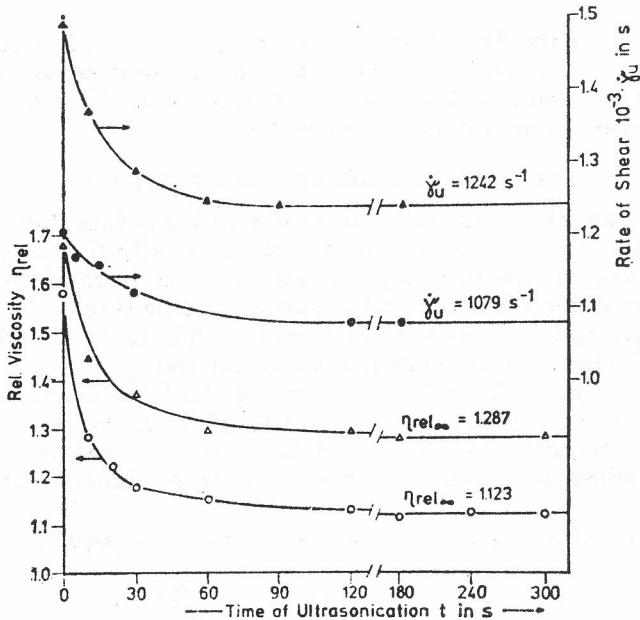


Figure 2. Dependence of the relative viscosity,  $\eta_{rel}$ , (O,  $\Delta$ ) and of the critical rate of shear,  $\dot{\gamma}_c$ , for the change from laminar to turbulent streaming ( $\bullet$ ,  $\blacktriangle$ ) on the time,  $t$ , of ultrasonication (20 Hz, 150 W); Aerosil 200,  $\text{H}_2\text{O}$ ;  $25^\circ\text{C}$ ,  $c_s = 0.01 \text{ g cm}^{-3}$  (O,  $\bullet$ );  $c_s = 0.02 \text{ g cm}^{-3}$  ( $\Delta$ ,  $\blacktriangle$ )

Figure 2 illustrates this transition with the dependence of the relative viscosity,  $\eta_{rel}$ , on the time,  $t$ , of ultrasonication. The viscosity of the sol decreases with increasing ultrasonication time for both sol concentrations used. For concentrations higher than  $c_s > 0.03 \text{ g cm}^{-3}$  the sols are characterized by Bingham behavior with a weakly marked yield value even after long ultrasonication.

Applying steadily increasing shear rates results in a sudden change from laminar to turbulent streaming conditions. In this case the rheogram is characterized by a marked break point indicating the sudden increase of energy dissipation. The rate of shear,  $\dot{\gamma}_c$ , at this break point in the rheogram is

also a sensitive measure of the degree of dispersion. The dependence of  $\gamma_c$  on the time,  $t$ , of ultrasonication follows the same trend as the relative viscosity shown in Figure 2.

By applying the principles of rheological behavior of colloidal dispersions given by Mewis and Spaull<sup>6</sup> for the interpretation of the results shown in Figure 2, it becomes clear that ultrasonication removes the agglomeration and the resulting sols have small aggregates with a limited size. However the rheological behavior of the sols prepared by the standardized shaking method, indicates that this technique only breaks the large agglomerates into smaller ones. The dispersion of Aerosil by ultrasonication and the rheological characterization of the resulting sols thus provides a suitable means of preparing reproducible and stable Aerosil hydrosols. Such sols with a viscosity,  $\eta_{N\infty}$ , were used after 12 hrs from the end of the ultrasonication process. These dispersions will be referred to as »standardized ultrasonicated« (us-standard).

In contrast to the flow behavior of the pyrogenic silica Aerosil in the same concentration region the shaken and ultrasonicated dispersions of the precipitated silica show a Newtonian flow behavior and the viscosity is only slightly increased in comparison with water.

#### CHARACTERIZATION OF SILICA PARTICLES

The sols were characterized by determining the sedimentation coefficients in an analytical ultracentrifuge, the translational diffusion coefficients with a photon correlation spectrometer, the viscosity concentration relationship in a concentric cylinder viscosimeter, the partial specific volume in an oscillating U-tube with a high precision density meter and, lastly the dimensions of the silica particles by transmission electron microscopy.

The hydrodynamically effective mass and the hydrodynamically effective volume of moving aggregates are not identical with the mass,  $m_2$ , and the volume,  $V_2$ , of the dry powder; in fact they are increased by the mass,  $m_1^*$ , and corresponding the volume of the comigrating immobilizing dispersion medium.

The degree of hydration  $\Gamma_h = m_1^*/m_2$  is given by equ. 1:

$$\Gamma_h = c_v (1/c_m + \bar{v}_2/v_1 - 1) - \bar{v}_2/v_1 \quad (1)$$

where  $c_m$  is the mass fraction of dry silica,  $v_1$ ,  $\bar{v}_2$  are the specific volumes of the medium and of the Silica. The volume fraction,  $c_v$ , of the hydrated particles in the hydrodynamic flow can be obtained from the viscosity with the Mooney equation, which in the case of very dilute systems corresponds to the Einstein law for spherical particles flowing independently in the dispersion.

$$\eta_{rel} = \exp \frac{2.5 c_v}{1 - k \cdot c_v} \quad (2)$$

Satisfactorily this Mooney equation can be used for the description of the measured viscosity concentration dependence for the ultrasonicated Aerosil-hydrosols near the isoelectric point with  $k = 2.02$ . With  $\Gamma_h$  the volume of the hydrated viscosity equivalent spheres can be calculated.

By using a Photon Correlation Spectrometer it is possible to measure the time-autocorrelation function of the laser-light scattered by the dispersed

particles. The first order time correlation function of the electrical field of ideal monodisperse spherical particles which have no interaction is an exponential function (eq. 3) of the correlation time  $\tau$  determined by the translational diffusion coefficient,  $D$ , and the amount of the scattering vector,  $\kappa$ .

$$g^{(1)}(\tau) = e^{-D\kappa^2\tau}$$

with:  $\Gamma = D\kappa^2 = \text{Line Width}$

$$\kappa = \frac{4\pi n}{\lambda_0} \sin \frac{\Theta}{2} = |\text{scattering vector}| \quad (3)$$

For polydisperse samples the portions of all particle sizes have to be considered in a summation of all correlation functions.

$$g^{(1)}(\tau) = \Sigma B(\Gamma_i) e^{-\Gamma_i\tau} \quad (4)$$

The measured correlation function of the intensity fluctuations of the scattered light is then given by  $g_K^{(2)}(\tau)$  with the adjusting parameter,  $\gamma$ .

$$g_K^{(2)}(\tau) = 1 + \gamma |g^1(\tau)|^2 \quad (5)$$

$$\ln \sqrt{g_K^{(2)}(\tau) - 1} = \ln \gamma - \bar{\Gamma} \tau + \frac{\mu_2}{2} \tau^2 - \frac{\mu_3}{3!} \tau^3 \quad (6)$$

with

$$\bar{\Gamma} = \Sigma B(\Gamma_i) \Gamma_i \quad (7)$$

$$D \equiv D_z = \bar{\Gamma} / \kappa^2 \quad (8)$$

$$\mu_2 / \bar{\Gamma}^2 = \frac{1}{\bar{\Gamma}^2} \Sigma (\Gamma_i - \bar{\Gamma})^2 B(\Gamma_i) \quad (9)$$

By expanding the logarithmic expression (6) into a Taylor series according the moment-method one gets the decay constant,  $\bar{\Gamma}$ , and the second moment,  $\mu_2$ , parameters from where we can deduce the z-average of the diffusion coefficient and the normalized variance of the diffusion coefficients around the mean value.

From the diffusion coefficient,  $D$ , together with the sedimentation coefficient,  $s$ , from ultracentrifuge measurements one can calculate the particle weight,  $M_{S,D}$ , using the Svedberg equation (10) as is well known.

$$M_{S,D} = \frac{RT}{1 - v_2 \rho_{LM}} \cdot s/D \quad (10)$$

From the mass,  $M_{S,D}$ , one can calculate the diameter,  $d_o$ , of the equivalent nonhydrated sphere and using relation (11) and (12) the corresponding friction coefficient,  $f_o$ , and diffusion coefficient,  $D_o$ .

$$f_o = 3\pi\eta_1 d_o \quad (11)$$

$$D_o = \frac{RT}{f_o} \quad (12)$$

Relating the measured diffusion coefficient,  $D$ , to the diffusion coefficient of the nonhydrated spherical particle,  $D_o$ , one can separate the relative value,  $f/f_o$ , in two contributions resulting from (1) the deviation from the sphere shape  $(f/f_o)_s$  and (2) from the increase in volume by the hydration of the particle, the immobilized water in the hydrodynamic volume  $(f/f_o)_h$ .

$$\frac{D_o}{D} = f/f_o = (f/f_o)_s \cdot (f/f_o)_h \quad (13)$$

Deviding the calculated  $D_o$  by the measured  $D$  produces a frictional ratio:

$$D_o/D = f/f_o = 2.96$$

The hydrodynamic fraction of the friction ratio,  $(f/f_o)_h$ , is represented by the ratio of  $D_o$  to the diffusion coefficient  $D_{oh}$  of an equivalent hydrated sphere

$$(f/f_o)_h = D_o/D_{oh} = 1 + \left( \frac{\Gamma_h}{v_2 \varrho_1} \right)^{1/3} \quad (14)$$

Given measured values of  $\Gamma_h$ ,  $\bar{v}_2$ ,  $\varrho_1$  a hydrodynamic ratio  $(f/f_o)_h = 2.1$  and a steric ratio  $(f/f_o)_s = 1.41$  results.

The steric fraction,  $(f/f_o)_s$ , represents the ratio between the diffusion coefficient,  $D_{oh}$ , of the hypothetical uniform hydrated sphere and that of the real hydrodynamic equivalent particle,  $D$ .  $(f/f_o)_s = \frac{D_{oh}}{D}$  is calculated directly or from the equ.  $(f/f_o) = (f/f_o)_s (f/f_o)_h$  (13).

The measured and deviated characterizing parameters are reported in Table I. A comparison of these parameters with geometric values from computer simulation of the kinetics of the aggregation according to the improved Smoluchowski equation shows remarkable agreement.<sup>4</sup>

TABLE I  
Characterization of Ultrasonicated Aerosil 200-Hydrosol: Measured and Derived Values

Isoelectric Point  pH = 2	Viscosity (Mooney-equation) $\eta_{rel} = \exp\left(\frac{2.5 c_V}{1 - 2.03 c_V}\right)$	Sedimentation  $s = 1.74 \cdot 10^{-10} \text{ s}$	Partial Specific Volume  $\bar{v}_2 = 0.4561 \text{ cm}^3 \text{ g}^{-1}$
Translational Diffusion Coefficient  $\bar{D} = 1.99 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$	Normalized Variance of Distribution around $D$  0.18	Diameter of primary Particles from EM  $\bar{d} = 12 \text{ nm}$	BET-specific Surface Area  $A = 211 \pm 20 \text{ m}^2 \text{ g}^{-1}$
Mass of the nonhydrated Particle  $m_2 = 6.6 \cdot 10^{-19} \text{ kg}$	Average number of primary Particles in one aggregate  $P = 333$	Degree of Hydration  $\Gamma_h = 3.75$	Hydrodynamic Volume  $V_h = 2.78 \cdot 10^{-21} \text{ m}^3$
Diffusion equivalent Particle Diameter  $d_D = 246 \text{ nm}$	Aggregate Density  $\varrho_A = 1.13 \text{ g cm}^{-3}$		

## ADSORPTION AND FLOCCULATION

The standardized, well-characterized silica hydrosols, were used for all adsorption and flocculation measurements; the dispersion medium was doubly distilled water, which was adjusted to the required pH values using HCl or KOH. The adsorbates (provided by Hoechst AG) were polyethylene glycols with molar mass  $M_w = 6.000$ ,  $M_w/M_n = 1.11$ , and  $M_w = 40.000$ ,  $M_w/M_n = 1.5$ .

For a direct comparison of the results from adsorption and stability measurements, the experimental conditions f.e. the mixing procedure were kept constant in both investigation.

## ADSORPTION ISOTHERMS

The amount of polymer adsorbed in gram per gram silica (adsorbance,  $A$ ) can be calculated from the mass balance, according to equation (15), using the measured supernatant concentration,  $c_L$ , of nonadsorbed polymer, the known initial concentration of polymer,  $c_E$ , and the sol concentration,  $c_s$ ,

$$A = (1/c_s) (c_E - c_L) \quad (15)$$

With the known specific surface areas of the silicas one can convert the  $A$  values in g/g to  $A$  values in g/m<sup>2</sup> or monomer mol/cm<sup>2</sup>. For the determination of the remaining concentration of nonadsorbed polymer, 20 cm<sup>3</sup> of the sol were removed after standing for half an hour and centrifuged for 10 min. at 200 p. m.. The concentration of the polymer in the supernatant was determined using a turbidity method.<sup>7</sup>

For both silica-types the adsorption isotherms (in Figure 3) for polyethylene glycol of molar mass 6000 and 40.000 (sol concentration  $c_s = 0.01$  g cm<sup>-3</sup>) are of the high affinity type; i. e. up to certain adsorption values practical no free polymer can be detected in solution. Then plateau values are reached, above which nearly all the polymer added remains in solution. The plateau values  $A_\infty$  obtained after a contact time of 24 hr were approximately 10% higher than those obtained after 1 hr. Thus, most of the polymer adsorption takes place within the first hour of contact. For a direct comparison of adsorption and flocculation results the adsorption isotherms were always determined

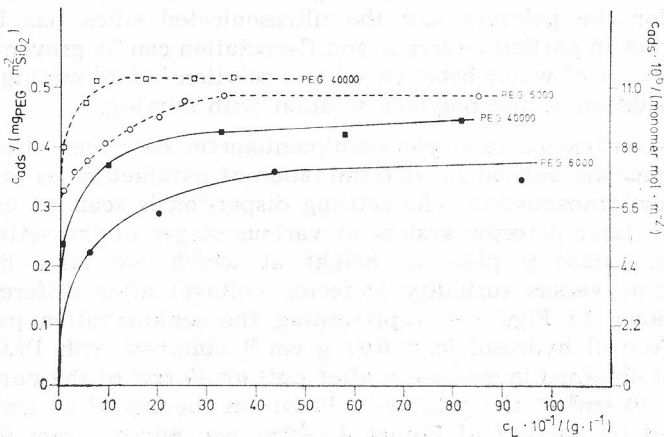


Figure 3. Adsorption isotherms of PEG 6000 (○, ●) and PEG 40000 (□, ■), pyrogenic silica Aerosil (○, □), precipitated silica (●, ■), water, 25 °C, pH 4.7.

after 1 hr of contact. The degree of coverage,  $\Theta$ , is defined as the ratio of adsorbance  $A$  to the adsorbance at the plateau,  $A_\infty$ .

$$\Theta = A/A_\infty. \quad (16)$$

The plateau values, and the affinity between PEG and the silica surface, increase with increase of molar mass of the polymer.

#### QUANTITATIVE DETERMINATION OF COLLOIDAL STABILITY

The stability of the silica suspensions in water, with and without polymer addition has been studied by sedimentation and rheology measurements as a function of pH and ionic strength. If polymer adsorption in an intrinsically stable colloidal dispersion causes flocculation, then the mobility of a part of the particles is throughly restricted as a result of interparticle interactions, causing them to settle together as floccules. Flocculation is strongly reflected in the sedimentation behavior and the optical properties of the dispersion. It leads to hindered sedimentation and multiple scattering, both of which prevent the application of common photometric methods, originally developed for particle size analysis in diluted suspensions. The strongly reduced transmission can no longer be described by the Beer-Lambert law. The sedimentation is characterized by a marked boundary layer and shows a distinct deviation from Stokes' law. However, the systematic determination of this hindered sedimentation behavior provides a method of characterization of colloidal stability and the structure of flocculated dispersions. For this purpose the following parameters need to be established.<sup>8</sup>

- a) The volume and specific properties of the settled phase in equilibrium;
- b) The settling velocity of the boundary layer;
- c) The turbidity/height-gradient along the total settling column, as a function of the settling time; and
- d) The turbidity profile in the settling boundary layer.

The Aerosils can be reproducibly flocculated with polyethyleneglycols of molar mass  $M_w$  6000 and 40000 even in the absence of electrolyte providing that the sol concentration is sufficiently large. The influence of different mixing procedures for the polymer and the ultrasonicated silica has been tested. Inhomogeneities in particle coverage and flocculation can be prevented by using a separating layer of water between sol and solution before mixing or by slow, continuous addition of the polymer solution with stirring.

The self-constructed laser-photosedimentometer described elsewhere<sup>9</sup> provide a simultaneous method for determination of parameters (a) to (d), even in systems of low transmission. The settling dispersion is scanned over its total height with a laser detector system at various stages of the settling process. Characteristic turbidity plots of height at which the laser beam passes (cuvette height) versus turbidity (detector voltage) after different standing times are shown in Figure 4, representing the sedimentation patterns of a flocculated Aerosil hydrosol ( $c_s = 0.01 \text{ g cm}^{-3}$ ) obtained with PEG 6000. The turbidity plot obtained immediately after putting 40 cm<sup>3</sup> of the pure dispersion medium and 10 cm<sup>3</sup> of the polymer solution on the top of 40 cm<sup>3</sup> of the sol, is represented by curve I of Figure 4. After one minute from finishing the standardized mixing procedure, the polymer coated sols are characterized by



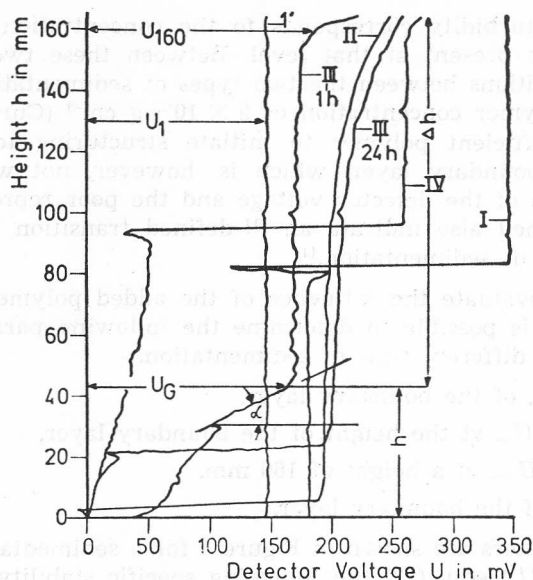


Figure 4. Sedimentation behavior of polymer treated Aerosil hydrosols. Aerosil 200; US-standard;  $C_s = 0.01 \text{ g cm}^{-3}$ ;  $T = 25.0 \text{ }^\circ\text{C}$ ;  $\text{pH } 4.7$ ;  $\lambda_0 = 632.8 \text{ nm}$ ; standard mixed.

Curve I: before mixing

Curve II:  $C_E = 6 \cdot 10^{-5} \text{ g cm}^{-3}$  PEG 6000. Example for »granular« flocculation

Curve III:  $C_E = 8 \cdot 10^{-5} \text{ g cm}^{-3}$  PEG 6000. Example for transition between »granular« and »structured« flocculation

Curve IV:  $C_E = 1.6 \cdot 10^{-4} \text{ g cm}^{-3}$  PEG 6000. Example for »structured« flocculation (boundary layer sedimentation)

the turbidity plot, marked  $I'$  in Figure 4. As a characteristic parameter the relative transmission,  $T(I')$ , is defined by

$$T(I') = U_1/U_0 \quad (17)$$

where  $U_1$  is the voltage reading at  $t = 1 \text{ min}$  and  $U_0$  that of the dispersion medium. The advancing sedimentation is followed from the turbidity plots in dependence of time. In general, there are two extreme types of sedimentation behavior: (a) free sedimentation according to Stokes' law and, (b) sedimentation of the totally structured systems. Hindered sedimentation lies between these two extreme cases. In extremely flocculated dispersions i. e. case (b) the particles settle together in a continuous network with the same velocity, independent of their size. The supernatant is practically free of particles and the low velocity of the settling, sharp boundary layer is determined by the upward streaming of the displaced dispersion medium through the flocculated structure, which acts like a solid bed.<sup>10</sup> The voluminous settling phase which, at any instant, has a constant composition along its height, possesses loose, structure that can be easily redispersed.<sup>8</sup>

On the other hand, the turbidity plots of the polymer free Aerosil hydrosols and those containing low polymer concentrations that are not sufficient to cause structured flocculation merely show a combination of particles in the form of granular, single floccules which settle, according to their different sizes, to a only closely packed, compact sediment. The supernatant liquid shows slight clearing with a continuous variation in turbidity over its height. At

each height the turbidity corresponds to the concentration and size of the granular flocs present at that level. Between these two extremes there are gradual transitions between the two types of sedimentation behavior. For example at a polymer concentration of  $8 \times 10^{-5} \text{ g cm}^{-3}$  (Curve III, Figure 8). There is just sufficient polymer to initiate structuring together with the formation of a boundary layer, which is, however, not well defined. The larger oscillations of the detector voltage and the poor reproducibility of the parameters obtained also indicate an ill-defined transition between the two extreme patterns of sedimentation.<sup>11</sup>

In order to evaluate the influence of the added polymer on the type of sedimentation, it is possible to determine the following parameters from the turbidity plots at different time of sedimentation.

- a) the position,  $h$ , of the boundary layer,
- b) the turbidity,  $U_G$ , at the height of the boundary layer,
- c) the turbidity,  $U_{160}$ , at a height of 160 mm,
- d) the angle,  $\alpha$ , of the boundary layer.

These parameters are shown in Figure 4 for a sedimentation time of 1 hr. In addition to  $T(I')$  equ. (17) the following specific stability criteria, derived from  $h$  and  $U_{160}$ , are used: The relative height,  $h_{rel}$ , of the boundary layer after the sedimentation times  $t = 6 \text{ hr}$  and  $t = 24 \text{ hr}$  referred to the initial height,  $h + \Delta h$ , at  $t = 0$ :

$$h_{rel} = h/(h + \Delta h). \quad (18)$$

The relative absorbance,  $E_{rel}$ , in the clear supernatant liquid at a height of 160 mm after a sedimentation period of 24 hr:

$$E_{rel} = E/E_o = \frac{\log(U_o/U_{160})}{\log(U_o/U_b)} \quad (19)$$

where  $U_b$  corresponds to the uncoated blanc sol.

As already mentioned, the transition from »granular« to »structured« flocculation behavior with increasing polymer concentration is reflected in the dependence of the relative boundary layer height on the time of sedimentation. From the increase of  $h_{rel}$  with time (Figure 5) one can see that at low polymer concentration ( $c_E = 6 \times 10^{-5} \text{ g cm}^{-3}$ ) »granular« flocculation occurs (see also curve II, Figure 4). With increasing the polymer concentration ( $6 \times 10^{-5} < c_E < 1.4 \times 10^{-4} \text{ g cm}^{-3}$ ) a transition between »granular« and »structured« sedimentation takes place, with the development of a hazy boundary layer (see also curve III, Figure 4). A further small increase in polymer concentration ( $c_E = 1.6 \times 10^{-4} \text{ g cm}^{-3}$ ) results in an abrupt change to »structured« flocculation with a sharp boundary layer, which settles very slowly (see also curve IV, Figure 4).

The stability criteria  $T(I')$ ,  $h_{rel}$  (6 hr, 24 hr) and  $E_{rel}$  are very sensitive to the specific changes in the sedimentation behavior due to flocculation. According to the flocculation models reported<sup>1</sup> one would expect that variations in sol concentration and in the molar mass of the adsorbed polymer to have

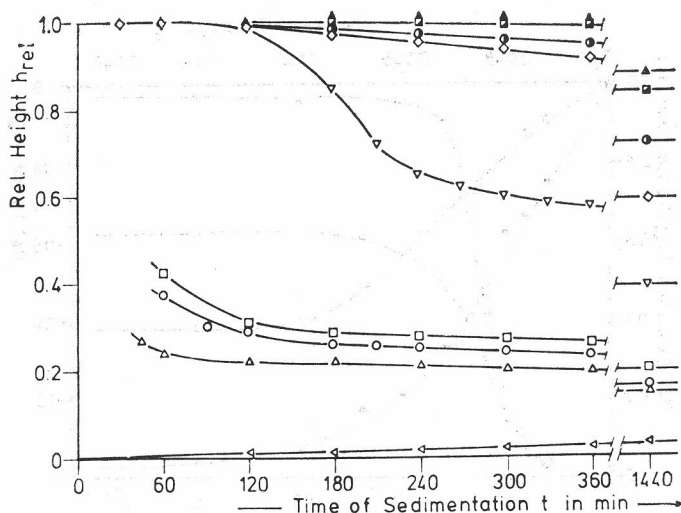


Figure 5. Dependence of the relative height of boundary layer  $h_{rel}$  on the sedimentation time,  $t$ ; Aerosil 200; US standard;  $c_s = 0.01 \text{ g cm}^{-3}$ ;  $T = 25^\circ\text{C}$ ;  $\text{pH} = 4.7$ ,  $\lambda_0 = 632.8 \text{ nm}$ ; MS-standard;  $\triangleleft$ ,  $\triangle$ ,  $\triangle$ ,  $\circ$ ,  $\square$ ,  $\nabla$ ,  $\diamond$ ,  $\bullet$ ,  $\blacksquare$ ,  $\blacktriangle$   $25 \cdot 10^{-5} \text{ g cm}^{-3}$  PEG 6000.

specific effects on the sol stability. The system was, therefore, investigated at sol concentrations,  $c_s$ , of  $0.01$  and  $0.0075 \text{ g cm}^{-3}$  using PEG of molar masses 6000 and 40.000.

The influence of the molar mass of the added PEG on the extent of flocculation of a sol of concentrations  $c_s = 0.01 \text{ g cm}^{-3}$ , is shown from a comparison of the parameters  $h_{rel}$  (6 hr, 24 hr),  $E_{rel}$ , and  $T(I')$ . These parameters are plotted as a function of polymer concentration in Figures 6 and 7 for PEG of molar mass 6000 and 40.000, respectively. According to Figure 6 with PEG

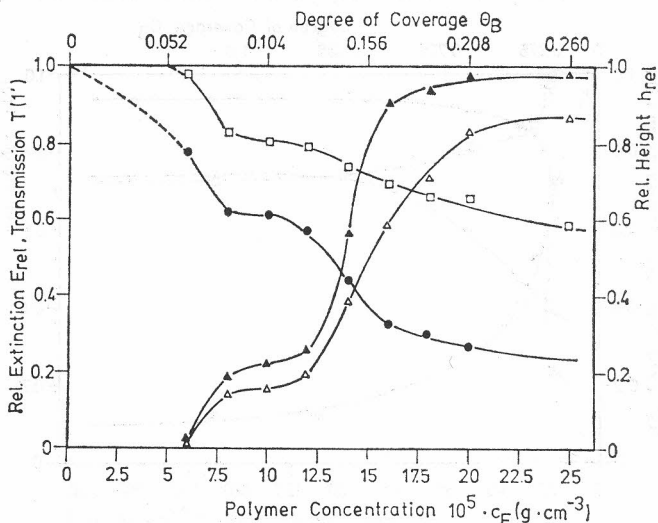


Figure 6. Dependence of the relative heights of boundary layer  $h_{rel}$  (6 hr)  $\blacktriangle$ ;  $h_{rel}$  (24 hr)  $\triangle$ ; the transmission  $T(I')$   $\bullet$  and the relative absorbance  $E_{rel}$   $\square$  on the polymer concentration  $c_E$ ; Aerosil 200, US-standard,  $T = 25^\circ\text{C}$ ,  $\text{pH} = 4.7$ , MS-standard,  $c_s = 0.01 \text{ g cm}^{-3}$ ; PEG 6000

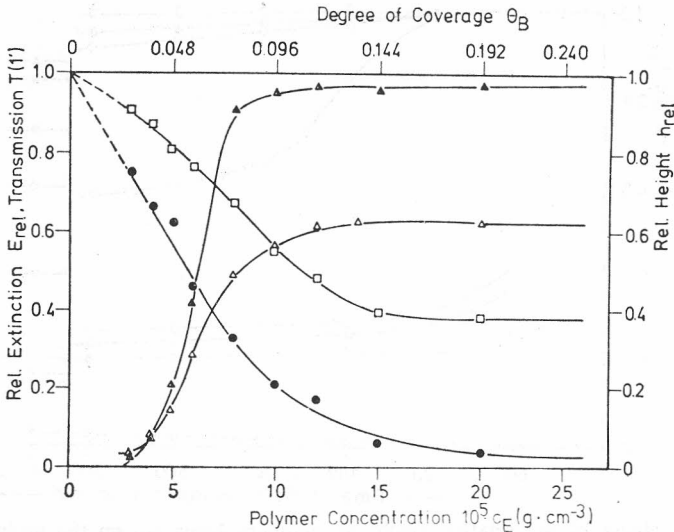


Figure 7. Dependence of the relative heights of boundary layer  $h_{rel}$  (6 hr  $\blacktriangle$ ;  $h_{rel}$  (24 hr)  $\triangle$ ; the transmission  $T(I')$   $\bullet$  and the relative absorbance  $E_{rel}$   $\square$  on the polymer concentration  $c_E$  Aerosil 200, US-standard, T 25 °C, pH 4.7, MS-standard,  $c_s = 0.01$  g cm<sup>-3</sup>; PEG 40000

6000 the onset of a measurable »granular« flocculation starts at about  $5 \times 10^{-5}$  g cm<sup>-3</sup> polymer, corresponding to a degree of coverage  $\theta$  of about 0.052. In contrast the results of Figure 7 show that the »granular« flocculation with PEG 40.000 starts at  $c_E = 2.5 \times 10^{-5}$  g cm<sup>-3</sup> ( $\theta = 0.026$ ). Moreover, with the high molecular weight polymers the transition between »granular« and »structured« flocculation behavior occurs within a narrow range of concentration ( $5 \times 10^{-5} < c_E < 8 \times 10^{-5}$  g cm<sup>-3</sup>). Above the upper limit of this range (corresponding to  $\theta = 0.075$ ), the building of the »flocculated« structure (that is

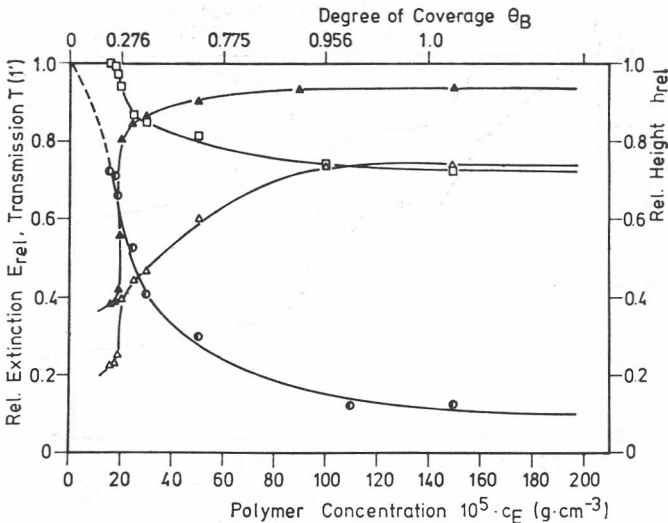


Figure 8. Dependence of the relative heights of boundary layer  $h_{rel}$  (6 hr  $\blacktriangle$ ;  $h_{rel}$  (24 hr)  $\triangle$ ; the transmission  $T(I')$   $\bullet$  and the relative absorbance  $E_{rel}$   $\square$  on the polymer concentration  $c_E$  Aerosil 200, US-standard, T 25 °C, pH 4.7, MS-standard.  $c_s = 0.0075$  g cm<sup>-3</sup>; PEG 6000

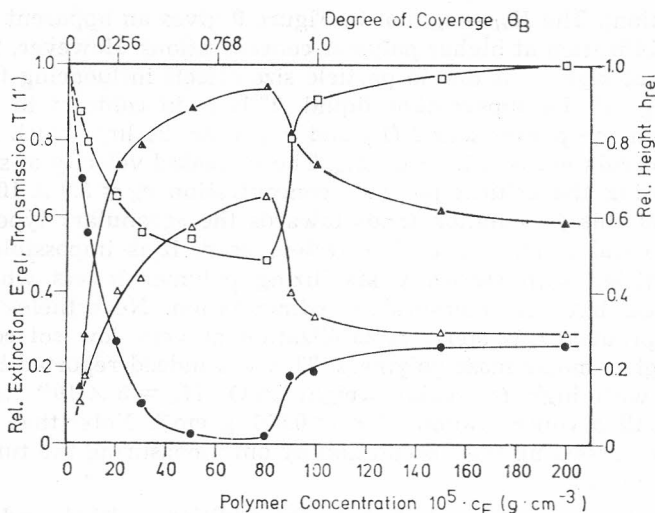


Figure 9. Dependence of the relative heights of boundary layer  $h_{rel}$  (6 hr)  $\blacktriangle$ ;  $h_{rel}$  (24 hr)  $\triangle$ ; the transmission  $T(I')$   $\bullet$  and the relative absorbance  $E_{rel}$   $\square$  on the polymer concentration  $c_E$  Aerosil 200, US-standard,  $T$  25 °C, pH 4.7, US-standard,  $c_s = 0.0075$  g  $\text{cm}^{-3}$ ; PEG 40000

characterized by a sudden change in the parameters) is practically complete. Further increase in  $c_E$  only causes »strengthening« of the structure, further aggregation of any remaining particles in the supernatant. This process results in a small increase of the transmission,  $T(I')$ , and the relative clear absorbance of the supernatant liquid,  $E_{rel}$ , and a very small increase of the sediment volumes,  $h_{rel}$  (6 hr, 24 hr). In contrast the transition between »granular« and »structured« flocculation obtained with PEG 6000 (Figures 6 and 7) is significantly broadened and is characterized by a plateau ( $7.5 \times 10^{-5} < c_E < 2.25 \times 10^{-4}$  g  $\text{cm}^{-3}$ ). This plateau can be seen for the parameters  $h_{rel}$  (6 hr, 25 hr),  $E_{rel}$ , and  $T(I')$ . This indicates also that the polymer adsorption is practically complete after the standardized mixing of sol and polymer solution. With the floccules formed by the addition of PEG 40.000 stronger light attenuation occurs than in the presence of those formed with PEG 6000. In addition the clearer supernatant liquid obtained with PEG 40.000, indicates that the settling floccules contain significantly larger number of Aerosil particles. In the period between 6 and 24 hr, the originally more voluminous structure obtained with PEG 40.000 settles more rapidly than the structure obtained using PEG 6000. With both polymers (even at highest polymer concentrations) there was no tendency for formation »granular« flocculation.

The results obtained with a sol concentration of  $0.0075$   $\text{cm}^{-3}$  are plotted for PEG 6000 in Figure 8 and for PEG 40.000 in Figure 9. In this case considerably higher polymer concentrations (coverages) are necessary before flocculation can be detected ( $6 \times 10^{-5}$  g  $\text{cm}^{-3}$  ( $\Theta = 0.13$ ) with PEG 40.000 and  $1.6 \times 10^{-4}$  g  $\text{cm}^{-3}$  ( $\Theta = 0.20$ ) with PEG 6000). In both cases »granular« flocculation was not observed within a standing period of 24 hr. While the addition of PEG 6000 causes a similar overall flocculation behavior for both sol concentrations, with PEG 40.000 at high values of  $c_E$  ( $8.0 \times 10^{-4}$  g  $\text{cm}^{-3}$ ,  $\Theta = 0.96$ ) a clear tendency towards granular flocculation was observed (note that at these polymer concentrations, the sol with  $c_s = 0.01$  g  $\text{cm}^{-3}$  exhibits completely »structur-

ed« flocculation). The  $E_{rel} - c_E$  plot in Figure 9 gives an apparent indication of a total restabilization at higher polymer concentrations. However, the reduction in intensity, at high  $c_E$ , is due to particle size effects influencing the scattering intensity,  $E_{rel}$ , of the supernatant liquid. This is in contrast to the evidence obtained from the parameters  $T(I')$  and  $h_{rel}$  (6 hr, 24 hr), which clearly show that some flocculation is still occurring. The increased velocity of sedimentation after surpassing the critical polymer concentration  $c_E = 8.0 \times 10^{-4}$  ( $\Theta = 0.96$ ) indicates that this flocculation tends towards the »granular« type. Thus given the experimental conditions of the system used, it is impossible to produce isolated particles with sterically stabilizing polymer layers which, like the bare particles, have no measurable sedimentation. Nevertheless, it may be possible to produce this steric restabilization at very low sol concentrations and with higher molar mass polymers. This was indeed reported by Rubio and Kitchener<sup>12</sup> with high molecular weight PEO ( $M_w = 5 \times 10^6$ ) using Cabosil-hydrosols with a concentration of  $c_s = 0.001 \text{ g cm}^{-3}$ . Note, that these results were obtained assessing the flocculation by only measuring the turbidity of the supernatant liquid.

The above phenomena obtained by the addition of PEG, and its variation with the mixing technique employed, are typical for the accepted model of flocculation by polymer bridging. Based on this model, the poor reproducibility obtained using the onestep method for mixing, I, Figure 10 without the separating layer of water can be attributed to inhomogeneities at the interface between sol and polymer solution. Probably, in this region differently coated flocculated

#### Methods of mixing.

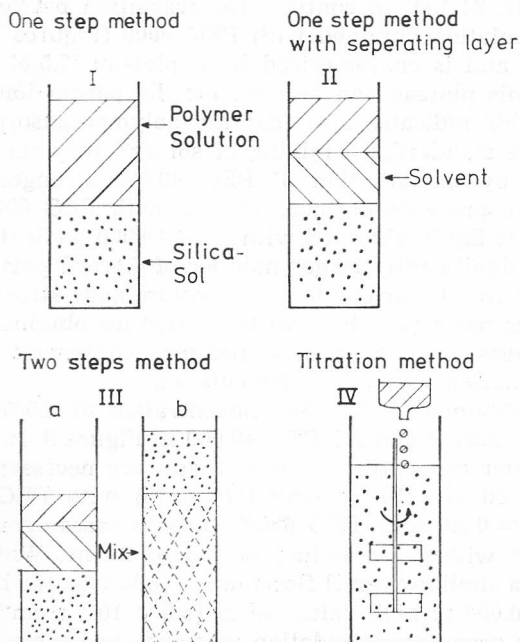


Figure 10. Methods of Mixing

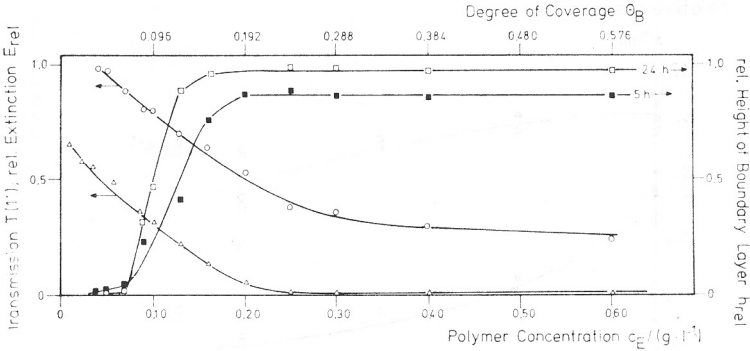


Figure 11. Dependence of the relative heights of boundary layer  $h_{rel}$  (5 hr)  $\square$ ,  $h_{rel}$  (24 hr)  $\blacksquare$ , the transmission  $T(I^0)$   $\triangle$  and the relative absorbance  $E_{rel}$   $\circ$  on the polymer concentration  $c_E$ ; Aerosil 200, US-standard  $T = 25^\circ\text{C}$ , pH 4.7,  $c_s = 0.01 \text{ g cm}^{-3}$  PEG 40000, Mixed by titration, time of titration 8 Min; time of stirring 20 Min, intensity of stirring  $\nu = 45 \text{ r. p. M.}$

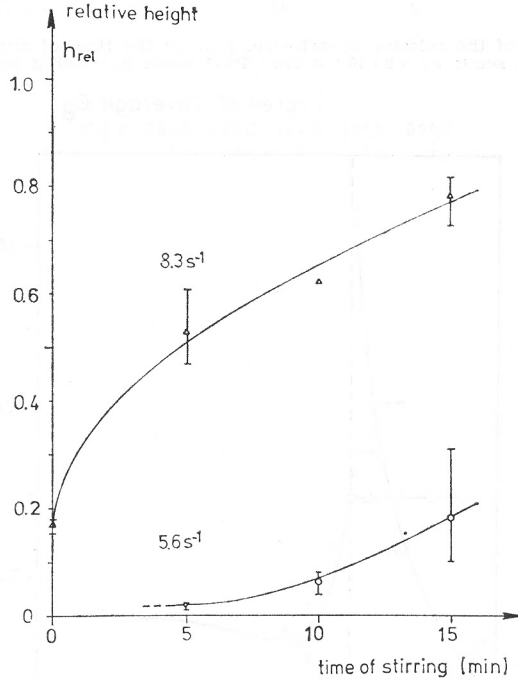


Figure 12. Dependence of the relative height,  $h_{rel}$ , of boundary layer on the time of stirring at stirring rates  $3.3 \text{ sec}^{-1}$  and  $5.6 \text{ sec}^{-1}$ ;  $c_E = 2 \cdot 10^{-4} \text{ g cm}^{-3}$  PEG 40000;  $c_s = 0.01 \text{ g cm}^{-3}$  Aerosil 200

or sterically stabilized particles are produced which, despite using the standardized mixing procedure give irregularities in the final flocculated structure. Using the separating layer of water, method II, these inhomogeneities in the particle coverage before mixing are in effect prevented, and bridging produces homogeneously flocculated sols.

Sols of such kind can be also obtained by titration, method IV, Figure 10. An example of that is shown in Figure 11. The influence of titration time,

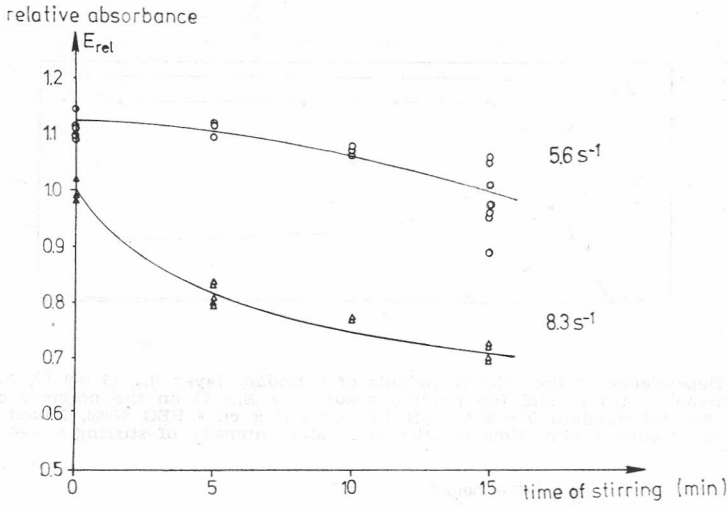


Figure 13. Dependence of the relative absorbance,  $E_{rel}$ , on the time of stirring at stirring rates  $8.3 \text{ sec}^{-1}$  and  $5.6 \text{ sec}^{-1}$ ;  $c_E = 2 \cdot 10^{-4} \text{ g cm}^{-3}$  PEG 40000;  $c_s = 0.01 \text{ g cm}^{-3}$  Aerosil 200

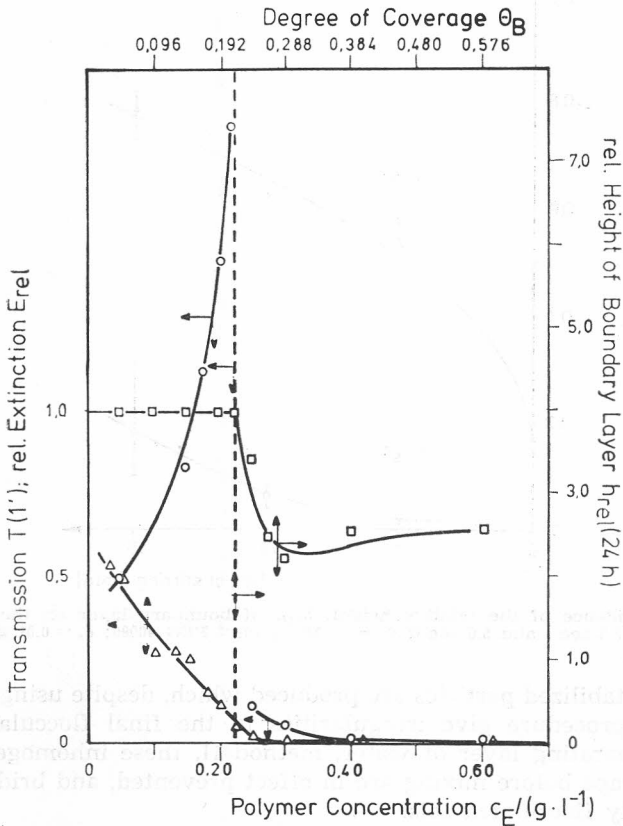


Figure 14. Dependence of the relative height of boundary layer  $h_{rel}$  (24 h) □, the transmission  $T$  ( $I'$ )  $\Delta$  and the relative absorbance  $E_{rel}$  ○ on the polymer concentration; PEG 40000;  $c_s = 0.01 \text{ g cm}^{-3}$  Aerosil 200; Intensity of stirring 107 U/Min, Time of stirring 20 Min.



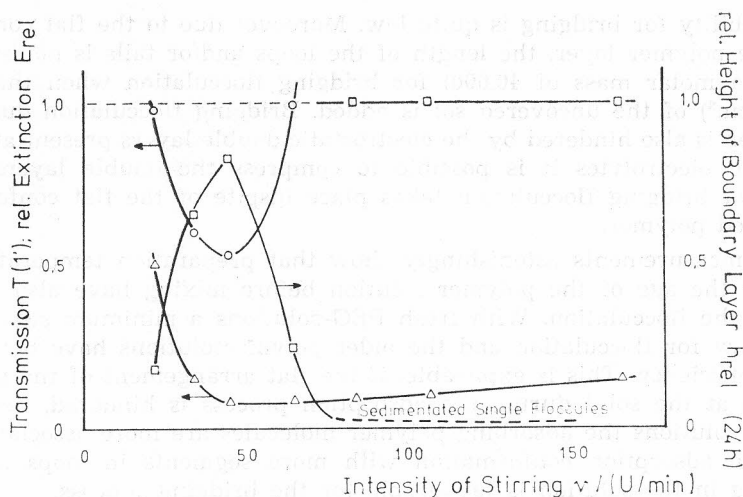


Figure 15. Dependence of the relative height of boundary layer  $h_{rel}$  (24 h)  $\square$ , the transmission  $T$  ( $1'$ )  $\triangle$  and the relative absorbance  $E_{rel}$   $\circ$  on the intensity of stirring;  $c_s = 0.01 \text{ g cm}^{-3}$  Aerosil 200;  $c_E = 2 \cdot 10^{-4} \text{ g cm}^{-3}$  PEG 40000; Time of stirring; 20 Min..

intensity and time of stirring can be analyzed quantitatively using the parameters of the sedimentogram.<sup>13</sup> With increasing titration time the granulated flocculation becomes more and more »structured« and the homogeneity and reproducibility of the suspension raise. Stirring after mixing has a small but definite influence. Deciding effect shows the stirring rate. When the stirring rate is increased to high intensity the behavior is changed strongly (Figures 12, 13).

With small polymer concentrations a strong decrease of the transmission  $T$  ( $1'$ ) accompanied by an increase in  $E_{rel}$ , but no boundary layer is observable and only a small number of granular flocs settle out. At  $\Theta = 0.2$  the behavior changes drastically, structured flocculation with a sedimenting boundary layer and a sudden decrease of  $E_{rel}$  is recognized (Figure 14). According Figure 15 the flocculation efficiency increases with stirring rate, shows a distinct maximum and decreases after that, especially at low polymer coverage.

The existence of an optimal stirring rate can be explained by the following:

- (1) A homogeneous distribution and adsorption of the polymer in the dispersion.
- (2) A particular relationship between the probability of polymer bridging between particles or the polymer adsorption on an individual particle and the rate of stirring.
- (3) The flocculation structure can be broken down by stirring stress at high stirring rates.

The model of polymer bridging also gives an explanation for the extremely weak flocculation obtained when using the two-step method of mixing (III Figure 10). The addition of the total amount of the polymer solution ( $10 \text{ cm}^3$ ) to the first part ( $25 \text{ cm}^3$ ) of the sol (which was separated from the polymer solution by a layer of water ( $40 \text{ cm}^3$ )) results in a sol ( $75 \text{ cm}^3$ ) with essentially isolated, polymer coated particles. As a result of the low particle concentration,

the probability for bridging is quite low. Moreover due to the flat conformation of the polymer layer, the length of the loops and/or tails is not sufficient (even at a molar mass of 40.000) for bridging flocculation when the second part (25 cm<sup>3</sup>) of the uncovered sol is added. Bridging flocculation during the second step is also hindered by the electrostatic double layers present at pH 4.7. By adding electrolytes it is possible to compress the double layers to the extent that bridging flocculation takes place inspite of the flat conformation of adsorbed polymer.

Last measurements astonishingly show that preparation temperature and especially the age of the polymer solution before mixing have also an clear effect on the flocculation. With fresh PEG-solutions a minimum stirring rate is necessary for flocculation and the older polymersolutions have better flocculation efficiency. This is explicable, if the flat arrangement of the polymer-molecules at the solid during the adsorption process is hindered, because in the older solutions the adsorbing polymer molecules are more associated. This incomplete adsorption conformation with more segments in loops and tails protruding in the solution is favourable for the bridging process.

Of the other mechanisms reported<sup>1</sup> the mechanism proposed by Iler<sup>14</sup> for destabilization of Aerosil by hydrophobization of the particles, as a result of PEG adsorption, could be also important. For a further analysis of the validity of the various models the flocculated sols were investigated using rheological measurements as shown below.

#### RHEOLOGICAL BEHAVIOR OF FLOCCULATED AEROSIL-HYDROSOLS

The rheograms of the Aerosil suspensions, with added PEG, are characterized by marked hysteresis loops and yield values (Figure 16). Both parameters provide information for the structure and strength of the colloidal dispersion.

The yield values  $\tau_{OC}$ , were determined by fitting the shear rates  $\dot{\gamma}_C$  and the shear stress  $\tau_C$  to the Casson Equation<sup>15</sup>

$$\dot{\gamma}_C = \frac{1}{\eta_C} (\tau_C^{1/2} - \tau_{OC}^{1/2})^2 \quad (20)$$

In every case it was possible to fit the measured values by an exact straight line.

In Figure 17 the yield values  $\tau_{OC}$  obtained are plotted versus the polymer concentration. Starting with a yield value of 1 Pa at  $c_E = 0.02$  the value increases with increase of the polymer concentration to a maximum of about 3 Pa at  $c'_E = 0.05$ , and thereafter it drops reaching an asymptotic value of about 2 Pa.

Moreover the flocculated structure produced by adding a certain amount of PEG 6000 ( $c'_E = 0.1$ ) and characterized by a yield value,  $\tau_{OC}$ , depends very strongly on the time,  $t$ , of ultrasonication of the uncovered sol before the addition of the polymer (Figure 18). For example, the addition of PEG 6000 to the standardized shaken sol produces a flocculated structure with a yield value of 0.2 Pa, whereas the addition of the same amount to sols which have been ultrasonicated for more than 2 min, results in yield values about 10 times higher.

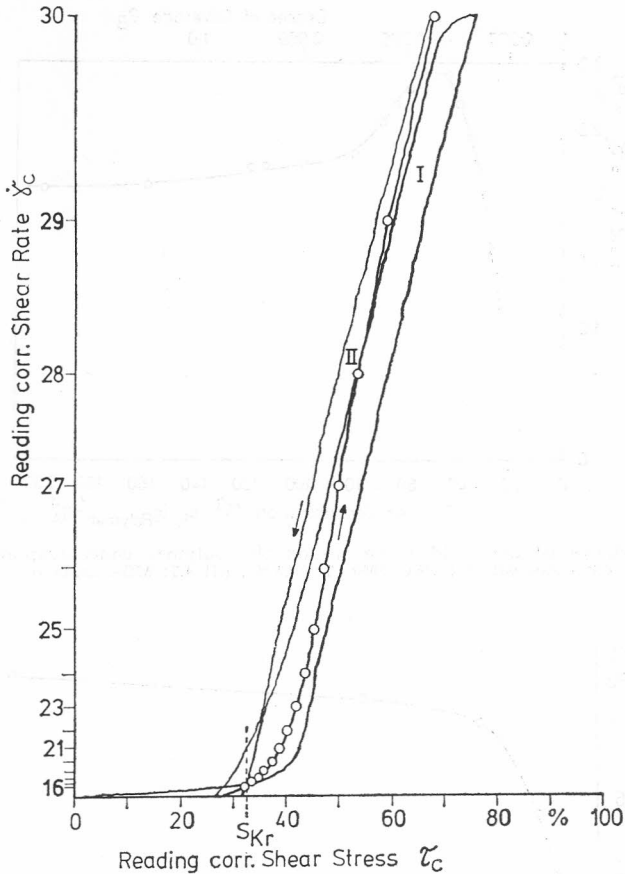


Figure 16. Rheogram of a polymer-treated Aerosil hydrosol I: Preshearing with sweep time 1 Min. II: Used rheogram with sweep time 8 Min.  $c_s = 0.02 \text{ g cm}^{-3}$  Aerosil 200; US-standard;  $c_E = 0.05 \text{ g PEG 6000/g Aerosil}$ ;  $T = 25^\circ\text{C}$ ; pH 4.7; MS-standard

The observed phenomena of structuring observed in sedimentation and the resulting yield values, obtained with Aerosil hydrosols, flocculated by PEG can be adequately interpreted only using the model of polymer bridging. Using the model proposed by Iller, the marked increase in the viscosity of the polymer treated sols could be explained by hydrophobic interactions between the polymer covered Aerosil particles, which could arrange themselves into a structure nearly free of water by repulsing the separating layers of water. Such a structure, however, is inconsistent with the observation of distinct yield values. Indeed, with this model, one would expect continuous destruction of the structure with increasing shear stress. Using the model of polymer bridging, the yield value can be considered the strain limit of the bridging polymeric network; the observed thixotropic effects (hysteresis areas) indicate a partial reversibility of the flocculated structures.

The reduction of the yield value after reaching a maximum in Figure 17 can be interpreted as a tendency toward steric restabilization at high polymer concentrations, as already discussed with the sedimentation behavior. Although

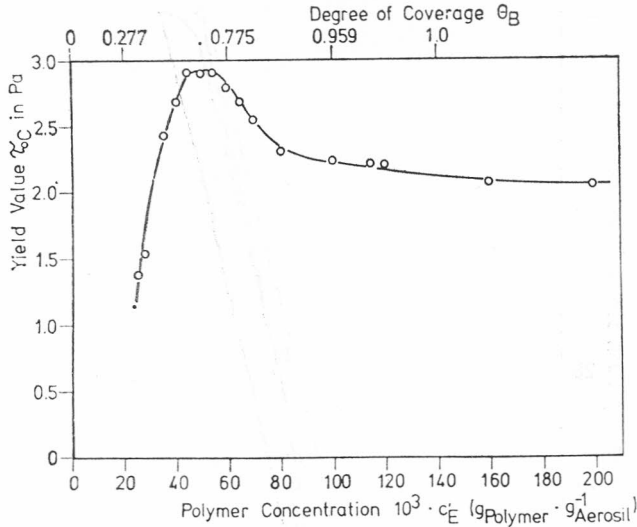


Figure 17. Dependence of the yield value  $\tau_{OC}$  on the polymer concentration  $c_E$ ;  $c_s = 0.02$  g  $\text{cm}^{-3}$  Aerosil 200; PEG 6000;  $T = 25$  °C; pH 4.7; MS-standard

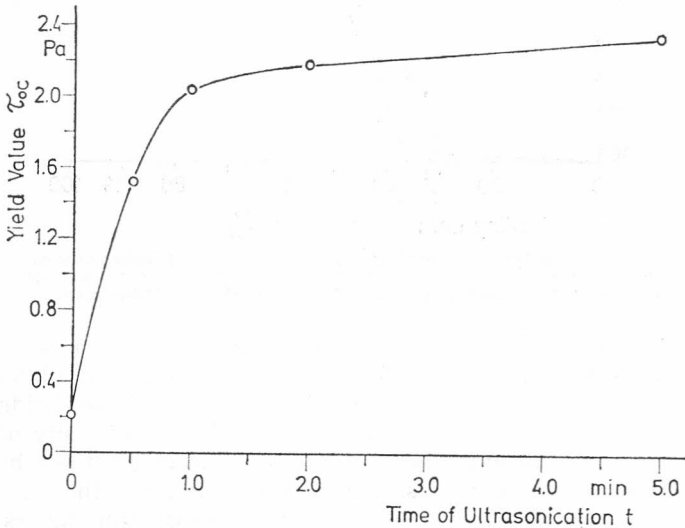


Figure 18. Dependence of the yield value,  $\tau_{OC}$ , on the time of ultrasonication,  $t$ , of the uncovered Aerosil 200 sol;  $c_s = 0.02$  g  $\text{cm}^{-3}$ ,  $c_E = 0.1$  g Polymer/g Aerosil,  $T = 25$  °C, pH 4.7; MS-standard

the values obtained from the sedimentation measurements for PEG 6000-treated sols do not show this kind of restabilization phenomenon, it is conceivable that this tendency can be only detected at the considerably higher yield stresses (encountered during rheological measurements). For example a floccule with singular, sterically stabilized portions has about the same streaming resistance for the repelled upward streaming dispersion medium as a totally structured sol, but a different resistance when high shear stress is

applied. The increase of the yield value with the time of ultrasonication of the sol before the addition of polymer in Figure 18 can be accounted for by the increasing number of isolated smaller particles, which produce more structured polymer-bridged sols.

The above results can be extrapolated for the control of stability of dispersions on an industrial scale. In practice the optimum method for mixing sol and polymer solution used here cannot be applied in exactly the same manner; however, it can be simulated. The inhomogeneities in the initial state of mixing can be nearly prevented by the slow addition of a dilute polymer solution to a stirred sol. The bridging flocculation process should be carried out with optimum polymer concentration at the optimal stirring rate and shear stress, in order to allow sufficient bridging and to prevent the destruction of already formed floccules. Commercial flocculants and stabilizers are mostly high molecular weight substances. Therefore, there is always the possibility of a sudden change of conformation causing a transition from flocculation to steric restabilization (or vice versa), particularly at unfavourable ratios of concentrations. It has also been shown that the affinity and irreversibility of the polymer adsorption increases with molar mass, thereby enhancing this effect. The results obtained using the present model system can, therefore, be expected to have some validity for real systems containing high molecular, nonionic polymers.

The consistency of all sedimentation parameters and the rheological measurements with the classical model of polymer bridging suggests that this is the most likely mechanism for the destabilization of the flame-hydrolysed silica hydrosols. From the adsorption and stability data derived from the results at various concentrations of silica and PEG's of various molecular weights at various mixing procedures the following generalizations can be made: The general picture of flocculation can be subdivided into granular and structured flocculation. The degree of flocculation increases with growing surface coverage and molar mass from granular to structured flocculation. At low sol concentrations there is a possibility of steric restabilization, which starts when there is a detectable remaining concentration of polymer in solution and which corresponds to nearly total surface coverage, due to the high affinity of polymer adsorption. The way of mixing has deciding effect on the efficiency of flocculation.

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#### REFERENCES

1. B. Vincent, *Adv. Colloid Interface Sci.* **4** (1974) 527.
2. E. Killmann, *Croat. Chem. Acta* **48** (1976) 463.
3. M. Korn and E. Killmann, *J. Colloid Interface Sci.* **76** (1980) 19.
4. J. Eisenlauer and E. Killmann, *J. Colloid Interface Sci.* **74** (1980) 108.
5. E. Killmann, J. Eisenlauer, and P. Kaniut, *Z. Naturforsch.* **34a** (1979) 68.
6. J. Mewis and A. J. B. Spaul, *Adv. Colloid Interface Sci.* **6** (1976) 173.
7. Y. A. Attia and J. Rubio, *Brit. Polymer J.* **7** (1975) 135.
8. G. D. Parfitt, *Dispersion of Powders in Liquids*, Applied Science Publishers, London, 1973.

9. E. Killmann and J. Eisenlauer, *Progr. Colloid Polym. Sci.* **60** (1976) 147.
10. H. A. Kearsley and L. E. Gill, *Trans. Inst. Chem. Eng.* **41** (1963) 296.
11. J. Eisenlauer, E. Killmann, and M. Korn, *J. Colloid Interface Sci.* **74** (1980) 120.
12. J. Rubio and J. A. Kitchener, *J. Colloid Interface Sci.* **57** (1976) 132.
13. J. W. Park, *Diplomarbeit*, 1980, Technische Universität München.
14. R. K. Iler, *J. Colloid Interface Sci.* **51** (1975) 388.
15. N. Casson, *Rheology of Disperse Systems*, CC. Mill Ed., Pergamon, London, 1959.

### SAŽETAK

#### Stabilnost hidrosolova SiO<sub>2</sub> pod utjecajem adsorpcije polimera

*E. Killmann*

Proučavana je stabilnost dobro dispergiranih solova SiO<sub>2</sub> pri različitim pH otopina. Solovi su pripremljeni ultrazvučnim raspršenjem SiO<sub>2</sub> (»Aerosil«), standardizirani su po koncentraciji i karakterizirani određivanjem ovisnosti viskoznosti o koncentraciji u cilindričnom viskozimetru, zatim određivanjem koeficijenta sedimentacije s pomoću analitičke ultracentrifuge, parcijalnoga specifičnog volumena (s pomoću visoko preciznog denzitometra sa vibrirajućom U-cijevi). Isto je tako određivan translacijski difuzijski koeficijent primjenom fotonskoga korelacijskog spektrometra, a oblik i veličina čestica određeni su transmisijskim elektronskim mikroskopom. Kinetika sedimentacije mjerena je laserskim fotosedimentometrom vlastite konstrukcije.

Rezultati pokazuju da je moguće reproducibilno flokulirati SiO<sub>2</sub> molarne mase 6000 i 40000 polietilenglikolom, ali je kod toga potrebno standardizirati postupak miješanja sola i polimera. Pokazani su rezultati utjecaja primjene različitih procesa miješanja, načina titracije, vremena i intenziteta miješanja, koncentracije sola i polimera, kao i molarne mase polimera i njegove adsorpcije na površinu SiO<sub>2</sub>.

Na osnovi ovih istraživanja, kao i nekih dodatnih reoloških mjerenja, utvrđeno je da klasični model stvaranja polimernih mostova najbolje opisuje mehanizam destabilizacije koloida.