THE EFFECTS OF SORPTIVE SURFACE MODIFICATION ON THE SEDIMENTATION AND RHEOLOGICAL PROPERTIES OF SUSPENSIONS OF ALUMINIUM OXIDE IN ORGANIC MEDIA

By

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Products were prepared from anhydrous aluminium oxide organophilized to various extents with an aqueous solution of ammonium methacrylate. The degrees of surface modification were selected on the basis of the results of preliminary sorption and sedimentation studies. An investigation was made of the effects of sorbed ammonium methacrylate on the sedimentation and rheological properties of aluminium oxide suspensions in an organic medium. Comparative examinations were performed in connection with the effects of methacrylic acid dissolved in the dispersion medium and of sorptive surface modification prior to the suspension process. Correlations were established between the results of the sorption, sedimentation and rheological investigations.

Introduction

It is a fundamental problem in several branches of industry (primarily the varnish, paint and plastics industries) that stable suspensions must be prepared from fillers and inorganic pigments with polar surfaces in dispersion media that are much less polar or even apolar. The interaction between the disperse phase and the dispersion medium is of determining importance from the aspect of the dispersion process and the properties of the dispersion. This is essentially indicated by the Ostwald—Buzágh continuity theory [1], which in its general form emphasizes that the more continuous the transition that develops on the solid — liquid interface, and the more harmonically the particle (together with its adsorption layer) fits into the structure of the dispersion medium, the more stable the dispersion will be, the smaller the adhesion forces, and the more favourable the practically-important properties of paint suspensions and filled polymer systems [2].

The harmonic fitting-in of the disperse phase into the dispersion medium may be promoted by regulating the lyophility of the surface. The lyophility is generally influenced with wetting agents (tensides) dissolved in the dispersion medium. However, the use of wetting agents may also lead to disadvantageous side-effects [3]. In the course of their sorption they are distributed between the solid surface and the solution, and thus the dissolved tenside considerably impairs the properties of films formed from the suspension. This deleterious effect can be eliminated by the systematic lyophilization (organophilization) of the surface of the particles of the disperse phase by the chemisorption of tensides before the suspension process [3—6].

Thermodynamically well-defined quantitative data for characterization of the lyophility of the surface are provided by the wetting heat values measured with an immersion microcalorimeter [7—9]. Conclusions regarding the interaction between the pigment surface and the tenside can be drawn from adsorption, sedimentation and rheological investigations [3, 5—7, 10,11]. At the same time, liquid mixture adsorption studies give a possibility for the quantitative determination of the size of the solid surface, as well as its hydrophilic-hydrophobic mosaic structure [12—14]. In a simple case the adhesion between the particles can be measured directly, while in general conclusions in this respect can be drawn from the sediment volume and the sedimentation rate [15—17].

The lyophility of the surfaces of the pigment and filler particles is modified by the sorption not only of tensides, but also of monomers capable of polymerization, oligomers and polymers. Many authors have made detailed studies of the effects of such solid substances on the kinetics of polymerization [18—20] and on the properties of filled polymer systems [21]. Substantially fewer data are available, however, in connection with the effects of sorbed monomer-type substances on the stability, sedimentation and rheological properties of suspensions in organic media [22, 23].

Experimental

Materials. Anhydrous Al_2O_3 of the highest analytical purity (Reanal) was used. Its specific surface area, measured by the BET method in an atmosphere of nitrogen, was 16.0 m^2/g. This specific surface area value did not change essentially as a consequence of the surface modification (organophilization). The dispersion medium was benzene of the highest analytical purity, or paraffin oil satisfying pharmacopoeia standards. As wetting agent and for organophilization, use was made of analytically pure methacrylic acid (Fluka), and of ammonium methacrylate prepared in the laboratory from methacrylic acid and ammonium hydroxide solution.

Methods. Surface modification of the aluminium oxide to various extents was carried out in a 10% benzene suspension, with a 0.1% solution of methacrylic acid in benzene. With a view to avoiding the disturbing effect of the water bound on the surface [24], before the suspension process the aluminium oxide was dried to weight constancy at 105 °C in a vacuum drying oven. The benzene was freed from water with metallic sodium.

In the organophilization with ammonium methacrylate, a 10% aqueous suspension of the Al_2O_3 was prepared; then, to the accompaniment of intensive stirring, ammonium methacrylate in a quantity equivalent to the methacrylic acid was added in the form of a 0.1% aqueous solution. After the adsorption equilibrium had been established (48 hours proved sufficient for this in both cases), the Al_2O_3 was separated from the equilibrium solution by centrifugation and then washed several times with the solvent. The washings were mixed with the equilibrium solution. The organophilized samples were dried to weight constancy at 60 °C in a vacuum drying oven, powdered, and then passed through a DIN-30 sieve.

The rheological examinations were made with a Haake rotary viscosimeter. The shear gradient was varied in 10 stages, in the interval $2.7-441\ sec^{-1}$. The suspensions for the rheological measurements were prepared in an Erweka rotatable homogenizer fitted with a closed agate vessel. In every case the suspension concentration was 62 mass%.

Results and Discussion

A detailed account was given earlier [6] of the effects of tensides dissolved in the dispersion medium, and of organophilization of the disperse phase prior to the suspension process, on the sedimentation and rheological properties of suspensions in organic media. A report is now presented of experimental results relating to studies comparing suspensions in an organic medium of Al_2O_3 hydrophilized with methacrylic acid dissolved in the dispersion medium, and suspensions in an organic medium of Al_2O_3 previously organophilized with ammonium methacrylate.

The effects of the quantity of sorbed methacrylic acid or ammonium on the rate of sedimenation of Al_2O_3 suspensions in a benzene medium are illustrated in Fig. 1. The Fig. 1 reveals that hydrophilic Al_2O_3 sediments out relatively quickly in pure benzene, with a sharp interface. On the action of a small amount of methacrylic acid, this rate is enhanced a little, presumably as a result of the transitional coagulating effect of the very small water content of the methacrylic acid. A larger quantity of methacrylic acid behaves as a markedly surface-active substance, and accordingly the sedimentation rate decreases rapidly; then, as a consequence of the development of an adsorption layer with reverse orientation, it increases once more. An essentially simpler variation can be observed between the sedimentation rate and the adsorbed quantity, if the surface of the Al_2O_3 is organophilized with an aqueous solution of ammonium methacrylate and the treated Al_2O_3 is then suspended in pure benzene. In this case the sedimentation rate falls progressively as the amount of ammonium methacrylate adsorbed increases.

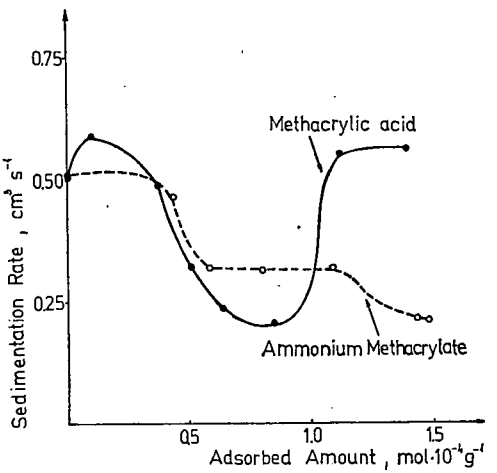

Fig. 1. Effects of surface modification on rate of sedimentation of Al_2O_3 suspensions in benzene medium

Interpretation of the phenomena is facilitated if we examine the similarities and differences for methacrylate adsorption from the organic medium. The adsorption-desorption isotherms of methacrylic acid and ammonium methacrylate are shown in Fig. 2.

It may be stated on the basis of Fig. 2 that in the first short section of the isotherms the equilibrium concentration is zero, and hence irreversible sorption may be assumed. The isotherms are two-stage isotherms characteristic of the sorption of tenside-type substances, and in both cases the sorbed quantity is comprised of parts bound by chemical and physical binding forces. After the inclined section of the isotherms, the specific adsorbed quantities before and after the desorption progressively diverge. In accordance with our earlier experience [3, 5], following the irreversible, chemisorption section, in a linearized plot the adsorption isotherm can be divided into two parts (Fig. 3). In the first section of the linearized isotherm

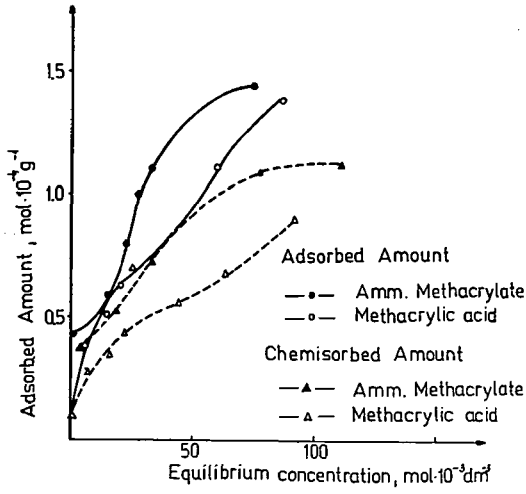

Fig. 2. Adsorption isotherms

the adsorption is partly reversible, while in the second section it is completely reversible.

Figures 2 and 3 strikingly reveal that, at more eleveated equilibrium concentration, the quantity of methacrylic acid sorbed from benzene (in contrast with the adsorption of stearic acid or ammonium stearate [6]) is greater than the amount of ammonium methacrylate sorbed from water. This may be correlated with the fact that methacrylic acid adsorbed from benzene causes greater decreases in the adhesion and sedimentation rate, and also with the fact that in this case a marked reaggregation process can be observed at higher methacrylic acid quantities, due to the development of an adsorption layer with reverse orientation.

The rheological measurement data can be discussed in good agreement with the results of the adsorption investigations. The extent of the organophilization of the Al_2O_3 used in the rheological examinations, and the amount of methacrylic acid dissolved in the paraffin oil dispersion medium, were determined from the characteristic points of the adsorption-desorption isotherms. In the course of the rheological examinations, the variation of the nature of the dispersion medium (benzene or paraffin oil) was made necessary by the desired increase in the reproducibility of the measurements and the decrease in their relative error.

It was demonstrated by comparative studies that the changed parameters result in changes in a similar direction when benzene is used as dispersion medium.

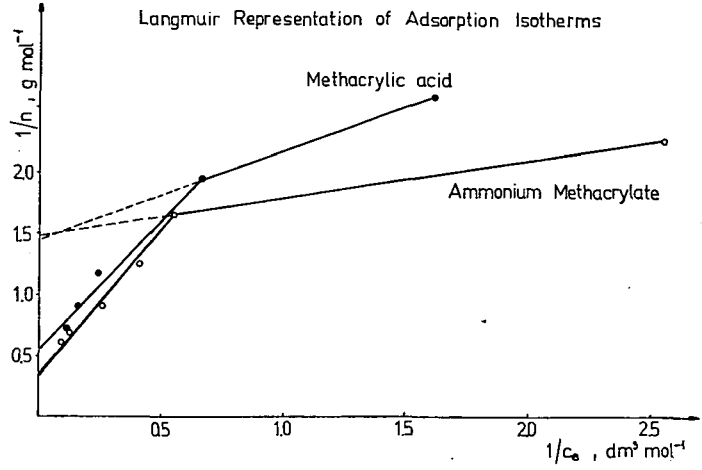

Fig. 3.

The paraffin oil suspensions of Al_2O_3 surface-treated with methacrylic acid dissolved in paraffin oil during the suspension process, or organophilized with an aqueous ammonium methacrylate solution before the suspension process, are characteristic plastic systems. The equilibrium flow curves exhibit a comparatively high yield value and plastic viscosity; appreciable thixotropy is displayed by the hydrophilic and the surface-treated Al_2O_3 suspensions. Instead of a detailed account of the flow curves, in Figs. 4 and 5 the variations in the plastic viscosity and Bingham yield values, calculated from the final linear section of the curves, are depicted as functions of the quantities of adsorbed methacrylic acid or ammonium methacrylate.

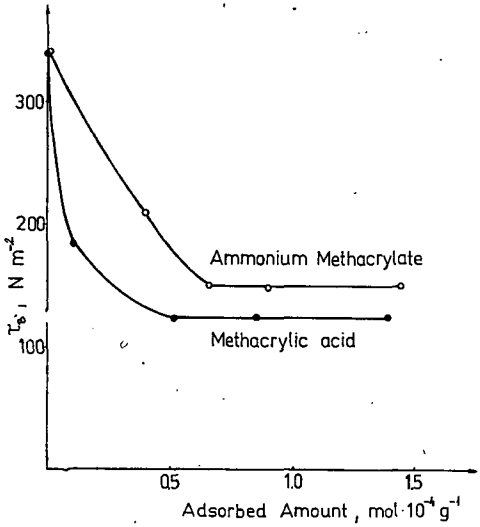

Fig. 4. Effects of methacrylic acid and ammonium methacrylate on Bingham yield value of Al_2O_3 suspensions in paraffin oil medium

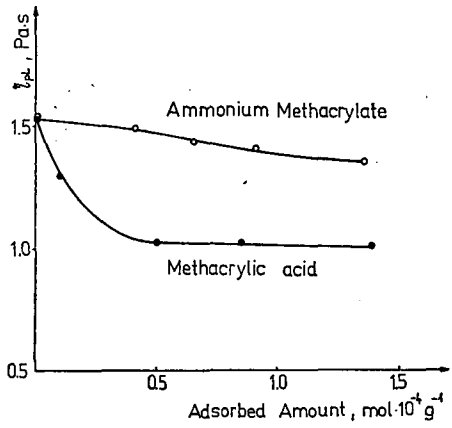

Fig. 5. Effects of methacrylic acid and ammonium methacrylate on plastic viscosity of Al_2O_3 suspensions in paraffin oil medium

On the basis of these Figures, it may be stated that the initial suspension of hydrophilic Al_2O_3 in a paraffin oil medium is a rigid system with a high adhesion; it possesses an outstandingly high yield value and a considerable plastic viscosity. Both the yield value and the plastic viscosity decrease to a limiting value as the amount of adsorbed methacrylic acid or ammonium methacrylate is increased. As a consequence of the fact that, at the same equilibrium concentration, the adsorbed quantity is very much higher for methacrylic acid than for ammonium methacrylate (Fig. 2), methacrylic acid exerts larger decreasing effects on the adhesion, and hence on the yield value and plastic viscosity. Both of the examined additives reduce primarily the yield value, the change in the plastic viscosity is very much smaller, presumably as a consequence of the large internal friction of the dispersion medium. It may also be observed that, in contrast with the results of the sedimentation examinations (Fig. 1), in concentrated dispersions with large amounts of adsorbed methacrylic acid no reaggregation accompanies the repeated increase in the adhesion. The reason for this is presumably that the loose adhesion interactions developing

between the particles are eliminated by the essentially greater mechanical effect applied during the preparation of the concentrated suspensions.

The reported experimental results permit the finding that the lyophility of the surface of solid grindings can be influenced to a significant extent not only by the adsorption of tenside-type substances of comparatively high molecular mass, but also by that of low molecular weight monomeric substances capable of polymerization. If the effects of such surface-treated solid substances on the kinetics of polymerization are investigated, it should not be forgotten that this surface modification considerably influences the sedimentation and rheological properties of the suspensions, and hence the physical and chemical properties of the filled polymer systems too.

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ВЛИЯНИЕ СОРБЦИОННОЙ ПОВЕРХНОСТНОЙ МОДИФИКАЦИИ НА СЕДИМЕНТАЦИОННЫЕ И РЕОЛОГИЧЕСКИЕ СВОЙСТВА СУСПЕНЗИИ ОКСИДА АЛЮМИНИЯ В ОРГАНИЧЕСКОЙ СРЕДЕ

А. А. Абд Эль Хаким, Я. Валаж и Ф. Санто

Приготовлены органофилизированные до разных степеней оксиды алюминия путем сорбции аммоний метакрилата из водного раствора. Изучено влияние степени органофилизации на седиментационные и реологические свойства суспензий оксида алюминия. Сравнена эффективность предварительной органофилизации метакрилатом алюминия непосредственного введения органофилизирующего агента — метакриловой кислоты, в систему. Показана, взаимосвязь между результатами сорбционных, седиментационных и реологических опытов.