EXPERIENCES WITH THE PREPARATION AND RATING OF CONCENTRATED SUSPENSIONS

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Summary

The parameters influencing the stability of a concentrated scourer suspension with a given chemical composition and gel structure were studied. We presumed that the system is stable if gelation proceeds through the adsorption layer. We stated that an optimum adsorption layer from the point of view of gelation can be established both by increasing the specific surface area of the scouring agent and by reducing the feed rate of the anionic tenside in the manufacturing process of the suspension. For in-plant quality rating of the product, we developed a simple test, the drop test, which was found fully satisfactory.

Introduction

Application of concentrated, structured suspensions has become increasingly widespread both in industry and in everyday life. However, manufacturing experiences demonstrated that formulation and processing of such complex systems is no easy task. In addition to the well-known technological difficulties, the main reason is that theoretical and experimental studies have, in their major part, dealt with low-concentration incoherent systems containing dynamically independent particles. There are relatively few papers in the literature reporting investigations on structured suspensions, that is, suspensions possessing a more or less coherent structure.

Structure formation related to thixotropy was first mentioned by Freundlich [1] and Buzágh [2] for clay mineral suspensions; later Hofman and Giese [3] set forth the card skeleton structure. Binghmam [4] and Roscoe [5] studied the plastic and elastic properties of particle lattices, Rebhinder and co-workers [6] dealt with the physico-chemical mechanics of coagulated structures, Szántó and co-workers [7] interpreted the sedimentation and rheological properties of structured clay mineral suspensions.

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The theory of concentrated suspensions is not yet fully elucidated; it is certain, however, that their stability is due to a more or less coherent structure (stability for concentrated suspensions is not identical with the true stability of dilute dispersed systems, it only implies that no settling-out occurs in the system).

Two border cases exist for forming coherent structures:

— In the first case, the dispersed particles form a coherent skeleton structure effected by increased adhesion forces or by cross-linking of macromolecules, preventing sedimentation. This structure exists in clay mineral suspensions and in flocculated industrial slurries.

— The second type of structured suspensions consists of a gel structure formed by the additives dissolved in the dispersion medium, preventing the dispersed particles from settling out. This type is frequent in cosmetic and household-chemical products.

Between these border cases numerous transitions exist, with both phenomena manifested to a certain extent (e.g. concentrated pesticide suspensions).

The stability of the structure depends on the interaction of the particles among one another and on their interaction with the medium. The interaction depends on the composition of the dispersion medium and on the value of adhesion forces, that is, on the nature, size and surface properties of the particles, as well as on wetting properties and on the structure of the adsorption layer. Hence, numerous possibilities exist to prepare suspensions with satisfactory stability.

One of these is to leave the composition of the dispersion medium unchanged, but modify the surface of the dispersed particles, by sorption pretreatment (e.g. organophilic bentonites) or by preparing the suspension in a manner to ensure that an adsorption layer with the desired characteristics from the view of stability shall be formed.

In this paper we report what parameters effected the formation of an optimum adsorption layer in the manufacture of a commercial suspension, leaving composition unchanged.

Experimental

Samples

The object of our study was a scourer suspension. Its industrial manufacture demonstrated that although composition and — on principle — technology was unchanged, quality of the product varied. Some batches were stable practically for months, that is, no settling-out of the particles was observed, while other batches settled out after a few days and it was difficult to re-disperse the sediment. The composition of the scourer is listed in Table 1.

The samples were prepared in the following manner: the two scouring agents were added to the aqueous solution of the complexing agent; subsequently, under constant stirring, the mixture of the non-ionic tenside and the C_{12-13} alcohol, and finally the anionic tenside and the usual supplementary additives were added.

Table 1

Composition of the studied suspension (per cent by mass)

Scouring agent *A*	10	($d_{0.5} = 6$ μm, specific surface area $= 11.6$ m^2/g)
Scouring agent *B*	15	($d_{0.5} = 53$ μm, specific surface area $= 0.27$ m^2/g)
Anionic tenside	7.5	
Non-ionic tenside	1.8	
Complexing agent	2.0	
$C_{12}-C_{13}$ alcohol	1.6	
Usual additives	0.5	
Water	66.6	
	100.0	

Conductivity and viscosity measurements demonstrated that the stability of the suspension was due to the gelation of the additives dissolved in the dispersion medium. Gelation time of the dispersion medium containing no scouring agent was three days.

Measurement of collective sedimentation

The samples were rated by their sedimentation properties. Obviously these more or less coherent suspensions do not follow the Stokes Law in sedimentation, the particles do not sediment individually, but collective sedimentation with a sharp interface proceeds.

Based on their collective sedimentation curves, concentrated suspensions may be classified into three groups shown in Fig. 1 [8]. Suspensions still containing individual, loose flocculates sediment as represented in Curve I. Sedimentation of suspensions in which a loose cross-linked aggregate has formed from the flocculates and sedimentation is controlled basically by the flow rate of liquid flowing through the pores (so-called semi-coherent suspensions) proceeds according to Curve II. Curve III, with its very small slope, characterizes suspensions with practically totally coherent structures. The sedimentation of these suspensions is in fact the shrinkage of the coherent skeleton structure.

Sedimentation curves were determined by pouring the suspension into calibrated test tubes and plotting the decrease of the volume of the slurry part (this being considered the sediment) *versus* time. In this concept, the total homogeneous suspension is regarded as sediment in the moment t = 0, that is, when sedimentation is started.

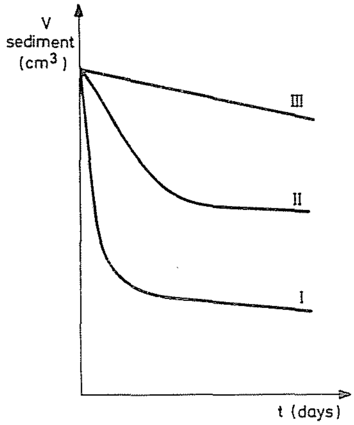

Fig. 1. Collective sedimentation curves of concentrated suspensions

Granulometric analysis

Particle size distribution of the scouring agents was determined with a Sartorius 4600 sedimentation balance. The suspension was diluted to 0.2 mass-% with a tenfold diluted solution of the dispersion medium.

Conductivity measurement

Conductivity of the samples in the course of preparation was measured at 20 °C using a conductometer type OK 102/1.

Results and discussion

Since the scourer suspension, at identical composition and — on principle — identical technology, showed varying sedimentation characteristics, we concluded that the optimum adsorption layer ensuring gelation is not established equally in all batches. Adsorption can be promoted by increasing the surface area of the scouring agent particles and by increasing the time of adsorption. We followed both paths in our investigation.

We determined particle size distribution of the two scouring agents *A* and *B* (Fig. 2) used to manufacture the scourer suspension. From the coarser scouring agent *B* we then prepared two finer fractions: one containing only particles below 63 μm, the other particles below 45 μm. With the scourring agent *B* represented in Fig. 2 (industrial sample) and the two fractions we prepared 1–1 kg samples and determined their sedimentation curves (Fig. 3) To our surprise, we found that while — as expected — sedimentation of the suspension prepared with the <45 μm fraction was less than that with the original scouring agent *B*, the suspension prepared with particles below 63 μm sedimented more rapidly than the suspension prepared with the original,

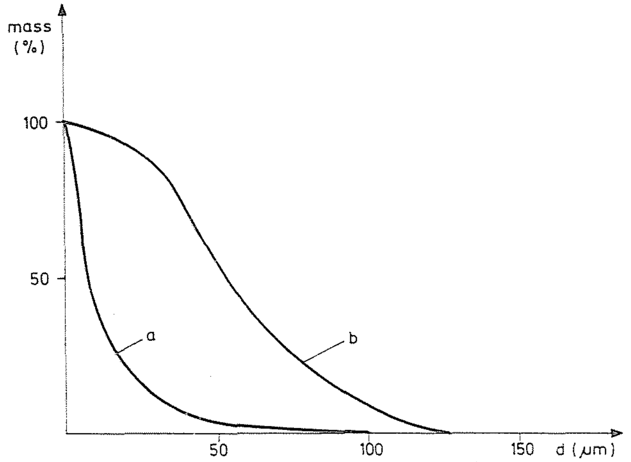

Fig. 2. Particle size distribution of the scouring agents determined with a Sartorius sedimentation balance

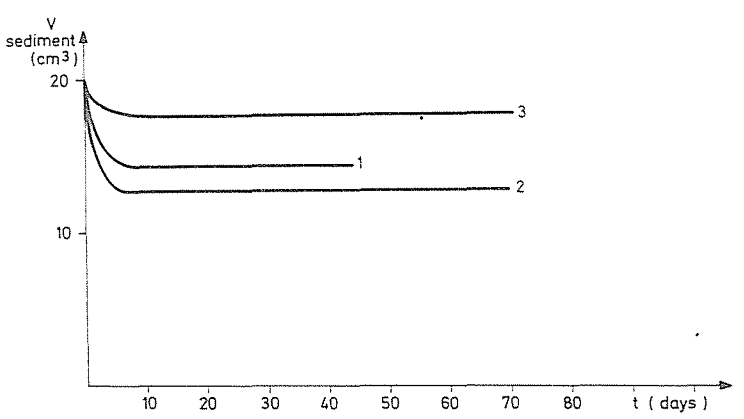

Fig. 3. Collective sedimentation curves of suspensions with different particle sizes: 1 — scouring agent *B*; 2 — fraction of scouring agent *B* with d<63 μm; 3 — fraction of scouring agent *B* with d<45 μm

coarser particles. This was equivalent to the finding that it is not only the particle size of the scouring agents that influences the quality of the product, but also contact time of adsorption, since nothing in the mode of preparation except perhaps feed rate and agitation rate could have changed.

We concluded from this finding that gelation only stabilizes the system if it takes place through the adsorption layer, that is, according to the continuity principle established by Buzágh, the particles fit into the structure of the medium continuously, together with their oriented adsorption layer. Since both gelation and adsorption are time-consuming processes, we now studied how stability of samples having identical composition change with changing feed rate of the tensides. We prepared 1 kg samples with the original scouring agent, at constant 120 rpm, with feed rates of 1, 2 and 4 cm^3/min, resp., using a peristaltic feed pump, and measured conductivity of the suspension during the preparation of the sample. The results are shown in Fig. 4.

The characteristic portion of the curves is the one where — as the anionic tenside is added — conductivity sharply decreases; it indicates coagulation and gel structure formation as the result of either physical or chemical forces.

We assumed that when the anionic tenside is being added slowly to the system, it has ample time to become adsorbed on the surface of the scouring agent particles; an adequate adsorption layer is formed and gelation proceeds across this layer, that is, the solid particles become incorporated in the gel net. To confirm this assumption, we recorded the collective sedimentation curves of the samples (Fig. 5). The figure demonstrates that the sample prepared with a feed rate of 1 cm^3/min settled much slower than the samples prepared with higher feed rates. This finding indicates that when the scouring agents used in

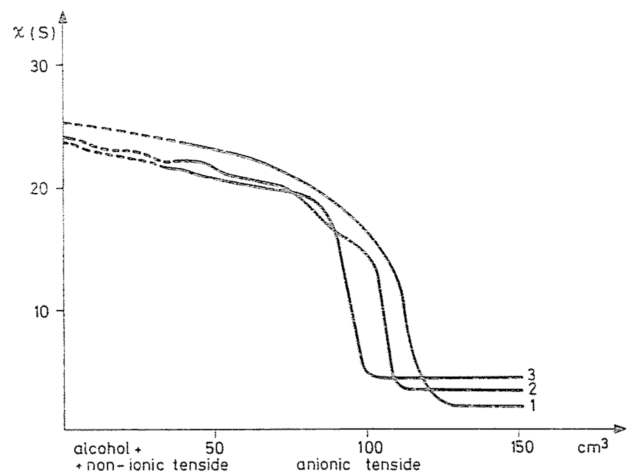

Fig. 4. Effect of tensides on the conductivity of the suspensions at different feed rates: 1 — 1 cm^3/min; 2 — 2 cm^3/min; 3 — 4 cm^3/min

commercial manufacture are being applied, only very slow feed rates will allow to manufacture a quasi-stable, but still semi-coherent suspension. The system is fairly sensitive even in this case: if a coarser fraction (d = 40–63 μm) of the scouring agent *B* is applied, already feed rates of 1 cm^3/min result in rapid sedimentation (Curve *4* in Fig. 5).

It follows from these results that the difficulties in manufacturing reproducibly high-grade products was due either to adding the anionic tenside

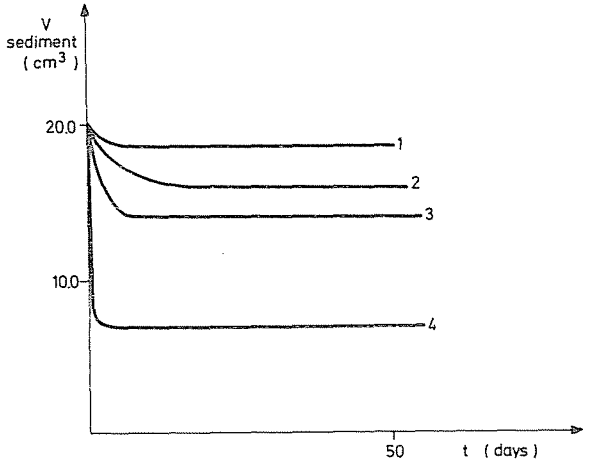

Fig. 5. Collective sedimentation curves of suspensions, prepared with different feed rates of the tenside: 1 — scouring agent *B*, feed rate 1 cm^3/min; 2 — scouring agent *B*, feed rate 2 cm^3/min; 3 — scouring agent *B*, feed rate 4 cm^3/min; 4 — fraction d = 40–63 μm of scouring agent *B*, feed rate 1 cm^3/min

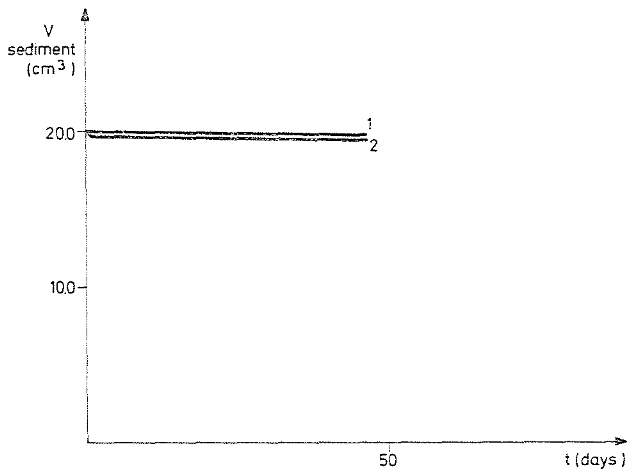

Fig. 6. Collective sedimentation curves of suspensions prepared with scouring agent *C* with different feed rates of the tenside: 1 — 1 cm^3/min; 2 — 4 cm^3/min

too rapidly to the suspension, or to the mine supplying the scouring agents not in conformity with particle size specifications. To control feed rate would have required technological investment; we therefore chose the path to reduce particle size of the scouring agent *B* to the extent that will not impair its scouring effect. The mine was able to deliver a product with a half-value of size distribution equal to 13.5 μm, marked in the followings by *C*. We repeated the feed rate tests with this material (Fig. 6) and found that owing to its higher specific surface area, the system was fully satisfactory regarding sedimentation both when the suspension was prepared at a feed rate of 1 and 4 cm^3/min.

A further problem had to be solved: to find a method suited for rapid rating of the suspensions, simple enough to be carried out at the plant level.

We started from the concept that if the suspension has a coherent gel structure, its drops will not disintegrate immediately when dropped into water, because their gel structure will hold the particles of the scouring agent. The simple test developed from this concept consists in the followings: a 50 μl drop of the sample is dropped from a defined height on top of a 20 cm high water column, and the behaviour of the drop is observed. The typical cases are:

— With high-grade suspensions, the drop remains on the surface of the water, and the scouring agents slowly diffuse out from the floating gel membrane.

— With satisfactory-grade suspensions, the drop falls intact through the water to the bottom.

— With unstable suspensions, the drop disperses spontaneously during its fall through the water column.

Experience demonstrated that the results of the test termed drop test are in good correlation with the sedimentation curves.

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