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PREFACE

Inorganic cementitious materials are usually transported and placed in forms as a mixture of unhydrated powder and water. The rheological properties of such mixtures are important not only from the standpoint of the handling of the materials but also because they influence structure formation resulting from hydration.

This paper deals with these basic questions as studied by the physical and colloid chemistry group headed by Professor P. Rehbinder of the University of Moscow, U.S.S.R.

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- Authors: P.A. Rehbinder and N.W. Michajlow (P.A. Rebinder and N.V. Mikhailov)

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FORMATION OF STRUCTURE IN DISPERSE AND MULTIMOLECULAR SYSTEMS, TYPES OF STRUCTURES AND THEIR RHEOLOGICAL PROPERTIES

The basic task of rheology is the investigation of the mechanical properties of structured systems and real substances which occupy an intermediate position between Newtonian fluids of various viscosity and ideally elastic solid materials. It is important here to determine the laws which govern the mechanical properties, which are the most fundamental or general properties, and which link them to special aspects of their composition and their structure.

An even more important task is the synthesis of various substances with predetermined mechanical properties and structures, and the synthesis of materials for a number of modern fields of engineering which exhibit certain rheological properties: elasticity, viscosity, plasticity, strength. The latter task is not so much one of rheology as one of physicochemical mechanics, a new marginal area of science which has arisen in the boundary regions between molecular physics and physical chemistry (especially the physical chemistry of disperse systems) on the one hand, and rheology with the mechanics of materials on the other.

Besides the synthesis of materials with predetermined structure and corresponding mechanical properties, physicochemical mechanics also embraces the scientific determination of the most favourable (optimum) conditions for the mechanical working of materials by deformation and dispersion by cutting, grinding and fine crushing, with utilization of the simultaneous effect of complex states of stress (in kinetic observation) the temperature and physicochemical factors, especially the adsorptive effect of the environment. It suffices to point out, and this will be confirmed in our studies, that the reversible effects of adsorption, given constant mechanical conditions, can bring about a considerable change in the deformation properties of the substance. For example, solid substances which appear practically as ideally elastic, i.e. show no appreciable elastic (sic) aftereffect when subject to stress in the vacuum or in dry air, nevertheless display high elasticity and creep capacity in the presence of boundary surface active substances, i.e. they are capable of irreversible flow. On the other hand, very plastic metal monocrystals in the presence of strong adsorptive effects become brittle and suffer a ten-fold reduction of strength.

These adsorption phenomena are associated with the appearance of the inhomogeneities or microcracks which are produced during the deformation of the substance by the state of stress and continue to develop as a consequence of various defects. The work required for the formation of new surfaces on a deformed body is determined by its surface energy, and decreases with the formation of adsorption layers which, during the deformation process, have just time enough to spread out along the newly formed surfaces by means of two-dimensional diffusion.

These two tasks - the production of structured systems and real solid substances with predetermined properties and structures, and still more that of studying and determining the optimum conditions for the destruction of materials - cannot be resolved with the methods of mechanics and classical rheology. Rather they must be regarded as physicochemical problems which are associated with two basic problems of modern colloid chemistry, namely the formation of structure and dispersal.

All real structured systems, structured suspensions, gels, polymers and their solutions, jellies, polycrystalline conglomerates, rocks, bituminous and cement-based building materials, ceramic and metallic-ceramic materials, and various alloys are divided into two main groups, depending on the nature of the formations between the particles forming the structure or between the individual structural elements (1-3).

These two groups are:

1. Coagulation structures, and

2. Condensation or crystallization structures.

Between these two groups we find structures of a mixed type with a continuous transition from coagulation to the condensation of crystallization structures.

In the coagulation structures in suspension or colloidal solutions (sols) with various concentrations of the dispersed phase, the spatial net takes the form of a disordered chain of particles subject to the effect of van der Waals' forces. Very thin layers of the liquid phase remain present between the particles. As a consequence of such weakened bonds with characteristic boundary lubrication at the places of contact between the particles, a comparatively low strength of the coagulation structures appears as our laboratory studies have shown, as well as a capacity for reversible reconstitution following a disturbance (thixotropy).

In coagulation structures two additional noteworthy features are also noted, namely the capacity for slow flow, given sufficiently small shearing stresses (creep), i.e. the presence of high Newtonian viscosity η_0 in practically undisturbed structure and in the structure which has reconstituted

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itself and shows an unusual high elasticity (elastic aftereffect)(1,4,5), combined with a slow increase in the shearing deformation after loading and a slow recovery after unloading (Fig. 1). These properties of very high viscosity in creeping flow and delayed elastic behaviour, together with thixotropy $^{(6)}$, are characteristic of coagulation structure as such and are almost totally independent of the nature or composition of the structure-forming particles.

The recording of complete rheological curves with elastoviscosimeters employing dynamometers of various types for a wide range of shearing stresses enabled us to investigate not only normally quasi-fluid coagulation structures, but also typically quasi-solid ones as well.

For such structures of the thixotropic type, e.g. very strongly structured aqueous and even very dilute bentonite suspensions⁽⁷⁾, an ability to flow with constant Newtonian viscosity at sufficiently small shearing stresses below a certain shearing stress boundary is characteristic. Such an initial viscosity η_0 of practically undisturbed type unlike the familiar cases observed by Philippoff⁽⁸⁾ exceeded by many powers of ten the viscosity η_m for completely destroyed structure (Fig. 2a and 2b). For a 10% aqueous bentonite suspension $\eta_0 \cong 10^7$ poise, i.e. it is eight powers of ten higher than the limiting viscosity $\eta_m \cong 0.1$ poise. A very abrupt transition, an avalanche-like structural destruction within a narrow range of shearing stresses at the limit of the flow capacity, combined with a discontinuous drop in effective viscosity by eight powers of ten characterize the degree of strength of the coagulation structure and determine its plastic properties (Fig. 3).

Unlike the coagulation structures, the condensation and crystallization space structures show maximum strength for the same density, since their particles are joined together by direct contact over minimum equilibrium distances with maximum forces. In the case of the condensation structures in the formation of polymers these are the main valence forces, for example in silicon dioxide jellies as distinct from aqueous gels of aluminium hydroxide, which can be regarded as typical coagulation structures. The forces in the crystallization structures are the ion bonds which act in the lattice.

Condensation and crystallization structures as such show no capacity for aftereffect or highly elastic deformations, and show high strength combined with brittle behaviour. However, where such structures do show plasticviscous creep properties or highly elastic behaviour, this can be attributed to the special character of the structural elements as such which form the condensation or the crystallization structures. These structural elements may either be the monocrystals of a metal or the flexible, long-chain

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macromolecules which are joined into a three-dimensional net by chemical bridges. The maximum plasticity can be recognized as a typical property of metallic monocrystals, and the maximum elasticity as typical of flexible macromolecules.

In the formation of a spatial network, e.g. during the disordered growing together of small crystallites to produce the crystallization structure, only the attenuation of these properties will occur; in the case of sharply expressed plasticity of an individual monocrystal this attenuation results from reciprocal blocking of crystals that have grown together in the absence of texture. Similarly in the solidification of a molten alloy, the more dispersed the structure, i.e. the smaller the crystallites that have grown together in a disordered manner, the greater will be the strength of the dense crystallization structure, and the more difficult it will be to deform plastically.

We see, therefore, that the rheological properties, especially in the presence of homogeneous shearing stress conditions, enable us to determine both the elastic and the viscous characteristics and make it possible to assess the type of structure, the particularities of structure formation, and finally the deformation properties of monocrystals or individual macro-molecules.

Let us turn now to a more detailed consideration of the characteristics of both coagulation structures and condensation or crystallization structures, and to a discussion of the possibility of continuous transition from one type of structure to the other.

As already mentioned, the reversible coagulation structures in suspensions and sols arise as a consequence of the weakened bonds between the particles of the dispersed, solid phase, separated by thin interlayers of the liquid phase at the points of contact. So that the three-dimensional structure can fill the entire volume, the number of particles in the unit volume, even where the content of the solid phase is small, must be sufficiently large, 1.e. the dispersity of this phase must be sufficiently great, and at the same time the coagulation must not result in the formation of compact aggregates; for this would immediately reduce the number of free particles so that the particles necessary for the formation of the spatial net in the given volume would be missing. Whence we get the following conditions for the formation of coagulation structure: (a) sufficiently high dispersion of the particles; (b) a mosaic character of surface forms, the lyophobic places on the particle surface, which are not wetted by the dispersing agent (not blocked), i.e. the unsaturated places, occurring rarely enough and forming the actual centres of coagulation.

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The anisotropy of the particles favours the voluminous spongy structure formation, even at a low concentration of the dispersion phase. In the case of rodlets or fibres, chain formation in the course of coagulation employs the ends of the particles, but in the case of platelets it employs the edges and the flat faces remain saturated. Coagulation structures in dilute colloid bentonite suspensions, hydrosols of vanadium pentoxide and many others are expressed in precisely this way. Even at very small concentrations by weight of the dispersed particles or the dispersed phase, from a few percent to a hundredth part of one percent, a quasi-solid system is obtained.

Coagulation leads to compact aggregation when, owing to the influence of the electrolytes or to a change in the nature of the particle surface, the side faces (rodlets or fibres) or the flat faces (platelets) become lyophobic, e.g. on account of compression of the diffuse double layer. If the particles have a symmetrical shape, e.g. spherical, the spatial structure formation is also possible for a low concentration of the dispersed phase, when the coagulation centres occur very rarely on the surface. In this case the particles (tiny spheres) form chains which become interwoven into a spatial structure. Small dimensions of the colloid particles, which favour a spatial structure formation, owing to the intense Brownian movement, which causes close interaction, ensure very rapid reconstruction of the structural strength after destruction. This is the reason for the thixotropy.

A complete stabilization of the particles, with lyophilization of their surfaces, eliminates the coagulation centres and thus prevents structure formation. For this reason, the addition of stabilizers always reduces the strength of coagulation structures in dilute systems to zero. No additives can play a peptizing (dispersing) part, by increasing the number of particles which appear as structural elements, so that with small additions of stabilizers this effect predominates over the suppression of coagulation centres, i.e. stabilization, and brings about maxima in the structure-strength curves (Fig. 4). For high concentration of the dispersed phase and the associated reduction in the thickness of the liquid layers between the particles the coagulation-structure formation comes about under arbitrary conditions, i.e. without the above-mentioned limiting conditions, even in sufficiently lyophilic systems. However, even in highly concentrated, already pasty suspensions, the structural strength is reduced to a minimum by the addition of stabilizers, and the liquid character becomes more strongly expressed. With concentrated dispersions the reinforcement of the double layer of ions or intensification of the lyophilic character by molecular absorption does not suffice for stabilization. Only boundary surface active substances, specifically of the protective colloid type which form a structural-mechanical

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barrier of sufficient thickness in the absorption layer, or in the entire space between the particles filled by the dispersing agent, have a stabilizing effect.

In concentrated dispersions the reestablishment of the structure occurs almost instantaneously after destruction and consequently the thixotropy appears considerably less strongly expressed; it is more evident in a number of intermediate concentrations of the disperse phase.

At a given concentration of the disperse phase this stabilizing effect is expressed in an increase of mobility. In the meantime, it must not be overlooked that the rheological properties of such concentrated, stabilized dispersion are determined by the nature of the stabilizers present in the intermediate layers between the particles. These particles of the disperse phase in this case play the part of an active filler and contribute as centres to the development of the coagulation structure which is formed by the micells or molecules of the stabilizers. The development of such a structure can by itself result in an increase of viscosity, and especially of initial viscosity, which corresponds to an undisturbed structure. Accordingly, it was shown in our laboratory that in the formation of a polymer in a sufficiently dilute solution (9-11), or for example in bitumin (12) of a sufficiently concentrated suspension of an active filler (or one activated with adsorption layers), two different space structures may be distinguished, namely, first the structure of the dissolved polymer, which is secured between the particles of the filler by the adsorption, and secondly the coagulation structure which is formed in the liquid phase owing to the interaction of the particles of the filler itself.

In the solution of linear polymers in which normally the absence of the space net, and hence the condensation structure, is assumed, the network of the jellies is always present which corresponds completely to the coagulation structure and is held together by the van der Waals' forces between the macromolecules along the unsaturated places or by the active groups, or finally, by less lyophilic groups. Of course, characteristic properties of such reversible space structures are determined mainly by the high elasticity of the individual macromolecules. Similar structures are no doubt present even in ordinary Newtonian, low molecular liquids, but in this case the structural strength is extremely small, and for ordinary viscosimetric measurements we have to deal with completely destroyed structures, the viscosity of which remains unchanged even under minimum stress or corresponding Should it be possible to apply still smaller shearing shear velocities. stresses, a measurable increase of effective viscosity might be expected and even the attainment of a maximum constant initial viscosity of the practically undisturbed structure.

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In the quasi-solid coagulation structures at stresses which are smaller than the flow limit, the creep viscosity η_0 is so great that in the course of measurements the residual deformation cannot be obtained within the relaxation period and only the elastic or highly elastic (aftereffect) deformation can be observed. Under these conditions the elastic aftereffects, i.e. the delayed highly elastic deformations, appear characteristic of the coagulation structures. At this quasi equilibrium a two to threefold reduction in the modulus compared with the value of the shear modulus occurs under instantaneous stressing of the system. Closely associated with this is the behaviour of thixotropic, highly solidified structures in measurements of the shearing stress relaxation at given constant deformations. In this case the shearing stresses relax comparatively rapidly up to a certain fraction of the arbitrary initial stress. This fraction (α) is in harmony with the theory that follows from the simple model representations

$$\alpha = \frac{E_2}{E_1 + E_2} = \frac{P_L}{P_0}$$

The relaxation process is described semi-quantitatively by the relation

$$P - P_L = (P_o - P_L) \exp\left(-\frac{\tau}{\theta X}\right); \frac{P_L}{P_o} = 1 - \lambda.$$

At the same time the natural high degree of elasticity is denoted by

$$\lambda = \frac{\varepsilon_{\rm m}}{\varepsilon_{\rm o} + \varepsilon_{\rm m}},$$

the instantaneous modulus by

$$E_1 = \frac{P}{\varepsilon_0},$$

the modulus of high elasticity by

$$E_2 = \frac{P}{\varepsilon_m},$$

and the equilibrium modulus by

$$E = P/(\varepsilon_0 + \varepsilon_m).$$

The moduli in turn are linked by the relation

$$\frac{1}{E} = \frac{1}{E_1} + \frac{1}{E_2}$$

For ideally elastic substances $\lambda = 0$, for coagulation structures and in aqueous bentonite dispensions becomes $\lambda = 0.5$, and for typical elastomers and

their solutions $\lambda \rightarrow 1$ ($\lambda \approx 0.9$). A true curve of the high elastic relaxation in general does not follow the simple exponential law, but the relations

$$P_{L} = P_{0}(1 - \lambda)$$

and the relaxation time

$$\theta^{\mathbf{X}} = \eta_2 / (\mathbf{E}_1 + \mathbf{E}_2)$$

in the rapidly falling branch of the relaxation curve are in harmony with the model theory, where η_2 is still the model viscosity determining the retardation. L.V. Ivanova-Tschumakova (compare the congress report) derived a kinetic equation for the slowly increasing elastic deformation $(13,1^4)$. This equation, which contains only one parameter, holds for the elastic relaxation of the stresses as well; it has been applied successfully to various polymers and their equations. Another very slow relaxation in the region P < P_L is of the Maxwellian type, i.e. it corresponds to the transformation of the elastic deformation time, which is determined by a high viscosity.

With uniform condensation and drying, concentrated coagulation structures, e.g. suitable clay-water suspensions, experience reduction in the thickness of the liquid interlayers at the points of contact and are gradually transformed into condensation structures. With this transition the strength increases greatly and the structure attains the strength of rocks in the order of magnitude of hundreds of kg/cm², but then, with progressive loss of plastic and thixotropic properties it is subject to an irreversible destruction. These condensation structures owing to the numerous inhomogeneities present in them, especially cracks, are not water resistant like crystallization structures that have grown together, so that when wetted they experience an almost complete loss of strength (limiting case of strength reduction by adsorption).

The crystallization structures, i.e. the polycrystalline solids, under normal conditions show only slight strength reductions due to adsorption which increase correspondingly with increases in porosity. The effects are entirely reversible and disappear after elimination of the liquid agent or adsorbed substance.

In systems of mixed structure the crystallization structure determines the strength and the coagulation structure, the creep capacity and the susceptibility to delayed elastic (aftereffect) deformation.

The laws of the formation of coagulation and crystallization structures and of mixed systems with various properties enable us to guide the structure forming processes in such a way that systems with predetermined mechanical properties and structures can be obtained.

A point worth noting is the difference between two types of structure which depends on the spontaneous change of crystallization structure and thermodynamic stability of the coagulation structure (15, 16). In the coagulation structure a thixotropic solidification and condensation analogous to syneresis develops in the course of time due to the action of adhesion and external forces owing to the reciprocal approach of particles which is associated with the expulsion of the liquid interlayers. The constant increase of structural strength (see Fig. 5, curve A) corresponds to this process. The spontaneous changes in the condensation structures, namely maturation, the irreversible solidification of jellies from polymers (silicic acid, gelatine, etc.) and their syneresis, which is linked with a strength increase, are of the same type. However, an entirely different picture is obtained both theoretically and experimentally for the crystallization structures. The place at which the crystallites grow together in this case are always thermodynamically unstable and they can therefore arise (like the crystallization structures themselves) only in the presence of adequate supersaturation, i.e. with sufficiently high rates of formation of the new phase, e.g. in the hardening of cements. If loose structures of this kind, when growing together, attain maximum strength and the liquid filling the pores (water) is not removed, a spontaneous dissolution of the contact takes place, i.e. of places with high solubility, which process goes side by side with the recrystallization of the solid phase in the form of separate crystals not grown together, i.e. with complete loss of strength and spontaneous destruction of the crystallization structure (see Fig. 5, curve B).

This phenomenon can easily be distinguished from loss of strength by adsorption (on moistening), because it is irreversible, i.e. it does not disappear again after drying. In practice such a decrease of strength can be eliminated after complete maturation of the crystallization structure, by reducing the solubility of the solid phase or by removing the solvent and also by decreasing the porosity or increasing the structural density.

In compact, i.e. highly condensed crystallization structures resulting from complete crystallization from melts, the thermodynamic instability of the finely dispersed polycrystalline substance is evident, of course, in the spontaneous recrystallization with increased grain size which occurs at sufficiently high temperature close to the melting-point, where in principle transformation occurs into a monocrystal accompanied by a reduction of the free surface energy.

The properties of the crystallization structure can also be varied within wide limits by additions of boundary surface active substance and by high frequency vibrations, i.e. by modifying the crystallization process

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through influencing of the form, the dimensions and the conditions of growing together of the crystallites, and modifying the character of the opened and closed porosity of the resulting structure.

The formation of highly condensed coagulation structures and of crystallization structures grown over them becomes very important in the strengthening of soils, in the manufacture of dense and very strong ceramic materials, and of various building materials. For extensive condensation it is first necessary to destroy the loose coagulation structure by vibrations, since it hinders the condensation process (17), and then to condense it, promoting the process by the addition of boundary surface active substances. The change of rheological processes of the concentrated coagulation structures in the course of dilution, together with their thixotropic properties explains the development of very unstable, water-soaked kinds of soils, and suggest how they may be improved, as the works of I.M. Gorkova⁽¹⁸⁾ and N.J. Denisov have shown.

A common example of a continuous transition from one structural type to the other consists in the semi-colloid of the soap type (19) in aqueous solutions, where control of rheological structural properties is also recogniz-In such equilibrium or thermodynamically stable systems the equilibrium able. distribution curve of particle sizes is displaced continuously with increasing soap concentration or with decreasing temperature towards greater micells or microcrystallites. At the same time a space structure develops which at first appears like the coagulation structure of a gel, but may subsequently be transformed into a crystallization structure of the solid (swollen) soap. This corresponds to a continuous transition from the true solution through a monophase, homogeneous system to the colloidal and eventually to the coarsely disperse two-phase systems. Of course, the equilibrium micells of the soap, which are occupied on the surface with hydrophilic groups, are capable of absorbing (solubilization) considerable quantities of hydrocarbons, the hydrocarbon components of micells acting as absorbents. On increasing the concentration of soap (sodium oleate in water) at 20°C up to 0.33 moles per litre, the initial viscosity $\eta_{\rm c}$ is increased only by one power of ten from 0.01 poise to 0.1 poise. Here the solubilization of hydrocarbons (dodecane) in moles per mole of soap remains constant. With a further increase of soap concentration (Fig. 6) from 0.33 to 0.53 moles per litres η_{a} attains the value of 10⁴ poise at which the transition to the solid gel occurs, and the specific solubilization increases.

This gel formation is associated with a progressive transformation of the spherical scap micells into platelets, which favours the development of the space structure and increases the specific solubility of the hydrocarbon.

When 0.22 moles dodecane per mole of soap are added to the solution of 0.8 moles sodium oleate per litre, the initial viscosity η_0 decreases from 10⁴ to 0.05 poise. This extraordinary effect probably comes about through vigorous swelling of the platelet-shaped micells owing to the increase in solubilization of hydrocarbon and their separation in the form of sphere-like micells of submicroscopic droplets which, surrounded by hydrophilic coatings of soap, are prevented from coagulating again. In one sense this is equivalent to a considerable dilution of the soap solution.

The addition of polar surface active substances has an opposite effect. For example, the addition of 0.08 moles n-octylalcohol to 1 mole of scap increases η_0 to more than 10⁷ poise and results in a definitely quasi-solid gel structure, which is apparently a consequence of additional structural bonding.

These examples show clearly what possibilities there are of controlling and guiding the structural formation and mechanical properties by means of various kinds of additives and by mechanical effects in the course of production (in statu nascendi).

Summary and Conclusion

1. Depending on the mechanism of formation, the nature of the bond and the characteristic rheological properties, space structures in disperse systems and in the solutions of polymers may be divided into two main groups:

(a) coagulation structures;

(b) condensation or crystallization structures, while at the same time transitional structures occur in a series of structural formations of a mixed type.

2. Coagulation structures are characterized by comparatively low strength, high plasticity and high creep capacity, considerable elastic aftereffects (delayed elasticity or high elasticity) and thixotropy, i.e. a definite capacity for the reestablishment of a destroyed structure. All these properties are determined by the presence of very thin interlayers of the fluid phase or of the dispersing agent at the points of contact between the particles of the disperse phase, or in the case of polymers, by the comparatively weak van der Waals bonds between the macromolecules.

3. Condensation or crystallization structures are distinguished from coagulation structures of equal concentration by great strength, even brittleness, and by the loss of plasticity and creep capacity. They are also characterized by the irreversible nature of the destruction and by the absence of thixotropic properties. Plastic or even high elastic properties occur only when these are characteristic of the particles themselves, depending on

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whether they are crystallites that have grown together or flexible change of polymers which are united by the principle valence forces to form a space net.

4. The investigation of the rheological (elastoviscous) properties of various types of structured systems from coagulation structures to solid substances permits far-reaching characterization of both the quasi-fluid and the quasi-solid structures if the properties of these systems are measured for homogeneous shearing stresses, especially when subjected to small shearing stresses, and flow curves are recorded.

5. The continuous transition from the coagulation to the condensation and crystallization structures were also investigated; similarly the ways of guiding the structural formation or the construction and of influencing the mechanical properties of the systems in question were noted. For this purpose mechanical vibrators are used in the presence of additional adsorbents for destruction and for subsequent condensation. To form crystallization structures control of the process of crystallizing of the new phase and of the growing together of the crystallites formed constitutes an additional method.

6. In the case of coagulation and condensation structures, the increasing thermodynamics stabilization is accompanied by a solidification of the system. After attaining maximum strength in crystallization structures, under certain conditions the strength may drop to zero or a minimum value owing to a recrystallization which is associated with a reduction in the free surface energy of the system.

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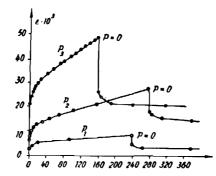


Fig. 1

The elastic aftereffect of thixotropic, highly solidified 15% aqueous suspensions of Turkman (Oglanlin) bentonite: $P_1 = 36 \text{ dyn} \cdot \text{cm}^{-2}$; $P_2 = 84 \text{ dyn} \cdot \text{cm}^{-2}$; $P_3 = 240 \text{ dyn} \cdot \text{cm}^{-2}$

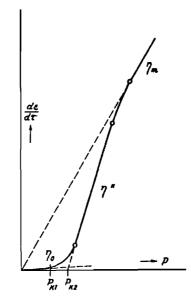
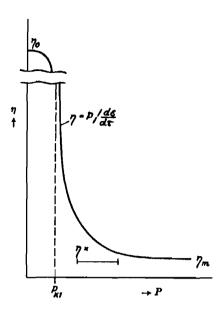


Fig. 2a

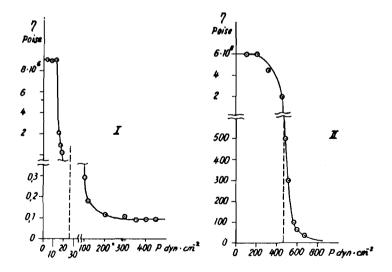
Complete flow curve of a thixotropic coagulation structure (schematic). Rate of deformation $d\epsilon/d\tau$ as a function of the shearing stress P (homogeneous, steady flow process)

 $\begin{array}{l} \eta_{o} = \text{initial viscosity} \\ P_{k\,i} = \text{lower flow limit} \\ P_{k\,2} = \text{upper (Bingham) flow limit} \\ \eta^{*} = \text{plastic viscosity} \\ \eta_{m} = \text{viscosity after total destruction} \end{array}$





The effective viscosity as a function of the shearing stress (schematic, corresponding to Fig. 2a)





The effective viscosity of aqueous suspensions of Turkmen bentonite as a function of the shearing stress under the conditions of steady flow

I = 10% suspension $P_{k_1} = 27 \text{ dyn} \cdot \text{cm}^{-2}$ II = 20% suspension $P_{k_1} = 480 \text{ dyn} \cdot \text{cm}^{-2}$

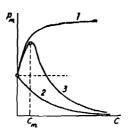


Fig. 4

Structural strength as a function of the concentration of a boundary surface active substance (schematic)

- 1 peptization influence (increase of number of particles of the elementary structure in the unit volume)
 2 - decrease of structural strength due to particle
 - stabilization 3 - resultant strength as a function of the additive concentration

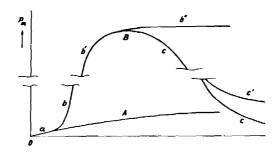


Fig. 5

Variation of strength of coagulation (A) and crystallization (B) structure as a function of time

- a induction period of formation and growth of crystallites of the new phase
 - b period of growing together of crystallites and development of framework
 - c decrease of strength owing to recrystallization

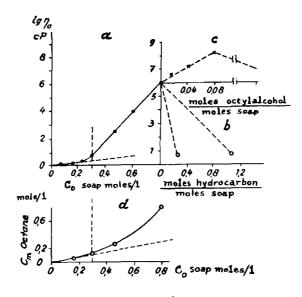


Fig. 6

The initial viscosity η_0 as a function of the concentration of sodium oleate in aqueous solution (a). Change of viscosity on solubilization of hydrocarbons (dodecane D and octane O) (b), or of octylalcohol (c) Solubilization of octane in aqueous sodium oleate solution as a function of the concentration (d)