The Rheological Properties of Concentrated Suspensions. II. Stationary Flow Properties and the Influence of Additives and of Particle Size

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It is generally accepted that the rheological properties of concentrated suspensions are connected with the state of flocculation and that the contribution of larger flocculates to the properties is predominant at low shearing stresses.[1,2] The rheological behavior of such flocculated systems is appreciably influenced by a trace of an adsorbate as well as by the size distribution of particles, which changes the energy of the interaction between particles. There is yet, however, no definite interpretation of the relations between the rheological properties and structures of the flocculates formed by particles in the ststem. In such concentratrated suspensions, it would be reasonable to assume that dispersed particles are partially linked with each other by weak attractive forces and that the links between particles are broken by a shearing force depending on the rate of shear.[2-5] A network model composed of links with various relaxation times would be an appropriate base for an explanation of the plastic behavior of such concentrated suspensions at low rates of shear where links between particles are not appreciably broken by the shearing force.[6,7]

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[1] M. Senô, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **78**, 66 (1957); *Month. J. Inst. Ind. Sci., Univ. Tokyo*, (*Seisan Kenkyû*), **11**, 36 (1959).

[2] I. M. Krieger and T. J. Dougherty, *Trans. Soc. Rheol.*, 3, 137 (1959).

[3] C. F. Goodeve and G. W. Whitfield, *Trans. Faraday Soc.*, **34**, 51 (1938).

[4] S. Peter and I. Stolle, *Z. physik. Chem. N.F.*, **11**, 251 (1957).

[5] T. Gillespie, *J. Colloid Sci.*, **15**, 219, 313 (1960).

[6] A. Tobolsky and H. Eyring, *J. Chem. Phys.*, **11**, 125 (1954).

[7] M. van den Tempel, *J. Colloid Sci.*, **16**, 284 (1961).

In a previous paper,[8] several equations were proposed for the stationary flow properties of concentrated suspensions at low rates of shear, assuming that there are certain circular structures in flocculates and that the links between particles can be conveniently distinguished into two parts at any instant in the stationary flow: the primary links, which are elongated without the separation of neighboring particles, and the secondary links, which are broken and reformed with the separation of particles.

It is the purpose of this paper to measure the stationary flow properties of various concentrated suspensions at very low rates of shear and to compare the findings with the theoretical predictions.

Experimental

Materials.—The characteristics of the pigments and media used in this work are listed in Table I. Barium sulfate-III was the same as barium sulfate-I except that the former was covered by sodium stearate. Linseed oil contains free fatty acids in itself and is more polar than polyisobutylene, which consists essentially of linear hydrocarbons with short methyl side chains, as shown in Table I.

The Preparation of Suspensions.—First a paste containing 70% pigments by weight was made. This paste was then passed through a paint mill three times and diluted by a medium to give a suspension of the required concentration. The diluted suspension was passed once more through the mill. Additives were added to the pigment before the pigment was mixed with the medium. An exact concentration of pigment was determined by igniting the suspension. Pigments had not been dried before being mixed with the medium except when the effect of water was examined experimentally.

Apparatus.—The stationary flow properties were measured with capillary viscometers and a rotational viscometer.

(a) Capillary Viscometers.—The capillary viscometers used in this work are improved Bingham viscometers, as illustrated in Fig. 1. The radii of the capillaries are 0.1493 and 0.1079 cm. and their lengths are 5.0 and 4.5 cm. respectively. The flow volume of measurement was selected so small as 0.10 cm^3 in order that the effects of head difference might be ignored during measurement. Measurements were made, alternately under pressure and by suction, in a water bath controlled at 30±0.02°C after the sample had been kept in it for 30 min.

The shear stress, S_a, and the shear-rate, $f(S_a)$,

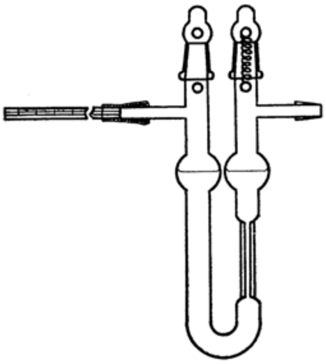

Fig. 1. Improved Bingham viscometer.

TABLE I-a. CHARACTERISTICS OF MATERIALS

Material	Density at 30°C g./cm^3	Viscosity at 30°C poises	Dielectric constant at 24.7°C, 50 kc./sec. e.s.u.
Linseed oil-I	0.9595	21.1	3.40
Linseed oil-II	0.9615	40.2	3.40
Linseed oil-III	0.9605	59.3	3.40
Polyisobutylene-I	0.883	137.3	1.90
Polyisobutylene-II	0.8825	129.6	1.90
Barium sulfate	4.50	—	10.25[a]
Water	0.996	0.008	76.5
Sodium stearate	1.07	—	3.125[b]

TABLE I-b. PARTICLE SIZES AND PURITY OF PIGMENTS

Pigment	Particle sizes			Weight loss		
	$(\overline{R})$ μ	$(\overline{R^2})^{1/2}$ μ	$(\overline{R^3})^{1/3}$ μ	at 105°C wt. %	by ignition wt. %	Total wt. %
Barium sulfate-I	0.075	0.079	0.082	0.32	1.34	1.66
Barium sulfate-II	0.265	0.283	0.311	0.20	1.51	1.71
Barium sulfate-III (covered by sodium stearate)	0.075	0.079	0.082	0.20	2.30	2.50

a) F. Wachholtz and A. Franceson, *Kolloid Z.*, **92**, 75 (1940).

b) K. D. Pathak and B. V. Bhide., *J. Indian Chem. Soc.*, **30**, 47 (1953).

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[8] M. Takano, This Bulletin, **36**, 1418 (1963).

at the wall of the capillary are given by the following equations:

$$S_a = a\Delta P/2L$$

$$f(S_a) = (1/\pi a^3)\{3Q + S_a(\mathrm{d}Q/\mathrm{d}S_a)\}$$

where a and L are the radius and the length of capillary respectively, ΔP is the pressure, and Q, the flow volume per unit time. The apparent shear rate is given as follows:

$$\dot{\gamma}_a = 4Q/\pi a^3$$

For the Bingham flow, the yield value, S_0, and the plastic viscosity, η_{pl}, are:

$$S_o = a\Delta P_o/2L$$

$$\eta_{pl} = (\pi a^4/8QL)\{\Delta P - 4\Delta P_o/3 + (\Delta P_o/3)(\Delta P_o/\Delta P)^3\}$$

$$\fallingdotseq (\pi a^4/8QL)(\Delta P - \Delta P_o)$$

where ΔP_o is the pressure below which the sample does not flow.

(B) Brookfield Rotational Viscometer.—The Brookfiedl viscometer used in this work is a commercial instrument which has a cylinder driven at the four constant speeds of 2, 4, 10 and 20 rev./min. However, three cylinders are exchangeable. The diameters of the cylinders are 3.039, 5.027 and 7.059 mm., and the lengths are 4.995, 5.053 and 5.009 cm. respectively. A container which had a radius of about 5 cm. and a depth of about 8 cm. was used directly as a vessel for the measurements.

Measurements were made after the sample had been kept for three hours in a water bath controlled at 30±0.02°C.

The stationary flow curves were obtained by using Engelhardt's extrapolation method.[9] The yield value and the plastic viscosity for Bingham flow have been calculated by means of the following equations:

$$S_o = M_o/2\pi a^2 L$$

$$\eta_{pl} = (M/4\pi\omega L)(1/a^2 - 1/b^2) + (S_o/\omega)\ln(a/b)$$

where M is the torque acting on the inner cylinder, M_o, the critical torque below which the sample does not flow, L, the immersed length of the inner cylinder, ω, the angular velocity of the inner cylinder, and a and b, the radii of the inner and outer cylinder respectively. The apparent rate of shear, $\dot{\gamma}_a$, is given as follows:

$$\dot{\gamma}_a = 2\omega/\{1-(a/b)^2\}$$

Experimental Results

Typical Newtonian and Bingham behavior was observed at lower rates of shear, as illustrated in Figs. 2 and 3.

The plastic viscosity and the yield value of various suspensions are listed in Tables II and III. The values listed in the tables were mainly obtained with capillary viscometers. However, some data were obtained by the Brookfield viscometer at 2 and 4 rev./min., as it was very difficult to obtain reproducible data at a stationary flow for thixotropic suspensions when capillary viscometers were used. The dependences of the relative plastic viscosity and the yield value are shown in Figs. 4 and 5.

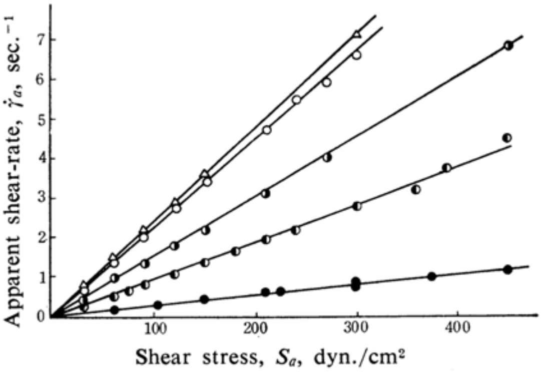

Fig. 2. Newtonian flow of suspensions of barium sulfate-I in linseed oil-II at various concentrations: (△) 0 vol.%, (○) 2.26vol. %, (◑) 8.18 vol.%, (◐) 17.14 vol.% and (●) 30.86 vol.%.

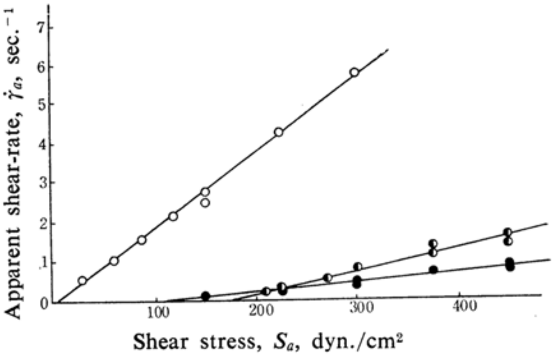

Fig. 3. Bingham flows of various suspensions: (○) 2.40 vol.% barium sulfate-III in linseed oil-II, (◐) 7.14 vol. % barium sulfate-III in linseed oil-II and (●) 2.09 vol.% barium sulfate-I in polyisobutylene-II.

When linseed oil was used as the medium, the yield value was not observed and the dependence of the relative plastic viscosity on the concentration was relatively simple, except when the particles were covered by sodium stearate. The adsorption of sodium stearate on the surfaces of particles increases the plastic viscosity and generates the yield value at lower concentrations.

When polyisobutylene is used as the medium, the yield value appears above the critical concentration determined by the particle size, and the plastic viscosity also increases remarkably above the critical concentration. The coating of the particles by sodium stearate

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[9] W. von Engelhardt and H. Lübben, *Kolloid Z.*, **147**, 1 (1956).

TABLE II. RHEOLOGICAL PROPERTIES OF SUSPENSIONS OF BARIUM SULFATE IN LINSEED OIL (30°C)

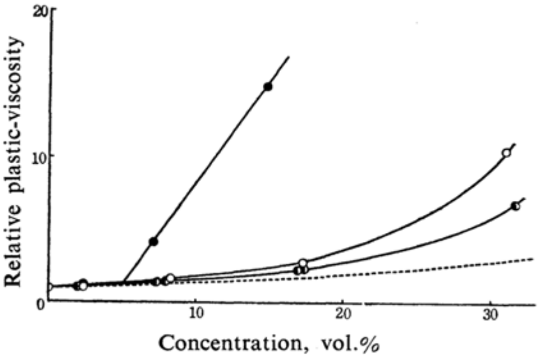
Suspension	Concn. vol. %	Plastic viscosity poises	Relative plastic viscosity	Yield value dyn./cm^2
Barium sulfate-I in linseed oil-II	0	40.2	1.00	0
	2.26	43.7	1.09	0
	8.18	67.1	1.67	0
	17.14	111.8	2.78	0
	30.86	420.8	10.45	0
Barium sulfate-II in linseed oil-I	0	21.1	1.00	0
	1.82	22.5	1.07	0
	7.16	30.2	1.43	8.2
	17.28	51.2	2.43	0
Barium sulfate-II in linseed oil-II	0	40.2	1.00	0
	2.04	45.1	1.12	0
	7.90	55.8	1.39	0
	16.67	89.0	2.21	0
	31.50	268.1	6.67	0
Barium sulfate-III in linseed oil-II	0	40.2	1.00	0
	2.40	51.2	1.27	7.34
	7.14	164.1	4.08	174.
	14.81*	595.	14.8	1060.

* Obtained by use of a Brookfield viscometer.

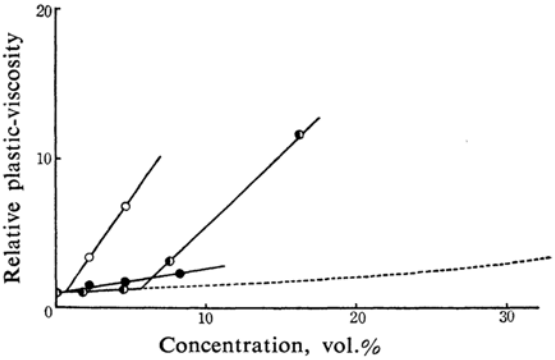
TABLE III. RHEOLOGICAL PROPERTIES OF SUSPENSIONS OF BARIUM SULFATE IN POLYISOBUTYLENE (30°C)

Suspension	Concn. vol. %	Plastic viscosity poises	Relative plastic viscosity	Yield value dyn./cm^2
Barium sulfate-I in polyisobutylene-II	0	129.6	1.00	0
	2.09	421.3	3.25	105.6
	4.57*	871.	6.72	364.
	7.50*	—	—	—
Barium sulfate-II in polyisobutylene-I	0	137.3	1.00	0
	1.81	145.0	1.06	0
	4.47	159.7	1.17	0
	7.50	412.0	3.00	119.9
	16.11*	1577.	11.5	683.3
Barium sulfate-III in polyisobutylene-II	0	129.6	1.00	0
	2.10	195.7	1.51	36.7
	4.54	218.6	1.69	49.2
	8.21*	280.	2.16	222.5

* Obtained by use of a Brookfield viscometer.



(a) Suspensions of barium sulfate in linseed oil.



(b) Suspensions of barium sulfate in polyisobutylene.

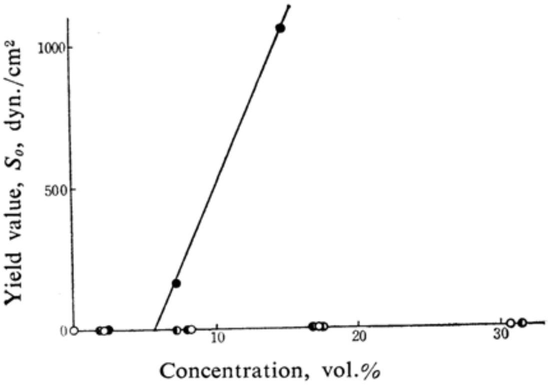
Fig. 4. Concentration dependence of the relative plastic-viscosity.
Symbols: (○) barium sulfate-I, (◐) barium sulfate-II and (●) barium sulfate-III. A dotted line represents Vand's equation.

lessens the appreciable dependence of the stationary flow properties on the concentration.

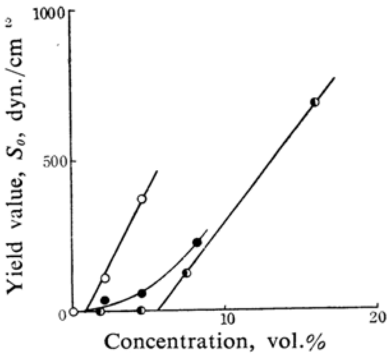
In both cases, suspensions of barium sulfate-I exhibit a higher dependence of the stationary properties on the concentration than do those of barium sulfate-II. In these cases, it seems not to be important that the particles had not been dried before being mixed with the medium. The effect of the adsorption of water on the stationary flow properties of suspensions of barium sulfate-I in linseed oil was examined experimentally; the findings are listed in Table IV. A minor quantity of water below 2 wt.% based on pigment does not appreciably change the flow properties of the system.

According to electron-microscopic observations, the shapes of these particles are approximately hexahedral, but the size distribution of particles differs from particle to particle, as shown in Table I-b. The weight losses of these particles by their being dried and by ignition are listed in Table I-b.

Sedimentation volumes of the particles in various media are listed in Table V. Barium sulfate-I shows a larger volume than barium sulfate-II in polar and non-polar media.



(a) Suspensions of barium sulfate in linseed oil.



(b) Suspensions of barium sulfate in polyisobutylene.

Fig. 5. Concentration dependence of the yield value.
Symbols: (○) barium sulfate-I, (◐) barium sulfate-II and (●) barium sulfate-III.

TABLE IV. INFLUENCE OF ADDITION OF WATER UPON THE RHEOLOGICAL PROPERTIES IN SUSPENSION OF BARIUM SULFATE IN LINSEED OIL (12.54 VOL. %, AT 30°C)

Suspension	Concn. wt. % based on pigment	Plastic viscosity poises	Relative plastic viscosity	Yield value dyn./cm²
Barium sulfate-I in linseed oil-III	0	116.7	1.97	0
	0.5	105.1	1.77	0
	1.0	113.6	1.92	0
	2.0	110.9	1.87	0
	3.0	207.9	3.50	0

TABLE V. SEDIMENTATION VOLUME OF PIGMENTS (cm³/g.) AT ROOM TEMPERATURE

Pigment	in H_2O	in CCl_4	in C_6H_6
Barium sulfate-I	2.34	3.64	2.12
Barium sulfate-II	1.06	1.04	1.20

The time dependence and shear-rate dependence of the flow properties were examined qualitatively by the Brookfield viscometer.

When linseed oil was used as medium, thixotropic behavior was observed slightly in suspensions of barium sulfate-I and -II, and remarkably in suspensions of barium sulfate-III.

When polyisobutylene was used as the medium on the other hand, anti-thixotropic behaviors¹⁰⁾ were observed, as illustrated in Figs. 6 and 7. Suspensions of barium sulfate-I have a greater tendency toward anti-thixotropic behavior than do those of barium sulfate-II. The anti-thixotropic behavior, however, disappears and normal thixotropic behavior is

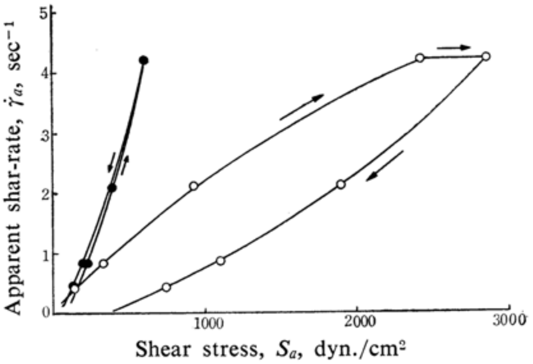


Fig. 6. Time dependence of flow property: (○) 4.54 vol.% suspension of barium sulfate-I in polyisobutylene-II and (●) 4.57 vol.% suspension of barium sulfate-III in polyisobutylene-II. Each point was obtained after rotating of the inner cylinder at a given speed for 5 min.

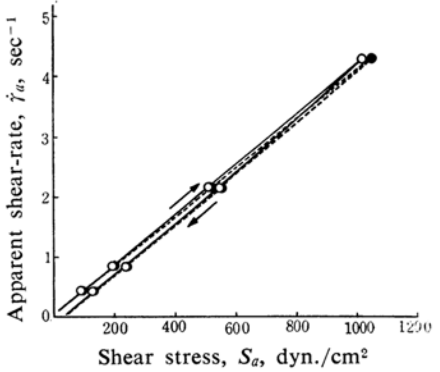


Fig. 7. Time dependence of flow property for a 4.47 vol.% suspension of barium sulfate-II in polyisobutylene-I: (○) after the sample was kept still for 30 min., and (●) after the sample was kept still for three weeks. Each point as obtained after rotating of the inner cylinder at a given speed for 5 min.

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10) J. Crane and D. Schiffer, *J. Polymer Sci.*, 23, 93 (1957).

observed when the particles are covered by sodium stearate.

Discussion

According to the experimental results described above, it is evident that the particle sizes and the polarities of the medium and of the additive appreciably influence the state of flocculation and the flow properties of the system.

In the previous paper,[8] it was proposed that the plastic viscosity and the yield value of flocculated systems at very low rates of shear may be given by the following equations:

$$\eta_{pl}=\eta+(g_1+g_2)\tau_2(2/\pi R_1)\sigma'(\phi-\phi'_{crit}) \qquad (1)$$

and

$$S_o=(2/\pi R_1)g_1\gamma_1\sigma'(\phi-\phi'_{crit}) \qquad (2)$$

where η is the effective viscosity of a medium involving the particles, g_1 and g_2 are the mean stiffnesses of the primary links and of the secondary links between particles respectively, τ_2 is the relaxation time of the secondary links, R_1, the diameter of the particles, ϕ, the volume fraction of the particles, σ', the mean number of links to be broken in order to separate two particles, γ_1, the mean strain of primary links in a stationary flow, and ϕ'_{crit}, the critical concentration above which stationary links between particles appear appreciably.

In Eqs. 1 and 2, the parameters, τ_2, σ' and ϕ'_{crit}, are given as follows at very low rates of shear:

$$\tau_2=(\boldsymbol{h}/2g_2\lambda_2^2)\exp(\Delta F/\boldsymbol{kT}) \qquad (3)$$

$$\sigma'=1+(12D_1'\boldsymbol{h}\phi_c/R_1^2\boldsymbol{kT})\exp(\Delta F/\boldsymbol{kT}) \qquad (4)$$

and

$$\phi'_{crit}=(\eta\pi R_1^3/8\boldsymbol{h})\exp(-\Delta F/\boldsymbol{kT})/\sigma' \qquad (5)$$

where $\boldsymbol{h}$ and $\boldsymbol{k}$ are the constants of Planck and Boltzmann respectively, ΔF is the mean free energy of activation for breaking the links between particles (which equals those of secondary links effectively), λ_2 is the distance increased whenever the secondary links are broken, T, the absolute temperature, D_1', the mutual diffusion constant of particles involved in a flocculate, and ϕ_c, the volume fraction occupied by particles in flocculates.

According to theoretical considerations, the plastic viscosity and the yield value must increase linearly above the critical concentration, ϕ'_{crit}, given by Eq. 5. After all particles are involved in one flocculate occupying the entire space available in the system, these flow properties must be quadratic functions of the concentration, since the ϕ_c included in σ' must be equal to the ϕ in such a region. These theoretical predictions seem to agree with the experimental findings, at least qualitatively, in flocculated systems.

The critical concentration, ϕ'_{crit}, can be obtained experimentally, and the mean free energy of activation for breaking the links between particles ΔF can be evaluated by using Eq. 5 with an assumption of the value of σ'. The critical concentration and the energy, ΔF, evaluated in this way are listed in Table VI. In these flocculated systems, the mean free energy of activation for breaking the links between particles seems to have the order of 30~36$\boldsymbol{kT}$, slightly depending on the assumed value of σ'. The order of energy, ΔF, agrees with the values, 38~46$\boldsymbol{kT}$, obtained by van den Tempel for suspensions of glyceryltristearate in either groundnut oil or paraffin oil.[7]

TABLE VI. CRITICAL CONCENTRATION AND THE MEAN FREE ENERGY OF ACTIVATION FOR BREAKING THE LINKS BETWEEN PARTICLES

Flocculated system	Critical concn. ϕ'_{crit}, vol. %	ΔF, $\boldsymbol{kT}$ $\sigma'=1$	$\sigma'=2$	$\sigma'=3$
Barium sulfate -III in linseed oil-II	5.0	31.0	30.3	29.8
Barium sulfate -I in polyisobutylene-II	0.8	34.0	33.3	32.8
Barium sulfate -II in polyisobutylene-I	5.6	36.0	35.3	34.9
Barium sulfate -III in polyisobutylene-II	0.5	34.4	33.7	33.3

In non-polar mediums, the most generally occurring type of interaction between particles may be considered to be the van der Waals-London attraction. For solvated spherical particles, the mean free energy of activation for breaking the links between two neighboring particles, ΔF, is given approximately by the following equation:[11-13]

$$\Delta F=(A_m^{1/2}-A_p^{1/2})^2R_1/24(\delta+2\Delta) \qquad (6)$$

where A_m and A_p are the Hamaker parameters of medium and particles, δ is the distance between the surfaces of solvated particles, and Δ is the thickness of the layer of the bound medium.

For particles adsorbed by an additive, the interaction energy is[13]

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[11] H. C. Hamaker, *Physica*, **4**, 1058 (1937).

[12] M. J. Vold, *J. Colloid Sci.*, **9**, 451 (1954).

[13] M. J. Vold, ibid., **16**, 1 (1961).

$$\begin{aligned}\Delta F=&(A_s^{1/2}-A_m^{1/2})^2(R_1+2\Delta)/24\delta\\&+(A_s^{1/2}-A_p^{1/2})^2R_1/24(\delta+2\Delta)\\&+(A_s^{1/2}-A_p^{1/2})(A_m^{1/2}-A_s^{1/2})\\&\times R_1(R_1+2\Delta)/12(\delta+\Delta)(R_1+\Delta)\end{aligned}\tag{7}$$

where A_s is the Hamaker parameter of the additive and Δ, the thickness of the layer of the additive.

The parameter, A, of a given homogeneous material with q_i, q_j atoms per cubic centimeter is defined as

$$A=\pi^2\sum_i\sum_j q_iq_j\lambda_{ij}\tag{8}$$

where λ_{ij} is the van der Waals parameter between two kinds, i and j, of atoms depending mainly on the polarizabilities of the atoms concerned. However, there is no simple method evaluate the value of A.

For the sake of simplicity, we will consider the van der Waals-London attraction between molecules. In this way, we have the approximate parameter for a given homogeneous material:

$$A=\pi^2q^2\lambda\tag{8'}$$

and the parameter, λ, between two molecules:[14]

$$\lambda=(3/4)\alpha^2eI\tag{9}$$

where q is the number of molecules per cubic centimeter, α, the polarizability of the molecule, e, the charge of an electron, and I, the first ionization potential of the molecule. The polarizabilities of non-polar molecules can be evaluated by measurement of the dielectric constant:

$$\alpha=(3M/4\pi d\boldsymbol{N})(\varepsilon-1)/(\varepsilon+2)\tag{10}$$

where M is the molecular weight, $\boldsymbol{N}$, Avogadro's constant, d, the density, and, ε, the dielectric constant at sufficiently higher frequencies.

By substituting Eqs. 9 and 10 into Eq. 8′, and by combining the result with the following relation:

$$q=(\mathrm{d}\boldsymbol{N}/M)$$

we obtain

$$A=(3/4)^3eI(\varepsilon-1)^2/(\varepsilon+2)^2\tag{11}$$

For non-polar materials, Eq. 11 will give an approximate value of the A parameter. For polar materials, however, Eq. 11 may only give an approximate order of the parameter.

Assuming $I=13.5$ eV., which is the first ionization potential of hydrogen atom for linseed oil, polyisobutylene and water, and using the dielectric constants listed in Table I-a, we estimated the magnitudes of A for each material. Similarly, for barium sulfate and sodium stearate, we assumed $I=5.21$ eV. for $Ba\rightarrow Ba^+$ and $I=5.09$ eV. for $Na\rightarrow Na^+$. The resultant evaluated values are listed in Table VII. Although these values were roughly estimated as described above, their orders of magnitudes of A agreed with those estimated in another way.[13]

TABLE VII. ORDERS OF THE MAGNITUDES OF PARAMETERS A

Material	A, erg.
Linseed oil	1.81×10^{-12}
Polyisobutylene	4.88×10^{-13}
Barium sulfate	2.00×10^{-12}
Sodium stearate	5.91×10^{-13}
Water	8.55×10^{-12}

By substituting these values of A into Eqs. 6 and 7 and by comparing the results with the experimental results stated above, we can estimate the distance between particles as shown in Table VIII. The thickness of the layer of sodium stearate was calculated from the concentration, ca. 1 wt.% based on pigment. In suspensions of barium sulfate-I and -II in linseed oil, the energy of the interaction between particles owing to the van der Waals-London attraction is very small when the distance between the surfaces of solid particles is larger than 10Å. The critical concentration, ϕ'_{crit}, given by Eq. 5 does not appaer up to the closest packing. This evaluation agrees with the experimental finding that no critical concentration can be observed up to the highest concentration.

The inefficiency of the addition of water to the suspensions in linseed oil can also be explained by assuming the van der Waals-London attraction between particles.

TABLE VIII. INTERACTION PARAMETERS BETWEEN PARTICLES

	$BaSO_4$-III in linseed oil-II	$BaSO_4$-I in P.I.B. -II	$BaSO_4$-II in P.I.B. -I	$BaSO_4$-III in P.I.B. -II
$\delta+2\Delta$, Å	11.8	12.1	43.3	55.3
2Δ, Å	10.3	—	—	10.3
δ, Å	1.5	—	—	45.0
$\Delta F/\boldsymbol{k}T$	30.5	33.6	35.4	33.1
σ'	1.5	1.5	1.8	1.3
g_1, g_2 dyn./cm.	2250.	64.7	5.35	33.5
λ_2, Å	108.	276.	471.	622.
$\gamma_1\times10^5$	4.51	134.	3460.	92.1
$\tau_2\times10^5$, sec.	3.52	254.	6980.	614.

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[14] F. London, *Z. Phys.*, 63, 245 (1930)

The mean stiffness of links between particles may be given by the following equation:

$$g=(1/3)(\mathrm{d}^2\Delta F/\mathrm{d}\delta^2) \qquad (12)$$

If we assume the D_1' in Eq. 4 can be approximated by the diffusion constant of unlinked particles $D_1=\boldsymbol{k}T/3\pi\eta R_1$, and that ϕ_c may be approximated by ϕ'_{crit}, the other parameters, σ', γ_1 and λ_2, may be evaluated from the concentration dependences of the plastic viscosity and the yield value by using Eqs. 1, 2, 3 and 4. The results are listed in Table VIII. However, it has been assumed that g_1 equals g_2 and that the interaction between particles is merely the van der Waals-London attraction.

Summary

The stationary flow properties of concentrated suspensions of barium sulfate in linseed oil and of those in polyisobutylenes have been measured at very low rates of shear with capillary viscometers and a Brookfield viscometer.

The dependence of the plastic viscosity and the yield value on the concentration, the particle sizes, and the polarizabilities of the medium and of the additive have been measured and explained by using a network model and by assuming van der Waals-London attraction between particles.

In suspensions of barium sulfate in linseed oil, the plastic viscosity and the yield value do not change on the addition of water below 2 wt. % based on pigments, and their dependence on the concentration of particles is monotonous. However, these values increase when the particles are covered with sodium stearate above a critical concentration.

In suspensions of barium sulfate in polyisobutylene, the plastic viscosity and the yield value appreciably increase above the critical concentration determined by the particle sizes, and these values decrease when the particles are covered with sodium stearate.

In both cases, a higher plastic viscosity and yield value are observed for suspensions of smaller particles in the same medium.

In suspensions of barium sulfate in polyisobutylene, antithixotropic behavior is observed at very low rates of shear. When the particles were covered by sodium stearate, the abnormal behavior disappears and normally thixotropic behavior is observed.

For plastic systems, the mean free energy of activation for breaking links between particles has been evaluated at 30～36$\boldsymbol{k}T$. If we assume van der Waals-London attraction between particles, the distance between the surfaces of solid particles is within the range of 10～55 Å, depending on the particle sizes and the presence of an additive.

Other parameters, the mean number of links to be broken for separating particles, the mean stiffness of links and other data have been approximately evaluated by assuming van der Waals-London attraction between particles.

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