The Thixotropic and Plastic Behaviour of Suspensions of Barium Sulphate with Clay.

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I. There are such cases known, in which non-thixotropic and non-plastic systems become thixotropic and plastic on adding certain amounts of other materials. A non-thixotropic and non-plastic suspension of quartz powder in water becomes, for instance, plastic and thixotropic when a small amount of lecithin is added.(1) A small amount of clay (1–2%) contained in the Solnhofen-slate was found to be responsible for the extreme plasticity of the slate, whose chief constituent was calcium carbonate.(2) A non-thixotropic suspension of barium sulphate can be made thixotropic on adding a certain amount of bentonite.(3) The phenomenon, which appears thus to be a general one, is interesting not only from a theoretical point of view but also from a technical one. The baryte-suspension with bentonite used as a drilling fluid in boring for petroleum in the United States marks a rather curious example of the technical application of the phenomenon. The stability of dispersions of such drilling fluids were discussed by Ambrose and Loomis(3) as a function of pH of the dispersion medium. For controlling the properties of such artificial systems, basic studies from many sides would be desirable.

Now a sort of a natural hydrogen-clay found in Japan, possesses more or less plastic and thixotropic properties but in a less degree than bentonite(4) in the United States, owing to its lower degree of dissociation and consequently the smaller capacity of its particles for binding water molecules. The Japanese hydrogen clay(5) with exchangeable hydrogen ions, can however be turned into an alkali-clay by treating it with alkali-salts or alkali-hydroxides.(6) The alkali-clay thus obtained is highly thixo-

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(1) H. Freundlich, *J. Soc. Chem. Ind.*, **53** (1934), 223.

(2) H. Freundlich and F. Juliusburger, *Trans. Faraday Soc.*, **30** (1934), 333.

(3) H. C. Lawton, H. A. Ambrose and A. G. Loomis, *Physics*, **2** (1932), 365; *ibid.*, **3** (1932), 185; H. A. Ambrose and A. G. Loomis, *ibid.*, **4** (1933), 265; *Ind. Eng. Chem.*, **25** (1933), 1019.

(4) H. Freundlich, O. Schmidt and G. Lindau, *Kolloid-Beihefte*, **36** (1932), 43.

(5) We would like to use this terminology instead of the widely used one: the Japanese acid clay.

(6) B. Tamamushi, *Kolloid-Z.*, **79** (1937), 309.

tropic and serves as a very effective adding material to make another non-thixotropic material such as barium sulphate or latex, thixotropic. The following experiments deal with the thixotropic and plastic properties of the suspensions of barium sulphate with various amounts of sodium-clay, where a certain correlation between thixotropy and related properties will be mentioned.

II. The natural hydrogen-clay taken at Itoigawa in Niigata prefecture, has a distinctly acidic reaction in its suspension in distilled water (pH of the ultrafiltrate of the suspension is equal to 5.8) and is slightly thixotropic in its concentrated suspensions (more than 35%) in water, whilst the sodium-clay formed by treating the former clay with dilute sodium hydroxide, is markedly thixotropic, its 10%-suspension in water solidifies on setting in about 60 minutes after strong shaking in a test tube of a diameter 14 mm. The sodium-clay greatly exceeds the hydrogen-clay in its swelling capacity in water according to the greater ability of the particles of the former clay in binding water molecules around them. The measurement of the swelling capacity was carried out by using the apparatus first designed by Freundlich, Schmidt and Lindau,⁽⁴⁾ the result of which is shown in Table 1 and in Fig. 1.

Table 1.

Swelling capacity of hydrogen-clay (per 1 g.)		Swelling capacity of sodium-clay (per 0.1 g.)	
Time	Water taken in c.c.	Time	Water taken in c.c.
0"	0.000	0"	0.000
5	0.100	2' 59	0.100
13	0.200	6 35	0.200
21	0.300	10 18	0.300
27	0.400	21 20	0.400
35	0.500	38 25	0.500
44	0.600	54 10	0.550
52	0.700	1° 18 15	0.600
1' 02	0.800	2 2 5	0.650
1 14	0.900	3 2 0	0.693
1 46	1.000	3 17	0.700
2 42	1.050	4 4	0.725
4 51	1.100	4 30	0.735
6 32	1.125	5 0	0.745
34 30	1.165	5 40	0.760
1° 14	1.175	18 30	0.930
1 37	1.180	54	1.165
2 3	1.185		
3	1.185		

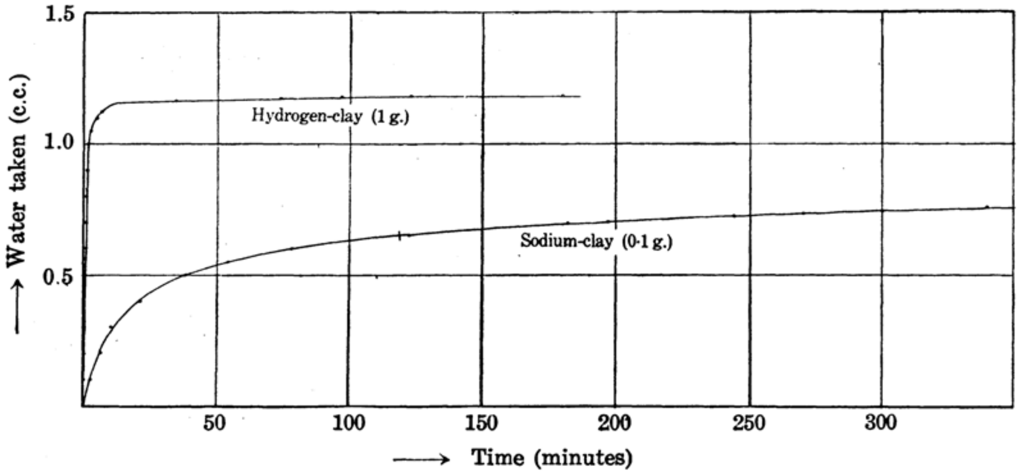

Fig. 1.

Moreover, the mass of the sodium-clay with a certain amount of water is strongly sticky and plastic, whereas the hydrogen-clay is rather brittle and non-plastic in the same conditions.

Now we prepared suspensions of barium sulphate according to the method of Weimarn(7) by the double decomposition of $Ba(CNS)_2$ and $MnSO_4 \cdot 7H_2O$, once with solutions of intermediate concentrations (N/5–N/10), and then with solutions of greater concentrations (about 5 N) of these salts. Consequently we obtained the suspensions of barium sulphate of smaller and larger particle size, radius of particles lying between about 2 μ and 10 μ, which was determined from the velocity of sedimentation by applying the Stokes formula.

The 25–30%-suspensions of barium sulphate without clay are certainly non-thixotropic, the suspensions of equal concentrations of solid matter with a small amount of the sodium-clay are however more or less thixotropic, as Table 2 shows.

It is to be remarked here that the suspensions with barium sulphate of larger particle size are thixotropic at the concentration of about 30%, while those with barium sulphate of smaller particle size are thixotropic at lower concentrations. The smaller size of particle is therefore advantageous to the thixotropy of the system.

It is further to be noticed that the suspensions with larger particles of barium sulphate seem to exhibit an optimum thixotropy at certain intermediate concentrations of the clay added, while those with smaller

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(7) P. P von Weimarn, "Die Allgemeinheit des Kolloidzustandes," Dresden (1925).

Table 2.

With $BaSO_4$ of greater particle size.

Composition (%)		Remarks
$BaSO_4$	Clay	
29.85	0.15	thixotropic
29.41	0.59	optimumthixotropic
29.08	0.92	thixotropic
28.57	1.43	thixotropic

With $BaSO_4$ of smaller particle size.

Composition (%)		Remarks
$BaSO_4$	Clay	
24.88	0.12	unstable
24.51	0.49	thixotropic
24.23	0.77	thixotropic
23.81	1.19	rigid and thixotropic

particles of barium sulphate become more and more viscous on increasing the amount of the clay. This apparently strange behaviour of the system in thixotropy has however, as we shall see later on, a certain parallelism with the behaviour in other related properties.

III. Thixotropy is, as generally accepted, related to a loose packing of particles in suspension.⁽⁸⁾ The volume of sedimentation, which is a good indicator for the degree of packing, was measured in the usual manner, 1 gram of the solid material being mixed with 10 c.c. of distilled water in a mess-cylinder, allowed to settle in an excess of liquid and the height of the powder settled down being determined after 24 hours. The results are shown in Table 3, in which the adopted values of the volume of sedimentation are the mean of several consecutive readings.

Table 3.

Composition of mixture (g.)		V. S. (c.c.)	Composition of mixture (g.)		V. S. (c.c.)
$BaSO_4$ (coarse)	Clay		$BaSO_4$ (fine)	Clay	
1.000	0.000	3.1	1.000	0.000	2.8
0.995	0.005	3.5	0.995	0.005	3.3
0.980	0.020	2.8	0.982	0.018	3.7
0.969	0.031	2.5	0.969	0.031	3.9
0.952	0.048	1.8	0.952	0.048	4.7
0.867	0.133	1.0	0.920	0.080	6.5
			0.831	0.169	9.1

As we see in the table, the volume of sedimentation is small in the suspensions of barium sulphate without clay and it increases steadily on

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(8) H. Freundlich, "Thixotropy," 16, Paris (1935).

adding the clay, in the case of $BaSO_4$ of smaller particle size, whereas it attains maximum in the case of $BaSO_4$ of larger particle size. The maximum volume of sedimentation in the latter case corresponds to the optimum thixotropy found in the same case. The correlation between thixotropy and the volume of sedimentation is evident.

IV. Now, the paste of $BaSO_4$ with water is more or less plastic.(9) For practical purposes we may determine the so-called plasticity number,(10) which gives the difference between the amount of water required to make the material sticky and that to make it just wet enough to be rolled in small thin rods. This number of plasticity was found once for pure $BaSO_4$ to be equal to 8, the amount of water in parts necessary for 100 parts of solid matter being 20 for the lower limit and 28 for the upper one. The same number was then determined for the mixture of $BaSO_4$ (95 parts) and clay (5 parts) to be 20, as the amount of water in parts necessary for 100 parts of solid matter was found to be 35 for the lower limit and 55 for the upper one. It is therefore obvious that the plasticity of $BaSO_4$ increases remarkably on adding a certain amount of clay.

The plastic behaviour of colloidal systems may however be more definitely characterized by determining the so-called yield value of Bingham.(11) The determination of this value was executed in the following way, with suspensions of various compositions of $BaSO_4$ and clay once for $BaSO_4$ of smaller particle size and then for $BaSO_4$ of larger particle size.

The adopted method of measurement is the capillary tube method, the suspension being passed through a capillary tube under a certain pressure difference at the two ends of the tube, and the rate of flow being recorded. The radius of the capillary tube $R = 0.069$ cm., its length $l = 50.09$ cm., and the value of the pressure difference applied varied from 15 mm. to 200 mm. Hg. Under these experimental conditions, the rate of flow could be measured with 17%-suspensions of $BaSO_4$ of larger particle size, but with suspensions of $BaSO_4$ of smaller particle size the concentration must be lowered to about 12%, since the latter suspensions of higher concentrations were found to be too viscous.

The relation between the stress pressure P and the rate of flow V/t obtained are given graphically in Fig. 2–5.

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(9) A. Atterberg, *Z. angew. Chem.*, **24** (1911), 928.

(10) R. Houwink, "Elasticity, Plasticity and Structure of Matter," 354, Cambridge (1937).

(11) E. C. Bingham, "Plasticity and Fluidity," New York (1922).

According to the theory of Bingham, the rate of the plastic flow in a capillary tube is expressed by the following equation:

$$\frac{V}{t} = \frac{\pi\mu R^4}{8l}\left(P - \frac{4}{3}p + \frac{p^4}{3P^3}\right),$$

where l is the length of the capillary tube, R its radius, P the pressure difference at the two ends of the tube, p a constant given by the relation:

$$p = \frac{2l}{R}f,$$

in which f is the friction or the yield value, and finally μ means a constant which is called the coefficient of mobility. The general feature of the curves in the above figures is justly represented by this equation.

For large values of the pressure applied, the last term of the equation becomes very small and the curve becomes nearly linear and coincides with its asymptote, namely:

$$\frac{V}{t} = \frac{\pi\mu R^4}{8l}\left(P - \frac{4}{3}p\right).$$

Putting herein $V/t = 0$, we obtain the intercept of the asymptote and from this we get the value of the true friction. From the inclination of the asymptote, we get further the value of $\frac{\pi\mu R^4}{8l}$ and consequently the value of the coefficient of mobility.

Applying the above relation to our experimental curves, we obtained the friction or the yield value f and the mobility coefficient μ in each case, the result being summarized in Table 4 and 5.

It is remarkable that in the case of $BaSO_4$ of larger particle size, the yield value attains its maximum at intermediate concentrations of the clay added, whereas it varies only in one direction with increasing amounts of clay in the case of $BaSO_4$ of smaller particle size. Such characteristic behaviour of the system in plastic flow may have a certain relation with what has been revealed in thixotropy and also in the packing of particles.

The existence of a definite yield value seems to be characteristic of all thixotropic systems. A system with a too low yield value might not be thixotropic. The mobility coefficient appears however to have no definite relationship with thixotropy, although a system with too low mobility would be unfavourable for the pronounced demonstration of the isothermal reversible sol-gel-transformation under the usual mechanical treatment.

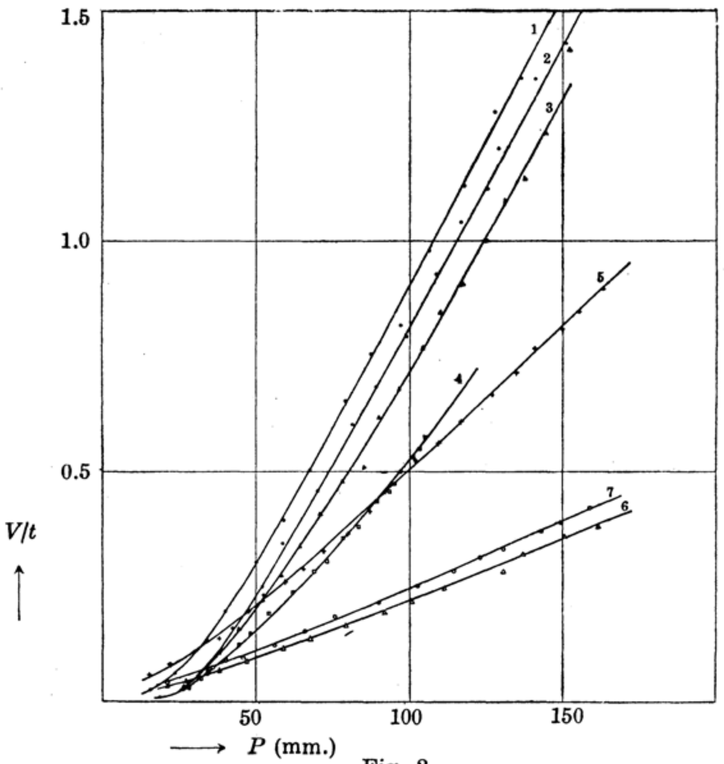
1.5
1.0
0.5
V/t
50
100
150
P (mm.)
1
2
3
4
5
6
7

Fig. 2.

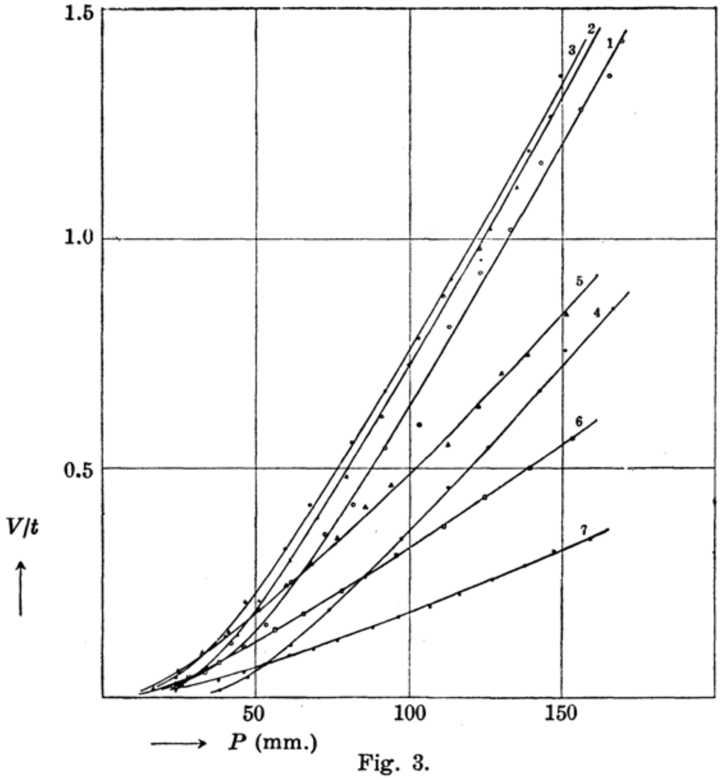
1.5
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Fig. 3.

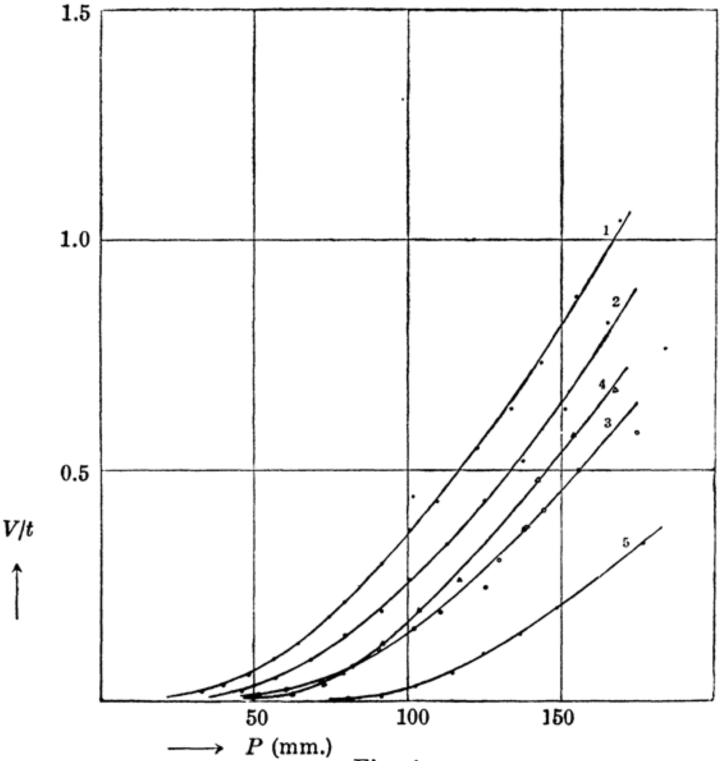

Fig. 4.

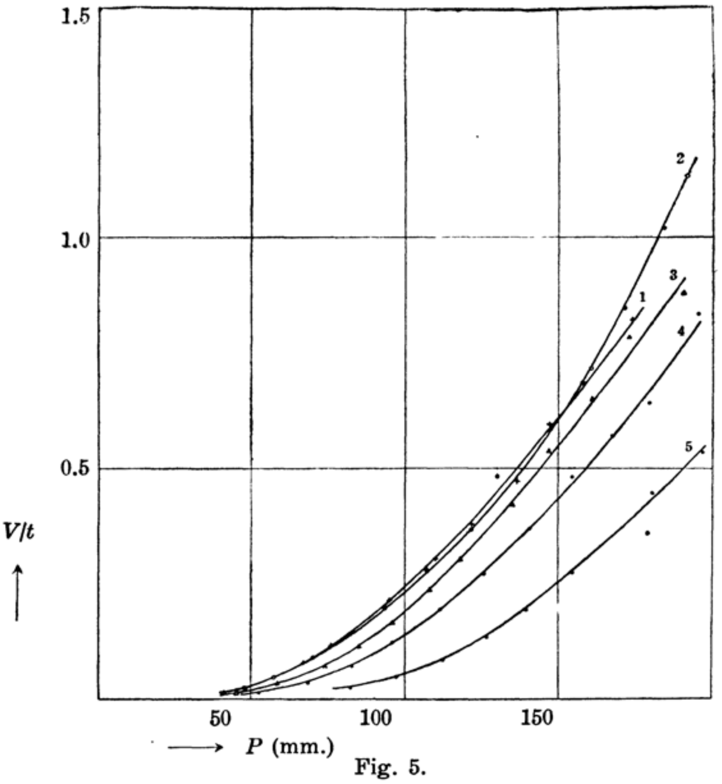

Fig. 5.

Table 4. With larger particles of $BaSO_4$.

Fig. No.	No. of curves in Fig.	Composition (%)		Yield value (dyne/cm^2.)	Mobility coef. (c. g. s.)
		$BaSO_4$	Clay		
2	1	17.0	0.00	1.72	10.58×10^7
	2	17.0	0.06	2.06	10.58
	3	16.9	0.61	2.54	10.36
	4	15.6	1.17	1.92	6.71
	5	15.4	2.22	1.17	5.25
	6	4.4	5.25	1.17	2.56
	7	0.0	5.48	1.10	2.74
3	1	17.00	0.00	2.81	9.00
	2	17.00	0.06	2.47	9.36
	3	17.00	0.19	2.40	9.75
	4	16.66	0.66	3.29	5.83
	5	16.45	1.22	1.65	5.43
	6	16.35	2.33	1.72	3.72
	7	15.95	3.37	2.06	2.39

Table 5. With smaller particles of $BaSO_4$.

Fig. No.	No. of curves in Fig.	Composition (%)		Yield value (dyne/cm^2.)	Mobility coef. (c. g. s.)
		$BaSO_4$	Clay		
4	1	17.00	0.00	4.94	8.66×10^7
	2	17.00	0.06	5.76	8.19
	3	17.00	1.13	6.17	6.03
	4	16.30	2.38	7.27	4.01
5	1	12.00	0.00	5.83	7.89
	2	12.00	0.03	6.31	8.83
	3	11.96	0.30	6.45	8.19
	4	11.92	0.60	6.65	6.95
	5	11.87	1.20	7.68	5.53

The values of the mobility coefficient obtained in the above are not quite certain owing to the narrow range of the pressure applied, nevertheless they show a general tendency to decrease with the increasing amount of the added clay.

V. Concerning the mechanism, how non-thixotropic $BaSO_4$-suspensions become thixotropic on adding the sodium-clay, it is not easy to give a conclusive explanation. The influence of electric charges of particles may be put aside, since both particles of $BaSO_4$ and of clay are equally negatively charged, which was demonstrated by the cataphoretic measurement under an ultramicroscope.

In non-thixotropic suspensions of $BaSO_4$, particles may be more or less independent of each other and they incline to settle in closer packing, whilst their independence will be lost when the clay is added, since the latter, adsorbed on the surface of $BaSO_4$-particles, will make the particles adhere to each other and thus facilitate the formation of a three dimensional net work in the whole system which favours thixotropy.(12)

Summary

(1) Non-thixotropic suspensions of $BaSO_4$ become thixotropic on adding certain amounts of a sodium-clay formed from a natural hydrogen-clay.

(2) The plasticity of the suspensions of $BaSO_4$ increases when the sodium-clay is added.

(3) The correlation among thixotropy, loose packing of particles (large volume of sedimentation), and isothermal plasticity, which is now generally accepted, is evident also in systems under investigation.

(4) A characteristic influence of the particle size of $BaSO_4$ on thixotropy and plasticity of the systems is mentioned.

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(12) B. Tamamushi, this Bulletin, **13** (1938), 234.