

subjected to the usual computational methods which permit estimation of rate constants.

The authors hope to show more fully in future studies how knowledge acquired from *in vitro* transfer systems can be applied to better understanding of the absorption, distribution, and excretion profiles of drugs studied *in vivo*. This should be possible even though *in vivo* profiles are complicated by the interposition of metabolizing machinery of the cells, extra drug compartments in the body, and excretion apparatus.

Also of much interest is the use of the *in vitro* model to evaluate the effects of placing additives in the various liquid phases or of altering the physical properties of a drug through functional group modifications.

#### REFERENCES

- (1) Doluisio, J. T., and Swintosky, J. V., *J. Pharm. Sci.*, **53**, 597 (1964).
- (2) Shore, P. A., Brodie, B. B., and Hogben, C. A. M., *J. Pharmacol. Exptl. Therap.*, **119**, 361 (1957).

## Rheology of Concentrated Dicalcium Phosphate Suspensions

By JOHN E. BUJAKE, JR.

The flow properties of concentrated (30–42 per cent by volume) dicalcium phosphate dihydrate (DCP) paste suspensions and model systems have been determined over a shear rate range of 0.045 to 6200  $\text{sec}^{-1}$  using concentric cylinder, cone-plate, and capillary extrusion viscometers at 25°. Apparent shear rates were corrected for non-Newtonian flow which gave optimum agreement of the data from the three instruments. Shear stress–shear rate data fitted the empirical power-law equation,  $\tau = K\dot{\gamma}^n$ , over most regions of the above shear rate range. Flow indices ( $n$ ) of 0.23–0.55 indicated appreciable shear thinning and suggested significant particle–particle interaction in these suspensions which are similar to consumer toothpastes. The greatest structural effects and non-Newtonian behavior were observed at low shear rates. Flow characteristics of the paste suspensions were comparable to those of a simple DCP–water model system. The effect of electrolytes on the viscosity of the DCP–water system was correlated with sedimentation volume data. The existence of a DCP network structure and reversible time-dependent bonds is postulated.

THE RHEOLOGICAL properties of concentrated paste systems are interesting from the viewpoint of both fundamental and applied research. Work reported in the literature on the quantitative characterization of the flow of highly concentrated suspensions has been somewhat limited. The Goodeve and Williamson equations have been applied with some success to suspensions at limiting high shear rates (1–4). Metzner has examined the flow of concentrated shear thickening suspensions and summarized some of the earlier work (5). Concentrated quartz powder suspensions have been studied by a number of workers (6). A review of some basic concepts of suspension formulation has also been presented (7).

It seemed that additional quantitative data on the flow properties of concentrated suspensions over a wide range of shear conditions would be of use in characterizing, controlling, and

predicting the behavior of suspensions under processing and use conditions. Such information would be particularly useful in gaining an understanding of flow in toothpaste and other similar systems.

Rheological investigations are basically concerned with the determination of the relationship between shear stress and shear rate. For Newtonian materials with their constant viscosity, this is relatively simple. However, concentrated suspensions have non-Newtonian and often time-dependent flow characteristics which necessitate a study over a wide range of shear rates under well-defined conditions. Low shear rates are particularly useful in structural studies. Shear stresses and shear rates must be calculated at an identical point in the system, *e.g.*, at the wall, and shear rates must be corrected for non-Newtonian behavior to obtain actual rates of shear.

In this work the non-Newtonian flow characteristics of some concentrated dicalcium phosphate dihydrate (DCP) paste suspensions and model systems have been examined using concentric cylinder, cone-plate, and capillary ex-

Received June 8, 1965, from the Research Center, Lever Brothers Co., Edgewater, N. J.

Accepted for publication August 24, 1965.

The author thanks Dr. E. D. Goddard, Mr. J. P. Anderson, and the Toilet Goods Section, Lever Brothers Co., for their assistance.

trusion viscometers to cover a wide shear rate range. Low shear was of particular interest, and shear rates at the wall were corrected for non-Newtonian deviations. The paste suspensions used were similar to commercial toothpastes, and the model systems were simply DCP in water with glycerin added in some experiments. The effect of varying the DCP particle size and concentration, and the effect of additives on the rheological and sedimentation behavior have been investigated.

### THEORY

A large number of equations have been suggested to describe viscous non-Newtonian flow. Of these the empirical two-parameter power-law equation is by far the most useful and widely applicable (8). It is given by

$$\tau = K\dot{\gamma}^n \quad (\text{Eq. 1})$$

where  $\tau$  is shear stress,  $\dot{\gamma}$  is the shear rate,  $n$  the flow index, and  $K$  the consistency index. The flow index (dimensionless) is a measure of the deviation from Newtonian behavior ( $n = 1$ );  $n < 1$  indicates shear thinning (pseudoplastic) behavior;  $n > 1$ , shear thickening (dilatant) behavior. The consistency index (dynes/cm.<sup>2</sup>) is a measure of consistency and is equivalent to an apparent viscosity (poises) at a shear rate of 1 sec.<sup>-1</sup>. With systems possessing a yield value ( $\tau_y$ ), the measured shear stress ( $\tau_m$ ) must be reduced by this amount, *i.e.*,  $\tau = \tau_m - \tau_y$ , to determine the flow and consistency indices.

The calibration of concentric cylinder viscometers is usually based on Newtonian assumptions, and shear rates thus determined are not valid for non-Newtonian flow. However, actual shear rates can be rigorously determined. It has been shown (9), assuming no slippage, that the shear rate at the surface of a rotating bob is given by

$$\dot{\gamma} = 4\pi N / (1 - S^{-2}) \left\{ 1 + K_1 \left( \frac{1}{n^n} - 1 \right) + K_2 \left[ \left( \frac{1}{n^n} - 1 \right)^2 + d \left( \frac{1}{n^n} - 1 \right) / d \log M \right] \right\} \quad (\text{Eq. 2})$$

where

$$\begin{aligned} K_1 &= (S^2 - 1) [1 + (2/3) \ln S] / 2S^2 \\ K_2 &= (S^2 - 1) (\ln S) / 6S^2 \\ S &= R_0 / R_i \\ n^n &= d \log M / d \log N \end{aligned}$$

$R_0$  and  $R_i$  are the radii of the outer cylinder (cup) and inner cylinder (bob), respectively, and  $S$ , the cup-bob ratio, is less than 1.2.  $N$  is the rotational speed and  $M$  the torque. If the fluid obeys the power-law equation, the  $d[(1/n^n) - 1]$  term in Eq. 2 is eliminated.

In the cone-plate viscometer, the fluid is sheared in a narrow gap between a rotating cone and a fixed plate. The shear rate is uniform throughout the gap and can be obtained directly from

$$\dot{\gamma} = 2\pi N / \alpha \quad (\text{Eq. 3})$$

where  $\alpha$  is the angle between the cone and plate which is usually less than 1°.

In a capillary tube of radius,  $R$ , it has been shown (10, 11) that the actual rate of shear at the wall for a non-Newtonian fluid is given by

$$\dot{\gamma}_R = 3 D_R / 4 + \tau_R (d D_R / d \tau_R) / 4 \quad (\text{Eq. 4})$$

where  $D_R = 4Q / \pi R^3$  ( $Q$  is the volumetric flow rate) and  $\tau_R$  the shear stress at the wall.

Then

$$\dot{\gamma}_R = (b + 3) D_R / 4 \quad (\text{Eq. 5})$$

where  $b = d \log D_R / d \log \tau_R$  and is obtained from a plot of  $\log D_R$  versus  $\log \tau_R$ .

Thus, actual shear rates can be obtained from concentric cylinder, cone-plate, and capillary viscometer data.

### EXPERIMENTAL

The flow characteristics of some concentrated toothpaste-like suspensions and simple DCP-water suspensions were measured using concentric cylinder, cone-plate, and capillary extrusion viscometers at 25°. The suspensions used (pastes *A-F*) were similar to typical consumer dicalcium phosphate dihydrate toothpastes which usually contain approximately 30–37% by volume DCP, CaHPO<sub>4</sub> · 2H<sub>2</sub>O, 17–34% by volume sorbitol and/or glycerin, and about 30% by volume water with the remainder consisting of surfactant, gum, sweetener, and flavor (12, 13). Other polishing agents, such as chalk, insoluble sodium metaphosphate, and tricalcium phosphate, are used in toothpastes, but this study was limited to DCP. Measurements were also made on simple DCP-water model systems in attempting to simulate toothpaste flow. The simple systems consisted of 32.5–42% by volume DCP in water; glycerin was added to some of the systems to minimize settling. The DCP used in these experiments had a mean particle diameter of 12  $\mu$  and a standard deviation of 2.1 and was supplied by the Monsanto Co.

Concentric cylinder and cone-plate shear stress-shear rate data were taken using the Haake Rotovisco Viscometer (Brinkmann Instruments, Inc., Great Neck, N. Y.). In these experiments the interchangeable concentric cylinders covered a shear rate range of 0.045–39 sec.<sup>-1</sup> and the cone-plate attachment 65–388 sec.<sup>-1</sup>. The Haake outer cup is fixed, and the bob is driven through a torque-measuring spring. The cup and bobs used had radius ratios of 1.05 and 1.14, and those used on toothpastes had 0.2 mm. vertical ridges to lessen slippage at the walls. A 28-mm. diameter cone with an angle of 0.5° was used with the cone-plate attachment. The rotational data were time-dependent; hence, a specific measuring procedure had to be used. Successive torque readings were taken at increasing, then decreasing, shear rates on the same paste sample in the lower shear region. At shear rates greater than 30 sec.<sup>-1</sup>, paste samples were sheared at one speed and then discarded. At any given shear rate, torque readings were taken as a function of time until an equilibrium reading was obtained; this took up to 5 min. at the lower shear rates. At very high shear rates the torque would decrease slightly with time after going

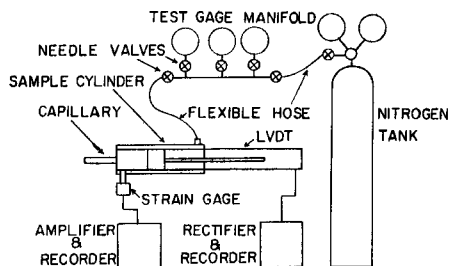


Fig. 1.—High-pressure gas-driven capillary extrusion viscometer.

through a maximum; this maximum value was noted and used in the shear stress calculations.

The capillary data were taken using a high pressure gas-driven capillary extrusion viscometer (Fig. 1) (14). The sample cylinder, 4.4-cm. i.d., 40-cm. length, had a highly polished stainless steel piston and was fitted with two threaded end caps and encased in a water jacket for thermostating. Interchangeable stainless steel capillaries were threaded in one end; a Quick coupler and high-pressure hose connected the other end cap to a gauge manifold and compressed nitrogen tank. In these experiments a 1.14-mm. radius capillary with a length-to-radius ratio of 200 and a  $90^\circ$  inlet angle was used. The pressure was monitored by the gauge manifold, and the flow rate determined by collecting extruded samples of known density for given time periods and weighing. A linear variable differential transformer (LVDT) was also used for flow measurement. Movement of the piston which was connected to the LVDT core produced a voltage which was directly related to the flow rate. Pressure measurements were also made using a Dynisco strain gauge screwed into the end cap near the capillary.

DCP sedimentation volumes were measured at  $25^\circ$  using 25-ml. glass-stoppered graduated cylinders. The suspensions contained 10 Gm. of DCP and 20 ml. of distilled water plus varying amounts of electrolytes and other additives. They were shaken for 1 min. to disperse the DCP and then allowed to settle. The sedimentation volume usually reached equilibrium after standing about 24 hr.

## RESULTS

**Flow Characteristics.**—The shear stress was measured as a function of shear rate with the concentric cylinder viscometer for pastes A and B containing 30 and 37% by volume DCP, respectively. The data were corrected to give actual shear rates at the wall (Eq. 2). A shear rate range of 0.045 to  $7.24 \text{ sec.}^{-1}$  was covered with a 1.84-cm. radius bob with  $S = 1.14$  (Fig. 2); and a range of 4 to  $39 \text{ sec.}^{-1}$  with a 1.01-cm. radius bob with  $S = 1.14$  (Fig. 3). The shear stress–shear rate curves indicated shear thinning characteristics. Apparent viscosities of 21,600 to 154 and 10,500 to 166 poises were obtained for pastes A and B, respectively. The characteristics of these pastes were also time-dependent; a thixotropic breakdown (hysteresis effect) was observed as indicated by the dashed curves (Fig. 2).

The shear stress–shear rate data for pastes A and

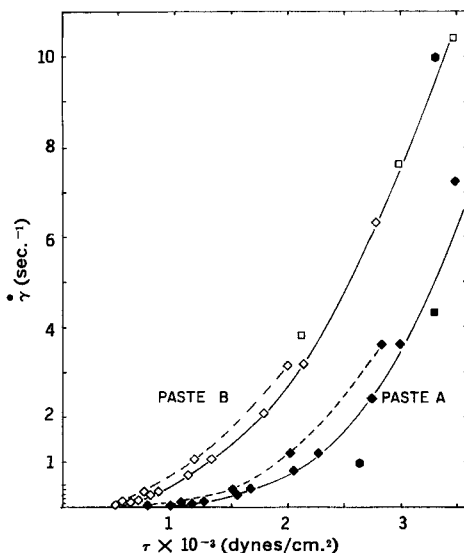


Fig. 2.—Shear stress vs. shear rate for paste A (30% DCP by volume) and paste B (37% DCP by volume) using the concentric cylinder viscometer ( $S = 1.14$ ) at  $25^\circ\text{C}$ . Paste A ( $\blacklozenge$ ) and paste B ( $\blacklozenge$ ) using a 1.84-cm. rad. bob. Paste A ( $\blacksquare$ ) and paste B ( $\blacksquare$ ) using a 1.01-cm. rad. bob. Paste A ( $\bullet$ ) using Weissenberg rheogoniometer.

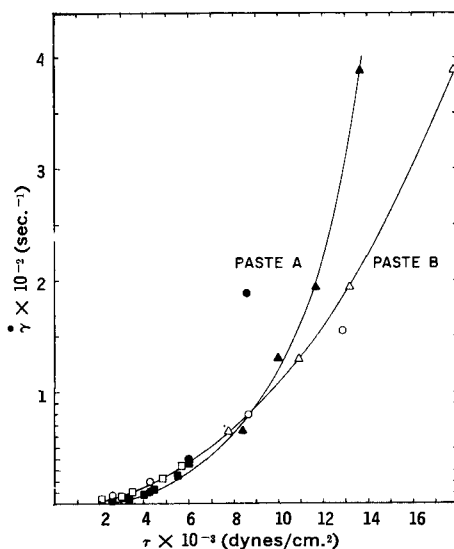


Fig. 3.—Shear stress vs. shear rate for paste A (30% DCP by volume) and paste B (37% DCP by volume) using concentric cylinder ( $S = 1.14$ ), cone-plate, and capillary extrusion viscometers at  $25^\circ\text{C}$ . Paste A ( $\blacksquare$ ) and paste B ( $\square$ ) using a 1.01-cm. rad. bob. Paste A ( $\blacktriangle$ ) and paste B ( $\triangle$ ) using  $0.5^\circ$  cone. Paste A ( $\bullet$ ) and paste B ( $\circ$ ) using the capillary viscometer.

B were also taken with the Haake cone-plate attachment over a shear rate range of 65 to  $388 \text{ sec.}^{-1}$  (Fig. 3). Shear thinning characteristics were observed. Apparent viscosities of 130 to 35 and 120 to 46 poises were obtained for pastes A and B, respectively.

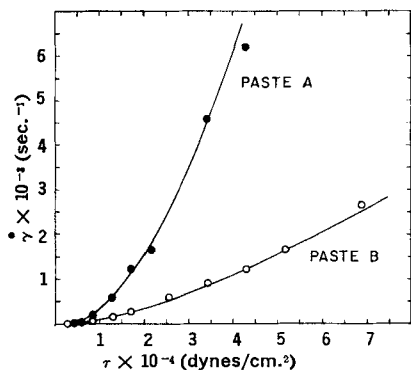


Fig. 4.—Shear stress vs. shear rate for paste *A* (30% DCP by volume) and paste *B* (37% DCP by volume) using the capillary extrusion viscometer at 25°C. Paste *A* (●) and paste *B* (○) using a 1.14-mm. radius capillary.

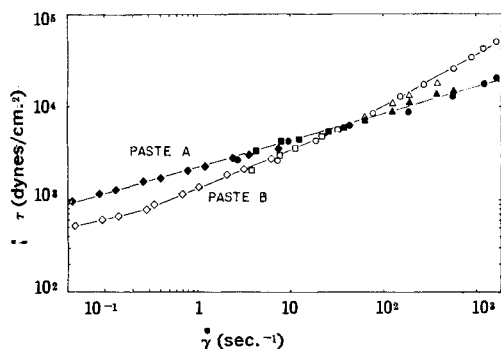


Fig. 5.—Shear stress vs. shear rate for paste *A* (solid symbols) and paste *B* (open symbols) using concentric cylinder (◆, ◇, ■, □), cone-plate (▲, △), and capillary extrusion viscometers (●, ○) at 25°C.

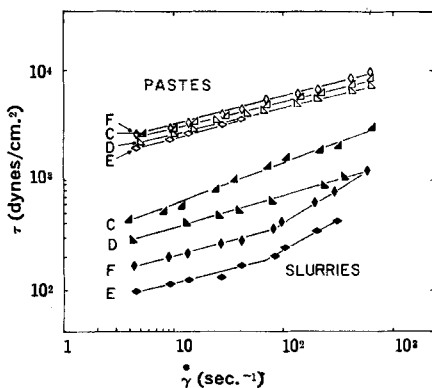


Fig. 6.—Shear stress vs. shear rate for pastes *C* and *D*, and *E* and *F*, 35% by volume DCP with 7.8 and 12  $\mu$  DCP, and 0.8 and 1.5% tetrasodium pyrophosphate, respectively, and for slurries *C* and *D* and *E* and *F*, 42% by volume DCP in water using the respective DCP samples.

A shear rate range of 2.6 to 6200  $\text{sec.}^{-1}$  was covered with the capillary extrusion viscometer using a 1.14 mm. radius capillary and pressures of 15 to 400  $\text{lb./in.}^2$  (Fig. 4). Apparent viscosities of 985 to 7.0 and 358 to 26 poises were obtained for pastes *A* and *B*, respectively. Shear thinning flow behavior was again indicated with the effect being greater in paste *A*.

**Power-Law Equation.**—The shear stress–shear rate data for pastes *A* and *B* fitted the power-law equation (Fig. 5). The fit was particularly good considering the different instruments used and the wide range of shear rates covered. Paste *A* had a flow index of 0.28, indicating appreciable shear-thinning characteristics. Paste *B* fitted the power-law in three shear regions. The flow index increased with increasing shear rate; it was 0.23 at 0.045–0.3  $\text{sec.}^{-1}$ , 0.41 and 0.3–50  $\text{sec.}^{-1}$ , and 0.55 at 50–1000  $\text{sec.}^{-1}$ . This implies less non-Newtonian behavior at the higher shear rates, *i.e.*, the apparent viscosity is decreasing less rapidly in this region. The paste structure caused by particle–particle linkages is broken down to a greater extent by the high shear rates giving a more Newtonian behavior. This indicates the desirability of working at relatively low shear rates in attempting to assess structural effects.

For paste *A*,  $K$  was 2130  $\text{dynes/cm.}^2$ ; for paste *B*,  $K$  was 1320  $\text{dynes/cm.}^2$ . Thus, paste *A* had an apparent viscosity greater than paste *B* at low shear rates. The effect of paste *A*'s lower solids content was overshadowed by a liquid phase viscosity, which was higher by a factor of about 2 (78.8 versus 39.3 poises at 10  $\text{sec.}^{-1}$ ).

**Particle Size and Pyrophosphate Variations.**—The effect of varying the DCP particle size and tetrasodium pyrophosphate concentration on the flow behavior was also determined. The pyrophosphate effect is of particular interest in DCP suspensions since even small amounts (<1%) of it can cause gelling of the suspension. Concentric cylinder and cone-plate measurements were made on pastes *C* and *D*, 35% by volume DCP, identical except for having 7.8 and 12.0  $\mu$  mean DCP particle diameters, respectively, and on pastes *E* and *F*, 35% by volume DCP, identical except for having 0.8 and 1.5% tetrasodium pyrophosphate added, respectively. The DCP sample used in *C* and *D* was different from that used in *E* and *F*. Data were also taken on simple model systems consisting of 42% by volume DCP in water slurries made with the above DCP samples using the concentric cylinder viscometer ( $S = 1.05$ ). Log-log plots of the paste and model system shear stress–shear rate data are given in Fig. 6. The apparent viscosity of the slurries was more sensitive to the particle size and phosphate variations than that of the pastes. Pastes *C*, *D*, *E*, and *F* had flow indices of 0.25, 0.25, 0.27, and 0.26, respectively, while slurries *C*, *D*, *E*, and *F* had flow indices (3–80  $\text{sec.}^{-1}$ ) of 0.36, 0.29, 0.27, and 0.27, respectively. Slurries *E* and *F* had larger flow indices in the high shear region which indicated a possible DCP–pyrophosphate structural breakdown. Increasing the particle size decreased both the paste and slurry apparent viscosity. Increasing the pyrophosphate concentration increased both the paste and slurry apparent viscosity; however, the apparent viscosities of slurries *E* and *F* were lower than those

TABLE I.—EFFECT OF ADDITIVES ON VISCOSITY OF 32.5% DCP-30% GLYCERIN-37.5% WATER SYSTEM AND ON DCP-WATER SEDIMENTATION VOLUME AT 25°C.

Additive	Apparent Viscosity (poises) at 25 sec. <sup>-1</sup>	Sedimentation Vol. <sup>a</sup> (ml./10 Gm. DCP)
...	1.75	13.8
0.002 M Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	10.3	18.8
0.02 M C <sub>12</sub> H <sub>25</sub> SO <sub>4</sub> Na	0.94	12.2
0.1 M NaOH	0.94	12.0
0.1 M CaCl <sub>2</sub>	1.85	18.6
0.1 M NaCl	2.22	14.2
0.1 M MgSO <sub>4</sub>	2.46	...
0.1 M HCl	2.58	14.4
0.2% Viscarin	19.5	...

<sup>a</sup> The total DCP-solution volume (V<sub>0</sub>) was 24.0 ml.

of C and D due to differences in the two respective DCP samples used. The agreement in most cases of the paste and slurry flow indices in the low shear region implied that the pastes and slurries have similar flow behavior. Hence, the DCP-water model appears to be a good approximation of the toothpaste system.

**Effect of Additives on Viscosity and Sedimentation.**—The effect of various additives on the apparent viscosity (at 25 sec.<sup>-1</sup>) of a 32.5% by volume DCP-30% by volume glycerin-37.5% by volume water slurry and on DCP sedimentation volumes was determined. (Table I.) The sedimentation volume gives an indication of the number and strength of particle-particle interactions. Large sedimentation volumes suggest many strong particle-particle interactions and a tendency to flocculate. The particles stick on contact, forming a porous structure. The addition of sodium lauryl sulfate and sodium hydroxide caused a reduction in both apparent slurry viscosity and sedimentation volume, whereas the sodium pyrophosphate, calcium chloride, sodium chloride, magnesium sulfate, and hydrochloric acid increased both the viscosity and sedimentation volume. Thus, the data indicate a relationship between DCP slurry viscosity and the sedimentation volume, suggesting that particle-particle interactions play a significant role in the flow of these systems. Also increasing the liquid phase viscosity by the addition of 0.2% Viscarin gum increased the suspension viscosity.

## DISCUSSION

The shear thinning characteristics of these concentrated suspensions can be related to a shear alignment of the asymmetric plate-like DCP par-

ticles and to a deformation and disengagement of the DCP aggregates. The resistance to flow decreases as the DCP linkages are broken up by the increasing shear rates. There was no indication of Newtonian flow at the lower shear rates examined (<1 sec.<sup>-1</sup>) or shear thickening at the higher shear rates (>100 sec.<sup>-1</sup>), as suggested by Metzner (5) for concentrated suspensions. The lack of Newtonian flow at low shear rates supports the hypothesis of considerable particle-particle interaction in the DCP suspensions.

The time-dependent thixotropic effects can be ascribed to the existence of primary and secondary bonds (15, 16) between the DCP particles. Primary bonds are relatively strong irreversible bonds which when broken reform with difficulty. Secondary bonds are relatively weak and reversible; they break and reform easily over short periods of time. Data on the apparent viscosity of toothpastes before and after mixing indicated that pastes lost up to 65% of their original viscosity on shearing and recovered most of the lost viscosity on standing several days. This recovery suggests the presence of reversible secondary bonds in toothpaste, which break on shearing and reform on standing. A breakdown with time was also indicated in some of the concentric cylinder experiments (Fig. 2).

The flow behavior of the DCP pastes and water slurries suggests significant particle-particle interaction. Electron photomicrographs have indicated that the DCP particles used were irregularly shaped and plate-like with sharp edges (17), which would contribute to hydrodynamic interaction. Sedimentation data suggested that the negatively charged DCP particles may also have positively charged sites (edges) due to lattice defects or surface impurities which would lead to an electrostatic edge-face interaction and the formation of a structure. Van der Waals attraction is also undoubtedly present. It is hypothesized that the deflocculating effect of the added hydroxyl and surfactant ions in the DCP slurry is caused by the neutralization of positive sites on the particle and a reduction of the edge-face interaction. The flocculating tendency of the inorganic chlorides and sulfates might be related to a compression of the electrical double layer to the extent that the Van der Waals attraction predominated. It is further suggested that the pyrophosphate ions facilitate linking between DCP particles and the formation of a network structure. The breakdown of this structure would cause the flow indices of the DCP-pyrophosphate slurries to increase at the higher shear rates. The pyrophosphate could also act as a sequestering agent and alter the DCP surface potential.

TABLE II.—COMPARISON OF FLOW INDICES AND APPARENT VISCOSITIES OF DCP-WATER SLURRIES WITH LITERATURE DATA

Ref.	Solid Phase	Liquid Phase	Solid Vol. %	Particle Diam. (μ)	Flow Index	Shear Rates (sec. <sup>-1</sup> )	Apparent Viscosity (poises) at 100 sec. <sup>-1</sup>
(5)	TiO <sub>2</sub>	H <sub>2</sub> O	42	0.2-1	0.62	40-200	1.38
(3)	SiO <sub>2</sub>	DOP <sup>a</sup>	45	6	0.86	16-500	7.69
	XPS <sup>a</sup>	DOP	44	3	0.85	16-500	9.42
(6)	SiO <sub>2</sub>	H <sub>2</sub> O	43	2-20	1.07	140-650	.06
This work	DCP	H <sub>2</sub> O	42	12	0.25-0.36	4-540	2.3-14.7

<sup>a</sup> XPS, crosslinked polystyrene beads; DOP, dioctyl phthalate.

Flow indices and apparent viscosities calculated from data on 42–45% by volume suspensions reported by other workers are summarized in Table II. The flow indices of the DCP–water suspensions (Fig. 6) were significantly lower than those of the titanium dioxide, silica, and polystyrene suspensions. The DCP slurries also had higher apparent viscosities. This indicated that, even with their smaller surface areas in most cases, the DCP particles interacted to an appreciably greater extent. In view of the effect of electrolytes on slurry viscosity and sedimentation volume, this greater DCP interaction appeared to be mainly electrostatic in nature. The degree of DCP interaction was also dependent on surface area; slurries of 7.8  $\mu$  DCP had higher apparent viscosities than those made with 12  $\mu$  DCP (Fig. 6).

The existence of a true yield value (intercept on shear stress axis) in these suspensions is questioned. The shear stress–shear rate data are curvilinear (Figs. 2–4), particularly in the low shear areas, making any attempted extrapolation inaccurate. It is even conceivable that the curve intersects the origin. Data taken at shear rates lower than those used in this study might help clarify this point.

The uncorrected shear stresses ( $\tau_m$ ) gave the best fit and were used in the power-law plots (Figs. 5 and 6). Even the existence of a yield value of 800 dynes/cm.<sup>2</sup> would have only a slight effect on the flow indices; they would increase from 0.28 to 0.41 for paste A and from 0.41 to 0.54 for paste B. These indices are still considerably lower than those reported by other workers (Table II).

No evidence of plug flow was observed under our experimental conditions, giving further support to the absence of a yield value in these systems. Observation of the flow streamlines in the concentric cylinder gap (0.13 cm.) indicated that a velocity gradient existed across the entire gap, even at the lowest shear rate used (0.045 sec.<sup>-1</sup>). This was accomplished by following the movement of a thin line of carbon black placed on the paste across the top of the gap.

In concentrated pastes a movement of the suspended particles away from the walls can occur under the influence of a velocity gradient resulting in slippage. In these experiments, slippage was

eliminated by going to low shear rates (0.01–10 sec.<sup>-1</sup>) and using ribbed cups and bobs. The effect of low shear was indicated by the fact that data taken with smooth cups and bobs agreed with that taken with the ribbed elements to within 2% below 10 sec.<sup>-1</sup> and to within 5% in the 10–39 sec.<sup>-1</sup> range. The accuracy of the viscometer was 1–2%.

It was observed that shear rates above 30 sec.<sup>-1</sup> caused fine cracks to form in the paste surface between the cup and bob rims. This could be attributed to the presence of small air bubbles in the paste and/or normal stresses. The existence of normal stresses was suggested in some experiments in which there was movement of the paste into the hollow bottom of the bob. Several experiments using a Weissenberg rheogoniometer (Martin Sweets Co., Louisville, Ky.), a unique cone-plate instrument that measures both torsional and normal stresses simultaneously in rotation or oscillation, indicated normal stresses of about 1200 to 1600 dynes/cm.<sup>2</sup> over a shear rate range of 0.1 to 10 sec.<sup>-1</sup>. The swelling of the paste extrudate observed in the capillary experiments also suggested the presence of normal forces.

#### REFERENCES

- (1) Goodeve, C. F., *Trans. Faraday Soc.*, **35**, 342(1939).
- (2) Gillespie, T., *J. Colloid Sci.*, **15**, 219(1960).
- (3) Gillespie, T., and Wiley, R. M., *J. Phys. Chem.*, **66**, 1077(1962).
- (4) Higuchi, W. I., and Stehle, R. G., *J. Pharm. Sci.*, **54**, 265(1965).
- (5) Metzner, A. B., and Whitlock, M., *Trans. Soc. Rheol.*, **2**, 239(1958).
- (6) Greenberg, S. A., Jarnutowski, R., and Chang, T. N., *J. Colloid Sci.*, **20**, 20(1965).
- (7) Hiestand, E. N., *J. Pharm. Sci.*, **53**, 1(1964).
- (8) Metzner, A. B., in Streeter, V., ed., "Handbook of Fluid Dynamics," 1st ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1961, Sec. 7, p. 5.
- (9) Krieger, I. M., and Maron, S. H., *J. Appl. Phys.*, **25**, 72(1954).
- (10) Rabinowitsch, B., *Z. Physik. Chem.*, **A145**, 1(1929).
- (11) Van Wazer, J. R., et al., "Viscosity and Flow Measurement," Interscience Publishers, Inc., New York, N. Y., 1963, pp. 191–192.
- (12) Van Wazer, J. R., ed., "Phosphorous and Its Compounds," vol. 2, Interscience Publishers, Inc., New York, N. Y., 1961, pp. 1645–1646.
- (13) Gershon, S. D., Pokras, H. H., and Rider, T. H., in Sagarin, E., ed., "Cosmetics Science and Technology," Interscience Publishers, Inc., New York, N. Y., 1957, pp. 296–360.
- (14) Bujake, J. E., Jr., *Rev. Sci. Instrum.*, **36**, 1368(1965).
- (15) Tobolsky, A., and Byring, H., *J. Chem. Phys.*, **11**, 125(1943).
- (16) Van den Tempel, M., *J. Colloid Sci.*, **16**, 284(1961).
- (17) Rapisarda, A. A., unpublished data.