high turbulence a steady state dynamic equilibrium is present in the saturated solution. The mass flux from the sphere (dissolution) is equal to the mass flux to the sphere (crystallization). The material going to the sphere must crystallize on the surface by the growth of existing crystals and possibly by the formation of new crystals. Some crystals may grow larger than others; this makes the surface more irregular and less densely packed than before. These new, fine crystals could have difficulty in adhering to the surface in the highly turbulent stream. Hence these enlarged, existing crystals or the new crystals could easily be broken off and carried away in the main stream.

This mass transfer at zero driving force could also be due to physical attrition, where eddies tear off or wear away minute particles of the cast solid other than those actually dissolved by true mass transfer. If mass transfer due to this type of attrition is present, it should be an additive effect along with the true dissolution mass transfer. However, as discussed previously, this correction gives constant J_D values for a given solute (Table 3) but does not give the same values for all solutes. Hence attrition alone is probably not causing these differences. It should be noted that the mass transfer at zero driving force for benzoic acid increases with increasing

Reynolds numbers (Figure 7). Preliminary hardness tests made on the cast spheres indicated that 2-naphthol was the hardest material and benzoic acid the softest.

Further studies should be made in mass transfer from dissolving solids in turbulent fluids on the role of physical properties of the solute such as hardness, crystalline structure, and ability to crystallize.

NOTATION

 C_D = total drag coefficient for spheres.

= concentration of solute in saturated solution, g./cc.

= concentration of solute in saturated solution, g./liter.

 $C_{L'} = \text{concentration}$ of solution, g./liter.

 C_L = concentration of solute in solution, g./cc.

 $D_L = \text{molecular diffusivity, sq. cm./sec.}$

 D_{p} = diameter of sphere, cm.

 J_D = dimensionless number for mass transfer.

 $K_L = \text{mass transfer coefficient, g./(sq.}$ cm.)(sec.), g./cc.

 $N_A = \text{flux, g./(sq. cm.)(sec.)}$

 $N_{Re} = \text{Reynolds number} = D_p V \rho / \mu$

 $N_{Sc} = \text{Schmidt number} = \mu/\rho D_L$ V' = average velocity in pipe, cm./sec.

V = average velocity in annular area between pipe and sphere, cm./sec.

= viscosity, g./(sec.)(cm.)= density, g./cc.

LITERATURE CITED

- 1. Binder, R. C., "Advanced Fluid Dynamics and Fluid Machinery," p. 116, Prentice Hall, New York (1951).
- 2. Chilton, T. H., and A. P. Colburn, Ind. Eng. Chem., 26, 1183 (1934).
- 3. Dryden, C. E., D. A. Strang, and A. E. Withrow, Chem. Eng. Progr., 49, 191 (1953).
- Garner, F. H., and R. W. Grafton, Proc. Roy. Soc. (London), A224, 64 (1954).
- 5. Garner, F. H., and R. D. Suckling, A.I.Ch.E. Journal, 4, 114 (1958).
 6. Goldstein, Sydney, "Modern Measure-
- ments in Fluid Mechanics," p. 16, 491, Clarenden Press, Oxford (1938).
- 7. Linton, W. H., and T. K. Sherwood, Chem. Eng. Progr., 46, 258 (1950).
- McCune, L. K., and R. H. Wilhelm, Ind. Eng. Chem., 41, 1124 (1949).
- 9. Seidell, Atherton, "Solubilities of Organic Compounds," 3 ed., Vol. II, D. Van Nostrand, New York (1941).

 10. _____, and W. F. Linke, "Solubilities of Inorganic and Organic Compounds," Supplement to 3 ed., D. Van Nostrand, New York (1952).
- 11. Wilke, C. R., and Pin Chang, A.I.Ch.E. Journal, 1, 264 (1955).

Manuscript received August 27, 1958; revision received November 6, 1958; paper accepted November 6,

Turbulent Flow of Pseudoplastic Polymer Solutions in Straight Cylindrical Tubes

ROBERT G. SHAVER and EDWARD W. MERRILL

Massachusetts Institute of Technology, Cambridge, Massachusetts

Experimental studies are described concerning the fluid dynamics, particularly in the turbulent region, of dilute solutions of free-draining, nonassociating, linear polymers; sodium carboxymethylcellulose, ammonium alginate, polyisobutylene, and carboxypolymethylene, all of which are pseudoplastic. These solutions were run in laminar, transition, and turbulent flow in a pipeline flow apparatus designed to permit measurement of dynamic pressure drop and impact pressure by radial traverse.

Photographic studies with dye injection used at the tube wall and at the tube center showed that turbulent flow of these pseudoplastic fluids has the following characteristics compared to Newtonian fluids: poor over-all radial mixing, thicker nonturbulent layer at the wall, and decreased rate of formation of horseshoe vortices at the wall.

A pseudoplastic fluid generally is defined as one which has a viscosity that decreases reversibly with increasing shear rate, which has no yield value, and which undergoes no time-dependent change in consistency. Dilute solutions of freedraining, essentially nonassociating polymers represent one class of pseudoplastic fluid, perhaps the most common. With

Robert G. Shaver is with the Dewey and Almy Chemical Company, Cambridge, Massachusetts.

one exception* the experimental studies described herein were concerned exclusively with this class of pseudoplastic

The shear-rate-shear-stress relationships of these polymer solutions can be correlated in general over a rather broad range of shear rates by the power-law model $\tau = b(du/dy)^s$ (4, 8, 9, 10).

Since the shear stress in a fluid flowing steadily in a straight cylindrical tube varies linearly from zero at the axis to a maximum $\tau_w = (\Delta P/L) \cdot (R/2)$ at the wall, the flow equations for pseudoplastics in laminar flow can be derived by assuming the power-law rheology (3, 8). The resultant expressions are friction factor:

$$f = [16b/(D^*V^{2^{-s}}\rho)] \cdot [2(3+1/s)]^s/8$$
 (1)

^{*}The exception is polyvinyl alcohol (Elvanol), which shows a strong tendency to associate by hydrogen bonding in dilute solution. The associating tendency in the Elvanol solution studies was so great that opalescence was noted, suggesting micelle formation. The results are irrelevant, since the solution behaved as a Newtonian fluid.

Poiseuille's law:

$$Q = \pi (\Delta p / 2Lb)^{1/s} \cdot R^{3+1/s} \cdot \pi / (3 + 1/s)$$
 (2)

Velocity distribution:

$$u/u_{max.} = 1 - (1 - y/R)^{1/s+1}$$
 (3)

Equation (1) is consequently analogous to the relation for a Newtonian fluid:

$$f = 16/N_{Re} \tag{4}$$

when the pseudoplastic Reynolds number is defined as $(D^{s}V^{2-s}\rho/b) \cdot 8[2(3+1/s)]^{-s}$. Previous work (4, 8, 9, 18) has shown that these expressions for the Fanning friction factor and Poiseuille's law agree with experimental data if the fluid can be characterized by a single value of s over most of the range of shear stress encountered in flow (say, from $0.25\tau_w$ to τ_w). However data for well-defined turbulent flow of pseudoplastic fluids have heretofore been lacking. Therefore it was the objective of this study to examine the nature of turbulent flow for one class of pseudoplastic fluids. For this purpose dilute solutions of sodium carboxymethylcellulose, ammonium alginate, carboxypolymethylene, and polyisobutylene were prepared, the rheology of which is unequivocally pseudoplastic according to

			Note A		Note B	
		Temperature,				2 sec1
\mathbf{Run}	\mathbf{Fluid}	°F.	b	s	b	s
1C-F, A1-7	Water	72 to 73	0.0095	1.00	Same	
B1	1.5% Elvanol	71	0.0254	1.00	Same	
2A, C1	0.18%, CMC-70	72	2.09	0.60	0.38	0.86
3A-B, D1	0.30% CMC-70	71	4.80	0.54		
3C, D2-4	0.30% CMC-70, degraded*	71	1.27	0.66		
3D	0.30% CMC-70, degraded*	71	1.05	0.68		
3E-F, D5-7	0.30% CMC-70, degraded*	71	0.505	0.75		
3H, D8	0.30% CMC-70, degraded*	71	0.120	0.85		
4A-C, E1-3	0.41% CMC-70	71	9.20	0.53	1.18	0.83
4D-E, E4-6	0.41% CMC-70, degraded*	71	4.01	0.59		
	0.41% CMC-70, degraded*	92	3.03	0.62		
5A-B, F1-5	0.35% CMC-70	71	2.22	0.64		
G1	1.0% alginate	76	3.47	0.70		
H1	0.83% alginate	74	2.15	0.73	1.20	0.78
6B-D, I1-4	0.62% alginate	72	1.38	0.74		
J1-2	0.46% alginate	72	0.422	0.82	0.39	0.86
K1-3	0.10% alginate	71	0.0302	0.95		
$\mathbf{L}1$	0.20% alginate	71	0.119	0.84		
M1	0.30% alginate	71	0.189	0.83		
8A-B, N1-4	0.50% CMC-70S	74	7.05	0.54		
9A-B, O1	0.25% CMC-70S	74	2.22	0.61	0.25	1.00
P1	0.12% Carbopol 934	70	0.710	0.78	4.9	0.85
Q2-3	0.52% Vistanex	77	0.644	0.71	0.095	0.98
m Q4	0.52% Vistanex, shear					
•	degraded	77	0.133	0.82		
R1	Impure cyclohexane	77	0.0108	1.00	San	ne

^{*}Upon aging in the storage vessel, presumably by enzymatic attack. Viscometric tests just before and just after the pipe-line runs showed identical values of b and s, thus eliminating degradation by shear as the cause

Note B: Data from modified Brookfield Synchrolectric viscometer. These values of s not applicable to transition and turbulent flow correlations.

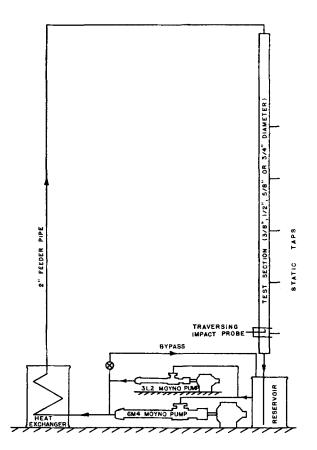


Fig. 1. Schematic diagram of the pipe-line flow apparatus.

the foregoing definition. The solutions were made highly dilute for two reasons, (1) to achieve a sufficiently high level of fluidity, so that turbulent flow might be achieved without inordinately large pumping requirements and (2) to avoid the complications of gel structure, concomitant false yield value, and gross elasticity that all these polymers exhibit in solutions of higher concentration. That gross elasticity in the solutions studied was totally absent cannot be proved rigorously, but qualitative observations that these solutions without exception poured like water without any trace of stringiness strongly suggest that gross elasticity was absent. That gel structure and yield value were absent is quantitatively substantiated by the viscometric data which show curves going to the origin (0, 0) at low shear rates and the total absence of time dependence in the curves over the entire range of shear rates.

EXPERIMENTAL APPARATUS AND PROCEDURE

The polymers used in this study were sodium carboxymethylcellulose, CMC-70 and CMC-70S of the Hercules Powder Co.; ammonium alginate, Kelco Co. Super-loid; carboxypolymethylene, Goodrich Chemical Co. Carbopol 934; and polyisobutylene, Enjay Co. Vistanex B-100. These commercial polymers were used as received

Note A: Data from Merrill-Brookfield viscometer. These values of s used in transition and turbulent flow correlations.

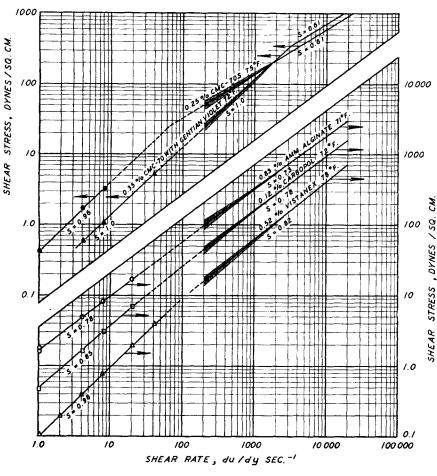


Fig. 2.

from the manufacturers and dispersed into solution according to the manufacturers' recommendations. With the exception of the cyclohexane solutions of the Vistanex all were aqueous solutions.

All these polymers in dilute solution are

Fig. 3. Friction factor f vs. Reynolds

$$\frac{D^{s}V^{2-s}\rho}{b}\cdot 8\left[\frac{1}{2(3+1/s)}\right]^{s}$$

For various values of s, in laminar, transition, and turbulent flow

Run, Fluid Table 1		Run, luid Table 1	
A 1-7	13	G 1	
R 1	14	E 7	
L 1	15	E 5,6	
P 1	16	E 1	
Q 2-3	17	D 8	
\bar{F} 1-5	18	J 1-2	
C 1	19	Q 4	
N 1-4	20	$ar{H}$ 1	
K 1-3	21	D 2-4	
M 1	22	0 1	
D 5-7	23	E 4	
I 1-4	24	E 2,3	
	Run, Table 1 A 1-7 R 1 L 1 P 1 Q 2-3 F 1-5 C 1 N 1-4 K 1-3 M 1 D 5-7	Run, Table 1 Fluid A 1-7 13 R 1 14 L 1 15 P 1 16 Q 2-3 17 F 1-5 18 C 1 19 N 1-4 20 K 1-3 21 M 1 22 D 5-7 23	

Note: The curves f vs. N_{Re} at constant s are identical in the three sections of this figure and are thus drawn to accommodate the data.

believed to be essentially nonassociating, free-draining, and random coiling. Sodium

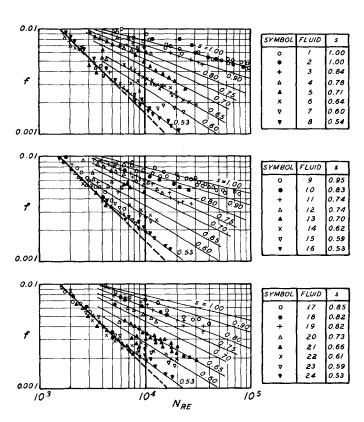
carboxymethylcellulose*, though having some degree of stiffness compared with the others, is nonetheless quite flexible by comparison with a truly rigid polysaccharide such as amylose in aqueous solution.

The rheological (shear-stress-shear-rate) curves were determined over a wide range that exceeded in all but one or two cases the maximum (wall) values achieved in the subsequent pipeline flow experiments, with the Merrill-Brookfield coaxial-cylinder viscometer (5, 7) in the range of 200 to 20,000 (sec.-1) (sec.) of shear rate and a Brookfield Synchrolectric viscometer modified with a coaxial-cylinder rotor and stator (2) in the range of 0.1 to 42 sec.-1. The salient feature of these two viscometers with respect to the fluids studied is the very small gap between rotor and stator relative to the diameter of the rotors. This permits one to achieve direct measurement of substantially point values of shear stress and corresponding shear rate.

The pipeline flow experimentation in this work was carried out in a recirculating system that could be fitted with smoothbore test sections varying in diameter from $\frac{3}{6}$ in I.D. to $\frac{3}{4}$ in I.D. These test sections were fitted so that frictional pressure drop might be measured at various locations along the tubes and so that impact pressure might be measured as a function of radial position. This system was pumped by either of two Moyno pumps in parallel which provided essentially pulse-free, positive-displacement pumping up to 40 gal./min. Figure 1 is a schematic diagram of this apparatus.

The impact-pressure traversing mechanism was designed and built to include positive, continuous location of the probe in the tube by means of a micrometer mechanism; detection of wall position by means of an electrical circuit and an insu-

^{*}As explained in connection with Table 1, the rheology of sodium carboxymethylcellulose under low rates of shear, irrelevant to this study, is unusual.



lated probe; great structural rigidity in the probe, together with small diameter of the probe tip, accomplished by the nesting of sections of successively smaller-diameter hypodermic tubing, the tip being 0.025 in. O.D. and 0.013 in. I.D.; and minimum disturbance of flow by use of a simple impact tube and a wall tap.

Dye-injection experiments (to be described) consisted of injecting a thin stream of pigmented test fluid at one of several radial positions in a ¾ in. I.D. Lucite tube, the dye stream being observed visually and photographically by means of a short-duration flash. The two main points of injection used were at the axis of, and at the entrance of, the Lucite test section, where an 0.025 in. O.D. hypodermic needle was aligned with the tube axis 185 diam, upstream of the point of observation, and through a wall tap located at, or slightly above, the point of observation. The injection was controlled by a hypodermic syringe compressed by a crank and screw-thread mechanism.

The purposes of these two injection positions were to observe the effect of turbulence on the fluid in the core of the tube and at the boundary of the tube.

RESULTS

Rheological Characterization

The power-law expression $\tau = b(du/dy)$. evidently is inapplicable at a shear rate du/dy = 0, because for all values of s < 1.0 it predicts an infinite value of the slope $d\tau/d$ (du/dy), contrary to experimental observation on these fluids. Therefore it is reasonable to expect that if the power-law expersion is applied over different ranges of shear rate, the values of b and s may have to be adjusted to correlate the data in each range, with $s \to 1.0$ as $(du/dy) \to 0$. In the case of each one of the solutions studied, as listed in Table 1, it was found that over the range of shear rate of 200 to 20,000 \sec^{-1} a single value of b and a single value of s could be used to correlate the shearstress-shear-rate data obtained on the Merrill viscometer (lower limit of readability 200 sec-1) and that over the range of 0.1 to 42 sec⁻¹, in which data were obtained from the modified Brookfield Synchrolectric viscometer, the shearstress-shear-rate relation could be fitted by a single value of s and single value of b. The value of s in the lower shear-rate range was invariably found to be higher than in the higher shear-rate range. substantially so for CMC and polyisobutylene solutions and only slightly so for alginate solutions. Figure 2 shows typical viscometric data as obtained on the Brookfield Synchrolectric viscometer (point readings of shear stress and shear rate) and on the Merrill-Brookfield viscometer. As the latter gives continuous curves on an x - y recorder, no points are shown for this high-range data. Instead the average of ten or more recorder traces is shown as the solid line, with the maximum and minimum variation shown as the shaded zone. It will be

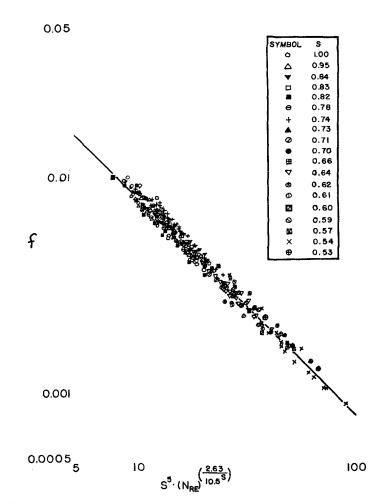
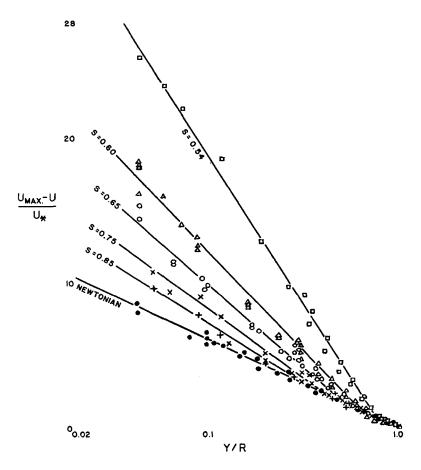


Fig. 4. Empirical correlation of friction factors in pseudoplastic turbulent flow. When the fluid is Newtonian (s=1), the expression reduces to the Blasius equation, $f=0.079/(N_{Re})^{\frac{1}{2}}$.

noted that the zone is broadest at the lower end of the shear-rate range (200 sec⁻¹), where the readability is the poorest. Dotted lines in Figure 2 represent the region over which viscometric data is lacking (usually 21 to 200 sec⁻¹). It will be noted that over the range of 200 to 1.000 sec⁻¹ the data obtained from the recorder plot are capable of correlation by other values of b and s than those given by the straight line. A major question, as yet unanswered, is whether the transition between the low shear-rate range and the high range ($>200 \text{ sec.}^{-1}$) is abrupt or gradual. It is reasonable to suppose that it is gradual in the case of alginate and Carbopol solutions. With CMC solutions it may well be abrupt owing to some reversible change in the molecular configuration. By the progressive addition of the dye Gentian violet (pararosaniline chloride) to CMC solution, it was found that two rheological curves with a sharp break point resulted, the lower curve being that of a Newtonian fluid and the upper curve that of a markedly pseudoplastic fluid. The higher the concentration of Gentian violet, the higher was the shear rate necessary to cause transition from Newtonian to

pseudoplastic flow. If the Gentian violet, which is capable of reacting with the -COO- group of the CMC through its group -NH3+, reinforces some mode of intramolecular association already inherent in CMC that holds the molecule inflexible up to some high level of shear, this abrupt Newtonian-pseudoplastic transition would be one of the phenomena anticipated. One such CMC-Gentian violet curve is shown in Figure 2. In this case the concentration of Gentian violet was sufficiently high to move the transition between Newtonian and pseudoplastic behavior up to about 3,000 sec. -1 shear rate. Accordingly the Newtonian nature of the fluid below this transition was detected over a substantial range by the Merrill-Brookfield viscometer, as well as by the Brookfield Synchrolectric viscometer.

Without exception all the transitionand turbulent-regime pipeline flow data have been correlated by using the high-range b and s values (range of 200 to 20,000 sec.⁻¹). The wall shear stresses achieved in these pipeline flow studies varied over a range such that maximum (wall) shear rate was usually in the range of 500 to 20,000 sec.⁻¹ and in a



WHERE U. = 17-/8

```
☐ - RUN 8B

Δ - RUNS 4E,F,G 8 9B

O - RUNS 5A,B 8 3C

X - RUNS 3E 8 6B,D

+ - RUN 3H

- RUNS 1C,D,E,F
```

Fig. 5. Turbulent velocity profiles for pseudoplastic and Newtonian fluids expressed as velocity deficiencies. The ranges of Reynolds Numbers are: Newtonian; 9,600 to 176,000

s = 0.85; 17,000 s = 0.75; 7,540 to 10,500 s = 0.65; 8,800 to 14,600 s = 0.60; 8,400 to 14,300 s = 0.54; 8,780

few runs was as high as 40,000 sec.-1 Under these conditions the volume of fluid contained within an imaginary coaxial cylindrical section, within which the shear rate was 200 sec. -1 or less, amounted to about one quarter of the total volume in the same section at the lowest values of wall shear stress and a negligible fraction at the highest wall shear stress. That the successful correlation of f vs. N_{Re} shown in Figure 4. is based entirely on s values in the 200 to 20,000 sec.-1 range suggests that low shear viscometry as a means of predicting the turbulent-flow characteristics of these polymer solutions would be in at least two cases (CMC and Vistanex) totally misleading. Stated in another way, if low shear viscometric data were used as a basis for predicting the turbulent-flow friction factors of CMC and Vistanex according to the correlations shown in Figure 4, the resulting values of f would be away out of line and would have to be reported as anomalous. When the high-range viscometric data are used, the predicted f values are in line with those of alginate and Carbopol and agree well with the experimentally determined values.

TURBULENT-FLOW FRICTION FACTORS

In turbulent flow the relationship between the friction factor and the pseudoplastic Reynolds number (Figure 3) was found to consist of a family of curves, each curve depending on s in such a way that the friction factor decreased with decreasing s at a given pseudoplastic Reynolds number.

All the experimental data, which form the basis of Figure 3, are correlated empirically by Equation $(5)_x$

$$f = 0.079/(s^5 \cdot N_{Re}^{\ \gamma}) \tag{5}$$

where

$$\gamma = 2.63/(10.5)^s \tag{6}$$

In Figure 4 it can be seen that Equation (5) correlates the experimental data in which the rheological behavior ranges from Newtonian to a pseudoplasticity of s = 0.53 with a maximum deviation of +33, to -15%. This correlation cannot be used with fluids having an s value less than about 0.4, since the predicted friction factor would be less than in laminar flow. In solutions of random coiling, nonassociating highmolecular-weight polymers sufficiently dilute to avoid gel structure and gross elasticity, the value of s has never been found lower than 0.5 from data obtained on either of the coaxial-cylinder viscometers used in this work. It is possible to attribute a very low value of s to a fluid with a yield value, which is really a Bingham plastic, or to a solution of rodlike molecules, for example amylose, but in either of these cases the power-law model $\tau = b(du/dy)^s$ is at best a very rough approximation of the rheology, which is far better described by other, unrelated equations.]

VELOCITY PROFILES AND MIXING LENGTHS

Figure 5 shows the experimentally obtained velocity-profile data for turbulent flow, expressed as velocity deficiencies and collected on one plot. In Newtonian turbulent flow it has been found (1) that this type of correlation brings together the profiles for all conditions of Reynolds number and tube roughness onto a single curve. However it can be seen that this correlation did not bring the pseudoplastic turbulent-velocity profiles onto a single curve but rather presented a series of curves, again depending on the value of s. In addition it can be seen that there is a region in the vicinity of the center of the tube in which a pseudoplastic curve coincides with the Newtonian, but this region gets progressively smaller as pseudoplasticity is increased. In general it can be said that at a given Reynolds number in turbulent flow in a smooth tube a pseudoplastic polymer solution of the type studied will have a lower friction factor and a less blunt velocity profile than a Newtonian fluid.

In addition it was found that the mixing-length distribution curves calculated from the velocity profiles did not coincide with the classical curves obtained with Newtonian fluids but also deviated

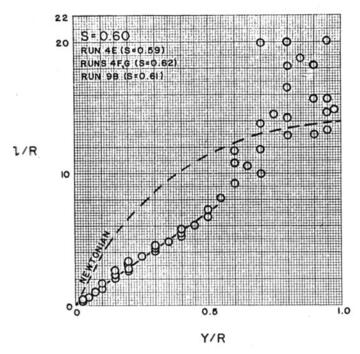
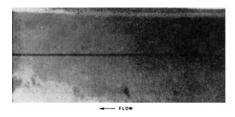
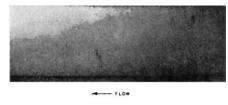


Fig. 6. Typical curve of mixing length distribution for pseudoplastic turbulent flow.



INJECTION 185 DIAWETERS UPSTREAM

Fig. 7. Laminar flow, dye injection at tube center.



INJECTION 1/2 DIAMETER UPSTREAM OF

Fig. 8. Laminar flow, dye injection at tube wall.

systematically with the value of s. Figure 6 shows a typical curve of mixing length vs. y/R. The interdependence of the velocity distribution curve and the distribution of mixing lengths was derived from the velocity distribution curves by the relation

$$l \cdot du/dy = u_* \sqrt{1 - y/R} \qquad (7)$$

DYE-INJECTION STUDIES

In a series of experiments designed to show something about the nature of the flow, pigmented liquid was injected at various points in a transparent tube and the path of the dye stream was photographed with a high-speed stroboscopic flash*. It soon became evident that the most informative experiments could be obtained by injecting at two different points, at the entrance of the test section in the center of the tube and at a small, carefully drilled wall tap. Axial injection was intended to show the effect of turbulence on the liquid in the

core of the tube and injection at the wall to show the effect on the fluid in the layer near the wall. The first type of injection was at the portion of the system where the large feed pipe necked down to the smaller test section. As the fluid was being accelerated at that section there was less tendency for flow separation and vortex formation to occur because of the presence of the hypodermic-tubing probe.

As seen in Figure 7, the dye injected at the center of the tube into a stream in laminar flow retains its radial position and identity in both the Newtonian and the pseudoplastic cases, making a straight filament as expected. The presence of the hypodermic probe did not seem to disturb this configuration until the flow increased almost to the transition region. Figure 8 shows that the dye stream injected at the wall retains its unity and runs a straight filament against the tube wall.

The dye stream injected from the axially positioned needle into a Newtonian liquid in turbulent flow as seen by the 40 µsec. flash 185 diam. downstream from the point of injection is completely

dispersed across the diameter of the tube (Figure 9). There is no filamental quality left to it, at least on the macroscopic scale. This is in accord with the understanding of Newtonian turbulence as a very rapid, violent mixing action.

Where the dye was injected at the wall, loops of dyed liquid were found emanating from the main body of the wall layer, shown in Figure 11. This effect is in accordance with the observations and calculations reported by Theodorsen (15) concerning horseshoe vortices formed in the vicinity of the wall and traveling toward the center under the influence of the main stream of flow. It indicates that turbulent eddies form at or near the wall and travel radially away from it, thereby mixing fluid from the region of the wall with fluid in the core of the flow. The force that produces the movement toward the center is a lift force generated by the rotating mass intruding into the flowing stream. It exchanges momentum with the fluid through which it is passing by means of normal drag forces and finally loses its identity.

When injected into a highly pseudoplastic CMC solution (s=0.61) in turbulent flow at the center of the tube, the dye stream takes on a strikingly different appearance 185 diam. downstream from the point of injection than it does in Newtonian turbulent flow (Figure 10). To a large extent the dye stream seems to be still intact, although it is highly distorted and grossly distributed across a large portion of the diameter of the tube.

The photographs of the dye stream injected at the center of the tube show that it does not readily lose its identity but rather is pushed aside by the turbulent vortices and does not become part of them. The action has been aptly described by Sherwood (19) as a kneading action.

With respect to the wall-injection study (Figures 11, 12), the smoothly flowing layer near the wall was found to be thicker in these pseudoplastic polymer solutions than in Newtonian liquids in turbulent flow. It was also found that the horseshoe vortices formed in the pseudoplastic liquid are relatively few in number and not at all well developed at this short distance from the point of injection.

On the basis of these observations it is concluded that the formation of horseshoe vortices is highly repressed in pseudoplastic turbulent flow leading to much lower energy dissipation and that the core fluid tends to retain its identity, although being distorted by the vortices that do penetrate it. An explanation appears to lie in the fact that the fluid in the center of the tube, under a low average rate of shear, has as a result a higher viscosity than the fluid near the wall, which is under a high rate of shear. Likewise the fluid in the core of a vortex

^{*}The pigmented liquid was carbon black dispersed in water. Initially Gentian violet was used. As noted above, this dye reacted with CMC and changed its rheology.

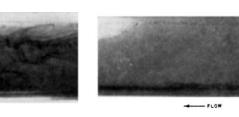
has a higher viscosity than the fluid that surrounds the core, thereby resisting intermingling with the more rapidly moving fluid. The mixing of two liquids of widely differing viscosity, such as water and heavy syrup, might be cited as a crude analogy.

It is apparent from the dye-injection experiments and from the velocity profiles obtained in the turbulent-flow regime that there is no plug flow in the core. That slip at the wall, as suggested as a possibility for some types of fluids (12), is absent in these pseudoplastic polymer solutions under all flow conditions was confirmed because the material balances calculated from the velocity

profiles which assumed zero slip checked with the measured flow rates.

FLUCTUATIONS IN PRESSURE

The manometer columns were observed to oscillate over the transition range of most of the fluids tested, giving the impression of periodic lapses into the turbulent form of flow from an unstable laminar form. The oscillations occurred between maxima and minima corresponding clearly to laminar and turbulent forms at the particular Reynolds number, as long as the frequency was low enough for the manometer to register. As the frequency of oscillation became higher,

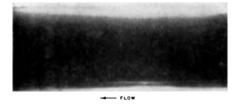


WATER, N_{RE}= 3720 Injection 185 Diameters Upstream

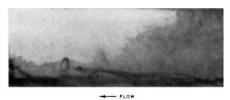
Fig. 9. Newtonian turbulent flow, dye injection at tube center.

WATER, N_{RE}=.3720 INJECTION 1/2 DIAMETER UPSTREAM OF EOGE OF PHOTO

Fig. 11. Newtonian turbulent flow, dye injection at tube wall.

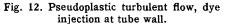


0.25% CMC-708, N_{RE} : 8400, S=0.61 Injection 185 Diameters Upstream



0.25% CMC-708, N_{RE}-12,800, S-0.61 Injection 1/2 Diameter Upstream of Edge of Photo

Fig. 10. Pseudoplastic turbulent flow, dye injection at tube center.



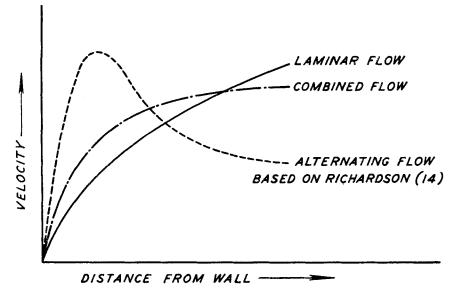


Fig. 13. Conversion of laminar to turbulent profiles.

the maxima and minima of the manometer readings fell between the extrapolated laminar- and turbulent-flow predictions, as would be expected owing to the inertia of the manometric fluid. This phenomenon has been noticed previously (13) and is probably due to the periodic formation of horseshoe vortices, with the consequent distortion of flow, at frequencies low enough to be seen on the manometers.

As the flow rate increased from the transition region into the turbulent region, the manometer oscillations increased in frequency and decreased in amplitude, becoming negligible for fluids of which the s value is 0.7 or more but persisting in highly pseudoplastic fluids (s < 0.7) as a flutter of very small amplitude (less than 1 mm.) and high frequency for a long way into the turbulent region, often up to the maximum obtainable flow rate. These observations suggest that the periodic change between two forms of flow that was observed in the transition region persists into the turbulent region.

A possible explanation for the apparent decrease in the frequency of the formation of vortices is the viscosity gradient present across the radius of a tube that carries a pseudoplastic fluid. If one considers such a fluid flowing in steady laminar flow at a high Reynolds number, the viscosity gradient in it would be defined by the linear shear-stress distribution and the rheological curve of the material. The effect would be to have a minimum viscosity at the wall and a maximum viscosity at the center of the tube. Thus a vortex formed at the wall of the tube in traveling inward toward the center penetrates layers of increasing viscosity. As a consequence of this it seems reasonable to expect that there would be a damping effect on the vortex over and above that imposed by a Newtonian system.

By means of this concept of viscosity gradient two effects observed in pseudoplastic flow can be explained: the persistence of stable laminar flow to abnormally low friction factors (high Reynolds numbers) and the relatively low frequency of formation of turbulent vortices in turbulent flow leading to lower friction factors than Newtonian and to flutter of manometer columns under certain conditions. One could reasonably expect such a viscosity gradient to retard both the point of incipient formation of vortices and the frequency of their formation once this point has been passed.

PERIODIC BOUNDARY LAYERS

In view of the foregoing it is interesting to consider the concept of periodic boundary layers as proposed by Richardson (14). Reported experiments were conducted in a pipe fitted with a loose section that could be oscillated in a

direction transverse to the flow. When a stable laminar flow was passed through the tube and the loose section oscillated the tube and the loose section oscillated. the resultant velocity profile was the blunt logarithmic type of turbulent flow (14). The effect is ascribed to an alternation between the laminar form of now and an alternating form the profile of which has a peak near the wall. The turbulent profile is then the time average between the two. (See Figure 13.)

If one ascribes the generation of turbulence to some process resembling the artificially induced one, the decreasing bluntness of pseudoplastic turbulent profiles (compared with the profiles of Newtonian fluids) with increasing pseudoplasticity can be explained in the following manner. Given the laminar form of flow in an unstable region, the vortex formation causes the flow to distort to the alternating form, with a peak near the wall. However the effect of pseudoplasticity, as deduced from other facts, is to reduce the frequency of the occurrence of these vortices. Therefore as pseudoplasticity is increased, progressively less of the alternating form is time averaged with the laminar form, resulting in progressively less blunt turbulent profiles and progressively lower friction factors. Since the laminar profiles become more blunt as pseudoplasticity is increased, it is apparent that the decrease in frequency of alternation must be such as to more than compensate for this effect in the resultant profile.

This concept of the oscillation between two forms of flow in the turbulent region is helpful in that it reasonably explains all the main phenomena observed with the turbulent flow of the pseudoplastic polymer solutions studied:

- 1. The decrease in friction factors at constant $N_{R_{\bullet}}$ as pseudoplasticity is increased
- 2. The progressively less blunt velocity profiles with increasing pseudoplasticity
- 3. The flutter of the manometer columns in the turbulent region with the highly pseudoplastic liquids
- 4. The relatively poor mixing of dye stream injected into the center of the tube
- 5. The thicker calm layer near the wall and fewer horseshoe vortices as seen by wall dye injection.

CONCLUSIONS

- 1. The degree of turbulent agitation in the turbulent flow region is progressively less at comparable Reynolds numbers as pseudoplasticity is increased (measured by decreasing value of s).
- 2. This is attributed to a progressively decreasing frequency of vortex formation at the tube wall.
 - 3. The result of this is lower friction

factors and less blunt velocity profiles in pseudoplastic turbulent flow than in Newtonian turbulent flow.

- 4. Laminar pseudoplastic velocity profiles are progressively blunter than Newtonian ones, as is predicted by the power model of pseudoplastic rheology.
- 5. Slip at the wall in these pseudoplastic polymer solutions under all measured flow conditions must be negligible, if it exists at all, to account for the excellent agreement in flow rates calculated by integrating the velocity profiles which assume zero wall slip and by measuring directly. Plug flow of a central core of fluid is shown not to exist by velocity profiles in the laminar regime, photography of axially injected dye streams in turbulent flow.
- 6. The laminar- and turbulent-flow behavior in tubes of the free-draining, nonassociating polymer solutions studied (despite significantly different features of molecular structure of the several polymers) is well correlated by using the power-law model $\tau = b(du/dy)$ to express the rheology, provided that b and s are determined over a range of shear appropriate to the conditions of the fluid at the wall and radially inward to roughly three quarters of the radius of the tube. For the flow conditions reported herein the range of 200 to 20,000 sec.-1 of shear rate was appropriate, and the values of b and s, found for all solutions to be constant over this range, vielded a satisfactory correlation of the tube-flow data. Viscometric determination in the low range of shear (0.1 to 42 sec.-1) was shown to be in general of no value.

ACKNOWLEDGMENT

The authors wish to thank the Esso Research and Engineering Company for a generous grant under which much of the apparatus was built; Brookfield Engineering Company, Stoughton, Massachusetts, for constructing and donating the two viscometers used in this study; Humble Oil and Refining Company for fellowship support; Dewey and Almy Chemical Company, Division of W. R. Grace and Company, for technical aid, supplies, and a substantial grant under which the Merrill-Brookfield. viscometer was developed; and H. H. Carter of the Chemical Engineering Department, Massachusetts Institute of Technology, Cambridge, Massachusetts, for his careful drawings.

NOTATION

L

= pseudoplastic rheological constant, (dyne)(sec.) /sq. cm.

d= differential operator

= tube diameter, cm. D

= Fanning friction factor

1 = turbulent mixing length, cm.

= length, cm.

 N_{Re} pseudoplastic Reynolds num-

$$\left(\frac{D^{s}V^{2-s}\rho}{b}\right) \cdot 8[2(3+1/s)]^{-s}$$

= pressure, dynes/sq. cm.

= volumetric flow rate, cc/sec.

= radius, cm. R

Q

u

= tube radius, cm. = pseudoplastic rheological exponent

= local velocity, cm./sec.

= maximum (axial) velocity in u_{max} tube, cm./sec.

 u_* = friction velocity, cm./sec.

V= average velocity, cm./sec.

= wall w

= distance from wall, cm.

Δ = difference

= exponent to N_{Re} γ

= viscosity, poises μ

= 3.1416 π

= density, g/cc. ρ

= shear stress, dynes/sq. cm.

 $\int T$ τ_w = wall shear stress, dynes/sq. cm. du/dylocal velocity gradient (shear

rate), sec.-1

LITERATURE CITED

- 1. Bakhmeteff, B. A., "The Mechanics of Turbulent Flow," Princeton, Princeton University Press, Princeton, New Jersey (1936).
- 2. Beerli, G. J., S.B. thesis, Mass. Inst. Technol., Cambridge (1957).
- 3. Bird, R. B., A.I.Ch.E. Journal, 2, 3, 428 (1956).
- 4. Dadekian, Z. A., and R. C. Engelken, S.B. thesis, Mass. Inst. Technol., Cambridge (1955).
- 5. Merrill, E. W., J. Colloid Sci., 9, 1, 7
- , Instrument Society of America Journal, 2, No. 2, 462 (1955).

7. Ibid., 3, No. 4, 124 (1956).

- —, J. Colloid Sci., 11, 1 (1956).
- 9. Metzner, A. B., and J. C. Reed, A.I.Ch.E. Journal, 1, 4, 434 (1955).
- 10. Metzner, A. B., and R. E. Otto, ibid. **3**, 1, 3 (1957).
- Mooney, M., J. Rheol., 2, 2, 210 (1931).
 Oldroyd, J. G., "Proc. Internat. Cong. Rheology, Holland, 1948," North-Holland Publishing Co., Amsterdam Sec-
- tion C, vol. II, p. 130 (1949).

 13. Prandtl, L., "Applied Hydro- and Aeromechanics," McGraw-Hill Book Co., Inc., New York (1934).
- 14. Richardson, E. G., "Dynamics of Real Fluids," Edward Arnold and Co.,
- London (1950). 15. Theodorsen, Theodore, "50 Jahre Grenzschichtforschung," edited by H. Gortler and W. Tollmien, Friedrich Vieweg, Braunschweig, Germany (1955).
- 16. Toms, B. A., J. Colloid Sci., 4, 511 (1949).
- 17. Weltmann, R. N., and P. W. Kuhns, Natl. Advisory Comm. Aeronaut. Tech. Note 3510 (August, 1955).
- 18. Weltmann, R. N., Ind. Eng. Chem., 48, 3, 386 (1957)
- 19. Sherwood, T. K., private communication.

Manuscript received January 7, 1958; revision received July 3, 1958; paper accepted July 10, 1958.