APPENDIX TRANSFER UNIT CALCULATIONS

The number of transfer units based on the liquid phase N is calculated from the simple equation for linear operating and equilibrium lines.

$$N = (x_2 - x_1) \left\{ \frac{\ln \frac{x_2 - y_2/\alpha}{x_1 - y_1/\alpha}}{(x_2 - y_2/\alpha) - (x_1 - y_1/\alpha)} \right\}$$

$$N = \frac{x_2 - x_1}{(x - y/\alpha)_{\text{in mean}}} =$$
(10)

While x_2 is measured directly, the other values needed to use Equation (10) must be calculated from other measurements. The volume flow rates of the liquid feed $L + v\epsilon_p$, the condensed foam $v\epsilon_p$, and the gas v were measured. The strontium tracer concentrations in the liquid feed x_2 , the effluent liquid x_B , and the condensed foam x_p were measured. An average bubble diameter d was determined from photographs of the foam (Figure 2) by a counting procedure described in detail else-

where (6). The surface flow rate was calculated from this diameter:

$$V = va = 6v/d \tag{3}$$

Since the liquid pool is assumed to be equivalent to one theoretical stage, the streams leaving this pool are in equilibrium and

$$y_1 = \alpha x_B \tag{11}$$

A solute material balance for this liquid pool can be rearranged to give

$$x_1 = x_B \left(1 + \frac{V\alpha}{L} \right) \tag{12}$$

A solute material balance for the condensed foam can be rearranged to give

$$y_2 = \frac{v_{\epsilon_p} x_p}{V + v_{\epsilon_p}/\alpha} \tag{13}$$

The values measured for calculation of N from these equations were checked for consistency by calculating solute balances for the whole column.

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Constitutive Equations for Viscoelastic Fluids with Application to Rapid External Flows

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A major problem in the analysis of complex flows of viscoelastic fluids lies in the development of a suitable constitutive equation relating stresses to the kinematics of deformation. In this paper an equation is developed from successive approximations to a very general theory of viscoelasticity. This equation, which predicts both a non-Newtonian viscosity coefficient and normal stress effects in simple laminar shearing flows, appears to reflect a reasonable compromise between simplicity and useful applicability to real materials.

The use of this equation is illustrated by means of a study of rapid flows about submerged objects. The results of this study are compared with the usual boundary-layer theory for Newtonian fluids, and the implications of this comparison are discussed in some detail.

One of the most important current engineering problems concerning non-Newtonian fluids involves the need for development of suitable constitutive equations with which to express the behavior of viscoelastic systems in complex flow fields, a problem to be distinguished from that of simple viscometric flow fields which have been studied extensively to date. While an understanding of viscometric flow fields does include a number of problems of engineering interest, at least as a useful approximation, most flow fields encountered in the processing of molten polymers are much more complex; an example of similarly complex flow fields involving dilute solutions occurs in the use of polymeric additives to reduce frictional drag in pipelines under turbulent flow conditions. In order to progress in the quantitative study of any of these flow fields by means of either mathematical analyses or experimental endeavors guided by dimensional analysis, it is necessary to have a suitably simple yet adequately general equation relating the stresses in the fluid to its deformational behavior.

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In this paper new methods are introduced for obtaining approximate constitutive equations describing viscoelastic materials. The resulting equations are applied to the study of rapid external flows, and the results of this study are discussed in terms of the boundary-layer theory of Newtonian fluid dynamics.

CONSTITUTIVE THEORY

The full nonlinear significance of constitutive theories was first realized by Oldroyd (33) in 1950; an accurate history of recent developments has been published by Rivlin (37). It would appear that the best approach to be used in developing a constitutive theory is to limit all assumptions to those which experience would suggest to be general enough to describe the stress-deformation behavior of polymeric media; of several approaches attempted to date one of the most satisfactory appears to be that in which it is assumed that the stress depends not only upon the instantaneous strain from some arbitrary state but upon the entire history of the deformation, the dependence being in such a manner that strains in

the distant past have less effect upon the stress than strains in the recent past. It is further presumed that the material is isotropic in its ground state and incompressible. Mathematically this is equivalent to taking the stress (aside from hydrostatic pressure) as an isotropic hereditary functional of the deformation history. Presentations of this general theory of viscoelastic materials have been published by Green and Rivlin (19), Coleman and Noll (8, 9, 10), and more recently by White (50, 51). In this theory the stress is expressed as an expansion of integrals of the strain tensor; the rheological properties of the medium are determined by a series of integral kernel functions, the first kernel being the relaxation modulus of linear viscoelasticity (7, 51).

This paper discusses motions in which the instantaneous strain developed in the fluid may be expressed or at least closely approximated by a Taylor series in time about the present instant. This permits the removal of kinematic parameters from the hereditary integrals and the expression of the stress in terms of instantaneous deformation rates and accelerations (19, 51). One thus writes for the stress

$$\tau = -p \mathbf{I} + \mathbf{F}(\mathbf{B}_1, \mathbf{B}_2, \dots, \mathbf{B}_n)$$
 (1)

in which the \mathbf{B}_n are acceleration tensors specified by the recurrence formula:

$$B^{ij} = v^{i}_{,m}g^{mj} + v^{j}_{,m}g^{im} - 2v^{m}_{,m}g^{ij}$$
(2a)
$$B^{ij} = \frac{D}{Dt} (B^{ij}) + 2 B^{ij} v^{m}_{,m} - v^{i}_{,m} B^{mj} - v^{j}_{,m} B^{im}$$
(2b)

In terms of the original concepts of Oldroyd (33), these equations represent rates of change and accelerations of the conjugate metric tensor and could be obtained by continual application of Oldroyd's equation (24). In the modern precepts of the Green-Rivlin theory (19), Equations (2) are equivalent to the Rivlin-Ericksen tensors (38). Extensive studies of acceleration tensors and their application have been published by Giesekus (15, 16).

Laminar shearing flows represent an important special case of the motions described by Equation (1). These flows, which include Poiseuille flow in a tube and Couette flow between coaxial cylinders, may be analyzed exactly, and the solutions are in the literature (8, 13, 15, 36). However, more complex flows are not as susceptible to analysis, and approximate procedures must be devised. To approach these more complex flow problems, one may expand Equation (1) in orders of deformation rate. Using this approach, one finds

$$\tau = -p \mathbf{I} + \mathbf{\Sigma} \mathbf{M}_n \tag{3}$$

in which the \mathbf{M}_n represent terms of order n in velocity: $\mathbf{M}_1 = \omega_1 \ \mathbf{B}_1 \tag{4a}$

$$\mathbf{M}_2 = \boldsymbol{\omega}_2 \ \mathbf{B}_1^2 + \boldsymbol{\omega}_3 \ \mathbf{B}_2 \tag{4b}$$

$$\mathbf{M}_{3} = \omega_{4} [tr \ \mathbf{B}_{1}^{2}] \mathbf{B}_{1} + \omega_{6} \ \mathbf{B}_{3} + \omega_{6} [\mathbf{B}_{1} \ \mathbf{B}_{2} + \mathbf{B}_{2} \ \mathbf{B}_{1}] \quad (4c)$$

$$\mathbf{M}_{4} = [\omega_{7} tr \ \mathbf{B}_{1}^{8} + \omega_{8} tr \ (\mathbf{B}_{1} \ \mathbf{B}_{2})] \mathbf{B}_{1} + \omega_{9} [tr \ \mathbf{B}_{1}^{2}] \mathbf{B}_{2}^{2} + \omega_{12} [tr \ \mathbf{B}_{1}^{2}] \mathbf{B}_{2}^{2} + \omega_{12} \mathbf{B}_{4} + \omega_{13} \mathbf{B}_{2}^{2} + \omega_{12} \mathbf{B}_{4} + \omega_{13} \mathbf{B}_{2}^{2} + \omega_{13} \mathbf{B}_{3}^{2} + \omega_{14} \mathbf{B}_{4}^{2}$$

$$\omega_{13}[B_1^2 B_2 + B_2 B_1^2] + \omega_{14}[B_1 B_3 + B_3 B_1]$$
 (4d)

Equations (3) to (4) may be interpreted in two senses. First they may be considered as a perturbation about a state of rest and secondly as a perturbation about Newtonian behavior.

The first-order fluid represented by Equations (3) and (4a) is identical to the classical Newtonian fluid (3, 39,

46). The concept of the second-order fluid, which represents the complete second-order correction to the Newtonian equation, was introduced by Coleman and Noll (9) in 1960. In laminar shearing flow the second-order fluid predicts normal stress effects but maintains a constant Newtonian viscosity; its range of applicability therefore appears to be limited to very low deformation rates or to materials which are only very slightly viscoelastic. The hydrodynamic theory of second-order fluids has been studied by Coleman and Markovitz (8) and White (51, 52).

Turning now to the third-order fluid, one has a material which exhibits both normal stresses and a variable viscosity in steady laminar shearing flows. The normal stresses may, in general, be unequal and are predicted to vary with the second power of the shear rate, as in the case of second-order fluids. The predicted relationships between the normal stresses thus are general enough to encompass all fluids, although the variation with shear rate does not appear to be (17, 24, 28, 42, 53). The viscosity is predicted to be a quadratic in shear rate. It is thus seen that the complete third-order approximation is a far more reasonable approximation to the behavior of real fluids than is that of second order and may be sufficiently good to warrant application to engineering problems. However, in this context caution and judgment must be exercised, since the predicted variations of the viscosity and of the normal stress terms with shear rate will be useful approximations only over limited ranges. The addition of three terms also increases greatly the complexity of the equations of motion for this fluid. With the exception of those kinematically simple problems which may be solved exactly (8, 15, 36), the available solutions are limited to exhaustive perturbation procedures in the absence of the inertial terms (6, 16, 23). Thus it would appear necessary for new simplifying and approximate procedures to be introduced even in this case to make hydrodynamic studies more tractable, and it would surely be required in the case of higher-order equations.

One procedure for obtaining simplifications which might be expected to be valid for slightly viscoelastic non-Newtonian fluids, that is dilute polymer solutions at moderate or high deformation rates and molten polymers at modest deformation rates, is the following: one may assume that only the viscoelastic tensors from the second-order fluid are significant beyond the purely viscous non-Newtonian term. Thus, the terms involving ω_5 and ω_0 are assumed to be negligible in the third-order fluid, as are all new coefficients of acceleration tensors in higher-order fluids. The stress is thus assumed to be of the form

$$\tau = -p \mathbf{I} + \overline{\mu} \mathbf{B}_1 + \omega_2 \mathbf{B}_1^2 + \omega_3 \mathbf{B}_2 \tag{5}$$

in which $\overline{\mu}$ is a function of the invariants of the B_s tensors:

$$I_s = tr \mathbf{B}_s$$
; $II_s = tr \mathbf{B}_s^2$; $III_s = tr \mathbf{B}_s^3$ (6a, b, c)

and of the mixed invariants $tr[\mathbf{B}_1^{a_1}\mathbf{B}_2^{a_2}\dots\mathbf{B}_n^{a_n}]$ in which $I_1=0$ because of incompressibility. From Equation (4) one sees that the function μ is of the form

$$\overline{\mu} = \omega_1 + \omega_4 II_1 + \omega_7 III_1 + \omega_8 tr[\mathbf{B}_1 \mathbf{B}_2] + \dots \qquad (7)$$

In laminar shearing flow, this constitutive equation predicts a viscosity which varies in an arbitrary manner with shear rate and normal stresses which increase as the second power of the shear rate. Thus, in the case of this motion, one is in a somewhat better position than with the third-order fluid; one may fit any set of shear stress data,

but the predictions of the normal stresses is not quantitatively verified except at low shear rates (17, 24). An expression similar to Equation (5) has been discussed by Ericksen (13) but mainly in the study of laminar shear flows

It is of interest to compare the material function μ with the laminar shear flow viscosity μ which is measured in capillary and coaxial cylinder experiments. The function μ is more limited than μ as in these fluid motions:

$$III_1 = 0 (8a)$$

$$I_n = II_n = III_n = 0 \quad (n > 2) \tag{8b}$$

The mixed invariants are all zero with the exception of $tr(B_1^{2a}B_2^{b})$ (compare 36). For purely viscous fluids, the viscosity is dependent only upon the invariants of B_1 and thus for laminar shear flows only upon II_1 . Since laminar shear flow viscosity data are very similar for purely viscous non-Newtonian and viscoelastic fluids, one might expect to be able to completely specify μ for viscoelastic fluids by II_1 and neglect the dependence upon the other invariants. It has been found that for many bulk polymers and polymer-solvent systems, viscosity data may be expressed over a limited but considerable range of shear rates by a power-law expression (26):

$$\mu = K \Gamma^{n-1} \tag{9a}$$

For purely viscous non-Newtonian fluids, the power law is equivalent to the expression (3)*

$$\mu = K \left[\frac{1}{2} II_1 \right]^{\frac{n-1}{2}} \tag{9b}$$

The material function $\overline{\mu}$ may be written as the expansion

$$\bar{\mu} = \mu(II_1) + \omega_7 III_1 + \omega_8 tr[\mathbf{B}_1 \mathbf{B}_2] + \dots \qquad (10a)$$

$$=K\left[\frac{1}{2}II_{1}\right]^{\frac{n-1}{2}}+\omega_{7}III_{1}+\omega_{8}tr\left[\mathbf{B}_{1}\mathbf{B}_{2}\right]+\ldots.$$
(10b)

Equation (10) is in a sense a superior expression $\overline{\mu}$ than Equation (7), as the function $\mu(II_1)$ contains terms of order higher than 2. Equation (7) represents the special case in which μ is linear in II_1 . It should be emphasized that choice of the power-law equation to express the viscous stress terms merely represents a choice which is computationally convenient; the fact that it may not represent a scientifically precise description of fluid behavior is frequently irrelevant, and, when this is not the case, other choices may be made which do lead to adequate approximations of these terms in those cases. Thus, the utility of Equation (5) is not likely to depend upon this choice but rather upon the adequacy of the last two terms for expressing the behavior of real fluids. An alternate interpretation of Equations (7) and (10) is also possible. Equation (7) represents μ as a perturbation about threedimensional Newtonian flow, while Equation (10) represents μ as a perturbation about the generalized laminar shear viscosity. It should be noted no information exists about the coefficients ω_7 , ω_8 For a large class of flows such higher invariants do not appear, for example in laminar shear flows in which, as has already been mentioned, both invariants are zero, while in planar two-dimensional flows III_1 is zero (44).

In the remainder of this paper the authors shall neglect all but the first term on the right-hand side of Equation (10). However, as they shall be entirely concerned with two-dimensional flows in Cartesian coordinates, nonzero coefficients of terms involving III_1 will not affect their results. Thus consider flows in which the equation of motion is

$$\rho \frac{D}{Dt} \mathbf{v} = -\nabla p + K \nabla \cdot \left\{ \left[\frac{1}{2} II_{1} \right]^{\frac{n-1}{2}} \quad \mathbf{B}_{1} \right\} + \omega_{2} \nabla \cdot \mathbf{B}_{1}^{2} + \omega_{3} \nabla \cdot \mathbf{B}_{2}$$
(11)

When one makes use of arguments of the type used for Newtonian fluids (3, 39), the dimensionless velocities and pressures arising from the solution of this equation must be functions of the following groups:

$$\frac{L^{n}U^{2-n}}{K}\rho, n, \frac{(-1)\omega_{3}U^{2-n}}{KL^{2-n}}, \frac{\omega_{2}}{\omega_{3}}$$
 (12)

The first group is, of course, the power-law Reynolds number representing the ratio of the inertial to viscous forces; the second group is simply the dimensionless flow index or power-law exponent n. The third dimensionless group is a generalization of the Weissenberg number, which was introduced in an earlier paper (51), and the final group is what was called the *viscoelastic ratio number* in this same paper. The drag coefficient for the fluid described by Equation (11) is then

$$c_t = c_t(N_{Re}, N_{Ws}, N_{VR}, n, \text{ geometric ratios})$$
 (13)

As in the case of second-order fluids, it may be shown that for planar flow fields the drag will be independent of $N_{\rm PR}$

Several authors have derived drag coefficient-Reynolds number expressions from dimensional analysis considerations for purely viscous non-Newtonian fluids (12, 26, 27, 45, 47), but only one paper appears to have considered the generalization of these concepts to viscoelastic materials (29). In that case, the drag coefficient for turbulent viscoelastic fluids was related to the normal stress-shear stress ratio at the wall shear rate. If one analyzes Equations (5) and (11) for laminar shearing flows, one finds that this stress ratio is identical to the Weissenberg number defined by Equation (12).

The above approach to formulation of approximate but useful constitutive equations may be supplemented by the introduction of a somewhat different approach which may be termed "the generalized Weissenberg conjecture." If one accepts the Weissenberg presumption of equality of normal stresses in the directions perpendicular to flow in laminar shear, it follows that ω_2 and ω_0 are zero. While this is a modest contribution, it can be greatly generalized as follows. White (51) has shown that the coefficients in Equation (4) may be represented by integrals of a series of functions $\Phi(s)$, $\Psi(s_1, s_2)$ etc. If one presumes that the reason ω_2 is zero is that the integral kernel which determines it is zero, it will follow from White's result (51) that in the first four orders of fluid behavior one may also set ω_0 , ω_{11} and ω_{14} equal to zero. Thus, this gives

$$\omega_2 = \omega_6 = \omega_9 = \omega_{11} = \omega_{14} = 0$$

This approach resembles recent proposals by Giesekus (16) and is discussed in more detail elsewhere (52).

SOME RAPID FLOW APPROXIMATIONS

In this section, hydrodynamic flow approximations to the problem of an infinite fluid moving past a submerged

⁶ An earlier properly invariant form of the power law was published by Mooney and Black (30). These authors expressed the viscosity in terms of the invariant dissipation function. For a purely viscous material, the Mooney-Black form may be inverted to give the above. However, for viscoelastic fluids this is not the case.

semi-infinite flat plate stretching from the origin along the x axis are considered. The continuity equation and the stress equations of motion for this planar problem become

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial u} = 0 \tag{14a}$$

$$\rho \left[u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right] = -\frac{\partial p}{\partial x} + \frac{\partial}{\partial x} t_{xx} + \frac{\partial}{\partial y} \tau_{xy} \quad (14b)$$

$$\rho \left[u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} \right] = - \frac{\partial p}{\partial y} + \frac{\partial}{\partial x} \tau_{xy} + \frac{\partial}{\partial y} t_{yy} \ \ (14c)$$

and the boundary conditions are

$$u(x, 0) = 0$$
 $v(x, 0) = v_s$
 $u(0, y) = U(0)$ $v(0, y) = 0$ (15a to f)
 $u(x, \infty) = U(x)$ $v(x, \infty) = 0$

where v_s represents suction, blowing, or dissolution of the plate. This is the problem which was attacked for Newtonian fluids by Prandtl and Blasius (4), Falkner and Skan (14), Goldstein (18), and others (39) and has become known as boundary-layer theory.* The first attempt to develop an equivalent boundary-layer theory for purely viscous non-Newtonian materials was Oldroyd's study (32) for Bingham plastics. More recently Schowalter (40) and Acrivos, Shah, and Petersen (1) have called attention to the possible existence of a comparable hydrodynamic boundary-layer theory for purely viscous fluids, and a significant number of solutions have appeared recently (1, 2, 5, 11, 20, 21, 41, 48, 54). As discussed elsewhere (25, 31), it is not yet clear to what extent these represent useful approximations, since the power law cannot portray the properties of real fluids accurately over the entire boundary-layer region; thus, some extension and numerical as well as experimental clarification of these studies would appear to be in order.

The primary simplifying assumptions required for the development of mathematical solutions for flow of an infinite purely viscous fluid over a flat plate are that first the component of the equations of motion perpendicular to the plate may be neglected, and second that the variation of the normal stress t_{xx} along the direction parallel to the plate is negligible. It does not appear that either of these assumptions is generally valid for viscoelastic materials owing to the existence of normal stresses produced by the sheared fluid elements. The difficulties incurred, as a result, in simplifying the equations of motion for viscoelastic flouds have been studied by Rajeswari and Rathna (35), Shinnar (20, 43), and Walters (49), the details of the work of the latter authors not being available at the time of writing.

Making use of the kinematic simplifications of Prandtl that in rapid flows the fluid velocity changes from zero at the surface of the plate to U in a small distance $\delta << x$

$$\frac{\partial u}{\partial x} \sim \frac{U}{x}, \quad v \sim U\delta/x$$

$$\frac{\partial u}{\partial x} \sim \frac{U}{x}, \quad \frac{\partial u}{\partial y} \sim U/\delta, \text{ etc.}$$
(16)

one may evaluate the components of the equations of motion, Equation (14), to yield

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{17a}$$

$$\rho \left[u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right] = -\frac{\partial p}{\partial x} + \frac{\partial t_{xx}}{\partial x} + \frac{\partial \tau_{xy}}{\partial y} \quad (17b)$$

$$0 = -\frac{\partial p}{\partial y} + \frac{\partial \tau_{xy}}{\partial x} + \frac{\partial}{\partial y} t_{yy}$$
 (17c)

Integration of Equation (17c) between y=0 and y=y and differentiation of the result with respect to x permits the elimination of the pressure gradient term from the x component of the equations of motion. Thus Equations (17b) to (17c) may be combined to give

$$\rho \left[u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right] = \frac{\partial}{\partial x} \tau_{yy}(0, x) + \frac{\partial}{\partial x} (t_{xx} - t_{yy}) + \frac{\partial}{\partial y} \tau_{xy} - \frac{\partial^2}{\partial x^2} \int_0^y \tau_{xy} dy$$
 (18)

The last term in this expression is obviously of the order $\tau_w \delta$, while the other terms must be of the order τ_w or τ_w/δ . Thus, this last term may be neglected. As $y \to \infty$, one obtains

$$\rho U \frac{dU}{dx} = \frac{d}{dx} \left[\tau_{yy}(0, x) + (t_{xx} - t_{yy})(\infty, x) \right] \quad (19)$$

and one thus has the equivalent form

$$\rho \left[u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} - U \frac{\partial U}{\partial x} \right] = -\left[\frac{\partial}{\partial x} \left(t_{xx} - t_{yy} \right) \right]_{y=\infty} + \frac{\partial \tau_{xy}}{\partial y} + \frac{\partial}{\partial x} \left[t_{xx} - t_{yy} \right]$$
(20)

In the remainder of this paper it is assumed that

$$\left[\frac{\partial}{\partial x}\left(t_{zx}-t_{yy}\right)\right]_{y=x}\simeq0\tag{21}$$

which implies, physically, that the fluid inertia is assumed to be dominant in the region far from the surface making stresses due to fluid "stretching" negligible.

Evaluating the components of the stress tensor by using

Evaluating the components of the stress tensor by using the constitutive equation which was previously developed and used in writing Equation (14), one obtains

$$\begin{split} \tau_{xy} &= K \left(\frac{\partial u}{\partial y} \right)^n + \omega_s \left[u \frac{\partial^2 u}{\partial x \partial y} + v \frac{\partial^2 u}{\partial y^2} + 2 \frac{\partial u}{\partial x} \frac{\partial u}{\partial y} \right] \\ \tau_{xx} &= -p + 2K \left(\frac{\partial u}{\partial y} \right)^{n-1} \frac{\partial u}{\partial x} + \omega_2 \left(\frac{\partial u}{\partial y} \right)^2 - 2 \omega_s \left(\frac{\partial u}{\partial y} \right)^2 \\ \tau_{yy} &= -p + 2K \left(\frac{\partial u}{\partial y} \right)^{n-1} \frac{\partial v}{\partial y} + \omega_2 \left(\frac{\partial u}{\partial y} \right)^2 + \\ 2 \omega_s \left[u \frac{\partial^2 v}{\partial x \partial y} + v \frac{\partial^2 v}{\partial y^2} - \left(\frac{\partial u}{\partial x} \right)^2 - \frac{\partial v}{\partial x} \frac{\partial u}{\partial y} \right] \end{split}$$

Terms of highest order for each of the components of the kinematic matrixes were retained in writing the above expressions; an order of magnitude analysis was then applied to eliminate the minor terms regardless of their origin.

Substituting these stress components into Equation (20) and simplifying, one obtains

$$\rho \left[u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} - U \frac{\partial U}{\partial x} \right] = \left[K \frac{\partial}{\partial y} \left(\frac{\partial u}{\partial y} \right)^{n} \right] + \omega_{3} \left[\frac{\partial}{\partial x} \left(u \frac{\partial^{2} u}{\partial y^{2}} \right) + v \frac{\partial^{3} u}{\partial y^{3}} + \frac{\partial u}{\partial y} \frac{\partial^{2} v}{\partial y^{2}} \right]$$
(23)

[•] In recent years, mathematicians have taken a closer look at the foundations of boundary-layer theory for Newtonian fluids. The authors will not discuss this work in any detail but refer to the paper by Lagerstrom and Cole (22) which argues that boundary-layer theory represents an infinite Reynolds number asymptote to the Navier-Stokes equations and introduces the use of singular perturbations and asymptotic expansions.

The class of solutions considered previously, for example by Schowalter (40) and Shah (41), are for this equation with ω_s set equal to zero.

The three sets of terms of Equation (23) (each set is enclosed by square brackets) represents the contributions of inertial, viscous, and elastic forces, respectively. In applying the order-of-magnitude analyses as usual, terms of second or higher order within each grouping have been neglected. This leads to an implicit, hidden assumption: namely that all three groups of terms are of comparable order of magnitude, for otherwise the neglected quantities in one grouping could become of the same import as the retained terms in another. This hidden assumption requires that

 $\frac{\rho U^2}{r} \simeq \frac{K U^n}{\delta^{n+1}} \simeq \frac{\omega_s U^2}{\delta^2 r} \tag{24}$

From this it follows that

$$N_{W*} \simeq \frac{1}{(N_{Re})^{(1-n)/(1+n)}}$$
 (25a)

where

$$N_{Re} \simeq \left(\frac{x}{\delta}\right)^{n+1}$$
 (25b)

As the length Reynolds number in the region of interest is of order of magnitude 10,000 and n varies from 0.2 to 1.0, the length Weissenberg number ranges from about 0.005 to 1.0 (with increasing n). The boundary-layer thickness Weissenberg number is of order of magnitude one hundred.

This may be looked at in an alternate manner if one returns to the stress equations of motion. Here the order of magnitude analysis yields

$$\frac{\rho U^2}{\kappa} \simeq \frac{(\tau_{xy})_w}{s} \simeq \frac{(t_{xx} - t_{yy})_w}{\kappa} \tag{26}$$

OI

$$(t_{xx} - t_{yy})_w \simeq \frac{x}{\delta} (\tau_{xy})_w \simeq \frac{1}{n+1} \frac{4}{(n+1)(\tau_{xy})_w} \simeq 10 \frac{\tau_{xy}}{(\tau_{xy})_w} (27)$$

This approximation indicates that the wall normal stresses must be from two to three orders of magnitude greater than the shearing stress in order for the approximation to be valid

Conversely, if the normal stresses are at least an order of magnitude smaller than this, the boundary-layer analyses for purely viscous fluids should become applicable.

In this light, it is perhaps instructive to consider the magnitudes of the ratio of elastic to viscous stresses exhibited by real fluids. Ratios of as great as 10° to 10° certainly appear to be attainable (17, 28, 42) but, under steady flow conditions, only at very high deformation rates. This would indicate that boundary-layer solutions for purely viscous fluids would apply to a considerable variety of slightly viscoelastic systems, at least if the deformation rates involved are not too great.

SPECIAL SOLUTIONS FOR FLOW AROUND SUBMERGED OBJECTS

It is the purpose of this section to transform Equation (23) to an ordinary differential equation, in order to determine what profiles U(x) will allow such a transformation. For Newtonian fluids, general classes of solutions were found by Falkner and Skan (13) and by Goldstein (18), and these have also been shown by Schowalter (40) to lead to transformations for power-law fluids. The

two classes of solutions are that U is a power function of x (Falkner-Skan) and an exponential function (Goldstein). Introduction of the stream function ψ (3, 39)

$$u = \frac{\partial \psi}{\partial u}, \ v = -\frac{\partial \psi}{\partial x} \tag{28}$$

permits reduction of the equations to a single dependent variable, while automatically satisfying continuity requirements. Equation (23) gives

$$\rho \left[\frac{\partial \psi}{\partial y} \frac{\partial^{2} \psi}{\partial x \partial y} - \frac{\partial \psi}{\partial x} \frac{\partial^{2} \psi}{\partial y^{2}} - U \frac{dU}{dx} \right] = K \frac{\partial}{\partial y} \left(\frac{\partial^{2} \psi}{\partial y^{2}} \right)^{n} + \omega_{s} \left[\frac{\partial}{\partial x} \left(\frac{\partial \psi}{\partial y} \frac{\partial^{3} \psi}{\partial y^{3}} \right) - \frac{\partial^{4} \psi}{\partial x} \frac{\partial^{4} \psi}{\partial y^{4}} - \frac{\partial^{2} \psi}{\partial y^{2}} \frac{\partial^{3} \psi}{\partial x \partial y^{2}} \right]$$
(29)

Considering first the case in which the velocity U(x) is given by the expression

 $U = c x^a \tag{30}$

and introducing the expression for the stream function

$$\psi = \left[\frac{Kx}{\rho U^{2-n}}\right]^{\frac{1}{n+1}} Uf(\eta, \xi) \tag{31}$$

in which

$$\eta = y \left[\frac{\rho U^{2-n}}{Kx} \right]^{\frac{1}{n+1}}, \ \xi = \frac{x}{L}$$
(32)

one obtains the following equation on seeking the equivalent Falkner-Skan solution:

$$\frac{d}{d\eta} (f^{II})^n + a[1 - (f^I)^2] + \frac{1 + a(2n - 1)}{n + 1} f f^{II} +$$

$$\frac{\omega_3}{\rho} \left(\frac{\rho U^{2-n}}{Kx}\right)^{\frac{2}{n+1}} \left\{ \frac{6a - 2}{n+1} f^I f^{III} - \frac{1 + a(2n - 1)}{n+1} f f^{IV} - \frac{3a - 1}{n+1} (f^{II})^2 \right\} -$$

$$\xi \left\{ f^I \frac{\partial f^I}{\partial \xi} - f^{II} \frac{\partial f}{\partial \xi} \right\} + \frac{\omega_3}{\rho} \left(\frac{\rho U^{2-n}}{Kx}\right)^{\frac{2}{n+1}}$$

$$\xi \left\{ f^I \frac{\partial f^{III}}{\partial \xi} + f^{III} \frac{\partial f^I}{\partial \xi} - f^{IV} \frac{\partial f}{\partial \xi} - f^{II} \frac{\partial f^{II}}{\partial \xi} \right\} = 0 \quad (33)$$
In this equation

If f is to be a function of η only, then it must follow that

 $f^s = \frac{\partial^s f}{\partial n^s}$

$$\left(\frac{\rho U^{2-n}}{Kx}\right)^{\frac{2}{n+1}} = \text{constant independent of } x$$

that is

$$a = \frac{1}{2 - n} \tag{34}$$

From Equation (32) one sees that this predicts η to be independent of x.

A n may vary from zero to unity, allowable values of a will be in the range of $\frac{1}{2}$ to 1. Interpreting this in terms

of the classical theory of inviscid fluids (39), one finds this to correspond to flow about blunt wedges.

When f is a function of η only, Equation (33) reduces to the ordinary differential equation

$$(2-n)\frac{d}{d\eta}(f^{II})^{n} + ff^{II} - (f^{I})^{2} + 1 = \frac{1-n}{N_{Ws}(N_{Re})} \frac{1-r}{1+n} [2f^{I}f^{III} - ff^{IV} - (f^{II})^{2}]$$
 (35) with boundary conditions

$$f'(0) = 0$$
 and $f(0) = \frac{(2-n)v_{\bullet}}{U_{L}} (N_{Re})^{\frac{1}{n+1}} \frac{x}{L}$

$$(36a, b)$$
 $f'(\infty) = 1$

$$f^{II}(\infty) = 0 \tag{36c, d}$$

The first boundary condition signifies a zero tangential velocity at the surface of the plate, while the second condition indicates the interfacial velocity due to suction, blowing, or dissolution. As may be seen, this velocity is restricted to be zero or to vary inversely as a function of distance along the plate; that is only for such a variation may a transformation be obtained. The third boundary condition means the velocity reaches the free stream value at infinity, and the fourth condition indicates that the y component of the velocity gradient is zero at this point. This latter boundary condition is not required in Newtonian boundary-layer theory but is added here because the viscoelastic properties of the fluid increase the order of the equation.

The drag coefficient is

$$c_t = \frac{2}{\rho U^2} \int_0^1 (\tau_{xy})_w d(x/L)$$
 (37)

When the transformation is applicable, this becomes

$$c_{t} = \frac{2 - n}{2} \frac{\left[f^{II}(0)\right]^{n}}{\left(N_{Re}\right)^{1/(n+1)}}$$
(38)

From Equations (35) and (38) one sees that viscoelasticity affects the drag coefficient through the dimensionless

product $N_{Ws}(N_{Rs})$, as well as through the Reynolds number itself.

Turning to the Goldstein free stream velocity

$$U = c' e^{bx} \tag{39}$$

and introducing for the stream function

$$\psi = \left(\frac{K}{h \, a \, U^{2-n}}\right)^{\frac{1}{n+1}} UF(\eta, \xi) \tag{40}$$

in which:

$$\eta = y \left[\frac{\rho U^{2-n} b}{K} \right]^{\frac{1}{n+1}}, \ \xi = x/L$$
 (41)

one finds, after carrying through the mathematical details as before, that F is a function of η alone if and only if n is equal to 2. In this case the differential equation for F

$$\frac{d}{d\eta} (F^{II})^2 + F F^{II} - (F^I)^2 + 1 = \frac{N_{Ws}}{(N_{Rs})^{1/3}}$$

$$[2F^I F^{III} - F F^{IV} - (F^{II})^2]$$
(42)

with

$$F(0) = 0$$

 $F'(0) = 0$
 $F'(\infty) = 1$
 $F''(\infty) = 0$ (43 a, b, c, d)

The surface velocity v_{\bullet} is here presumed to be zero.

As in the case of the Falkner-Skan analysis, a similarity transformation is possible only when η may be taken to be independent of x. The corresponding situation in the case of Newtonian fluids as discussed by Schlichting (39) is seen to be of limited engineering interest, which is further restricted in this case by the required value of the flow behavior index n.

While the Goldstein free stream velocity result is thus seen to be of little value, the equivalent Falkner-Skan solution does include a region of moderate interest and could be pursued further. However, it would be of far more interest to obtain solutions for more general velocity fields. Fortunately, considerable progress has been made in recent years in the area of the direct numerical integration of the equations representing nonsimilar boundary layers (34). While this alternative is one requiring a large expenditure of computational effort, it also is one which concomitantly enables the investigator to relax the limitations imposed by use of a power-law relation to describe the viscosity function. Hence, it may serve to resolve more than a single difficulty.

One additional problem remains. Except in the important special case of a constant external (free stream) velocity, a number of difficulties would appear to arise in the determination of the external velocity field. The use of inviscid flow theory, as in the Prandt-Blasius boundarylayer procedure, may not be applicable to viscoelastic fluids. Slattery (44) has discussed some of the reasons for this difficulty.

CONCLUSIONS

In this paper a series of approximate constitutive equations has been developed, some of which may be used in the analysis of complex flow problems. As an application of one of these equations, the problem of rapid flows about submerged objects has been discussed, and the partial differential equation describing the velocity field has been derived. The solution of this equation by means of the similarity transformation procedure of conventional boundary-layer theory is shown to be impossible except perhaps in a small number of uninteresting special cases.

Three paths for further work appear to be open. First, it might prove to be profitable to reapproach this problem from the asymptotic expansion procedure of Lagerstrom and Cole (22) in which one might even choose to use Equation (3) as a constitutive equation. Secondly, one might take recourse to numerical methods, and, thirdly, one may investigate the use of approximate (integral-momentum) techniques. The utility of such further activities is limited by the comments following Equation (27).

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NOTATION

= exponent in Equation (30)

= coefficient of exponential term, Equation (39)

= acceleration tensors, defined Equation (2)

= proportionality coefficient, Equation (39)

= drag coefficient D()∂()

 $-+\mathbf{v}\cdot\nabla$ () Dt

= function defined by Equation (40)

f = body force

f

= function defined by Equation (31)

 g^{ij} conjugate metric tensor (see textbooks on tensor analysis for a discussion of definition and uses)

1 unit matrix

K = consistency index

L= characteristic length dimension

 \mathbf{M}_n = terms defined by Equation (4)

= power-law exponent or flow behavior index n

 $N_{\rm O}$ = dimensionless group (see subscripts)

= hydrostatic pressure p

= stress tensor

t = time

tr= trace (operation denoting summation of the diagonal terms of a matrix)

U= mainstream velocity

= x component of the velocity u

= velocity vector having components v^i

= y component of velocity vector

= surface velocity normal to plate

= distance variables

 I_s , II_s , III_s = invariants defined by Equation (6)

= del operator (3, 39)

= boundary-layer thickness δ

Г = shear rate

coefficients of acceleration tensors (material coω, efficients or material properties to be determined experimentally)

= density

quantity defined by Equations (32) or (41), deη pending upon analysis under consideration

ξ

= viscosities defined by Equations (7), (9), (10) μ, μ

= stream function, defined by Equation (28) ψ

= stress tensor

Subscripts

= covariant differentiation with respect to the x_i ,j coordinate(s)

Re= Reynolds number [Equation (12)]

VR= viscoelastic ratio number [Equation (12)]

= Weissenberg number [Equation (12)]

= components of the quantity to which they are appended, the shearing stress τ_{xy} evaluated at the wall is denoted by τ_w or $(\tau_{xy})_w$

LITERATURE CITED

- 1. Acrivos, Andreas, M. J. Shah, and E. E. Petersen, A.I.Ch.E. Journal, 6, 312 (1960).
- 2. Bizzell, G. D., and J. C. Slattery, Chem. Eng. Sci., 17, 777 (1962).
- 3. Bird, R. B., W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," Wiley, New York (1960).
 4. Blasius, H., Zeit. Math. u Phys., 56, 1 (1908), (translated
- in NACA TM 1256).

5. Bogue, D. C., Ind. Eng. Chem., 51, 874 (1959).

- 6. Caswell, B., and W. H. Schwarz, J. Fluid Mech., 13, 417 1963).
- 7. Coleman, B. D., and H. Markovitz, J. Appl. Phys., 35, 1
- ______, and W. Noll, Arch. Rat. Mech. Anal., 3, 289 (1959); J. Appl. Phys., 30, 1508 (1959); Ann N. Y. Acad. Sci., 89, 672 (1961).
- , Arch. Rat. Mech. Anal., 6, 355 (1960). Rev. Mod. Phys., 33, 239 (1961).

11. Collins, M., and W. R. Schowalter, A.I.Ch.E. Journal, 9,

98, 804 (1963).

12. Dodge, D. W., and A. B. Metzner, *ibid.*, 5, 189 (1959).
13. Ericksen, J. L., in "Viscoelasticity, Phenemonological Aspects," Academic Press, New York (1960).

14. Falkner, V. M., and S. W. Skan, Phil. Mag., 12, 865 (1931).

15. Giesekus, H., Rheologica Acta, 1, 404 (1961); 3, 59 (1963).

-, Z.A.M.M., **42**, 32 (1962).

- 17. Ginn, R. F., and A. B. Metzner, Trans. Soc. Rheology, to be published.
- 18. Goldstein, S., Proc. Camb. Phil. Soc., 35, 338 (1939).
- 19. Green, A. E., and R. S. Rivlin, Arch. Rat. Mech. Anal., 1, 1 (1957).
- 20. Gutfinger, C., and R. Shinnar, A.I.Ch.E. Journal, 10, No. 5, 631 (1964).
- 21. Kapur, J. N., and R. C. Gupta, Z.A.M.M., 43, 135 (1963). See also Kapur, J. N., and R. C. Srivastava, Z.A.M.P., 14, 383 (1963).
- 22. Lagerstrom, P. A., and J. C. Cole, J. Rat. Mech. Anal., 4,814 (1955)
- Langlois, W. E., Quart. Appl. Math., 21, 61 (1963). See also Langlois, W. E., and R. S. Rivlin, Rend. di Mat., 22, 169 (1963), and Langlois, W. E., and R. S. Rivlin, Tech. Rept. No. 3. to U. S. Army, Div. Appl. Math., Brown University (1959).

24. Markovitz, H., and D. R. Brown, Trans. Soc. Rheology, 7, 137 (1963)

25. Metzner, A. B., in "Advances in Heat Transfer," Vol. 2, J. P. Hartnett and T. Irvine, ed., Academic Press, New

York, to be published.

———, in "Handbook of Fluid Dynamics," V. L. Streeter, ed., McGraw-Hill, New York (1961).

_____, and J. C. Reed, A.I.Ch.E. Journal, 1, 434 (1955).
_____, W. T. Houghton, R. A. Sailor, and J. L. White, 27. 28. Trans. Soc. Rheology, 5, 133 (1961).

-, and M. G. Park, J. Fluid Mech., 20, 291 (1964).

- 30. Mooney, M., and S. A. Black, J. Colloid. Sci., 7, 204 (1952).
- 31. Napolitano, L. G., Private communication (1964).
- 32. Oldroyd, J. G., Proc. Camb. Phil. Soc., 43, 383 (1947).

- 33. ——, Proc. Roy. Soc., **A200**, 523 (1950). 34. Parr, W., U. S. Naval Ordnance Report NOLTR 63-261 (1964).
- 35. Rajeswari, G. K., and S. L. Rathna, Z.A.M.P., 13, 43 (1962).

36. Rivlin, R. S., J. Rat. Mech. Anal., 5, 179 (1956). 37. ———, in "Phenomenes de Relaxation et de Fluage en Rheologie Non-Lineaire," Editions de Centre National de la Recherche Scientifique, Paris (1961).

-, and J. L. Ericksen, J. Rat. Mech. Anal., 4, 323 (1955).

39. Schlichting, H., "Boundary Layer Theory," 4 ed., McGraw-Hill, New York (1960).

40. Schowalter, W. R., A.I.Ch.E. Journal, 6, 24 (1960).

41. Shah, M. J., Ph.D. thesis, Univ. California, Berkeley, California (1961). See also Shah, M. J., E. E. Petersen, and Andreas Acrivos, A.I.Ch.E. Journal, 8, 542 (1962).

42. Shertzer, C. R., and A. B. Metzner, Trans. Plast. Inst., 31, 148 (1963); 32, 217 (1964).

Shinnar, R., Personal communication (1964).
 Slattery, J. C., Chem. Eng. Sci., 17, 689 (1962).

, and R. B. Bird, ibid., 16, 231 (1961).

- 46. Stokes, G. G., Trans. Camb. Phil. Soc., 8, 105 (1845). 47. Thomas, D. G., Ind. Eng. Chem., 55, No. 11, p. 18
- 48. Tomita, Y., Chem. Eng. (Japan), 23, 66, 525 (1959); Bull. Jap. Soc. Mech. Eng., 4, 77 (1961).
- 49. Walters, K., Personal communication (1963).
- 50. White, J. L., J. Appl. Poly. Sci., 8, 1129 (1964).

51. *Ibid.*, p. 2339.

- 52. White, J. L., Ph.D. thesis, Univ. of Delaware, Newark, Delaware (in preparation).
- -, and A. B. Metzner, J. Appl. Poly. Sci., 7, 1867 53. (1963).
- 54. Yau, J., and C. Tien, Can. J. Chem. Eng., 41, 139 (1963).

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