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Time dependent power law behaviour at low shear rates for paint systems

By M. Camina and C. G. Roffey

With 3 figures

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G. W. Scott Blair and W. Tuszyński (1) have observed a power law behaviour with coagulating milk, and Nedonchelle and Schutz (2), have observed this behaviour in the retrogradation of starch, in which the equation:

$$\log \tau = \log K + M \log \dot{\gamma}$$

is obeyed with the power exponent M and constant K varying with time. τ is the shear stress and $\dot{\gamma}$ the shear rate. The straight lines on the $\log \tau / \log \dot{\gamma}$ plots obtained for specific times were found to converge through a common point $\tau', \dot{\gamma}'$ and all the stresses can, therefore, be written as τ/τ' and all the shear rates as $\dot{\gamma}/\dot{\gamma}'$ which eliminates the awkward dimensions of a log-log equation as mentioned by these workers. They speculate that this behaviour could apply to other systems. We have studied several highly pigmented paints (commercial undercoats) and found similar behaviour.

Several undercoats that exhibited pseudoplastic behaviour, i.e., at high shear rates giving $\tau = K\dot{\gamma}^N$ with N being less than unity, were subjected to shear at 1.134 sec^{-1} for about one minute on a Weissenberg Rheogoniometer to break down any structure present and were then subjected to a slow shear ($< 10 \text{ sec}^{-1}$). An increase of viscosity with time was observed, the viscosity/time build up being followed on an ultra-violet chart recorder. Some of the undercoats reached an equilibrium viscosity after shearing for about 1 min,

others showed no apparent equilibrium within 2 min. For the latter paints a computer programme was used to estimate an equilibrium viscosity. The time interval between changing from the high shear rate to the low shear rate was found not to affect the reproducibility, if kept short. This viscosity/time build up was proved not to be an artefact for no build up was found when a Newtonian oil thinned with solvent was treated in a similar manner.

Typical data are shown in fig. 1 for one of the paints used. Linearity of the $\log \tau / \log \dot{\gamma}$ plots was confirmed although only over two decades of shear rate.

Plots were made of the varying M values against the respective $\log K$ values for each line in fig. 1. The fact that these graphs were reasonably linear as shown in fig. 2 is indicative of a common point of intersection.

Fig. 1. Plot showing time dependent slow shear rate power law behaviour for a paint undercoat

Fig. 2. Graph showing plots of $\log K$ versus exponent M , obtained from fig. 1, where $\log \tau = \log K + M \log \dot{\gamma}$ is shown. The fact that the plot in fig. 2 is linear indicates that all the lines in fig. 1 converge to a common point at shear rate $\dot{\gamma}'$

The shear rate corresponding to the point of intersection, $\dot{\gamma}'$, found from fig. 2 was identical within experimental error to the shear rate at which deviation from linearity was first observed on a normal power law plot at relatively higher shear rates.

Fig. 3. Graphs showing linearity resulting from plots of $\log \left(1 - \frac{\tau_e}{\tau_t}\right)$ against time for viscosity/time build up observed in several undercoat paint systems.

Hahn, Ree, and Eyring (3) have proposed a kinetic model to explain time dependent flow behaviour. According to this model a plot of $\log (1 - \tau_e/\tau_t)$ against

time should produce straight lines at given shear rates, where τ_e is the equilibrium shear stress and τ_t the shear stress at time t . It was found for these paint systems that such plots were linear, see fig. 3. Also, using Scott Blairs figures from his coagulating milk system and estimating a τ_e value from his data by computer techniques, we found that this plot was also linear.

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Authors' address:

M. Camina, C. G. Roffey
The Paint Research Association
Teddington, Middlesex (England)