

expression for viscosity, of the form suggested by Geddes and Dawson³ for the paddle-type Stormer viscometer.

By plotting W against $1/t$ in the applicable range of the simple equation given above, straight lines through the origin are obtained for Newtonian liquids in the commercial viscometer. Deviation from Newtonian flow will be readily indicated, and the curves obtained for non-Newtonian materials will be related qualitatively to the fundamental flow curves, although they will not be of identical shape⁴.

We have used this instrument in the rheological examination of various types of cold-setting adhesives which are characterized by a rapid increase in viscosity—an effect additional to any which may be produced by the evaporation of part of the liquid phase from the system. W vs. $1/t$ curves for any particular instant during setting were obtained indirectly by plotting t against T (the period between the incorporation of the final ingredient and the observation of t) for a series of values of W . By interpolation the corresponding values of t and W were found for arbitrary values of T , and the plotting of $1/t$ against W provided the appropriate curve.

Some thickening aqueous systems which have been explored by this method, at 25° C., include casein-lime-sodium silicate, casein-caustic soda, urea formaldehyde resin-sulphuric acid-urea, and resorcinol formaldehyde resin-formaldehyde. The casein-lime-sodium silicate glues were characterized by a fairly rapid increase in yield value with T ; in casein-caustic soda glues the yield value was low and increased very slowly until the gel stage was reached. Urea formaldehyde adhesives, on the addition of the hardener, displayed considerable yield values which increased with T . Resorcinol formaldehyde resin was prepared in aqueous solution and adjusted to pH 6.25, which was compatible with a working life of several hours when the formaldehyde:resorcinol molar ratio was afterwards raised to 1.1:1, a value suitable for hardening the resin at 25° C. Practically Newtonian behaviour persisted until the abrupt transition to the gel stage. It is intended to discuss in detail elsewhere the molecular significance of these various phenomena.

The demonstration of instantaneous Newtonian flow in a system in which the viscosity is rapidly increasing may warrant the recognition of this behaviour as a distinct type. Both the criteria of Newtonian deformation suggested by the British Rheologists' Club⁶ (the proportionality of shear stress and rate of shear for an arbitrary time, and of shear strain and time for constant stress) evidently refer to purely rheological conditions. The latter criterion is meant to imply, presumably, that no structural change takes place as a result of shearing: it is not intended specifically to exclude the case where viscosity is changing with time, irrespective of whether the system is subjected to stress, with consequent lack of strict proportionality between shear strain and time during any test extending over a finite period. However, where such a condition obtains and the first criterion is simultaneously applicable, as in some thickening colloidal dispersions, there is no reason to suppose that departure from proportionality between shear strain and time would necessarily be produced by the rheological conditions set up by shearing. The difficulty in separating the effects of flow and of polymerization nevertheless suggests the recognition of the proposed category.

The work described here was carried out as part of the programme of the Division of Forest Products of the Council for Scientific and Industrial Research, Australia. We are indebted to Mr. R. T. Leslie of the Council's Section of Mathematical Statistics for establishing, from our data, the applicability of the equation given.

H. G. HIGGINS
K. F. PLOMLEY

Division of Forest Products,
Council for Scientific and Industrial Research,
Melbourne.

June 7.

¹ *J. App. Phys.*, **18**, 988 (1947).

² See, for example, Barr, "Monograph of Viscometry", 235 (Oxf. Univ. Press, 1931).

³ *Indust. Eng. Chem.*, **34**, 163 (1942).

⁴ Alfrey, "Mechanical Behavior of High Polymers", 39 (Interscience Publishers, 1948).

⁵ *Nature*, **149**, 708 (1942).

Supercooling of Mercury

BEFORE the War, when we were working at University College, Southampton, on the solid/liquid phase change, some experiments were started on the supercooling of mercury, in order to find the degree attainable, the factors controlling it, the effect of external influences and the cause of the onset of freezing.

Mercury of very high purity was distilled *in vacuo* into two twin 'Pyrex' vessels, of a few c.c. capacity, held in identical cavities in a copper block. The space above the surface of the two samples of mercury could be evacuated or filled with known gas, as desired. More than two hundred observations were made.

Some of the results are: (1) The amount of supercooling (ΔT_f) of pure mercury in air is not usually more than a degree or two, but *in vacuo* can be increased at least to 12° C. by previous heating *in vacuo* for some hours at about 200° C. (2) Change of atmosphere above the mercury surfaces effects ΔT_f , but not necessarily immediately; for example, there was usually a lag between the admission of air and the consequent decrease of ΔT_f . (3) The direction of the change in ΔT_f produced by a given treatment (for example, heating to 200° C.) was usually the same for each twin, but the amount of change was usually different. (4) The amount of ΔT_f shown by a given twin remained roughly constant for times of the order of days, and consistently greater or less than that of the other. (5) The onset of freezing was never simultaneous in the two twins. (6) Vibration and even deliberate bumping of the whole apparatus did not induce freezing.

It seems probable that the values of ΔT_f observed were less than those characteristic of really pure mercury. The onset of freezing appears to be controlled by some additional component which can enter the mercury via the gas phase, and not by external disturbance, such as mechanical shock.

It is proposed to study the matter further.

L. G. CARPENTER
L. J. C. CONNELL
A. B. OSBORN

22 Manor Road,
Farnborough,
Hants.
July 27.