Table 1. X-RAY DIFFRACTION DATA FOR HIGH PRESSURE Zn_2SiO_4 PHASES

Phase *A* 110 kbar, 120 kbar, 900° C		Phase *B* 150 kbar, 900° C	
d Å	*I*	d Å	*I*
5·46	1	6·78	4
3·75	1	4·74	7
3·60	6	3·48	1
3·11	4	3·24	< 1
2·972	5	2·870	< 1
2·815	10	2·712	5
2·766	10	2·641	5
2·621	6	2·507	2
2·568	3	2·454	10
Four weak lines omitted		2·366	3
2·244	5	2·256	< 1
		2·215	3
		2·094	3
		2·029	8
		Several weak lines omitted	
		1·458	7
		1·435	3

I, Estimated relative visual intensities.

an olivine, but the resemblance of the X-ray diffraction pattern to those of other olivines is not striking. A further run was carried out on Zn_2SiO_4 at a higher pressure—150 kbar. Complete transformation into an even denser birefringent phase with a mean refractive index of about 1·87 was observed. From the difference of refractive indices, this phase is estimated to be about 23 per cent denser than willemite. The X-ray diffraction pattern is complex—the spacings of the principal reflexions are given in Table 1.

A mixture of ZnO and SiO_2 in equimolar proportions crystallizes at one atmosphere to Zn_2SiO_4 (willemite) + SiO_2, but at 30 kbar at 500° C. Hayashi *et al.*[4,5] reported that the mixture crystallizes to a pyroxene structure. We have confirmed this synthesis. At 35 kbar, 1,100° C, and at 120 kbar, 900° C, the mixture crystallized to a pyroxene like structure.

An oxide mixture of $ZnGeO_3$ crystallizes at one atmosphere to Zn_2GeO_4 (phenacite structure) + GeO_2. This was also found to be the stable assemblage at 10 kbar, 1,100° C, but at 20 kbar, 35 kbar (1,100° C) the mixture crystallized to Zn_2GeO_4 (spinel structure) + GeO_2 (rutile structure). A further transformation was found in the 110 kbar, 900° C run. The $ZnGeO_3$ composition was found to crystallize completely to an ilmenite structure, similar to the high pressure modifications of $MgGeO_3$ and $MnGeO_3$. Thus, in this case, we have the reaction

$$Zn_2GeO_4 \text{ (spinel structure)} + GeO_2 \text{ (rutile structure)}$$
$$2\,ZnGeO_3 \text{ (ilmenite structure)}$$

occurring with increase of pressure from 35 kbar to 110 kbar.

These results contribute towards a broader understanding of the behaviour at high pressures of $M(SiGe)O_3$ and $M_2(SiGe)O_4$ compounds (M = Mg, Fe, Ni, Co, Mn, Ca, Cd, Zn) which have formed the subject of many previous investigations in this laboratory[6]. Nearly all these compounds which have been investigated so far display major phase transformations at high pressures. A systematic understanding of these transformations has important applications to studies of the constitution of the Earth's mantle.

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PHYSICS

Aging and Degradation in Dilute Polymer Solutions

WE have studied the properties of dilute solutions of polymers which have been found to reduce friction in turbulent flows[1]. The substances tested, in solution in tap water, were guar gum, polyethylene oxide (Union Carbide 'Polyox' *WSR* 301) and polyacrylamide (Dow 'Separan' *AP* 30). It had been previously found that solutions of 'Polyox' and 'Separan' exhibit normal-stress difference effects[2]. Correspondingly for 'Polyox' solutions, it has been reported[3] that the pressure increment at the mouth of a pitot tube, or open-ended tube facing into the flow, can be reduced below the value $\frac{1}{2}\rho V^2$ normal for Newtonian liquids, where ρ is density and V is speed. The present experiments began as a further investigation of this loss of pitot pressure. It was found that the pitot loss reduced with time, and that with 'Polyox' solutions other normal-stress difference effects showed a similar aging, without apparently impairing the ability of the liquid to produce turbulent drag reduction. Continued exposure of the liquid to intense turbulence does, however, lead to a degradation of the drag reduction.

The apparatus used was as in Fig. 1. Liquid in a header tank H could have an air pressure p, positive or negative relative to the atmosphere, applied to its upper surface. The liquid descended through a nozzle N and emerged through a smoothly rounded orifice O, of 2·5 mm narrowest diameter, to form a jet, which flowed over a pitot tube, of 0·9 mm outside diameter, and then into a receiver tank R, from which the fluid was returned by a peristalic pump to the header tank. The liquid pressure in the header tank was observed in an open-ended manometer tube, in which the liquid level rose, of course, by an amount p above the level in the header tank. The level to which the liquid rose in a manometer tube attached to the pitot enabled the pitot loss L to be determined as a fraction of the true pitot pressure P.

Typical results are shown in Figs. 2 and 3. In Fig. 2 results for two solutions of 'Polyox', both of 70 p.p.m. concentration, are shown. One was tested 4 days after mixing, and the other within 3 h of mixing. Pitot loss is shown as a fraction of time after starting up the flow in the apparatus, with P held constant at 34 cm ($V = 260$ cm/sec in the jet at the pitot mouth). The liquid level in the pitot manometer tube was made equal to that in the header tank tube at the beginning. The time taken for L to reach a maximum represents the response time for adjustment of the pitot manometer level by outflow through the small bore (0·6 mm diameter) of the pitot tube. The maximum loss with the fresher solution is greater than that with the older, but the aging process is evidently accelerated by the flow in the apparatus.

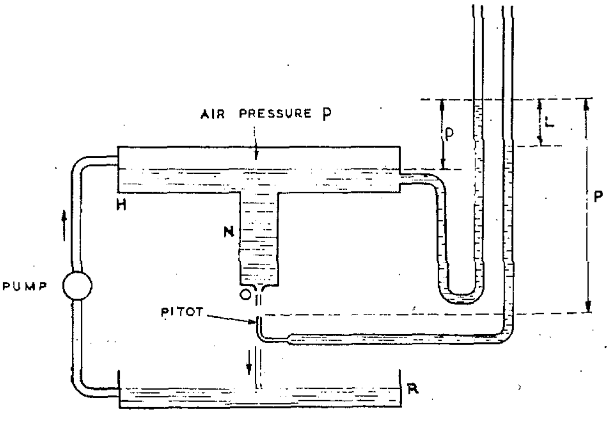

Fig. 1. Pitot tube apparatus.

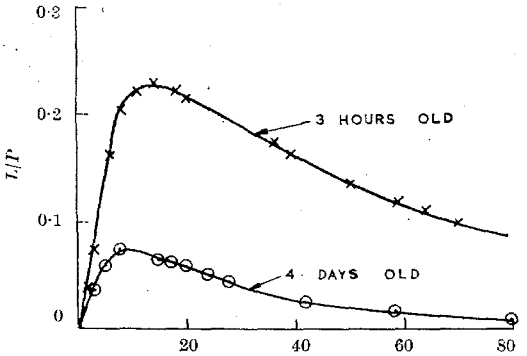

Fig. 2. Pitot loss as a function of time.

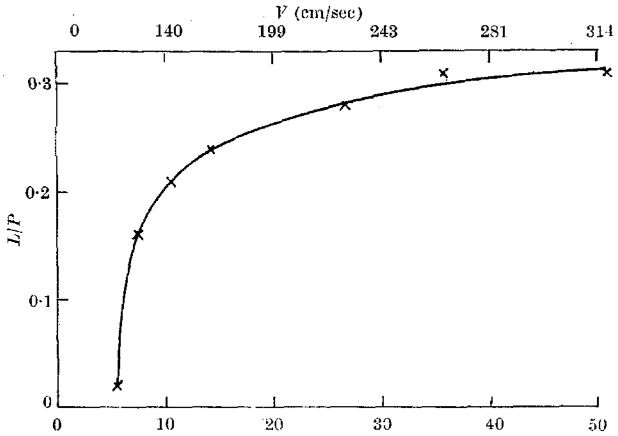

Fig. 3. Pitot loss as a function of speed.

More dilute 'Polyox', of 20 p.p.m. concentration, shows only a very small pitot loss even when fresh, but at 50 p.p.m. concentration the loss is about half as great as at 70 p.p.m. Results for 'Separan' solutions of 100 and 130 p.p.m. concentration are similar to those for 'Polyox', except that the pitot loss does not diminish with aging to zero, but attains a final limiting value smaller than the maximum for fresh solution. Guar gum solution of 160 p.p.m. concentration shows no pitot loss at all.

For 70 p.p.m 'Polyox' solution tested within 2 h of mixing the maximum pitot loss is shown as a function of pitot pressure P, or equivalently of jet speed V, in Fig. 3. At very low speeds there is no effect. Goren[3] suggests that at higher speeds than those of the present experiments the pitot loss may fall off, to diminish to zero at sufficiently high speeds. The reduction of pitot loss, however, with increasing speed which Goren[3] reported might be due to accelerated aging at the higher speeds in the turbulent flows of those experiments.

Turbulent drag reduction was measured in the rotating wheel rig we described elsewhere[4]. A flanged wheel rotates in a casing containing liquid, and the frictional torque exerted on the casing is measured and compared with the torque for the same speed of rotation when the liquid is replaced by the same amount of water. 'Polyox' solutions, aged in the pitot rig so as to show no remaining pitot loss, produced just as much drag reduction as freshly mixed solutions, with no greater tendency to degradation with time.

The viscosities of various solutions, some of which had been aged in the pitot rig of Fig. 1, and others of which had been degraded in the turbulent friction apparatus, were measured. A capillary instrument was used in which the wall shear rate was about 1,200 reciprocal seconds. Results are shown in Table 1. The measured viscosities can be compared with the value of 1·0038 centistokes for distilled water at 20° C. Concentrations quoted are only approximate.

Table 1. VISCOSITIES OF VARIOUS SOLUTIONS

Case No.	Fluid	Kinematic viscosity (centistokes) at 20° C
1	130 p.p.m. 'Separan' aged in pitot rig	1·158
2	Same mixture not put into pitot rig	1·162
3	70 p.p.m. 'Polyox' aged in pitot rig	1·056
4	Same mixture not put into pitot rig	1·055
5	70 p.p.m. 'Polyox' degraded in turbulent flow rig	1·036
6	Same mixture not put into turbulent flow rig	1·056
7	70 p.p.m. 'Polyox' filtered 1 h after mixing, and viscosity of filtrate measured 5 h after mixing	1·081
8	Same fluid, 5 days later	1·064

In cases 1 to 6, the fluids were stored at rest for 5 or more days before the measurements were made. Evidently, aging in the pitot rig does not make the viscosity any different from that of liquid kept for several days at rest, but degradation in turbulent flow (so that the resulting fluid produces much less drag reduction than when fresh) reduces viscosity, probably as a result of molecular scission. Fresh solution has a higher viscosity than aged solution.

The apparent viscosity of both fresh and aged solutions in filtration is much greater than the figures given here. It was measured by the following procedure: 50 ml. of water was put into a funnel lined with wet fine grade filter paper, and the time for the first 30 ml. to pass through was found. When all the water had drained through, 50 ml. of the solution at the same temperature was put in and the time for the first 30 ml. to pass through again was found. The average value from several tests of the ratio of these times is the apparent viscosity ratio, because for a completely homogeneous fluid containing nothing to block the filter pores the time of filtration would be proportional to viscosity. For fresh 70 p.p.m. 'Polyox' solution, which had been previously filtered once to remove any undissolved impurities, the ratio was about 2·3, and for the same solution, aged either by leaving it to stand for five days or by circulating it in the pitot rig for three hours, it was about 1·4. After degradation in the turbulent flow rig, so that the drag-reducing effectiveness was only a quarter of its initial value, the ratio was about 1·1. The average filter pore size is of the order of 3μ, so at this scale the fluid evidently cannot be regarded as a continuum with the same rheological properties as for larger-scale flows. Presumably molecules or molecular aggregates of a size comparable with the pore diameter are present in the fluid.

The second normal-stress difference, between directions perpendicular to the streamlines, was investigated with the concentric-tube instrument we described elsewhere[2]. It had been found that 'Polyox' solutions, unlike solutions of guar gum or 'Separan', exhibited a significant second normal-stress difference. Further tests have now shown that this difference is less for solutions mixed 1–3 days previously than for freshly mixed solutions, while solutions aged in the pitot rig, so as to have zero pitot loss, also have zero normal-stress difference.

As described earlier[4], a laminar jet of coloured 'Polyox' solution emerging from a capillary tube into uncoloured fluid and impinging obliquely on a flat surface may remain as a narrow jet over this surface, whereas a corresponding water jet spreads out into a wedge-shaped region. It now appears that narrow jets, probably attributable[2] to non-Newtonian tensile stresses along the streamlines, are characteristic only of fresh 'Polyox' solutions, for aged 70 p.p.m. solution has been found to behave like water. Thus here is another instance where non-Newtonian effects disappear with aging.

We have noted[4] that jets of coloured 'Polyox' solution squirted from a fine bore capillary into uncoloured 'Polyox' solution, so that the initially laminar jet became turbulent, in some cases showed a greatly modified turbulence structure. Other experiments on turbulent jets[3,5,6] at higher Reynolds numbers have suggested, however, that the turbulence is unaffected by the additive. This discrepancy may be due to accelerated aging in these flows at higher Reynolds number which are initially turbulent rather than laminar, as it has now been found that even initially laminar jets of 'Polyox' solution, aged in the pitot rig, show much less drastically modified turbulence than jets of fresh solution.

Many of the anomalous non-Newtonian effects found for some dilute polymer solutions seem to diminish or disappear with aging, which may be accelerated by gentle mixing such as that which takes place in the pitot apparatus. This aging may simply represent a more complete dissolving of the additive, though Pruitt *et al.*[7] attributed it to polyer adsorption on the walls of the containing vessel, and Shin[8] to biological attack. Shin[8], however, showed that while biological degradation could evidently be important over longer time periods, for periods of less than a week, over which large reductions of viscosity could occur, the turbulent drag reduction was little affected, which is in agreement with the present findings. The suggestion of polymer adsorption also seems hard to reconcile with undiminished turbulent drag reduction, which is more consistent with the suggestion, made to explain certain anomalous turbulence measurements by Fabula[9], that molecular aggregates occur in freshly mixed solutions but tend to break up with aging. These molecular aggregates would appear to be the cause of some normal-stress difference effects in fresh solutions. 'Polyox' solution, which for the concentration range 50–100 p.p.m. shows marked non-Newtonian effects when fresh, is, when aged and thoroughly dissolved, not very different from water in all viscometric and rheogoniometric measurements so far tried, except those for which the flow passages are only a few microns wide. Thus it may well be impossible to find constitutive equations which are significantly non-Newtonian for such aged liquids. Because these liquids are still fully effective in producing turbulent drag reduction, it would seem to be difficult to explain that phenomenon in terms of non-Newtonian equations.

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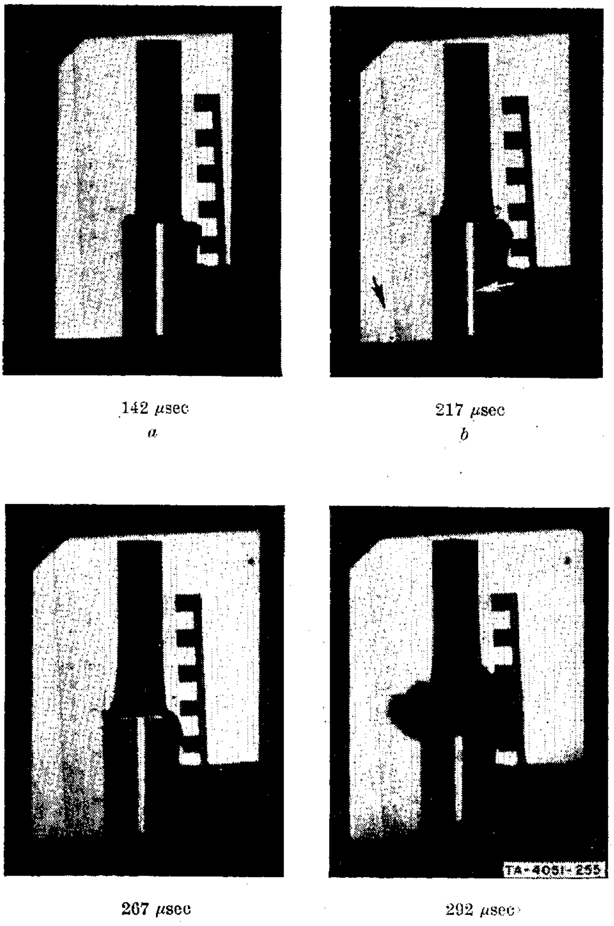
Anomalies in Detonation Initiation of Liquid Explosives

ATTENTION has recently been directed to the study of low velocity detonations (LVD) (refs. 1 and 2), which propagate at velocities only slightly supersonic with respect to the unreacted liquid and may be very easily initiated in some liquids. It is the purpose of this communication to show that both the shape and material of the container and the presence of a witness plate affect LVD initiation. Theories proposed for LVD (refs. 1–3) require that the container sound speed be greater than that of the liquid explosive. We have tested this prediction by using lead tubes with 1,2-difluoroaminopropane, a liquid known to sustain normal and low velocity detonations[4]. Because of the low sound velocity, we expected that weak initiating shocks would not yield LVD in lead though identical shocks would in steel. Unexpectedly, there was definite evidence of LVD propagation. The experiments were repeated and photographed with a high speed framing camera. The lead tubes used were 1·27 cm inner diameter × 0·635 cm wall × 10·4 cm long, and the shock source consisted of an exploding bridge-wire detonator, a small (~ 1 g) RDX pellet, two pressed tetryl pellets (each 3·87 cm diameter × 2·54 cm long; density ~ 1·51 g/cc; weight ~ 90 g), and a 'Plexiglas' attenuator (3·87 cm diameter × 30·5 cm long). The shock strength at the end of the attenuator was about 1 kbar compared with about 60 kbar required to initiate normal detonation.

Frames selected from the photographic record are shown in Fig. 1. The experiment was backlit with an electronic flashgun and the principal features appear as shadows. These include a transparent ruler and a notched strip to serve as fiducial markers, the lead tube (the large black rectangle in the upper half of each frame), and the 'Plexiglas'. Because of its shape the 'Plexiglas' transmitted a thin strip of light parallel to its axis. Irregularities at the 'Plexiglas'–lead interface arise from bits of cement used in assembling the shot. Numbers below each frame are the lapsed time from initiation of the detonator. Fig. 1(*a*) shows the still unshocked system. From independent measurements the time at which the shock reaches the 'Plexiglas'–lead interface is known. Then the lead expands and wrinkles (Fig. 1(*b*)). The air shock from the donor (marked by arrows) is apparent in the discontinuities across the ruler and the light strip along the 'Plexiglas' axis. (This situation may not be evident in the half-tone; a limited number of photographic prints are available from the author on request.) At 267 μsec after initiation (Fig. 1(*c*)) the air shock has reached the lead which has now separated from the 'Plexiglas'. The



142 μsec
a

217 μsec
b

267 μsec
c

292 μsec
d

Fig. 1. Low velocity detonation in lead.