

that the slope of the straight-line portion of the curve should correspond to a viscosity which is nearly equal to the viscosity of the Newtonian component of the dispersion. Goodeve and Whitfield have found this to be true for carbon black pastes⁶. The second test is that the temperature coefficient of the flow should indicate an activation energy in the low-stress region typical of the Type 1 bonds, while the activation energy in the high-stress region should have the much lower value typical of the Type 2 bonds. This is confirmed by the reported observations of Eley and Pepper, who find 30 kcal. and 11 kcal. respectively in the two regions.

Thus we conclude not that the relaxation theory of flow treated according to statistical mechanics is in question, but that, given the data on flow of a complex system, one can discover its mechanism.

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¹ Eley and Pepper, *Nature*, **154**, 52 (1944).

² Eyring, *J. Chem. Phys.*, **4**, 283 (1936).

³ Tobolsky, Powell and Eyring, "Chemistry of Large Molecules", 125 (Interscience, 1943).

⁴ Powell, thesis, Princeton University (1943).

⁵ Blott and Samuel, *Ind. Eng. Chem.*, **32**, 68 (1940).

⁶ Goodeve and Whitfield, *Trans. Far. Soc.*, **34**, 511 (1937).

Powell and Eyring have shown that the form of the flow/stress relation observed by us may be described by the addition of a second flow-process. Since this second process is postulated to involve weak bonds, it will be Newtonian on their theory.

We would note that the need to assume two types of bond is not so clear for a plasticized polymer as for a solid-liquid dispersion. In fact, Tobolsky and Eyring² have considered only one bond, of the strong type, in the flow of plastics, and have derived a theory of extrusion on this basis. Some point may be added to this objection by the observation that the test of Powell and Eyring, that the limiting viscosity of the system should nearly equal the viscosity of the Newtonian component (that is, plasticizer), fails when applied to our system. The former is 10^8 poises, while the latter is 0.2 poises.

Powell and Eyring quote experiments on solid-liquid dispersions. It seems a somewhat lengthy extension of the theory of relaxation, to apply it to the forces between macroscopic solid particles. However, assuming this to be correct, their theory implies that as the stress is increased, the flow should first be exponential, then Newtonian, and then once again exponential, the last effect occurring when the stress f_2 on the weak bonds reaches values where $f_2 \lambda_2 \lambda_3 \gg 2kT$. This last effect has never been observed, but it would offer a possible test of their theory.

We would not claim that the above remarks definitely rule out some form of two-bond mechanism for our system, but we would submit that there is a case for examining all possible 'one-bond mechanisms'. The general notion of a potential barrier may be taken as essential to any theory of flow in plastics, but the specific features of Eyring's theory, such as the hyperbolic sine law for stress, have never been properly established. For example, a test of this law carried out by Tobolsky and Eyring on creep and stress relaxation in rubber and steel² was

successful only up to a point, in that the viscous volume parameter, $\lambda_1 \lambda_2 \lambda_3$, was found to depend upon initial stress. The position cannot be clarified until a larger body of evidence is available on the flow of plastics and liquids, including especially Newtonian liquids, over the widest possible ranges of stress and temperature.

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¹ Tobolsky and Eyring, *J. Chem. Phys.*, **11**, 131 (1943).

² Tobolsky and Eyring, *J. Chem. Phys.*, **11**, 128 (1943).

Formation of Apatite from Superphosphate in the Soil

THE bulk of the phosphate added to soils as fertilizer remains in forms unavailable to plants. In calcareous soils it has been said to form hydroxy-apatite. From a study of the reversion of mixtures of superphosphate and liming materials, MacIntire and his associates¹ have recently suggested that the ultimate form of some of the phosphate applied to heavily limed soils may be fluorapatite; but, so far as we have been able to ascertain, no direct evidence has ever been obtained of the actual presence in the soil of apatite formed from fertilizers.

The Broadbalk continuous wheat plots at Rothamsted provide favourable conditions for studying this question. Superphosphate has been applied to some of the plots annually for nearly a century, and the whole field had been heavily dressed with local chalk some decades before the experiments commenced. Since it appeared likely that the phosphate would accumulate in or around the soft porous chalk particles, these were isolated from samples of two plots taken in the spring of 1944. Such fragments (0.5-2 mm. diameter) from the plot (No. 5) with superphosphate but no nitrogenous fertilizer contained about 3 per cent P_2O_5 , which is ten times as much as on the plot (No. 3) without fertilizer. On heating the chalk from plot 5 to 800° and extracting with carbon dioxide-free sucrose solution to remove calcium oxide, a residue was left which gave the X-ray powder diagram of apatite. A partial analysis of a 140 mgm. sample of the residue gave 47 per cent CaO, 26 per cent P_2O_5 , 1.5 per cent F and 10 per cent insoluble in hydrochloric acid. (Some fluorine was lost during the ignition.) The refractive index was n_D 1.601. Efforts to isolate the phosphate from the chalk without heating have not yet been successful, but X-ray diffraction data suggest that apatite is present.

Further analyses showed that where superphosphate had been applied, the phosphate content increased rapidly with decreasing grain size of the chalk fragments. The values for individual grains were highly variable, but consistent results were obtained by separating the whole of a given fraction from a bulk soil sample.

P ₂ O ₅ PERCENTAGE OF CHALK FRAGMENTS FROM BROADBALK SURFACE SOIL (SECTION 4), 1944.			
Mean values in whole fraction from 500 gm. soil			
		Plot 5	Plot 3
	0.5-2 mm.	2.8	0.33
	2-5 mm.	2.0	—
Individual grains 3-7 mm.			
	Mean	1.4	0.13
	Extremes	0.09-5.5	0.045-0.23