matters arising

Deposit-forming by zinc dithiophosphates in base oils during oxidation

A RECENT report by Bird and Galvin[1] has described experiments in which specimens of En 31 steel were immersed in solutions of zinc dialkyldithiophosphates in white oil and either heated over a range of temperatures for 16 h or rubbed for 10 min against a disk of the same material. Electron spectroscopic investigations of the surface films formed at 140 °C showed a product having a zinc–phosphorus–sulphur ratio of 1 : 1 : 0.6, and this ratio was said to be constant over a range of conditions, and was thus assumed to be a decomposition product of the original additive. Zinc phosphate, sulphide and sulphite formations were not observed.

Work in our laboratories on the oxidation stabilities of mineral oil blends of zinc dithiophosphates has revealed similar decomposition residues. The formation of these was, however, found to depend on both the hydrocarbon group in the dithiophosphate and the nature of the base oil. Thus, when a solution of a zinc disecondary alkyl dithiophosphate in a high sulphur content base oil was heated at 120 °C for 164 h and subjected to a stream of dry oxygen, a residue was formed which had a zinc (24.6%)–phosphorus (12.6%)–sulphur (4.5%) ratio of 1.0 : 1.08 : 0.37, which was not too dissimilar from that found at the iron surface by Bird and Galvin[1]. Further, X-ray examination of this residue showed that it was a complex inorganic material in which zinc oxide, sulphide or phosphate was absent. When blends of this additive in low sulphur content mineral oil base fluids were similarly tested this residue was not produced.

Substitution of zinc diprimary alkyl or diaryl dithiophosphates in the above range of base oils failed to produce any residues. It was therefore concluded that the decomposition was a function both of the base oil and the hydrocarbon group in the dithiophosphate. Previous work has suggested[2] that the decomposition of zinc dialkyldithiophosphates is dependent on the number of β-hydrogen atoms attached to the alkyl constituent, and this is fully consistent with the results obtained in our present work.

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[1] Bird, R. J., and Galvin, G. B., *Nature*, **254**, 130 (1975).
[2] Dickert, J. J., and Rowe, C. N., *J. org. Chem.*, **32**, 647 (1967).

Haemoglobin type and superovulation in ewes

PANT and Pandey[1] reported that haemoglobin (Hb) type in Binaneri ewes influences the ovulatory response to exogenous gonadotropin (pregnant mare's serum gonadotropin, PMSG). The practical and physiological implications of this finding prompt us to present the results of a study of the relationship between Hb type and ovulatory response to PMSG in parous, non-lactating Welsh Mountain ewes.

Eighty-six ewes were given 1,000, 1,100 or 1,250 IU PMSG (Folligon, Intervet) on day 12 (day 0 is the day of oestrus) of the oestrous cycle and ovulation rate assessed by counting the corpora lutea present at laparotomy on days 2–8 of the subsequent cycle. Hb type was determined by starch gel electrophoresis in a Tris-EDTA borate buffer system, *p*H 8.2 (ref. 2). An analysis of variance of ovulation rate, after transformation of the raw data to $(x + 1)^{\frac{1}{2}}$, showed no significant effect of either Hb type or dose of PMSG. Table 1 shows the mean ovulation rates for Hb type, the data being pooled for dose of PMSG.

A further 16 ewes were given 500 IU PMSG and ovulation rate examined as before. Mean ± s.e. (number of ewes) ovulation rate for AA, BB and AB Hb types were 1.3 ± 0.21 ($n = 6$), 1.6 ± 0.24 ($n = 5$) and 2.2 ± 0.37 ($n = 5$), respectively.

These results argue strongly against a correlation between Hb type and ovulatory response to superovulation in Welsh Mountain ewes. Breed or environmental differences may, however, explain the discrepancy between our results and those of Pant and Pandey[1]. It is clear that Hb type in Welsh Mountain ewes is not a major determinant of the very substantial individual variation in ovulation rate observed after administration of PMSG.

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[1] Pant H. C., and Pandey, M. D., *Nature*, **258**, 738–739 (1975).
[2] Gahne, B., Rendel, J., and Venge, O., *Nature*, **186**, 907–908 (1960).

Volcanic triggering of glaciation

IN his latest contribution to the discussion of the links between volcanism and glaciation[1], Bray perpetuates a concept that he proposed in much stronger terms in his two earlier contributions on the same subject[2,3]; namely that there is evidence of "an apparent correlation between major phases of global ice advance and ash eruptions in New Zealand, Japan and southern South America over the past 42,000 yr". This represents a slight modification of his earlier view that there were worldwide 'waves' of volcanic activity that could be correlated with the same ice advances[3].

I am not in a position to comment on the evidence from Japan or New Zealand, but in my opinion the postulation of correlatable episodes of volcanic activity and ice advance in southern South America is extremely unwise, simply because there is so little factual evidence. All such postulations are based on the widely quoted but rarely read work of Auer[4–7]. It is clear from his descriptions that the ash horizons that Auer used in his work, were, in most cases, air-fall ashes from single volcanic eruptions, which may have been quite small. There is no evidence for any massive eruptions, nor for any waves of eruptions. The weakness of the evidence for such waves is compounded by the very small number of published radiocarbon dates; there are probably less than a dozen such dates for volcanic eruptions in the whole of South America.

It is quite correct, as Bray states, that "the possibility that large Pleistocene

Table 1 Hb type and ovulatory response to PMSG* in Welsh Mountain ewes

Hb type	AA	BB	AB	Total
Ovulation rate (mean ± s.e.)	8.6 ± 0.96	8.2 ± 0.90	10.0 ± 1.29	8.9 ± 0.63
No. of ewes	20	35	31	86

*PMSG at 1,000–1,250 IU.