

The conditions for polyvinyl chloride to exert a catalytic effect are therefore: (a) that it is present in an undissolved state; and (b) that benzoyl peroxide, or some other source of reactive free radicals, is also present in the system. It is suggested that this co-catalytic effect is due to a gradual increase in the total number of active centres as the polymer accumulates in the system. The additional centres are believed to be derived by a chain transfer reaction between free radicals and conglomerates of polymer, thus producing immobile radicals in the surface of the polymer which are largely free from the process of self-neutralization which occurs in the liquid phase. The number of these radicals will be proportional to the surface area of the polymer and also to the number of mobile radicals present, while the latter will depend upon the concentration of the catalyst. As the reaction proceeds there will therefore be an increase in the number of radicals present and consequently an increase in reaction-rate.

It is well known that 'polymer begets polymer'. For example, with vinyl chloride it has been found in technical operation that if a small amount of polymer be formed at a bend or constriction of a pipe conveying the liquid monomer under pressure, this will grow in course of time, often with serious results. Upon the above ideas it is easy to see that, even in the absence of catalyst, adventitious centres in the monomer can react, by transfer with the polymer as they flow past, to produce an active surface, which will cause the initial seed to grow continuously though slowly until the pipe is blocked.

A detailed kinetic analysis has been made, and this, together with full experimental results, will appear elsewhere.

W. I. BENGOUGH  
R. G. W. NORRISH

Department of Physical Chemistry,  
University of Cambridge,  
Jan. 4.

<sup>1</sup> Prat, *Mem. Serv. Chim. Etat, Paris*, **32**, 319 (1945).

<sup>2</sup> Dostal and Mark, *Z. phys. Chem.*, **29 B**, 299 (1935).

<sup>3</sup> Cuthbertson, Gee and Rideal, *Proc. Roy. Soc., A*, **170**, 300 (1939).

<sup>4</sup> Nozaki and Bartlett, *J. Amer. Chem. Soc.*, **68**, 2377 (1946).

### Photo-chemical Activity of Paint Pigments

RECENT experience has shown that certain grades of zinc oxide of local manufacture markedly accelerated the initiation of chalking in paint films. In the course of an investigation into these differences, it was observed that they corresponded to differences in the fluorescent behaviour of the zinc oxides when irradiated with ultra-violet light. The zinc oxides (Series A, three samples from two manufacturers), prepared by burning zinc vapour in air (French process), showed no visible fluorescence at room temperature and markedly accelerated the initiation of chalking, as compared to the zinc oxides (Series B, four grades from three manufacturers) prepared by burning zinc vapour in air containing reducing gases (as in the American process), which showed a strong yellow fluorescence.

This result is in apparent conflict with some statements made in the literature<sup>1</sup>, but a comparative test for fluorescence using an 'Osira' lamp has provided a useful means of selecting non-chalking grades of zinc oxide available in Australia.

A distinct difference in the photo-chemical activities of (A) and (B) was also noted. An aqueous

suspension of (A), after irradiation for a short period with an 'Osira' lamp, was found to contain hydrogen peroxide<sup>2</sup>, liberating iodine from potassium iodide solution, decolorizing permanganate solution and giving a yellow colour with titanium sulphate solution. Longer irradiation by direct sunlight also caused formation of hydrogen peroxide. A suspension of (B) treated in the same way gave no reaction for peroxide.

The major contributing factor in the different performances of paints containing (A) and paints containing (B) must be that in the former the high-energy portion of the solar radiation is utilized as photo-chemical energy, whereas in the latter it is dissipated as lower-energy radiation<sup>3</sup>. From (A) the energy may be transferred directly to the unsaturated fatty oil, providing the energy required for the removal of hydrogen from the  $\alpha$ -methylene group, this being the initial step of the oxidation suggested by Farmer<sup>4</sup>. From the above evidence, however, it appears to be more likely that transfer of energy to oxygen takes place followed by entrance of molecular oxygen at the double bond, as suggested by Hilditch<sup>5</sup>. The production of hydrogen peroxide in the presence of water also provides an explanation for the observed acceleration of chalking under moist conditions.

It is hoped that a detailed study of the fluorescence spectra and their dependence on environment for a number of differently prepared zinc oxides and other pigments will provide further information about their influence on the photo-chemical oxidation of paint vehicles.

G. WINTER

General Chemistry Section,  
Defence Research Laboratories,  
Melbourne. Aug. 19.

<sup>1</sup> Kekwick, *J. Oil and Col. Chem. Assoc.*, **21**, 118 (1938).

<sup>2</sup> Narasimha, Chari and Qureshi, *J. Ind. Chem. Soc.*, **21**, 97 (1944).

<sup>3</sup> See Goodeve, *Trans. Farad. Soc.*, **33**, 346 (1937).

<sup>4</sup> Farmer and Sutton, *J. Chem. Soc.*, 119 (1943). Farmer, Koch and Sutton, *J. Chem. Soc.*, 541 (1943).

<sup>5</sup> Hilditch, *J. Oil and Col. Chem. Assoc.*, **30**, 1 (1947).

### Thermal Activation of the Dehydrogenase Systems of the Unfertilized and Fertilized Eggs of the Sea Urchin, *Paracentrotus lividus*

Runnström<sup>1</sup> and Örström<sup>2</sup> were the first to try to compare the dehydrogenase activity in the sea urchin egg (*Paracentrotus lividus*) before and after fertilization by means of methylene blue reduction experiments. They could not reveal any difference. However, Ballantine<sup>3</sup>, carrying out similar experiments, was able to demonstrate a rise in the rate of methylene blue reduction in the sea urchin *Arbacia punctulata* ranging from 2.2 to 3.7 times. In 1939 Miss Inger Stordal, in preliminary experiments in collaboration with one of us (P. E. L.), proved the methylene blue reduction by fertilized eggs to have a higher temperature coefficient than that of the unfertilized egg. The completion of these experiments was postponed because of the outbreak of war.

Our experiments carried out at Roscoff (France), at a temperature of about 12°, 16°, 20° and 24° C., confirm this result; thus the difference in reduction-rate is nil, or comparatively small, at 12°, but rather considerable at 24° C. This is due to the different slopes of the temperature curves, and also to the different forms of the curves, those of the fertilized