$$Z = V_2/V_1 =$$

$$\frac{\left[v_2^{1/3}/3 \left\{ (a_1'^2 + a_2'^2 + a_3'^2) - \frac{1}{b^2}(a_1^2 + a_2^2 + a_3^2) \right\}(a_1' \cdot a_2' \cdot a_3')^{-\frac{2}{3}} - 2v_2 - \frac{1}{f(1/v_2 - 2 + 1/\sigma)} \right]}{v_2^2 \left[(\frac{1}{2} - \mu) + \frac{v_2}{3} + \frac{v_2^2}{4} + \cdots \cdots \right]} \quad (4)$$

16. Studies on the Temperature rise and its Iufluence on the Degree of Polymerisation in the Emulsion Polymerisation of Vinyl acetate

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By many investigations on the emulsion polymerisation, it has already been recognized that the locus of polymerisation is in the micelles of detergent molecules in the earlier stage of polymerisation and is in the monomer–polymer particles in the later one. Recently through the studies by S. Okamura ("Synthesis and Applications of Polyvinyl Emulsion" (in Japanese) 1949.) and by M. Matsumoto ("J. Chem. High Polymer (Japan) 7, 390, 1950) it has also been found the different ıelationships between the degree and the conversion of polymerisation in both stages.

In the paper reported here are considered the relations between the degree of polymerisation and the rise of temperature in the emulsion polymerisation of vinyl acetate. By the usage of sodium lauryl sulphate as emulsifier, the size of emulsion particles and also the amount of heat accumulated in the polymerising particles are both found to diminish markedly. From these effects, the branching polymerisation occurs to the less extent than in the case without any emulsifiers, and so the difference of the degree of polymerisation as polyvinyl–acetate ($\overline{P}_{Ac}$) and as as alcohol ($\overline{P}_A$) is very small. The effects of agitation on the relationships mentioned above are shown in Figure–1. At the strong agitation the polymerisation occurs mainly in the swollen polymer particles and so $\overline{P}_{Ac}$ are found to increase but $\overline{P}_A$ to decrease during the polymerisation proceeds.

Assuming that the heat of polymerisation is spent to warm the emulsion liquid and the emulsion particles and also to escape at constant rate through the wall of reaction vessel, the elevation of temperature in the emulsion particles is evaluated as shown in Figure 2. At the maximum temperature shown in figure (e. g. ca. 77°C.), the amount of monomer remaining in particles reaches 50% or more. The boiling point of monomer in swollen state is considered to be higer than normal value (73°C)) and these relations are calculated by the Huggins–Boyer's equation

$$\ln a_1 = \ln (1 - x/100) + x/100 + \mu(x/100)^2$$

and by the following formula:

$$\Delta T = \frac{RT^2}{L} \ln a_1 \ ,$$

where x is the yield of polymerisation, μ the constant of interaction between polymer and monomer, L the latent heat of vaporization, T the normal boiling point of monomer and ΔT is the degree of boiling point elevation.
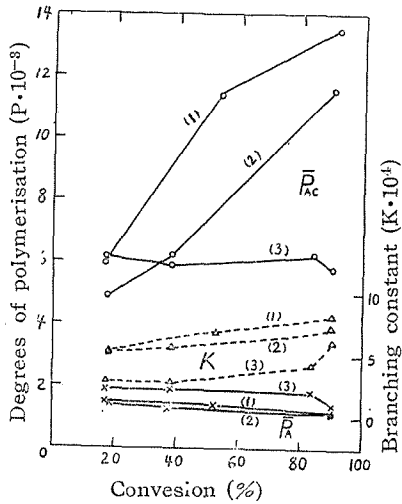

Figure 1. Effects of agitation on the emulsion polymerisation (VAc. 10cc, H_2O 50 cc, APS. 0.05 g. at 70°C.)
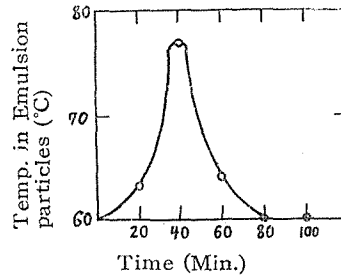(1) Strong agitation,
(2) Weak agitation
(3) Stand-still

Figure. 2. Estimated temperature in emulsion particles. (VAc. 4 cc, H_2O 50cc, APS. 0.1 g at 60°C.