Action of p-Toluenesulfonyl Chloride as the Cold-setting Accelerator for Thermosetting Resins

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As the cold-setting accelerator for thermosetting resins, *p*-toluenesulfonyl chloride (PTSC) is widely used, but differing from free acids it does not readily develop its action. The fact is evident when we observe the viscosity and temperature changes with the setting time of cold setting resin solutions containing PTSC.

For this purpose the measurement of the electric resistivity change serves to a certain extent.

The platinum electrodes of 1 mm diameter were set in the resin solution at intervals of 10 mm and in the depth of 3 mm. The D.C. voltage of 3V was applied between these electrodes and the current was measured with setting time from which the resistivity was calculated.

PTSC used was colorless crystal with the exact m.p. of 69°C. Furfuryl alcohol used as the resin monomer, was distilled at 81°C under 20 mm Hg prior to use.

The results were summarized and indicated in Fig. 1.

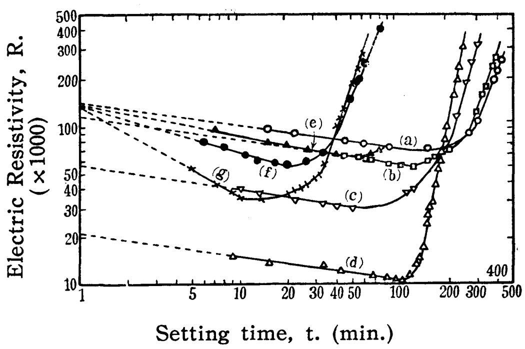

Fig. 1. The curves of electric resistivity versus setting time of the furfuryl alcohol containing PTSC.
Furfuryl alcohol 7.00 g, PTSC (a) 0.207 g, (b) 0.300 g, (c) 0.600 g, (d) 1.003 g, temp. 31.7±03°C.
Furfuryl alcohol 7.00 g, PTSC 0.207 g, (e) 37.3±0.3°C (f) 47.7±0.3°C (g) 57.7±0.3°C.

It can be seen in this figure that each curve consists of three parts. Of these, the initial part of resistivity decrease satisfying the approximate formula $R=kt^{-z}$, indicates the decomposition of the sulfonyl chloride, and the final increase following the relation $R=K'\cdot t^{z'}$, can be explained only by the resinification. The intermediate part is supposed to be transitional.

As for the initial stage, a similar change was also observed in the case of the measurement on the furfuryl alcohol in dioxane and the resole in dioxane using 500 V megger.

The constants of the above two formulas, K, Z, and Z' were calculated from Fig. 1, which were found to satisfy the following approximate formulas.

$$K=Ae^{-\alpha c}, \qquad Z=Be^{\beta\theta}, \qquad Z'=Sc^{b}$$

(A, B, S, α, β and b are constants, c the catalyst concentration, and θ the setting temperature).

Further, the point of intersection made by the extension of initial and final linear portions can be regarded as the point of complete decomposition of PTSC. The time T corresponding to this point was approximately expressed by

$$T = pc^{-q} \ (p,\ q \text{ are constants}).$$

In addition, it was observed that the time T required for the complete decomposition, was remarkably affected by the setting temperature. (Change of temperature from 32°C to 58°C reduces T to ca. 1/10, while 5 times increase of concentration of the accelerator only reduces T to ca. 1/2 of the value at 32°C).

Thus it is suggested that to develop the accelerator action of PTSC, the temperature rise is more effective than the accelerator increase.

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