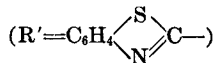


$\text{Me}_2\text{N}^+\text{C}^-\text{NMe}_2$). The anions of thioacetic acid ($\text{R}' = \text{MeCO}$) which have a marked accelerative effect also meet the theoretical requirement. Conversely, one would expect retardation of vulcanization where the group R' is less reactive towards basic nucleophils than is the thiocarbonyl center, X. This has recently been demonstrated by Swift⁵ who has shown, first, that the rate of crosslinking in a NR-TMTD-ZnO system is decreased when mercaptobenzothiazole



is included, and second, that there is complete inhibition of cure when naphthalene-2-thiol is added to the system.

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Particle Identity Point in Suspension Polymerization

One important parameter which should be known for the understanding and control of the suspension polymerization process is the per cent conversion after which the particles

retain their identities for the rest of the polymerization. In all cases the monomer was styrene, the suspending agent was a combination of polyvinyl alcohol and a sodium salt of an alkyl-aryl sulfonic acid used in 0.7 wt.-% based on the monomer, and the oil-to-water weight ratio was one-to-one. The polymerization conditions were 0.22 wt.-% of benzoyl peroxide, 95°C. for 10 hours duration, followed by 3 hours at 120°C. under nitrogen pressure. The procedure was as follows: A batch of clear polystyrene beads were made under the standard conditions and the -18 +20 screen fraction isolated as Material I. Another batch was made with the monomer saturated with a high molecular weight dye (National Carbanthrene Printing Golden Orange G Double Powder). The -18 +20 screen fraction of these deep orange beads was isolated as Material II. Appropriate weights of I and II were then suspended together in water, equilibrated under agitation with styrene monomer (containing the appropriate amount of catalyst) at room temperature for 48 hours, to yield the equivalent of the standard suspension polymerization at 25% or at 50% conversion. The temperature was then raised to 95°C. and the appropriate remainder of the polymerization cycle completed. To establish the "0% conversion" behavior, the standard polymerization was conducted with the only variation being that the monomer was added in two equal successive increments, the latter containing the orange dye.

From each of the last three polymerizations described, the beads were recovered, dried, randomly sampled, and each sample completely categorized. Results are given in Table I.

The discrepancy between the half-count and the full count is attributed to the very large number of tiny clear beads which sifted to the bottom of the sampler; these beads are presumably formed from the small amount of monomer reflux returned to the kettle. Unfortunately, the counted beads were not weighed as then the influence of these small clear beads could have been shown to be negligible.

From the data in Table I it is concluded that, under the specific conditions employed, almost all the particles in these suspension polymerizations of styrene retain their identities after 50% conversion. Further, at 25% conversion about one-half of the particles will continue to retain their identities throughout the rest of the polymerization.

TABLE I

Run No.	% conversion at which color was added	Number of beads in sample	One-half count ^a				Full count			
			% orange	% yellow	% clear	% $1/2 \times 1/2^b$	% orange	% yellow	% clear	% $1/2 \times 1/2^b$
3	0	ca. 5000	0	100	0	0	0	100	0	0
4	25	6062	31.3	29.3	36.3	3.1	22.1	29.6	46.7	1.6
5	50	4493	45.1	2.2	48.0	4.7	40.4	2.1	53.9	3.6

^a Score after counting one-half of the total sample.

^b Any bead containing clear and colored portions was placed in this category.

retain their identities for the rest of the polymerization. This "particle identity point," PIP, has not been explicitly determined insofar as this writer is aware. This letter is to record an attempt to determine a PIP for a particular system.

The experimental equipment used was a standard laboratory glass stirred polymerization autoclave with a 1-liter ca-

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