

NOTES

The Mechanism of Scale Formation in PVC Reactors

Suspension polymerization of vinyl chloride is almost invariably accompanied by the formation of scale on the internal surfaces of the polymerization reactor, including moving surfaces such as those of the impeller. This deposit consists of a PVC which is generally of a lower porosity than the particles of suspension polymer produced concurrently in the reactor. This scale impairs heat transfer, interfering with temperature control. If allowed to build up, it can produce changes in the internal reactor topography which can affect the suspension system. This will be particularly marked if the build-up is on the impeller. The difference in character, particularly porosity, between the scale and the suspension particles gives rise to problems if particles of scale become detached and mix with the bulk of the polymer particles. The lower porosity of the scale results in a markedly slower uptake of plasticizer and other compounding additives compared to the particles of the bulk of the resin. The presence of scale particles in a resin will become apparent on compounding ("fish eyes") and reduces the quality of the resin.

Scale must, therefore, be removed periodically. This involves reactor down-time, is expensive,¹ and is generally done mechanically by scraping or high velocity water jet or by the use of solvents. Some of these methods necessitate the entry of personnel into the reactor, which today is considered to be highly undesirable in view of the carcinogenic nature of the monomer. Mechanical scraping can damage the reactor surface, which increases the rate of scale formation. The use of solvents involves solvent recovery problems. Scale formation is, therefore, a totally negative phenomenon; and though numerous efforts have been made to overcome this problem, as evidenced by the number of patents on this subject, the total prevention of scaling does not appear to have been achieved. Nor has a satisfactory explanation of this phenomenon appeared in the literature. An understanding of the causes of this phenomenon hopefully will contribute to its eventual prevention.

Published information on this subject is sparse. A number of findings indicate that the initial stage of scale formation is a nucleation phenomenon. Two examples suffice to demonstrate this: the initiation of scale formation is faster on stainless steel than on glass,¹ and for both materials it is much faster on surface imperfections such as scratches. Glass has a smoother surface than stainless steel, if the latter has not been specially treated. The rapid formation of polymer along scratches is particularly noticeable when working in transparent glass reactors. PVC is known to have a very low solubility in the monomer,² which is already evident at low molecular weights,³ so that polymer radicals growing in the liquid monomer phase precipitate out almost as soon as they are formed.⁴ The tendency will be for these radicals to precipitate out onto existing nuclei such as polymer particles rather than for them to form new nuclei which is less favored thermodynamically.³ At the beginning of the polymerization, when few or no nuclei exist in the suspension, these macroradicals will, therefore, tend to precipitate out on any available imperfections on the reactor walls. The same mechanism also accounts for the rapid build-up of scale once its formation has been initiated. This precipitation of macroradicals almost as soon as they are formed results in a rapid transfer of radical activity from the monomer phase to the polymer phase.^{5,6} As a direct result of this, the rate of polymerization is greater in the polymer phase than in the monomer phase.^{7,8} In fact, already at 5% conversion, 84% of the polymerization occurs in the polymer phase⁵ and the rate increases with conversion.⁷ If a reaction is started in a reactor which contains scale, this is equivalent to starting a reaction with added polymer, and this is known to increase the rate.⁹ The point of interest here is that this increase in rate occurs almost exclusively in the polymer phase^{5,6} which, in this case, is the scale. This is the mechanism which causes scale to build up more rapidly with each additional batch run in the reactor.

In the presence of monomer, the scale is swollen with the latter. At 50°C, the polymer phase contains 6 moles/l. vinyl chloride,⁵ that is, the polymer phase contains approximately 32% vinyl

chloride. It is this monomer which polymerizes in the polymer phase, and the resulting interstitial polymerization³ reduces the BET specific surface² and the porosity of the polymer. This explains why the scale becomes less porous and harder with each batch run in the reactor. The mechanism proposed here to explain scale formation indicates that, although it may be possible to delay the formation of scale by various stratagemms such as using reactors with highly polished internal surfaces, once the formation of scale has been initiated its rapid build-up is inevitable.

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