The term polysulfide polymers referred at one time exclusively to the high-sulfur-containing polymers as manufactured by the Thiokol Chemical Corp. From 1928 to 1960 they were the only high-sulfur polymers available. The solid polysulfide polymers contained 37–82% bound sulfur, while the liquid polymers contain approximately 37%, which gives them their unique chemical properties.

Between 1960 and 1976 several new mercaptan terminated polymers having varied polymer backbones were introduced. These are covered in the section entitled "Other Mercaptan Terminated Polymers." The chemical resistance of these various polymers can vary depending upon their backbone structure and, on this basis, should be evaluated on their own relative merits.

POLYSULFIDE SEALANTS

Sealants based on polysulfide liquid polymers originally found wide acceptance for applications requiring a flexible, adhering, chemically resistant composition of matter. Since they were the first liquid polymers available that could be cured at room temperature, they were soon specified for a number of military applications. Their use as aircraft sealants for fuel tanks still remains as a major outlet. Other military applications included a quick hose repair compound, a sealant for bolted steel tanks for quick assembly on the battle front, electrical potting compounds, caulks for wooden flight decks which were designed as a stop gap in the early days of aircraft carriers, sealing and adhering methacrylate bubbles on aircraft, sealing cocoons in the mothball fleets, adhering aluminum strips on wings for reducing air turbulence during flight, and many others. Most of these were emergency measures adopted for immediate use during the early 1940s and covered by quick-issue military specifications.

Use of polysulfides is at present largely restricted to sealants and insulating glass. Where these polymers were dominant in the 1960s and early 1970s, they are now a poor third as building sealants, giving way to silicones and urethanes. The decline of polysulfide sealants in the U.S. has been due in part to a price war which resulted in inferior-quality building sealants, causing many suppliers to switch to urethane. Some companies made their own urethane-base polymers while others bought a prepolymer from several sources. Another reason for the decline was the better performance available with urethane and silicone sealants. In Europe, the polysulfide sealants have a better market because of more rigid control of performance, application, and specification.

One continuing large application for polysulfide sealants is as a glass adhesive for making insulating glass units. This application started out in a small way in the early 1940s using a plasticized solid polysulfide polymer; but this was quickly replaced by the more versatile liq-
uid polymer. In recent years, polysulfide sealant, while still first, has been steadily giving ground to other systems including butyl hot melt and the dual system of silicone/polysisobutylene. The hot melts are cheaper, and lend themselves to automation and lower labor costs. The polysulfide systems are ending up as lower quality units for public housing and the home repair market which are not greatly affected or controlled by specifications. The high quality market for industrial and high rise buildings is now using some polysulfide, but the best units are made using a dual system of silicone/polysisobutylene. The trend will continue, with polysulfide losing out where high quality and good performance specification will prevail.

Another large market in the past was the use of polysulfide sealant as a glass adhesive for installing automotive windshields. In the original process, the glass was attached by metal trim on the assembly line. General Motors designed a three-part mixer which was made by Pyles Industries, and the use of the very fast-curing polysulfide actually lowered total costs. Thus polysulfide was adopted by General Motors for many of their models; later, Chrysler joined. This market lasted for approximately five years; but eventually the polysulfide was replaced by a simpler system consisting of a one-part urethane activated by mixing water into the sealant just before use. Here again, cost savings dictated the final selection.

The replacement market started out using a two-part polysulfide which was difficult to handle. This was quickly replaced by the one-part silicone, which was more expensive but more foolproof. In the replacement market, labor costs were less important.

Another large market which held sway for approximately 6 years in the early 1960s was the use of the sealant for military runway expansion joints. These sealants were highly extended with filler and coal tar, and used specialty polymers to meet the required low cost. The bubble burst when the sealants hardened with time, lost adhesion, and had to be replaced. The new system was a hot melt of plasticized PVC, which has done an admirable job with a simpler system and was eventually covered by ASTM specifications.

Areas where the polysulfide sealants are still used include dental impression compounds, cast printing rolls, casting compounds for flexible molds, electrical potting, and miscellaneous adhesives.

Polysulfide sealants are excellent adhesives and adhere to a wide variety of surfaces; but price inevitably plays a major role in the final selection of material used for high-volume applications.

Chemistry

Many of the sealants have been prepared using Thiokol® LP®-2, LP®-32 or LP®-31 as the base polysulfide liquid polymer; the chemistry, cure mechanisms, reinforcement, and applications will thus be restricted to these polymers. The chemistry and applications of polysulfide polymers, crudes, water dispersions, and various liquid polymers are covered completely in extensive bibliographies by Berenbaum and Panek. 21

The general preparation of polysulfide liquid polymers, as discussed by Patrick and Ferguson 22 involves first the reaction of bischloroethyl formal with a sodium polysulfide solution containing specific emulsifying and nucleating agents as shown below:

\[ nClC_2H_4OCH_2OC_2H_4Cl + nNa_2S_{2.25} \rightarrow (\text{C}_2\text{H}_4\text{OCH}_2\text{OC}_2\text{H}_4\text{S}_{2.25})_n + 2n\text{NaCl} \]

The sulfur is present as a mixture of disulfide and trisulfide.

In the next step, the high molecular weight polymer is split into segments which are simultaneously terminated by mercaptan groups as shown below:

\[ \text{RSSR} + \text{NaSH} + \text{NaHSO}_3 \rightarrow 2\text{RSH} + \text{Na}_2\text{S}_2\text{O}_3 \]

The concentration of splitting salts controls the average molecular weight of the LP®2 and

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