Polysulfide polymers have the following general structure:

$$HS - (R - S_x)_n SH$$

where x is referred to as the rank and represents the average number of sulfur atoms in the polysulfide unit. This article is limited to polymers of this type where R is an aliphatic group and x > 1. The rank, x, usually ranges from slightly less than two to about four. A recent monograph (1) provides extensive information on the history, properties, and uses of aliphatic polysulfides. Other sulfur-containing polymers have been reviewed (2).

The history of polysulfides began over 150 years ago. In 1838 chemists in Switzerland reported that the reaction of chloraetherin (1,2-dichloroethane) with potassium polysulfide gaveambivalent a rubbery, intractable, high sulfur semisolid. Subsequently there were reports of similar products obtained by various methods, but the first useful products were developed from studies in the late 1920s. This led to the formation of Thiokol Corp. which began production of the ethylene tetrasulfide polymer Thiokol A in 1928, the first synthetic elastomer manufactured commercially in the United States. One of the first successful applications of Thiokol A [14807-96-6] was for seals where its resistance to solvents justified its relatively high price.

These new synthetic rubbers were accessible from potentially low cost raw materials and generated considerable worldwide interest. For a time, it was hoped that the polysulfide rubbers could substitute for natural rubber in automobile tires. Unfortunately, these original polymers were difficult to process, evolved irritating fumes during compounding, and properties such as compression set, extension, and abrasion characteristics were not suitable for this application.

During the 1930s gradual improvements in the product and processing overcame some of the drawbacks of this material. Nonetheless, the applications were limited and Thiokol Corp. struggled to remain solvent. The first year Thiokol reported a profit was in 1941, 13 years after its foundation. This was realized when the U.S. Air Force discovered that the aliphatic polysulfides were useful as a fuel-resistant sealant for aircraft tanks and hoses. Polysulfides also began to be used as sealants for boat hulls and decks.

The most significant improvement came in the early 1940s when a method for preparing thiol-terminated liquid polysulfides was developed. Cure of the liquid polysulfides could be accomplished by oxidative coupling. Thus, in effect, a rubber could be compounded without the need of heavy mixing equipment. One of the first large-scale applications of the liquid polysulfides was as a binder for solid rocket fuel. From about 1946 until 1958, these binders were used in various rocket systems and the aliphatic polysulfides achieved commercial success. The switch to predominately liquid-fueled rockets in 1958 ended this phase of the polysulfide business.

Since then, uses have shifted more toward civilian applications. Polysulfides have unusually good resistance to solvents and to the environment and good low temperature properties. This makes them particularly useful in a variety of sealant applications. For example, the outstanding resistance of polysulfides to petroleum

Table 1. Properties of LP Liquid Polysulfide Polymers^a

Property	LP-31	LP-2	LP-32	LP-12	LP-3	LP-33	LP-977	LP-980
		Sı	pecification red	quirements				
viscosity at 25°C, Pas b	95-155	41-52.5	41–52.5	41–52.5	0.94 - 1.44	1.5-2	10-15	10-15
moisture content, %	0.12 – 0.22	0.3 max	0.27 max	0.27 max	0.1 max	0.1 max	0.26 max	0.26 max
mercaptan content, %	1.0-1.5	1.50-2.00	1.50 - 2.00	1.50 - 2.00	5.9 - 7.7	5.0 – 6.5	2.5 – 3.5	2.5 – 3.5
-			General pro	perties				
average molecular weight	8,000	4,000	4,000	4,000	1,000	1,000	2,500	2,500
pour point, °C	10	7	7	7	-26	-23	4	4
branching agent, %	0.5	2.0	0.5	0.2	2.0	0.5	2.0	0.5
average viscosity								
at 4°C, Pa·s ^b	740	380	380	380	9	16.5	77	77
at 65° C, mPa·s(=cP)	14,000	6,500	6,500	6,500	150	210	1,100	1,100
low temperature flex, ${}^{\circ}\mathrm{C}^c$								
at 69 MPa^d	-54	-54	-54	-54	-54	- 54	-54	-54

^aAll products listed have flash point (PMCC) $> 177^{\circ}$ C. The specific gravity at 25°C ranges from 1.27 to 1.31. CAS Registry Number for all the LPs listed is [68611-50-7], ie, they are copolymers made from (3) and 1,2,3-trichloropropane, and sodium polysulfide.

^bTo convert Pa .s to P, multiply by 10.

(qv) products has made them the standard sealant for virtually all aircraft integral fuel tanks and bodies. Another important application is in insulating glass window sealants (qv). Sealants based on liquid polysulfides have had an excellent record since the 1950s and are the worldwide market leader in this application.

Polysulfides also have a long record as construction sealants. In 1953, the Lever House in New York, New York, was one of the first high rise buildings to abandon the traditional structural masonry for the attractive curtain wall construction. Originally, the joints were sealed with a typical oil-based caulk. Within 6 months, there were serious leakage problems through virtually every joint. The original sealant was removed and replaced with a polysulfide-based elastomeric sealant that could expand and compress with the movements of the panels. Much of this original sealant is still performing in the 1990s. Polysulfides became the first high performance elastomeric sealants to be used in building construction and have been applied successfully to many large-scale projects around the world (see Building materials).

Some of the early Thiokol solid rubbers are still made and used in printing rolls, solvent-resistant spray hose, gaskets, and gas-meter diaphragms. Many of the polysulfide products have been in use since the 1940s with an excellent track record. Continuing improvements in technology keep these products competitive.

1. Physical Properties

The commercial polysulfides are made from bis-chloroethylformal (formal) as shown later in equation 11. In some products trichloropropane is added as a branching agent. Table 1 shows typical properties of polysulfides available from Morton International. These products were acquired from Thiokol Corp. in 1983.

The solid polysulfide products are light brown millable rubbers. Thiokol ST [9065-29-6] (2) is made as in equation 11 with 2% branching agent added. Its

 $[^]c$ Cured compound.

^dTo convert MPa to psi, multiply by 145.

ClCH₂CH₂OCH₂OCH₂CH₂Cl

(3)

Mooney viscosity (ML 1+3 at 100°C) ranges from 28 to 38. Thiokol FA [68611-48-3] is a copolymer made from formal (3) and ethylene chloride with sodium polysulfide; Mooney viscosity (ML 1+4 at 121°C) ranges from 60 to 112. Both rubbers have excellent resistance to a wide range of chemicals. They also have low permeability to gases, water, and organic liquids, excellent low temperature flexibility, and superior resistance to the effects of sunlight, ozone (qv), aging, and weathering.

2. Chemical Properties

2.1. Oxidative Curing

The rich chemistry of the thiol end group provides versatility in modifying and curing polysulfide polymers. The most common means of curing polysulfides is by chain extension with oxidizing agents, eg, equation 1, where R-SH represents liquid polysulfide; O, oxidizing agent; and the product is a disulfide.

$$2R \longrightarrow SH + O \longrightarrow R \longrightarrow S \longrightarrow S \longrightarrow R + H_2O \tag{1}$$

Because thiols are easily oxidized, a host of organic and inorganic oxidants may be used. Mild oxidants such as oximes, nitro compounds, or air can be effective. Various oxidants have been used in special applications, but only a few are used in large-scale applications.

For a long time, lead(IV) oxide, PbO_2 , was the most widely used oxidizing agent for the high molecular weight liquid polysulfides (mol wt > 2500). It was not suitable for lower molecular weight polymers because of the difficulty in controlling the strongly exothermic reaction. Since the early 1970s manganese dioxide, MnO_2 , has become the predominate oxidizing agent. Manganese dioxide [11129-60-5] has several advantages over lead, such as reduced toxicity, better pot life stability, and better light resistance, elasticity, and recovery for the cured rubber.

The newest curing system is sodium perborate monohydrate [10332-33-9], $NaBO_2H_2O_2H_2O_3$, a well-known bleaching agent used in certain laundry cleaning formulations. Therefore, it is produced on a large scale at a reasonable price. Sodium perborate offers several advantages as a curing agent for building sealants. One is that it has a light color rather than the dark color of manganese or lead oxides. Thus, it is nonstaining and sealants can be manufactured in a variety of colors. Sealants cured with sodium perborate have low modulus, excellent elasticity, and outstanding resistance to water, weather, uv light, and mold, even without additives. They have good adhesion to most surfaces and are environmentally friendly.

2.1.1. One-Part Oxidative Curing Systems

The inorganic peroxide curing agents for liquid polysulfides are activated by water. By formulating and packaging polysulfides under anhydrous conditions, one-part sealants are prepared. These cure when exposed to atmospheric moisture and are used in construction sealant applications. The curing agents most commonly used have been calcium peroxide, zinc peroxide/amine, zinc/lithium peroxide, or manganese dioxide. Sodium perborate is also effective in preparing light-colored, fast curing, one-part sealants and is growing in importance.

2.1.2. Epoxy Resins

Polysulfides may also be cured by reaction with epoxy resins (qv) according to the reaction in equation 2. Amines or other catalysts are used and often primary or secondary amine resins are cured together with the polysulfide.

LP-3, the lowest molecular weight liquid polysulfide, is used as a reactive diluent to lower the viscosity of the formulation and to facilitate mixing and application of the resin. The liquid polysulfide also acts as a flexibilizer. The addition of LP-3 to epoxy formulations gives products with good flexibility, high impact strength, excellent chemical resistance, and good adhesion. ELP-3 [117527-71-6] (4) is an epoxy-terminated polysulfide derived from LP-3. An advantage of this product is its low odor, especially in comparison with the thiol-terminated LP-3.

$$\underbrace{\text{CH}_2-\text{CHCH}_2-\text{S}+\text{C}_2\text{H}_4-\text{OCH}_2\text{O}-\text{C}_2\text{H}_4-\text{S}-\text{S}}_{x}\underbrace{\text{C}_2\text{H}_4\text{OCH}_2\text{O}-\text{C}_2\text{H}_4-\text{S}-\text{CH}_2\text{CH}-\text{CH}_2}_{Q}$$

2.2. Diisocyanates or Polyisocyanates

The thiol end groups of the liquid polysulfides are quite reactive with isocyanates (eq. 3). Typical diisocyanates, such as 1,3-toluene diisocyanate (m-TDI) and diphenylmethane-4,4'-diisocyanate (MDI), are effective in curing liquid polysulfides. Using liquid polysulfides in-

$$2RSH + O = C = N - R' - N = C = O \longrightarrow RSC - NH - R' - NH - CSR$$

$$0$$

$$0$$

$$0$$

$$0$$

stead of the common hydroxy-terminated polymers brings the advantages of the polysulfide to the cured product. Thus, good chemical and solvent resistance, weatherability, adhesion, etc, can be attained. The isocyanate-cured systems have some advantages over oxidative-cured systems, such as improved adhesion to plastic substrates. There are also drawbacks to this method of curing. For example, water must be eliminated from the formulation to prevent foaming. This requires additional steps to dry all of the formulation ingredients (fillers, plasticizers, liquid polysulfide, etc) and to protect them from atmospheric moisture. Also, the mix ratio must be tightly controlled to give close to stoichiometric amounts of polysulfide and isocyanate. Actually, a slight excess of isocyanate is usually used. For the oxidative-cured formulations, a significant excess of oxidant is used and the ratio is more forgiving. Furthermore, the isocyanates are more hazardous to work with than the commonly used oxidizing curing agents.

2.3. Phenolic Resins

At elevated temperatures, phenolic resins are cured with polysulfide resins through a condensation reaction. The product may be considered a block copolymer of the rigid phenolic resin and the flexible polysulfide. Thus, the polysulfide acts to flexibilize the resulting polymer.

2.4. Miscellaneous Curing Reactions

Other functional groups can react with the thiol terminal groups of the polysulfides to cross-link the polymer chains and build molecular weight. For example, aldehydes can form thioacetals and water. Organic and inorganic acids or esters can form thioesters. Active dienes such as diacrylates can add to the thiols (3). Examples of these have been mentioned in the literature, but none have achieved commercial significance.

2.5. Reactions of the Disulfide Group

Besides the thiol end groups, the disulfide bonds also have a marked influence on both the chemical and physical properties of the polysulfide polymers. One of the key reactions of disulfides is nucleophilic attack on sulfur (eq. 4). The order of reactivity for various thiophiles has been reported as $(C_2H_5O)_3P > R^-$, HS^- , $C_2H_5S^- > C_6H_5S^- > C_6H_5P$, $CN^- > SO_3^{2-} > OH^- > 2$, $4 - (NO_2)_2C_6H_3S^- > N_3^- > SCN^-$, I^- , $C_6H_5NH_2(4)$. These thiophiles are capable of splitting the disulfide bond and thus reducing the molecular weight of the polymers.

$$RS \longrightarrow SR + X^- \longrightarrow RS \longrightarrow X + RS^-$$
 (4)

An important aspect of this is the splitting of the polymer chain with thiol (eq. 5) or mercaptide ion (thiol + base catalyst). In fact, sodium sulfide or organic monothiols, eg, mercaptoethanol or decylmercaptan, are utilized to lower the molecular weight of polysulfides or to limit the extent of curing reactions.

$$RSSR + R'SH \rightleftharpoons R'SSR + RSH \qquad (5)$$

This reaction also plays a role in the degradation of polysulfides. A back-biting mechanism as shown in equation **6** results in formation of the cyclic disulfide (**5**). Steam distillation of polysulfides results in continuous gradual collection of (**5**). There is an equilibrium between the linear polysulfide polymer and the cyclic disulfide. Although the linear polymer is favored and only small amounts of the cyclic compound are normally present, conditions such as steam distillation, which remove (**5**), drive the equilibrium process toward depolymerization.

$$-\operatorname{SSCH}_{2}\operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{CH}_{2} \xrightarrow{\operatorname{CH}_{2}\operatorname{CH}_{2}} \xrightarrow{\operatorname{CH}_{2}\operatorname{CH}_{2}} \xrightarrow{\operatorname{CH}_{2}\operatorname{CH}_{2}} \xrightarrow{\operatorname{CH}_{2}\operatorname{CH}_{2}} \xrightarrow{\operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{CH}_{2}} \xrightarrow{\operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{CH}_{2}} \xrightarrow{\operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{CH}_{2}} \xrightarrow{\operatorname{CH}_{2}\operatorname{C$$

Another aspect of the splitting reaction (eq. 5) is that it allows for the potential recycle of cured polysulfide. Oxidatively cured polysulfides can be broken down by adding low molecular weight liquid polysulfide with mixing and heating. The resulting liquid material can be reworked and cured again (5). A related reaction is disulfide interchange (eq. 7). This process leads to redistribution of the polymers. For example, if thiol-terminated polymers made from different monomers are combined, they redistribute to form a random polymer. Thus, block copolymers of polysulfides are difficult to obtain. One way to make use of this phenomenon is shown in equation 8. Here a high molecular weight thiol-terminated polysulfide polymer is reduced to a lower molecular weight polymer with hydroxyl terminals. In this way a different functionality can be introduced into the end group.

$$RSSR + R'SSR' \longrightarrow 2RSSR' \tag{7}$$

$$RSSR + HOCH_2CH_2SSCH_2CH_2OH \longrightarrow 2RSSCH_2CH_2OH$$
 (8)

Disulfide interchange also effects the physical properties of the cured polysulfide polymers. Polysulfide polymers undergo stress relaxation in a manner markedly different from conventional rubbers. Stress applied to stretch a sample of polysulfide rubber rapidly falls to zero. There is no change in the chemical and physical properties of the polymer recovered after the tests. The polysulfide polymer can be repeatedly recycled through the relaxation process. With vulcanized hydrocarbon rubbers, the stress decay takes place much more slowly and the activation energy for the relaxation is higher. Studies have attributed the behavior of the polysulfides to interchange between the polysulfide linkages of adjacent polymer chains (6). Addition of free sulfur or free thiol groups dramatically increases the rate of relaxation. Small amounts of free thiol can increase the rate several hundredfold (6).

Disulfides are susceptible to attack by strong oxidizing agents and this can result in decomposition of polysulfides. For example, nitric acid causes violent decomposition of polysulfide polymers.

3. Manufacture and Processing

Polysulfide polymers are made commercially according to the reactions shown in equations **9–12**. Details of the process and alternative approaches have been described (1, 7). Although other dihalides can be used, its favorable economics, minimal competition with ring formation, and the desirable physical properties of the resulting polymer have made bis-chloroethylformal the monomer of choice. Only occasionally are other dihalides used in special applications. 1,2,3-Trichloropropane [96-18-4] is sometimes added as a branching agent.

Many of the reagents used are hazardous and require special equipment and handling. At Morton International, there has been ongoing effort to minimize waste from the processes. In equation $\bf 9$ excess HCl is used to avoid formation of higher homologues from reaction of ethylene oxide with itself. Excess HCl is recovered and recycled. Similarly, excess 2-chloroethanol (eq. 10) is removed from the product by distillation and recycled. Little waste is generated in these steps. In the polymerization reaction (eq. 11), excess sodium polysulfide is required to drive the reaction to completion. Specialized equipment is used for washing and collecting the high molecular weight solid polymer in order to optimize its recovery. The wash water contains NaCl, the excess sodium polysulfide, and only small amounts of organics. The amount of excess Na_2S_x is minimized and efforts are under way to recover the sulfur species from the aqueous stream. High molecular weight solid (2) is converted to liquid polysulfide (2) by reaction with NaSH and Na_2SO_3 .

$$CH_2$$
— CH_2 + HCl \longrightarrow $HOCH_2CH_2Cl$

$$2HOCH_2CH_2Cl + CH_2O \longrightarrow (3)$$
 (10)

$$(3) + NaS_x \longrightarrow (2)$$
 (11)

3.1. Formulation

Polysulfide-based sealants are formulated with appropriate ingredients to obtain the desired properties for a particular application. A typical formulation contains liquid polysulfide polymer, curing agent, cure accelerators (bases) or retarders (acids), fillers, plasticizers, thixotropes, and adhesion promoters.

For a two-part (A and B) sealant, Part A consists of liquid polysulfide, filler, plasticizer, thixotrope, and adhesion promoter. Part B contains the curing agent, plasticizer, a small amount of filler, and the accelerator or retarder. Part A can be mixed on any type of mixer that will ensure thorough dispersion. Generally, the equipment should utilize a double-arm kneading action mixer or a combination kneading action and high speed dispersing blade. Representative types are Change Can, Ross Planetary or Power Mixer, Meyers Mixer, Kneader Extruder, and Hockmeyer Mixer. Optimum dispersion of the fillers is obtained on a paint mill where the fillers are subjected to a grinding action which breaks down the agglomerates. If the mixer itself provides sufficient grinding of the pigments, then milling can be eliminated. The curing paste (Part B) can be prepared either by ball milling or three-roll paint milling. Paint milling is generally preferred, however, solvent-based pastes are best prepared in a ball mill to minimize solvent loss. In order to obtain the most uniform results, pastes containing the accelerators or retarders should be aged for at least two weeks at room temperature prior to use.

The one-part sealant bases require drying the ingredients. Predrying the ingredients before manufacturing is cumbersome and expensive. Other alternatives include vacuum drying during manufacture, azeotropic distillation to remove water before moisture-sensitive components are added, and use of desiccants (qv). The most common method is through the use of the desiccant barium oxide (8). The mixing is done on equipment as described except the processes are carried out under an atmosphere of dry nitrogen and the final step is to combine the pastes into a single mix.

4. Specifications and Testing

Typical specifications for the polysulfide polymers are summarized in Table 1. Specifications for the sealants vary widely depending on the specific application and the needs of the applicators. Standards for sealant testing vary in different countries. Ultimately, the tests should simulate the environment the sealants will be exposed to and measure their performance under these conditions.

Examples of typical tests for sealants include those for stability, curing characteristics, and cured sealants. Stability varies with formulation and storage temperature, and may range from 3 months to over 1 year. Curing characteristics include tack-free time, which varies with relative humidity and can range from hours to days; work life; and cure time. Cured sealant tests are adhesion to appropriate substrates; measurement of physical and mechanical properties such as tensile strength, elongation, modulus, hardness, compression and recovery, and low temperature flexibility; and environmental effects, eg, uv light, water or special fluids, and high and low temperature.

5. Health and Safety

Because they are sulfur-containing polymers, the polysulfides have a characteristic odor. Although the odor is somewhat objectionable it probably arises from small amounts of lower molecular weight compounds. In fact, the lower molecular weight polymers exhibit the strongest odor. Toxicity tests conducted on a representative LP brand liquid polysulfide used in Morton sealant applications indicate that the polymers are not eye irritants and have a low order of oral toxicity ($LD_{50} > 5$ g/kg). Tests on the lower molecular weight liquid polysulfide products show similar findings. These materials are not eye or skin irritants, do not cause allergic skin reactions, and are

not toxic when administered orally ($\rm LD_{50} > 3.4~g/kg$). Rats exposed to a low molecular weight LP at a level of 230 mg/L for four hours developed apparent eye and respiratory tract irritation. However, this level far exceeds that which would be encountered in an industrial setting and is not indicative of real life exposure. Under the criteria set forth under OSHA's Hazard Communication Standard (29 CFR 1910.1200), Morton classifies liquid polysulfide products as nonhazardous. When used in accordance with prescribed procedures, they do not pose a health hazard (9).

When considering sealants or other formulated products, the health and safety considerations relating to the other ingredients should be taken into account.

6. Economic Aspects

Worldwide production capacity of liquid polysulfides is about 33,000 t with manufacturing sites in the United States, Japan, and Germany. Total consumption is about 28,600 t. Approximately 50% is for insulating glass sealants, 30% for construction applications, and \sim 10% for aircraft sealants. In addition, \sim 909 t of the solid polysulfide rubbers are sold each year.

Polysulfide sealants have $\sim\!83\%$ of the market share of insulating glass sealants in Europe, 35% in the United States, and a total of $\sim\!60\%$ worldwide. Some growth in this area is expected as polysulfides are gaining market share in the United States and sales of insulating glass windows is expected to increase overall. Polysulfides have only a modest share of the building sealant market. The perborate-cured sealants offer advantages and some increase in sales is expected in this area. Polysulfides are virtually the only sealant specified for aircraft integral fuel tanks worldwide. In addition, they comprise about 90% of other aircraft sealant applications. The total volume used in the aircraft sealant market fluctuates with aircraft construction and repair. This segment is expected to remain fairly constant (see Sealants).

Most of the polysulfide sales are in Europe, the United States, and Japan. Over the next few years, there should be some expansion into other countries.

7. Uses

7.1. Insulating Glass Sealants

One of the largest scale applications of polysulfide polymers is as a sealant for insulating glass windows. The window consists of two panes of glass separated by a hollow spacer that is filled with desiccant to remove moisture or volatiles from the air space. This prevents condensation and fogging of the window at low temperature. Dual seal windows contain a primary seal along the edge of the spacer that is usually made from polyisobutylene (PIB). PIB has good resistance to moisture vapor transmission and extends the life of the unit. The outer edge of the unit is closed off with the secondary seal of polysulfide or other sealant material. The intermediate air space is sometimes filled with an inert gas such as argon to improve insulation and reduce noise. Polysulfide sealants have low permeability for water vapor or inert gas and can be used either in dual- or single-seal units. In the dual-seal units, if there are small leaks in the primary seal, the polysulfide provides a good backup. Other sealants such as silicones have high permeability, and can only be used in dual-seal units that rely on the integrity of the primary seal.

Besides water vapor and gas diffusion, other requirements for good edge sealants are water resistance, uv resistance, heat/cold resistance (-40 to 80° C), adhesion to glass and metal, and good characteristics for application. Polysulfide sealants have maintained an excellent record in use since the 1950s. Development of new polysulfides and sealant formulations continues in order to meet market needs of the 1990s.

7.2. Aircraft Sealants

Polysulfides have been used for sealing fuel tanks and aircraft structural components since the 1940s. There are stringent requirements for these sealants. They must have outstanding resistance to fuels and excellent adhesion to many different materials such as various metal alloys and protective coatings used in aircraft construction. The sealants must also perform in extremely variable weather conditions (10). The polysulfides have an excellent performance record.

7.3. Construction Sealants

In the 1950s, curtain wall construction became dominant in high rise buildings. This technique requires sealing of the joints against wind and weather. Sealants used up until that time were not suitable to withstand the temperature changes, sun, wind, rain, vibration, etc. Polysulfide-based sealants were developed for this application and have served in many large-scale projects since that time. Polysulfide construction sealants are used to seal glass in aluminum frames, concrete moving joints, steel/stone joints, and in other applications. For earlier sealants, in order to obtain good adhesion to the variety of substrates, primers were usually used. Besides the disadvantage of requiring application of the primer, there was the risk that the primer would not be properly or uniformly applied. More recently, polysulfide sealants have been developed that incorporate adhesion promoters in the formulation and eliminate the need for primers. These sealants have been tested against ASTM C920 as a class 25 building sealant on glass, anodized aluminum, and concrete and meet all requirements (11).

Other advancements in construction sealants are the improvements in one-part curing of polysulfide sealants. In the past, one-part polysulfide sealants had a reputation for being very slow to cure through. In the 1990s, one-part sealants have been developed that cure much faster. These use either manganese dioxide or sodium perborate as the curing agent. Sodium perborate has several advantages over other curing agents. This is especially true in construction sealants, where the neutral color, low modulus, good mold resistance, and low physiological effects make it attractive for both one- and two-part sealants.

7.4. Below-Ground Sealants

Immersion in water for long periods or continuous exposure to high humidity are especially difficult conditions for organic-based materials to withstand. Sealants for use in water purification plants or wastewater treatment plants have special demands for physical, chemical, and microbiological properties. Polysulfide based sealants have proved themselves useful in this area. Special consideration must also be given to the other ingredients, eg, fillers, plasticizers, adhesion promoters, or curing agents, in formulating for these applications (12).

The chemical and fuel resistance of polysulfides makes them useful as sealants and coatings for secondary containment areas, where they prevent chemicals, solvents, fuels, etc, from seeping into the ground in the event of spillage or a storage tank leak. Polysulfide-based coatings and sealants are also used for bridges, air fields, and road construction.

7.5. Epoxy Flexibilizers

Polysulfides are useful as flexibilizers in epoxy resin formulations. Compounders can target the properties desired for a particular application through the selection and balance of the epoxy, the liquid polysulfide–epoxy ratio, curing agent, and filler. Most of the compounds are two-component: one containing the epoxy resin, the second containing polymer and curing agent. Probably the most important factor is the ratio of polysulfide to epoxy resin. The most effective ratio ranges from 1:2 to 2:1 liquid polysulfide to epoxy. Liquid polysulfide–epoxy formulations are used for a variety of applications including adhesives, protective coatings, barrier coatings,

electrical potting compounds, resilient plastic tooling materials, aggregate liquid polysulfide—epoxy mortars, and surface sealers.

7.6. Water Dispersions

Polysulfide products are offered as aqueous dispersions (Thiokol WD-6). These are useful for applying protective coatings to line fuel tanks, and for concrete, wood, and in some cases fabrics, felt, leather (qv), and paper (qv). It has been found that a stable emulsion can be made that contains both LP and manganese oxide curing agent. The emulsion can be thinned and applied as a spray coating. After it is applied, water evaporates and the LP cures to form a solid rubber (13).

7.7. Rubber Articles

The solid polysulfide rubber products, Thiokol FA and Thiokol ST, are used in the manufacture of printing rollers, printing blankets, gas meter diaphragms, O-rings, and specialty molded items.

BIBLIOGRAPHY

"Polymers Containing Sulfur, Polysulfides" in *ECT* 2nd ed., Vol. 16, pp. 253–272, by M. B. Berenbaum, Thiokol Chemical Corp.; "Polysulfide Resins" under "Polymers Containing Sulfur" in *ECT* 3rd ed., Vol. 18, pp. 814–831, by S. M. Ellerstein and E. R. Bertozzi, Thiokol Corp.

Cited Publications

- 1. H. Lucke, ALIPS Aliphatische Polysulfide, Hüthig & Wepf, Basel, Switzerland, 1992; English transl. in press.
- 2. A. Duda and S. Penczec, in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, Wiley and Sons, Inc., New York, 1989, 246–368.
- 3. S. J. Hobbs, Polym. Mater. Sci. 67, 415 (1992).
- 4. W. A. Pryor, Mechanisms of Sulfur Reactions, McGraw-Hill Book Co., Inc., New York, 1962, 59-64.
- 5. Ger. Pat. Appl. DE 4142500 (1991), R. J. Hecktor, F. Specht, R. Theobald, and G. Unger (to Metallgesellschaft AG).
- 6. A. V. Tobolsky and W. J. MacKnight, Polymeric Sulfur and Related Polymers, Interscience, New York, 1965.
- 7. D. E. Vietti, Comprehensive Polymer Science, Vol. 5, Pergamon Press, Oxford, U.K, 1989, 533-542.
- 8. U.S. Pat. 3,912,696 (1975), J. I. Doughty (to Minnesota Mining and Manufacturing Co.).
- 9. D. Wienckowski, personal communication, Morton International, Inc., Woodstock, Ill., 1994.
- 10. D. B. Paul, P. J. Hanhela, and R. H. E. Huang, Polymer Science and Technology, Plenum Press, New York, 1988, 269-280.
- 11. A. R. Fiorillo and J. R. Harding, in D. H. Nicastro, ed., *Science and Technology of Building Seals, Sealants, Glazing and Waterproofing*, Vol. 4, ASTM STP 1243, ASTM, Philadelphia, Pa., 1994.
- 12. T. Lee, T. Rees, and A. Wilford, in C. J. Parise, ed., Science and Technology of Building Seals, Sealants, Glazing and Waterproofing, STP 1168 ASTM, Philadelphia, Pa., 1992, 47–56.
- 13. U.S. Pat. 5,073,577 (1991), P. H. Anderson (to Morton International, Inc.).

General References

- 14. M. B. Berenbaum, in N. G. Gaylord, ed., Polyethers, Part III, Vol. 13, Interscience, New York, 1962, p. 43.
- 15. E. R. Bertozzi, Rubber Chem. Technol., 41, 114 (1968).
- 16. S. M. Ellerstein, in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, Vol. 13, John Wiley & Sons, Inc., New York, 1988, p. 186.
- 17. E. M. Fettes, in N. Kharasch, ed., Organic Sulfur Compounds, Vol. 1, Pergamon, London, 1961, p. 266.
- 18. H. Lucke, ALIPS Aliphatische Polysulfide, Hüthig & Wepf, Basel, Switzerland, 1992; English transl. in press.

- 11
- 19. J. R. Panek, in N. G. Gaylord, ed., Polyethers, Part III, Vol. 13, Interscience, New York, 1962, p. 115.
- 20. A. V. Tobolsky and W. J. MacKnight, Polymeric Sulfur and Related Polymers, John Wiley & Sons, Inc., New York, 1965.
- 21. A. V. Tobolsky, The Chemistry of Sulfides, Interscience, New York, 1968.
- 22. D. E. Vietti, Comprehensive Polymer Science, Vol. 5, Pergamon, London, 1989, p. 533.

DAVID VIETTI Morton International, Inc. MICHEAL SCHERRER Morton International, Inc.

Related Articles

Sealants; Polymers containing sulfur, poly(phenylene sulfide); Polymers containing sulfur, polysulfones