There are different types of insulating glass sealant available on the market, all meeting the requirements of sealant manufacturers as well as IG unit users. Among these products, sealants based on polysulphide polymers have a leading position because of their low viscosity, fast curing, insensitivity to mixing failures and rapid adhesion. These processing properties, virtually tailor-made for IG applications, have contributed to the success of polysulphide-based IG sealants. This article details the evolution, applications and properties of this vital IG unit component.

Last year - 2002 - polysulphide polymers celebrated their 75th anniversary; it was in 1927 that J.C. Patrick of the United States invented polysulphide rubber. This first synthetic rubber was a speciality mainly used for hoses, blankets and textile coating because of its excellent chemical resistance. The commercial breakthrough of polysulphides was achieved by the development of liquid types. Patrick and co-workers invented the first liquid rubber in 1941-42. In Greiz, Germany, polysulphide rubber was produced under the trade name Perthiokol from 1944 to 1950; the manufacture of the liquid types started in 1963. At around this time, the manufacture of liquid polysulphides started in other countries too.
There were also a few more companies that planned to manufacture polysulphides but never actually started production on an industrial scale. Today, there are still four manufacturers of liquid polysulphides. They meet the worldwide demand of approximately 22,000 tonnes per year.

**MODERN-DAY USE**

Nowadays, products based on liquid polysulphide polymers enjoy wide acceptance in many fields, including the construction, aerospace, marine and insulating glass industries.

Approximately 94 per cent of liquid polysulphides are used in the manufacture of sealants for a wide variety of applications. Approximately 75 per cent of these sealants are used in insulating glass units. Besides this main application area, high-performance polysulphide sealants are successfully used in the building and aircraft sectors. Additional industrial applications are specialities such as printing blankets, binders for grinding wheels, and mouldings. The long-time use of polysulphide sealants in these different applications for more than 40 years has demonstrated the outstanding performance of polysulphide-based sealants.

Just to demonstrate how important polysulphide sealants are in the aircraft industry, a modern aircraft like a Boeing 747 contains more than 1,000 kilograms of polysulphide sealants. These sealants have to perform during the entire service life of an aircraft, more than 30 years.

As mentioned before, insulating glass sealants represent by far the largest application area of liquid polysulphide polymers. The development history of insulating glass is inseparably joined with that of polysulphide sealants. In the early 1960s, the organically sealed IG system could only be launched by the use of polysulphide sealants because, at that time, there were no alternative organic sealants available. Still today, polysulphide IG sealants have the leading position among elastic insulating glass sealants.

According to current standards, an insulating glass unit is double sealed; the inner sealant is mainly polyisobutylene, the outer or secondary sealant functions
as a structural adhesive. Insulating glass significantly contributes to energy saving and the reduction of energy waste. Thus, the challenges of environmental care and greenhouse gas reduction are supported by high-quality insulating glass. This explains the continuously growing market of insulating glass worldwide.

More than 280 million square metres of insulating glass were manufactured worldwide in 2002. Europe is the largest IG producer, North and South America together are in second position, while a fast-growing market is to be found in the Asia-Pacific region. Worldwide, polysulphide-based IG sealants have a market share of around 60 per cent.

Why have polysulphides been so successful for more than 40 years? The reason is the unique combination of product and processing properties which are based on the special features of liquid polysulphides.

**POLYSULPHIDE MOLECULAR STRUCTURE**

- **Formal-, Methylene-Linkages**: low temperature flexibility
- **Trifunctional Branching**: cross-linking/elastic deformation
- **Disulphide Linkages**: exchange reactions, stress relaxation
- **Thiol End-Groups**: highly reactive, SS by curing
- **No Unsaturated Linkages**: good weatherability

**POLYSULPHIDE EXCHANGE REACTIONS**

- **Disulphide - Disulphide**: 
  \[ R-S-S-R \rightarrow R-S + S-R \]
- **Thiol - Disulphide**: 
  \[ R-S-H + R'-S \rightarrow R-S + S-R' \]

**UNIQUE MOLECULAR STRUCTURE**

The most important reason for the outstanding performance of the polysulphides is their molecular structure. Liquid polysulphides belong to the group of aliphatic polysulphides which are produced in aqueous dispersion by polycondensation of an organic halide with alkali polysulphide. By introducing a tri-functional co-monomer as a cross-linking agent, a macromolecular network is formed during synthesis. The macromolecules are then reduced to the required chain length by reductive splitting. At the same time, the split disulphide groups are converted into reactive thiol terminal groups. Polysulphides based on bis-(2-chloroethyl)-formal, 1,2,3-trichloropropane as co-monomer and sodium polysulphide are the most commercially successful polysulphide types.

The structure of the liquid polysulphides consists of:

- formal-, methylene linkages which provide low temperature flexibility;
- tri-functional branching which provides cross-linking during curing; cross-linking is a base requirement for elastic deformation;
- disulphide linkages: these make exchange reactions possible which are important for the manufacturing process as well as for the mechanical properties; the total sulphur content of approximately 37 per cent leads to high chemical resistance;
- thiol terminal groups: these are highly reac-
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High-performance contributor to IG efficiency

Oxidative Curing Process

2 R- SH + MnO₂ → R- SS- R + H₂O + MnO

- fast reaction (activated MnO₂ quality)
- heterogeneous reaction
- non-stoichiometric (MnO₂ excess 2-3 times)
- relatively insensitive to mixing failures
- curing almost without shrinking

Positive Characteristics of Polysulphides

- unique molecular structure
- exchange reactions
- robust oxidative curing process
- adapted to the requirements
- not harmful to human and environment
- can be recycled

Optimized sealant formulations have been developed by the sealant manufacturers

Polysulphide Suitability

Wide product range of polysulphide types defined by:
- viscosity
- branching
- mechanical properties
- reactivity
- narrow product specifications

Tailor-made polysulphide polymers are available

Exchange reactions, curing

As mentioned, the capability of the polysulphides to exchange linkages is key to the understanding of their deformation (and also of the manufacturing process).

These reactions can take place between disulphide/disulphide and thiol/disulphide linkages and lead, for example, to the well-known stress relaxation behaviour of cured polysulphides.

The highly reactive thiol terminal groups can be linked together via oxidative curing or addition reactions. Cross-linking via oxidation is the most important curing route and manganese dioxide is the most important curing agent for liquid polysulphides.

Curing with manganese dioxide is a heterogeneous, non-stoichiometric reaction, which is very fast and relatively insensitive to mixing failures. Manganese dioxide provides curing almost without shrinking, as well as excellent chemical and weather resistance of the cured product.

Last but not least, polysulphide types are well adapted to the requirements of sealant manufacturers and the end-users.

A wide range of polysulphide polymer types have been developed in close cooperation with our customers. The types differ in viscosity (molecular weight) and branching. As a result of these characteristics, polysulphide types are different in their reactivity and mechanical and chemical properties. Tailor-made polysulphides can also be developed on request.

Beside these advantages, polysulphides are not harmful to humans or the environment and can be recycled. The latter advantage is a further consequence of the exchange reactions: cured products can be softened by using low molecular weight types and those blends can be re-used.

In spite of all these special advantages, pure polysulphides cannot be used to seal insulating glass units. For this application, optimized sealant compounds are needed which reinforce the good properties of the base polymer and provide the desired adhesion and processing properties.

IG Sealant Suitability

The requirements of the properties and the performance of IG sealants come from two sources. The IG unit user is interested in the performance of the final product; the IG unit manufacturer is interested in the performance of the final product and in excellent processing properties.

IG sealants manufactured by the leading European producers have been evaluated in order to demonstrate how polysulphide-based
products meet the requirements compared with elastic sealants based on other polymers.

**Rheology**

Liquid polysulphides are almost Newtonian liquids. The flow behaviour of an insulating glass sealant is completely different to that of the polymer:
- pseudo-plastic flow;
- non-sag flow is required.

The viscosity is influenced by the type of polysulphide polymer (see figure below) but the special flow characteristic can only be achieved by sealant formulation.

The pseudo-plastic flow of the sealants - the viscosity decreases at higher shear rates - permits a high output for production lines and good contact of the sealant to surfaces of glass and spacer, and also diminishes wear and tear of equipment.

**Curing**

If monitoring the curing process by measuring the viscosity versus time, the curing curve of the polysulphide sealants is S-shaped: long pot life (flat induction period of 35-45 minutes) followed by a rapid curing phase. The tack-free time is less than an hour. In comparison to other insulating glass sealants based on polyurethanes or silicones, the curing of polysulphide sealants is unique, caused by oxidative curing with manganese dioxide. This excellent curing behaviour can also be monitored by the evolution of the Shore A hardness.

Well-formulated polysulphide IG sealants can achieve 80 per cent of their final hardness after four hours curing at room temperature. Products based on other polymers cure more slowly, as shown below. The final hardness level of approximately 50 Shore A is achieved by most
of the IG sealants we evaluated and is sufficient for secondary IG sealants.

The IG manufacturer is interested in a robust curing process. Because of the excess of curing agent, the curing process of polysulphide IG sealants is relatively insensitive to mixing defaults.

The above figure shows pot life, tack-free time and Shore A at different mixing ratios of commercially available polysulphide IG sealants. Between 100:8 and 100:12 (the recommended ratio is 100:10), the curing rate and the evolution of hardness are sufficient. Pot life and tack-free time drop with increasing amounts of curing agent.

The hardness after four hours curing time also varies considerably - less curing agent leads to slower curing. Fortunately, the hardness after 24 hours is roughly the same if the mixing ratio varies between 100:8 and 100:12. Importantly, the adhesion on glass and aluminium at all different mixing ratios was 100 per cent. In other words, no adhesion failures were observed.

Although these results show that polysulphide IG sealants tolerate mixing variations, the recommended mixing ratio should be carefully observed. Only at the optimum ratio can perfect results be achieved. In the case of PU- or silicone-based sealants, deviations from the recommended mixing ratio are only permitted within considerably smaller limits because the curing mechanism via addition reactions is much more sensitive to deviations of the mixing ratio.

In short, the examples demonstrated that polysulphide-based IG sealants meet requirements in terms of processing properties very well and are superior to IG sealants based on other polymers in some aspects.

**IG SEALANT REQUIREMENTS**

What about the requirements and the properties of the insulating glass unit? The chart below shows the function of an IG sealant with respect to the performance of the IG unit.

The following figures show some examples referring to the performance of the same IG sealants that were used to demonstrate the processing properties.

Fast evolution of adhesion is a major concern. As faster adhesion is achieved, fewer problems appear during transportation of the
IG units. Well-formulated polysulphide IG sealants achieve full adhesion within four hours’ curing at room temperature.

Moreover, after exposure to water and UV for 1,000 hours, polysulphide IG sealants continue to perform well. No adhesion failures were found. PU- and silicone-based sealants also show excellent results. Their strength values are higher because of their higher peel resistance.

The service life of insulating glass units depends on the function of the sealant as a barrier against moisture and its ability to keep the gas filling inside. Consequently, the gas loss rate and moisture vapour transmission (MVT) rate of the sealant are very important. Polysulphide sealants have a low MVT rate; PU sealants have a minor advantage in this respect, whereas silicone sealants show higher values.

The gas loss rate is very low in the case of polysulphide sealants, whereas sealants based on PU or silicones possess higher values. It is obvious from the calculations that the expected lifespan of IG units sealed with polysulphide sealants is 20-40 years. Tests on windows in use have impressively confirmed these results.

It has to be mentioned, however, that despite the differences in some properties between the investigated sealant types, the test results show that all types of well-formulated IG sealant meet the requirements.

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