Monsanto

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SUBJECT: ~~Technical Aspects of~~ Polysulfide Sealants

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This report covers a recent literature survey and is aimed at updating plasticizer's background in polysulfide sealants. Some suggested leads are currently under investigation. Other leads and comments are welcome.

Polysulfide

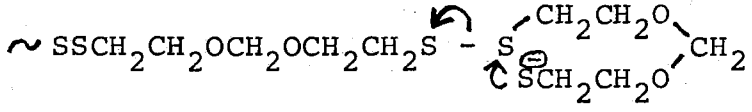
Polusulfides are made from the reaction of sodium polysulfide with bis-chlorethyl formal. Approximately 3:1 of Na_2S_2:Na_2S_3 is used. Approximately 0.1-4.0% 1,2,3-trichloropropane is added as a crosslinker. The reaction is finished with sodium bisulfide and sodium sulfite in order to get -SH termination. Alkyl naphthalene sulfonate with magnesium hydroxide solutions are used as suspending agents for the polymerization.

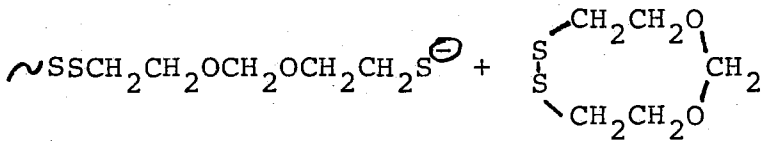
The cure proceeds by the oxidation of the mercapto termination groups with formation of labile disulfide linkages. Metal oxides are commonly used as the oxidizing agents for initiating cure. Amines, rubber accelerators, fillers, plasticizers, adhesion promoters, etc. are added for given formulations.

One of the major problems with polysulfides is thermal degradation at high temperatures. This is accelerated by water and/or UV making moist UV tests very severe. When water is added to a polysulfide linkage the formal linkage hydrolyzes forming a hydroxy terminated disulfide with free formaldehyde. This free formaldehyde then attacks the disulfide linkage forming formic acid. This results in a less flexible backbone and causes weight loss with hardening. Calcium oxide is an example of a temperature stabilizer as it is both an acid and a water scavenger. Acidity may also come from oxidation of the formal linkage, forming a hydroperoxide which decomposes to formic acid and water. This is, of course, a free radical process and is one reason why antioxidants are added to polysulfide rubbers. This also brings up a problem in that the metal oxidizers added to initiate the cure may be a problem in high temperature stability. Diepoxides and diisocyanates as curing agents will give a better high temperature performance but result in a lower flex.

The recent problems with our plasticizers have been caused to a large extent by the replacement of lead dioxide with manganese dioxide as a cure initiator because manganese dioxide gives better high temperature properties. Lead dioxide, while a good overall curing agent, will react after oxidation of the mercaptan to form a disulfide and lead oxide. This lead oxide can react with additional mercaptan to form S-Pb-S-bonds. With heat, the lead leaves the backbone to form lead sulfide with a C-S-C linkage in the backbone. This sulfide linkage is much less flexible than the desired disulfide linkage. Free sulfur will limit the degree of interaction (but not sufficiently to form a good sealant for high temperature uses in comparison with manganese dioxide). Very poor compression set properties also result from the appearance of lead in the backbone. The elimination of lead from the backbone can also be UV catalyzed as well as heat catalyzed. Along with some weight loss, a severe loss of adhesion occurs. While sulfur addition will help thermal properties it will destroy adhesion, rheology, and eventually also harm heat stability (through another mechanism).

The presence of the mercaptan in the polymer can also cause cyclodepolymerization with a loss of virtually all the polymer weight. Equations for this reaction are as follows:





To get the best strength one eliminates unreacted mercaptan, ionic salts or other activators. Approximately 24 kilo calories/mol is the activation energy for the mercaptide/disulfide process. This value is not firm and does vary according to the formulation.

Curing Agents

Group 2A metal oxides, halides, and perchlorates are polysulfide polymerization catalysts. In the literature it is noted that tellurium oxide, manganese dioxide, and chromate salts will work as catalysts. Magnesium perchlorate is good in polysulfides to lower corrosion, and to give better cross-link density in water containing formulations. Sodium dichromate will increase the cross-link density (desired) but in combination with 1,2,3-trichloropropane (commonly used in the base polymer synthesis) will cause a decrease of cross-link density.

Metal alkoxides and alkyl metals (as thalium) are good curing agents. Tetraalkyl titanates with organic acids give very quick cures. The reaction products of the tetraalkyl titanates with a carboxylic acid (as maleic, succinic, etc.) with a group 2A metal dioxide gives a very high strength cure. It has also been shown that diethyl zinc adducts with water can act as synergistic catalysts.

Commonly used group 2A metal dioxide catalysts are normally activated. Manganese dioxide is activated by 50% caustic at 250°C. Dry manganese dioxide is more stable. Manganese dioxide/polysulfide systems are retarded by anhydrides. Often, for overall strength, mixtures of metal dioxides are usable. Thus, a 1:3.2 ratio of lead dioxide: manganese dioxide is very effective. About 24% by weight manganese dioxide is most effective in the formulation and up to 42% by weight is the maximum usable level. These levels are never, to my knowledge, used commercially. When accelerators as diphenyl guanidine are used, lead dioxide is more efficient than sodium dichromate and both are more efficient than manganese dioxide. About 1.5-2.0 times the stoichemometric amount is needed. Group 2A dioxides are also used with other oxides as iron oxide, nickel oxide, etc. Iron or manganese dithiocarbamates are reported to be good in cure. It is noted that iron and manganese will accelerate oxidation but copper is inert unless a morpholino (or other amine) compound is present. In that case the manganese is still the most efficient but copper becomes more active than iron. Amines such as aminophenols, aminobenzaldehydes, or amino benzyl alcohols are also good cure agents particularly with oxides such as zinc dioxide, lead dioxide, etc.

It is noteworthy that sulfonamides accelerate cures. This has been confirmed in our laboratory with Santicizer® 8. Carbonates, as zinc carbonate, also are good accelerators and curing agents, but are not normally effective enough for commercial utilization. Permanganates,as potassium permanganate, are good curing agents. Calcium oxide, previously recognized as a good heat and acid stabilizer, is also a latent cure agent. Our own work indicates that it also increases adhesion.

The use of acrylics or unsaturated materials with polysulfide results in tougher cures. The polysulfide extends through the olefinic linkage and allows disulfide cross-linking.

Cross-linkers

One normally can cross link many unsaturated rubbers with polysulfides. Monsanto holds several patents in this area. As polysulfides will vulcanize natural rubber it is obvious additions of such things as alpha-beta unsaturated polymers will result in a cross-linked system. This is good for moisture vapor transmission, adhesion, etc. Disulfide or sulfur-nitrogen accelerators can also react with polysulfide cross links. Peroxides will lead to carbon-sulfur cross links and result in aging problems. This is partially discussed in the polysulfide chemistry section. Cresol and benzimidozole are synergistic antioxidants to prevent this.

The crosslinking aspects of dichromates are also to be remembered in this area.

Adhesion

It is shown that carbon black helps adhesion to glass particularly when triethylene amine is in the formulation. A maleic anhydride/amine mixture with polysulfides results in a tacky adhesive. This is obviously caused by a strong interruption of chain extension and cross-linking. Resorcinol and formaldehyde systems, particularly with thiochloride polymers, give very good adhesion, particularly of metal to rubber. This is used in tire cord primers. Terminating a polysulfide with TDI will result in increased glass adhesion. Unsaturated polyesters are very good adhesion promoters for polysulfide rubber. Conversely, mercaptan-containing polyesters will interact with polysulfides also to increase adhesion. Polyterpenes, silanes, and epoxies are also used as adhesion promoters. Epoxies, as vinyl cyclohexene diepoxide, will increase adhesion about 5% as reported. Glycidal trialkyl oxysilanes will increase adhesion particularly in the partially hydrolyzed state. To improve adhesion to wet surfaces butyl rubber or polyester butylene can also be used. Polyethylene amines and epoxies are also used on wet surfaces.

Polysulfide usually sticks to an acid surface and wetting agents aid adhesion. As previously shown calcium oxide can be an adhesion promoter on glass. Alkyl titanates can be primers for polysulfides as can reactive carbonates. In many cases UV adsorbers can be adhesion promoters for polysulfide. Diphenyl phthalates have a use here.

It has been shown that if the sealant is degased adhesion can be improved by a factor of three. The IR adsorption of the sealant versus the peel strength is linear.

Moisture Vapor Transmission

Moisture vapor transmission decreases with increasing crosslinking. Sodium dichromate, manganese dioxide, lead dioxide, and p-quinonedioxime decrease (in this order) water adsorption. Tars, bitumens, and crosslinked diepoxides (as vinyl cyclohexene diepoxides) will also improve moisture vapor transmission. With epoxides paratoluene sulfonic acid is a good catalyst. Phenolics are also used in this area but must have methylol groups in order to react. B-chloroethanol may accelerate polymer formation. It is to be noted that the dichromates give redox reactions with polysulfides. The mercaptan oxidation is ionic. It is catalyzed by dimethyl formamide and other tertiary amides and amines. Both disulfide and coordination bonds appear when dichromates are used as catalysts. This may also indicate why better crosslinking occurs with subsequent better adhesion and better moisture vapor transmission.

Rubber Modification

Polysulfide rubbers have been treated with acrylates, phenol, furfurals, butadienes, isocyanates, epoxides, phenolics, etc, to give reactive termination. Apparently if 5-10% reactivity is built into the polysulfide polymers much better stability is found.

Moisture Curing

Metal alkoxides are moisture cure agents. These systems are used in one-shot polysulfide caulks. Magnesium dipropoxides and calcium dibutoxide are used. Cuprous chloride, pyradine, tertiary amines and acetylacetonates are also used. Potassium permanganate, molecular seives, and chlorinated paraffins form a very good system. Vinyl siloxanes (no tin allowed) are very good. Surfactant increase the hydroscopic nature of the system as do barium oxide, barium carbonate, and calcium carbonate. With calcium hydroxide, imino bis(propylamine) sulfate and diethylenetriamine sulfate are good moisture cure agents.

Plasticizers in Formulations

Plasticizers should act as a sulfur solubilizer. Mesamols are good as are polyalkylene or polyphenylene plasticizers in oil resistance and adhesion. Benzyls, alkylates, acetates and formaldehyde resins, etc. are also seen to be polysulfide plasticizers.

Paraquinonedioxime with manganese dioxide gives less shrinkage. Epichlorohydrin rubbers in polysulfides increase resistance. Light curable sealants are formed with benzoin and acrylates. Peroxides with polyamines in polysulfide latexes give good vulcanizates. It has been found that polysulfides react with coal tars and aqueous sodium silicates to form good sealants. Epoxy/polysulfide bonds can be hardened by anhydrides with substituted amino phenols. Polybutene succinic anhydrides may be useful here. Barium titanate gives a good microwave cure. Ferrocenes with polysulfides give improved electrical insulation. It is noted that the Thiocol sealants shelf life can be mathematically predicted. It is also to be noted that hydroxy wastes can be partially used in polysulfides. This may be an HOE outlet.

Physical Chemical Properties

Urethane prepolymers with manganese oxide increase tensile. Groups 1 through 3A hydrides, alkyls, amides, polysulfoxides and polysulfones increase molecular weight. Manganese dioxide requires 8.68 kilocalories/mole versus sodium dichromate's 13.37 kilocalories/mole for vulcanization. The sedimentation coefficients are not affected by pH in the 4.1-11.2 range unless a polyacrylamide polymer is present. Curing rates of polysulfides decrease with

water levels equal or less than 0.2% by weight. The rate increases with water levels above 0.2%. The rate is R.H. dependent below a R.H. of 45%. Increased dispersion of carbon black can decrease the effective density of polysulfide vulcanization, particularly in latexes. Fatigue and tensile failures may be crack growth related. Polysulfide can increase the oxidation resistance of nitrile rubbers. Note: One can increase the heat resistance with a peroxide, copper abietate, amino phenol, etc. in the presence of manganese oxide. Phosphorus in the backbone gives a positive heat stability effect. Antioxidants cut the degree of the disulfide breakage. Trichloromethyl groups cut the amount of polymerization. Manganese dioxide with diphenyl guanidine will degrade readily in the presence of polysulfide with free sulphur. Carbanion terminated polysulfides react with vinyls. Most epoxy/polysulfide viscoelastic properties are non-linear. 30° stress relaxation of manganese dioxide systems are greater than those with lead dioxide. Potassium permanganate is also greater than lead dioxide in stress relaxation.

Miscellaneous

It is unusual that isocyanates, sulfides and triethylene amine react to give polysulfide foams. Diethylene glycol with a surfactant in polysulfide (catalyzed by H_2EtCl_3 and heat) will make a foam. Alkyl thiochlorides will act as detackifiers on unsaturated rubber surfaces. Polysulfide acts as a filler in epoxy systems at -90°C to 50°C.

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