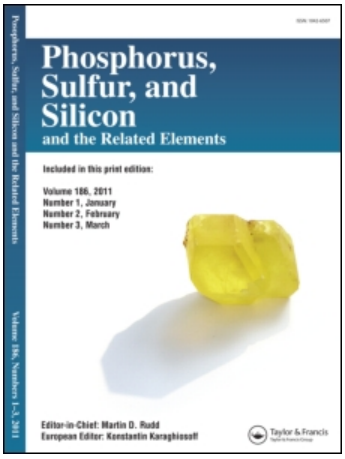

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Polysulfides - Natures Organic Soluble Sulfur

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POLYSULFIDES - NATURE'S ORGANIC SOLUBLE SULFUR

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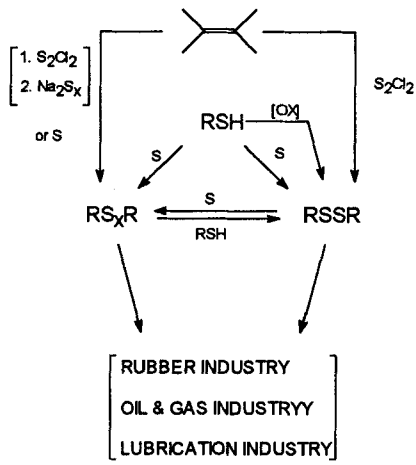
Abstract An overview of the chemistry of organic polysulfides will be presented with an emphasis placed upon their use in industrial applications.

Introduction

Sulfur plays a crucial role in many applications within the chemical industry. The lubrication industry relies on sulfur for the machining of metal parts, and the prevention of metal surfaces (ie., gears) from seizing. Vulcanization of rubber was made possible through its use as a cross-linking agent, while the presulfiding of metal oxide catalysts employed in the petroleum industry increases catalyst life. Since sulfur is a solid at room temperature and possesses poor solubility in many organic solvents, organic polysulfides have become the sulfur source of choice because they are an excellent vehicle for transporting sulfur to the reaction site.



Lubrication Industry

Polysulfides are used to prevent two metal surfaces from welding during extreme load-carrying conditions by reacting with the metal surface to form a protective layer. There are four phases of protection that function during lubrication: Full Fluid Film; Oiliness/Lubricity; Anti-Wear; and Extreme-Pressure. The first two stages occur under mild conditions when a thin film of fluid prevent the metal surfaces from touching. Anti-wear compounds provide protection during the third phase of lubrication in which surface asperities are in full contact under mild loads. The final phase of protection occurs with the use of extreme-pressure (EP) agents. Extreme-pressure agents contain either chlorine, phosphorous, or sulfur, and under severe localized conditions, react with the metal surface producing a protective layer that shears from the metal surface before welding occurs. Sulfurized fatty acids, sulfurized olefins, and organic polysulfides have been the most widely used sulfur-based EP-agents. Organic polysulfides are considered premium products, because they contain no olefinics, chlorine, or color producing trithiones. In addition, organic polysulfides may be used in a wider range of applications since their distribution can be manipulated to produce a sulfur rank from three to five.

Petroleum Industry

Petroleum feedstocks are hydrotreated to remove nitrogen, sulfur, oxygen, halide, and metals. Hydrotreatment involves the reaction of the petroleum feed with hydrogen over molybdenum oxide on alumina-based catalysts. Cobalt oxide and nickel oxide are added as promoters for the removal of sulfur and nitrogen in the feed, respectively. In order to prevent coking (carbon build-up) and the reduction of the metal oxides to their respective inactive free metals, the metal oxides are presulfided with sulfur. Presulfiding converts the metal oxides to their corresponding metal sulfides. Many forms of sulfur such as elemental sulfur, hydrogen sulfide, carbon disulfide, alkyl sulfides (dimethyl sulfide), alkyl disulfides (dimethyl disulfide), and alkyl polysulfides (t-nonyl polysulfide) have found use as presulfiding agents. Of those employed, dimethyl disulfide has emerged as the preferred presulfiding agent throughout the world due to its excellent activity and relatively low odor.

Oil and Gas Industry

Aliphatic disulfides, especially dimethyl disulfide, have found great utility as "sulfur solvents" in the Oil and Gas Industry. Sour gas (natural gas containing hydrogen sulfide) contains various levels of soluble sulfur which is deposited in the well pipe during production until the well plugs off. Catalyzed disulfides are then injected into the well, dissolve the sulfur plugs, and production is resumed. Although disulfides are poor physical solvents, the use of effective catalyst systems enable them to take-up 1.5 times their weight in sulfur, via chemical incorporation.

Manufacture

Polysulfides have been manufactured commercially by reacting olefins, polyolefins, and fatty acids with sulfur, sulfur halides, and sulfur/hydrogen sulfide. However, the sulfurization of olefins and polyolefins produces crude polysulfides, which in many cases contain unsaturation, chlorine, and may be oligomeric in nature. Higher quality polysulfides are produced by reacting a mercaptan with sulfur in the presence of a basic catalyst. This process not only occurs at much lower temperatures but provides greater control over the polysulfide distribution and side reactions. During the initial stages of the reaction, polysulfides of a high sulfur rank (many sulfur atoms) are generated. As the reaction proceeds, mercaptan reacts with these high-rank polysulfides producing lower-rank polysulfides. A disulfide is finally formed if the reaction is left to proceed to completion.

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References and Notes

1. For a list of References, please contact the author at Elf Atochem NA, 900 First Ave, King of Prussia, Pa, USA, 19406.