



Standard Classification for Rubber Compounding Materials—Sulfur¹

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ϵ^1 NOTE—Section 5, Keywords, was added editorially in June 1993.

1. Scope

1.1 This classification covers the variety of sulfur grades used in the rubber industry. Typical chemical and physical properties for sulfur are shown. Sulfur is principally used in unsaturated rubbers as a vulcanizing agent.

2. Referenced Documents

2.1 ASTM Standards:

- D 4569 Test Method for Rubber Chemicals—Determination of Acidity in Sulfur²
- D 4571 Test Methods for Rubber Chemicals—Determination of Volatile Material²
- D 4572 Test Methods for Rubber Chemicals—Wet Sieve Analysis of Sulfur²
- D 4573 Test Method for Rubber Chemicals—Determination of Oil Content in Oil-Treated Sulfur²
- D 4574 Test Methods for Rubber Chemicals—Determination of Ash Content²
- D 4578 Test Methods for Rubber Chemicals—Determination of Percent Insoluble Sulfur by Solvent Extraction²

3. Significance and Use

3.1 Sulfur is one of the principal rubber vulcanizing agents. It is a critical additive. When chemically combined with rubber, sulfur develops basic performance properties in the vulcanized compound such as: tensile strength, elongation, modulus, and hardness. In soft or elastic rubber compounds, sulfur is an essential but minor additive. In semi-hard rubber and ebonite, sulfur becomes a major compounding material while retaining its role as a vulcanizing agent.

3.2 The most stable molecular form of sulfur at ambient conditions is a ring structure containing eight sulfur atoms. Depending on conditions these molecules orient into one of two crystalline structures. At room temperature the crystals are rhombic and above 95°C they rearrange to monoclinic. Less than 1.5 % of either crystalline structure of sulfur is soluble in any rubber at room temperature.

3.3 The second common molecular form of sulfur is polymeric sulfur, made up of unbranched chains of sulfur atoms. It is commonly referred to in the rubber industry as insoluble sulfur. When this material is created by rapid heating to above 160°C and quenching to room temperature, the sulfur is amorphous. If formed under other conditions, the polymer chains may develop regions of pseudo crystallinity.

3.4 Insoluble sulfur is an important form of sulfur used only in the rubber industry. It is not soluble in any type of rubber hydrocarbon. When it is mixed in rubber, it disperses but remains undissolved in the rubber. The use of insoluble sulfur prevents the development of a supersaturated solution of sulfur in rubber that occurs when rhombic sulfur is used. No sulfur bloom will develop on the surface of uncured rubber pieces when the rubber cools after mixing or processing; therefore, building tack is preserved. At curing temperatures, insoluble sulfur rapidly transforms to a soluble species, dissolves in the rubber, and enters into the vulcanization process.

4. Basis of Classification of Sulfurs

4.1 *Rhombic Sulfur* (ordinary ground sulfur)—Rhombic sulfur, which is the ordinary form of sulfur under normal conditions, is ground and classified to meet specific particle size requirements. The various grades of this type of sulfur contain less than 1 % polymeric sulfur. The ground types of sulfur may also contain additives to enhance performance. Oil is added to sulfur to help control sulfur dust and improve dispersion in rubber. Finely ground solid minerals are also added to improve dispersion in rubber. Ordinarily the total additive level is 5 % or less of the sulfur formulation. Many of these types of sulfur may be added to rubber compounds as 100 % sulfur.

4.2 *Insoluble Sulfur* (polymeric)—There are two general types of insoluble sulfur and the general description of each is detailed as follows:

4.2.1 *Low Insoluble Content Sulfur or Flowers of Sulfur*—This product is made by vaporizing pure sulfur and quenching the vapors in an inert gaseous atmosphere. A select grade of this product contains between 30 and 40 % of polymeric sulfur. This level of insoluble sulfur is often insufficient to prevent bloom, and its use is restricted to rubber compounds containing high levels of fillers or rubber compounds using modest amounts of sulfur. Historically, this was the first commercial insoluble sulfur available.

¹ This classification is under the jurisdiction of ASTM Committee D-11 on Rubber and is the direct responsibility of Subcommittee D11.20 on Compounding Materials and Procedures.

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² *Annual Book of ASTM Standards*, Vol 09.01