AEROSIL® and AEROXIDE® for Liquid Silicone Rubber (LSR/LIMS)

Technical Information 1253
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1 Introduction

Synthetic silicas from Evonik Industries AG have been known for many years in the silicone industry. Both fumed and precipitated silicas are used to control the properties of silicone rubber.

The fumed silicas, in the form of different hydrophilic and hydrophobic AEROSIL® products, are applied in numerous silicone systems (see Figure 1).

For example, as effective thixotropic additives, they control the viscosity and stability of uncured silicone sealing compounds. Their efficiency as reinforcing component also positively affects the mechanical properties of the different silicone products. The use of special AEROSIL® grades even makes it possible to manufacture products with excellent optical properties (transparency).

Manufactured by flame hydrolysis of chlorosilanes, and with a silicon dioxide content of more than 99.8 %, AEROSIL® is one of the purest silicas commercially available. These inorganic substances, which are completely amorphous, fulfill all consumer requirements regarding reliable, physically safe raw materials.

Metallic oxide AEROXIDE® TiO₂ P 25 from Evonik is also manufactured using the well-known AEROSIL® process. AEROXIDE® can be used in silicone rubber to improve the heat stability.

In this Technical Information brochure, we would like to present the properties of hydrophilic and hydrophobic grades of AEROSIL®, and of AEROXIDE® TiO₂ in liquid silicone rubber applications. A series of new and innovative experimental products for this growing silicone application are currently undergoing trials, making it necessary to revise this present Technical Information fairly soon. In the event of further questions, please feel free to contact our team of specialists at any time.

1.1 Liquid Silicone Rubber (LSR/LIMS) – A material of growing significance

Addition cross-linking liquid silicone rubber (LSR) was developed at the end of the 1970’s by Dow Corning. Liquid silicone rubbers have become increasingly important over the past few years, as a result of their good material and processing properties. Due to their fluid consistency and short cross-linking times, a high rate of productivity can be achieved with high-speed, automatic, environmentally-friendly processing methods using liquid injection molding systems (LIMS).

The changeover in production from compression molding to automatic processing is an economic factor requiring serious consideration. The result would be a tangible reduction in the piece price. Here are some of the most significant fields of application:

- Construction of automobiles and other vehicles
- Electronics and electrical engineering
- Human and food sector
- Medical technology
- Sanitary and household goods
Consequently, fields of application for LSR products are to be found in almost all branches of industry. Some important products, for example, are keypads, seals and gaskets, insulators in high voltage technology, and baby bottle nipples. Due to the fact that the material can be sterilized and displays good biocompatibility properties, it is also used in numerous medical applications. The spectrum of building components ranges at present from small and precision parts weighing less than 0.05 g per piece, and produced in large quantities, to high-volume components of up to 80 kg in weight, manufactured in small or medium-sized series.

The diversity of suitable applications is currently undergoing a new revolution. Thanks to the two-component or dual color injection molding technology now available for use with liquid silicone rubber, it is also possible to bond plastics with silicone rubber in one working step.

1.2 Components of the LSR system
LSR is made up of a two-component system, whose components A and B generally require mixing in a ratio of 1:1. They consist of polysiloxane polymers or copolymers, containing active or inactive fillers and additives. Prior to vulcanization, LSR is a mixture of silicone polymers containing vinyl groups and a cross-linking component with Si-H groups.

Their consistency and cross-linking behavior allow excellent processibility. Their viscosity is very low compared to that of solid silicone rubber (HCR). In a resting state, they have paste-like characteristics. Vulcanization works on the mechanism of hydrosilation. The result of this chemical reaction is a highly elastic, three-dimensional network with excellent mechanical, electrical, and optical properties. Unlike with peroxide curing, no by-products are released during the vulcanization of LSR compounds. Good storage stability is achieved by the use of inhibitors and the right choice of silica.

1.3 Processing of LSR
The much faster vulcanization process, compared to peroxide curing, is a deciding factor for the processing. Short cycles mean lower piece prices. Generally, the injection molding of LSR is fully automatic. As Figure 2 shows, components A and B are metered during production at room temperature, together with a pigment paste or other additives, if required, from a dosing apparatus into a static mixer, and subsequently injected into a hot mold. During the dwell time in the hot mold, the mixture cures to a solid, elastic component, which may be extracted by means of an automatic handling system, or manually, after the mold is opened.

The cycle times obtainable with liquid silicone rubber vary between a few seconds and several minutes. In order to release volatiles, and to bring about a more complete vulcanization, the molded parts can be then postcured at about 200 °C. In many cases, a curing time of four hours is sufficient for this.

Figure 2  Operating diagram of an injection molding machine for processing LSR
The high requirements made on silicas from Evonik during the production of LSR compounds, and during the processing and application of LSR products

The high standards are not just expected of the silicas during the production of the LSR compounds, but also during the processing of the finished compounds using injection molding technology (see Figure 3). The challenge issued to the silica is to provide very high mechanical properties in the finished product and the lowest rheological properties in the compound – a somewhat contradictory demand in itself! Top quality LSR products requiring a high level of mechanical and optical properties (transparency), are produced exclusively with fumed silicas. Precipitated silicas may also be used in certain applications requiring dynamic properties, for example in keypads made of silicone rubber.

Demands on the silica in different LSR products

- Very good mechanical properties (e.g. hardness, tensile strength, resistance to tear)
- Excellent optical properties (e.g. highly transparent baby bottle nipple)
- Very good dynamic properties (low compression set, e.g. for key pads)
- Good electrical and dielectric properties (e.g. for insulators)
- Excellent physiological compatibility (e.g. in medical applications)
- Good temperature resistance (e.g. molds for baking or ice cubes)

Demands on the silica during the production of LSR

- A high degree of purity (no metallic contamination)
- Good storage stability (low moisture adsorption)
- Rapid incorporation behavior
- Good and rapid dispersibility
- Minimal thickening, i.e. very low level of rheology at high levels of loading

Demands on the silica in the LSR compound and during the processing of LSR

- Good level of rheology (low viscosity)
- Good flow properties (low yield point)
- Good storage stability (no subsequent thickening)

Figure 3  LSR injection molding machine; Manufacturer: ARBURG GmbH + Co., Lossburg, Germany

Figure 4  Highly transparent bottle nipple made of LSR for baby food
3 The production and properties of fumed grades of AEROSIL®

3.1 Production
AEROSIL® is a synthetic, amorphous silicon dioxide manufactured by hydrolysis of chlorosilanes in an oxyhydrogen flame, in accordance with the reaction formula SiCl₄ + 2H₂ + O₂ → SiO₂ + 4 HCl. The production process was patented by DEGUSSA back in 1942, used for largescale manufacturing in the 1950’s, and has been continuously developed ever since. AEROSIL® is classified as a fumed silicon dioxide or fumed silica, due to the process of flame hydrolysis used in its production, and is also described as a finely-divided silicon dioxide, due to the small size of its particles.

High degree of purity
The raw materials used are entirely of chemical origin and are very pure. With its SiO₂ content of more than 99.8 % by weight (related to the ignited substance), AEROSIL® is one of the purest silicas commercially available. The heavy metal content lies below the detection limit of standard methods of analysis. Neither animal- nor plant-based raw materials are used in the manufacture of AEROSIL®, and neither are solvents. The AEROSIL® process is used by Evonik to manufacture fumed titanium and aluminum oxides, together with a variety of mixed oxides.

Diversity of product modifications
The properties of AEROSIL® may be greatly varied. For example, the specific surface of AEROSIL® OX 50 is only 50 m²/g, whereas that of AEROSIL® 380 is almost eight times as much. The surface and structure of AEROSIL® may be modified in many different ways, to suit the requirements for modern silicone rubber products. For instance, dimethyl silyl, trimethyl silyl, or siloxane groups may be chemically anchored on the AEROSIL® surface by means of chemical reaction with organic silicon compounds. Examples of surface-modified products are AEROSIL® R 972, AEROSIL® R 812 S and AEROSIL® R 202. AEROSIL® R 8200 is a structurally-modified product that was developed specially for the applications LSR and RTV-2 component. Special fumed silicas in beaded form are available from Evonik under the trade name AEROPERL®.

3.2 Properties
Finely-divided Structure
AEROSIL® is a fine, white, amorphous powder, made up of primary particles ranging from approx. 7 to 40 nm in size—depending on the specific surface of the product. The primary particles are not present in an isolated state, but are clumped together as stable aggregates, which may be several hundred nanometers in size. These aggregates group together to form agglomerates in the micrometer range that readily disintegrate during application.

Hydrophilic and hydrophobic grades of fumed silica
Silanol and siloxane groups are situated on the surface of untreated AEROSIL®. As a result of these, AEROSIL® has a strong affinity with water—it is hydrophilic—and may be totally wetted. AEROSIL® 200, for instance, is able to absorb considerable quantities of water. This does not change its aggregate state: it remains a free-flowing powder. By converting the silanol groups with silanes or siloxanes, as described above, alkylsilyl-groups become chemically anchored on the surface. The resulting products now repel water—they are hydrophobic—and adsorb only very small quantities of water. These products are labeled with the suffix “R” (R = repellent), e.g. AEROSIL® R 812 S.
### Table 1  Physico-chemical properties

<table>
<thead>
<tr>
<th>Test method</th>
<th>200</th>
<th>300</th>
<th>380</th>
<th>R 812 S</th>
<th>R 8200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Behavior in the presence of water</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>hydrophilic</td>
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<tr>
<td>Appearance</td>
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<tr>
<td></td>
<td>loose white powder</td>
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<tr>
<td>Surface</td>
<td>m²/g</td>
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<td>acc. to BET</td>
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<td>380 ± 30</td>
<td>220 ± 25</td>
<td>160 ± 25</td>
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<tr>
<td>approx. value</td>
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<td>Loss on drying</td>
<td>%</td>
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<tr>
<td>(2 hours at 105 °C) on leaving the production plant</td>
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<tr>
<td></td>
<td>≤ 1.5</td>
<td>≤ 1.5</td>
<td>≤ 2.0</td>
<td>≤ 0.5</td>
<td>≤ 0.5</td>
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<tr>
<td>pH value</td>
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<td></td>
<td>3.7–4.5</td>
<td>3.7–4.5</td>
<td>3.7–4.5</td>
<td>5.5–9.0</td>
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</tr>
<tr>
<td>C content</td>
<td>%</td>
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<td></td>
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<td></td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3.0–4.0</td>
<td>2.0–4.0</td>
</tr>
<tr>
<td>SiO₂ content</td>
<td>%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>≥ 99.8</td>
<td>≥ 99.8</td>
<td>≥ 99.8</td>
<td>≥ 99.8</td>
<td>≥ 99.8</td>
</tr>
</tbody>
</table>

1 In acc. to DIN ISO 9277  
2 In acc. to DIN EN ISO 787-11  
3 In acc. to DIN EN ISO 787-2  
4 Water: methanol = 1:1  
5 related to the substance ignited for 2 hours at 1000 °C  
6 The data have no binding force.
4 The production of LSR systems

A variety of kneaders and other mixers with high shearing action are used to produce LSR compounds. Figure 7 shows a planetary dissolver, Type PMH 1400 from the company Netzsch Feinmahltechnik GmbH, Germany, with a usable volume of 1400 liters, as used on a production scale. Basically, LSR compounds can be manufactured using hydrophilic and/or hydrophobic silicas. Mixers and silicas should be chosen according to the method of production used. In principle, there are two different manufacturing options: these are briefly described in the following section.

4.1 Compounding by means of the “in situ” hydrophobizing of hydrophilic silicas

The so-called “in situ” hydrophobizing of hydrophilic silicas, combines several processing steps. This involves the loading of batches containing different LSR polymers and/or silicone oils with hydrophilic silicas. These highly viscous raw compounds are then blended using mixers with strong shearing action. The mixing process is carried out at a high temperature. At the same time, the hydrophilic silica, is rendered hydrophobic “in situ” by the addition of silanes (e.g. Dynasylan® HMDS), i.e. the silanol groups on the surface of the silica react with the silane used. This causes the silica to become extremely hydrophobic and, due to the strong shearing action, it also undergoes structural modification at the same time. Outstanding flow characteristics, combined with excellent mechanical and optical properties, can be obtained in this way, after the LSR batch has been cut back to the desired level of silica loading using a pure polymer.

In addition to the know-how required to carry out this complex process, large investments in special equipment and mixing aggregates are necessary. High energy costs are also incurred, due to the necessary processing temperatures of up to 200 °C, and the relatively long batch times (approx. 4 hours). A further major disadvantage of this compounding method is the release of reactive by-products that require proper disposal.
4.2 Compounding with hydrophobic silicas

In order to offer an alternative to the compounding method described above, with its "in situ" hydrophobizing, we would like to give you a closer look in this Technical Information brochure at two special products made by Evonik. These hydrophobic grades of AEROSIL® make it possible to simplify the compounding process based on the LSR formulation. By using the hydrophobic grades AEROSIL® R 812 S and AEROSIL® R 8200, it is possible to dispense with the "in situ" technology described in Chapter 4.1. The effects obtainable with these hydrophobic products are summarized below. Detailed results are described in Chapter 5.

AEROSIL® R 812 S

By means of a special modification, trimethylsilyl groups are chemically anchored on the surface of this fumed silica. AEROSIL® R 812 S can be used in LSR without the use of processing additives, such as hexamethyldisilazane (Dynasylan HMDS). The very hydrophobic nature of AEROSIL® R 812 S enables rapid incorporation and dispersion of the silica in the LSR polymer. Vulcanisates of unusually high transparency can be produced with this silica.

AEROSIL® R 8200

AEROSIL® R 8200 was specially developed for the application LSR and can also be incorporated without the use of processing additives. Special modification has also left this fumed silica with trimethylsilyl groups chemically anchored on the surface. AEROSIL® R 8200 is not merely very hydrophobic, but has been structurally modified by means of an additional processing step.

This silica is characterized by its very low thickening effect even when high levels of loading are used. Hence, it is possible to produce easily dispersible compounds with very good flow properties by using AEROSIL® R 8200. Based on its special structural modification, high levels of loading produce excellent mechanical properties, together with very low levels of viscosity, and good storage stability. The relatively high tapped density of approx. 140 g/l, and comparatively low BET surface of 160 m²/g, enable a very rapid incorporation of AEROSIL® R 8200 in polymer systems.

Advantages of compounding with hydrophobic silicas:

- No "in situ" hydrophobizing necessary
- Low investment costs (mixers and safety equipment)
- Savings in the cost of raw materials, as no silanes are needed
- Savings in energy costs, as no high temperatures are needed
- Environmentally-friendly processing, as no by-products (ammonia) are released
- Rapid incorporation of the silica is possible, resulting in short batch times and capacity expansion
- Continuous production of LSR possible
- Production site can be independent of location
5 The effects of different grades of hydrophobic AEROSIL® in an LSR formulation

In order to test the technical application properties of various hydrophobic grades of AEROSIL®, planetary dissolvers (see Figure 11) were used to produce a variety of LSR mixtures on a laboratory scale, that were subsequently cured. Detailed information on the formulation used, together with the test procedure, is given in the experimental section (chapter 6.1).

The following technical application properties were determined: the time required to incorporate the silica, the rheological properties (viscosity and yield point), the mechanical properties of the vulcanisates (hardness, resilience, tensile strength, resistance to tear propagation and elongation at break), and the optical properties (transparency). The individual results will be presented and discussed in the following chapter. Two ready-to-use two-component LSR products were used as reference materials.

5.1 Rheological properties of the uncured LSR compounds

As the name of this application LSR (Liquid Silicone Rubber) implies, the rheological properties of these systems are of elementary primary significance. A low level of rheology is required during the processing of the LSR compounds, i.e. low levels of viscosity combined with good flow properties (low yield points).

The length of time needed for incorporation is additionally important for the processing of the silica. Table 2 shows the required incorporation times, the viscosities, and the yield points of various compounds based on differing levels of loading of AEROSIL® R 812 S and AEROSIL® R 8200.

The measurement of the rheological properties shows a clear result. When a 20–25% loading level of AEROSIL® R 812 S is used, the viscosity level and yield point of the compounds are approximately the same as those of the reference material L 2–4.

<table>
<thead>
<tr>
<th>Silica / Product</th>
<th>Level of Loading [%]</th>
<th>IT/Sil* [min]</th>
<th>Yield Point [Pa]</th>
<th>Viscosity η [Pas; D = 10 s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEROSIL® R 812 S</td>
<td>20</td>
<td>12</td>
<td>0</td>
<td>183</td>
</tr>
<tr>
<td>AEROSIL® R 812 S</td>
<td>25</td>
<td>20</td>
<td>171</td>
<td>432</td>
</tr>
<tr>
<td>AEROSIL® R 812 S</td>
<td>30</td>
<td>28</td>
<td>370</td>
<td>1,050</td>
</tr>
<tr>
<td>AEROSIL® R 812 S</td>
<td>35</td>
<td>40</td>
<td>1,800</td>
<td>6,000</td>
</tr>
<tr>
<td>AEROSIL® R 8200</td>
<td>20</td>
<td>3</td>
<td>0</td>
<td>34</td>
</tr>
<tr>
<td>AEROSIL® R 8200</td>
<td>25</td>
<td>4</td>
<td>0</td>
<td>62</td>
</tr>
<tr>
<td>AEROSIL® R 8200</td>
<td>30</td>
<td>5</td>
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<td>128</td>
</tr>
<tr>
<td>AEROSIL® R 8200</td>
<td>35</td>
<td>6</td>
<td>312</td>
<td>340</td>
</tr>
<tr>
<td>AEROSIL® R 8200</td>
<td>40</td>
<td>8</td>
<td>1,680</td>
<td>1,530</td>
</tr>
<tr>
<td>AEROSIL® R 8200</td>
<td>45</td>
<td>10</td>
<td>5,500</td>
<td>6,000</td>
</tr>
<tr>
<td>L 2–4, Component A</td>
<td>–</td>
<td>–</td>
<td>52</td>
<td>344</td>
</tr>
<tr>
<td>L 2–4, Component B</td>
<td>–</td>
<td>–</td>
<td>180</td>
<td>244</td>
</tr>
<tr>
<td>L 2–7, Component A</td>
<td>–</td>
<td>–</td>
<td>228</td>
<td>372</td>
</tr>
<tr>
<td>L 2–7, Component B</td>
<td>–</td>
<td>–</td>
<td>380</td>
<td>340</td>
</tr>
</tbody>
</table>

* Incorporation time required for silica
As illustrated in Figure 8, the viscosity and the yield point increase as the level of loading is raised. In order to use a higher level of loading than 35%, the structure of the silica must be modified.

The results based on AEROSIL® R 8200 demonstrate that higher levels of loading are possible when using a structurally modified product, without negatively influencing the level of rheology. The rheological properties, especially the flow properties, are comparable to those of the reference material L 2–7 when a 35% loading level of AEROSIL® R 8200 is used.

5.2 Mechanical properties of the cured LSR samples,

The mechanical properties of the cured LSR samples, based on differing loading levels of AEROSIL® R 812 S and AEROSIL® R 8200, are compiled in Table 3.

As can be expected, the mechanical properties of the LSR vulcanisates improve as the loading level of silica is increased. Depending on the level of loading, vulcanisate durometer hardness levels (Shore A) of around 40, 50, 60 or 70 were achieved. Figure 10 clearly demonstrates how the tensile strength improves as the concentrations of AEROSIL® R 812 S and AEROSIL® R 8200 increase.

However, of particular interest is the considerable improvement of the resistance to tear propagation with increasing loading level of silica.
5.3 Optical properties of the cured LSR samples

The optical properties of the cured LSR samples based on differing loading levels of AEROSIL® R 812 S and AEROSIL® R 8200, are presented in Table 4.

The optical properties of the silicas examined are of a high level throughout. The use of higher loading levels can initially cause a reduction in the transparency of the vulcanisates. A possible explanation for this can be the less effective dispersion, which depends on the small sized lab equipment.

### Table 3  Mechanical properties of the cured LSR samples

<table>
<thead>
<tr>
<th>Silica / Product</th>
<th>Level of Loading [%]</th>
<th>Tensile Strength [N/mm²]</th>
<th>Elongation at Break [%]</th>
<th>Resistance to Tear Propagation [N/mm]</th>
<th>Hardness [Shore A]</th>
<th>Impact Resilience [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEROSIL® R 812 S</td>
<td>20</td>
<td>5.0</td>
<td>350</td>
<td>19</td>
<td>43</td>
<td>59</td>
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<td></td>
<td>25</td>
<td>6.1</td>
<td>350</td>
<td>27</td>
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<tr>
<td></td>
<td>30</td>
<td>6.3</td>
<td>300</td>
<td>34</td>
<td>62</td>
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<td>7.3</td>
<td>240</td>
<td>34</td>
<td>71</td>
<td>37</td>
</tr>
<tr>
<td>AEROSIL® R 8200</td>
<td>20</td>
<td>8.1</td>
<td>600</td>
<td>37</td>
<td>45</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>8.9</td>
<td>320</td>
<td>44</td>
<td>71</td>
<td>61</td>
</tr>
</tbody>
</table>

### Table 4  Optical properties of the LSR vulcanisates

<table>
<thead>
<tr>
<th>Silica / Product</th>
<th>Level of Loading [%]</th>
<th>Transparency directly after curing [DE*/D 65]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEROSIL® R 812 S</td>
<td>20</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>38</td>
</tr>
<tr>
<td>AEROSIL® R 8200</td>
<td>20</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>41</td>
</tr>
<tr>
<td>AEROSIL® R 8200</td>
<td>40</td>
<td>34</td>
</tr>
<tr>
<td>AEROSIL® R 8200</td>
<td>45</td>
<td>35</td>
</tr>
<tr>
<td>L 2–4</td>
<td>–</td>
<td>54</td>
</tr>
<tr>
<td>L 2–4</td>
<td>–</td>
<td>54</td>
</tr>
</tbody>
</table>
6 Experimental section

6.1 LSR formulation and LSR compounding
Liquid silicone rubber is generally a ready-to-use mixture of paste-like or liquid consistency. In practice, the addition curing rubber system consists of two components. In order to test all the relevant technical application properties, it is necessary to produce vulcanisates.

The necessary components A and B were combined into a one-component system in the following formulation to allow better handling on a laboratory scale.

First of all, the polysiloxane is placed into a planetary dissolver (see Figure 11). The silica is then incorporated at a low rotational speed. Subsequently, this basic mixture is dispersed under vacuum and with water cooling for 30 minutes at a higher velocity speed. The rheological properties can now be determined from this basic mixture (see Chapter 5).

<table>
<thead>
<tr>
<th>Table 5  LSR base-formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formulation (1000 g batch)</td>
</tr>
<tr>
<td>60–80 % Silicone polymer</td>
</tr>
<tr>
<td>20–40 % Silica</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 6  LSR standard formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSR formulation [350 g batch, Example for 20 % silica]</td>
</tr>
<tr>
<td>Polysiloxane</td>
</tr>
<tr>
<td>Synthetic silica</td>
</tr>
<tr>
<td>Platinum catalyst (10 ppm pure Pt/ECH)</td>
</tr>
<tr>
<td>Inhibitor (340 ppm pure Pt/CH)</td>
</tr>
<tr>
<td>SiH cross-linking agent</td>
</tr>
</tbody>
</table>

Figure 11  Planetary dissolver; Manufacturer: Hermann Linden, Marienheide, Germany
The remaining formulation components were added step by step to the basic mixture in the order given in Table 5, and were well homogenized. The compounds were then de-aerated in a vacuum drying cabinet oven.

6.2 Cross-linking and postvulcanization

Cross-linking

In order to produce a variety of LSR vulcanisates for different test purposes, specially prepared plates containing defined amounts of LSR compound were cured in a vulcanization press (see Figure 12) for between 10 and 12 minutes, according to the thickness of the vulcanisates, at a pressure of 100 bar, and a temperature of 120 °C.

Postvulcanization

The cured compounds released from the mold were then post-cured for 4 h at 200 °C in a convection oven to achieve a total vulcanization, and to remove any volatiles. The mechanical and optical properties were determined (see Chapter 5) after the vulcanisates had been stored for 72 h in a standardized climate at 23 °C and 50% humidity.
7 Heat stabilizer for LSR formulations

As mentioned in Chapter 1, the finely divided metallic oxide available from Evonik, AEROXIDE® TiO₂ is also manufactured using the well-known AEROSIL® process.

AEROXIDE® TiO₂ P 25 and AEROXIDE® TiO₂ PF 2 can be used in silicone rubber to improve the heat stability.

7.1 Production and properties of AEROXIDE® TiO₂ P 25

7.1.1 Production

AEROXIDE® TiO₂ P 25 is manufactured by flame hydrolysis of titanium tetrachloride (see Figure 13).

The more effective product AEROXIDE® TiO₂ PF 2 is also produced by this method. The addition of FeCl₃ gives a AEROXIDE® TiO₂ mixed with 2 % Fe₂O₃.

Figure 13 Chemical reaction

\[ \text{AEROXIDE® TiO}_2 \text{ P 25} \]
\[ \text{TiCl}_4 + 2 \text{H}_2 + \text{O}_2 \rightarrow \text{TiO}_2 + 4 \text{HCl} \]

\[ \text{AEROXIDE® TiO}_2 \text{ PF 2} \]
\[ \text{TiCl}_4 + 2 \text{H}_2 + \text{O}_2 \rightarrow \text{TiO}_2 + 4 \text{HCl} \]

and

\[ 2 \text{FeCl}_3 + 3 \text{H}_2 + 1.5 \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 6 \text{HCl} \]

Figure 14 Liquid silicone rubber high temperature resistance

7.2 LSR Shore-A Hardness Change during storage at high temperatures

Further information on heat stability properties of our AEROXIDE® products can be found in Technical Information No. 1218.

8 Summary and product recommendations

8.1 Summary

In principle, both hydrophilic and hydrophobic fumed silica are suitable for use in the manufacture of LSR products. The choice of silicas should be made according to the most significant properties for the processing of the LSR compound, such as

- low level of rheology
- good flow properties
- rapid vulcanization behavior
- good storage stability

and the properties that are to be achieved in the corresponding final product, e. g.

- good mechanical properties
- high transparency
- good electrical properties
8.2 Product recommendations
We would like to recommend the following Evonik products for LSR applications:

**AEROSIL® 200, AEROSIL® 300, AEROSIL® 380**
These fumed silicones are hydrophilic. The BET surface of AEROSIL® 200 is approximately 200 m²/g, whereas the higher surface areas are displayed by AEROSIL® 300 with approx. 300 m²/g, and 380 m²/g in the case of AEROSIL® 380. Each of these products is readily dispersible and very well suited for “in situ” hydrophobizing. The favorable reaction behavior of these products with processing additives, such as silanes (Dynasylan® HMDS), results in compounds with very good flow properties, and good storage stability. In addition to the excellent mechanical properties (high tensile strength and high tear resistance), it is possible to achieve cured LSR compounds with a very high degree of transparency. The choice of product depends on the desired rheological level of the LSR compound. Since the viscosity of the compound increases as the BET surface gets bigger, and the transparency of the vulcanisates is also dependent on the size of the active surface, the commitment to a certain product can only be made after a series of tests have been carried out.

**AEROSIL® R 812 S**
This fumed specialty product has undergone special modification to chemically anchor trimethylsilyl groups on its surface. AEROSIL® R 812 S can be used in LSR without additional processing auxiliaries. This product stands out especially due to its extremely hydrophobic nature, which permits rapid processing (incorporation) and very good dispersibility. Vulcanisates of high transparency can be achieved, due to its relatively high BET surface of approx. 220 m²/g.

**AEROSIL® R 8200**
This fumed specialty product also underwent special modification to chemically anchor trimethylsilyl groups on its surface. AEROSIL® R 8200 is not just extremely hydrophobic, it has also been structurally modified by an additional processing step. AEROSIL® R 8200 was developed for use in LSR applications, and is characterized by its very low thickening effect even at high levels of loading. For this reason, it is possible to manufacture compounds with very good flow properties by using AEROSIL® R 8200. Due to its special structural modification, high levels of loading result in very low viscosity, combined with excellent mechanical properties. AEROSIL® R 8200 can be very rapidly incorporated into polymer systems as a result of its relatively high tapped density of approx. 140 g/L and its comparatively low BET surface of about 160 m²/g.

**AEROXIDE® TiO₂ P 25**
AEROXIDE® TiO₂ P 25 is a effective heat stabilizer in silicone rubber and is produced by flame hydrolysis of titanium tetrachloride. A financially favorable and effective stabilization up to 250 °C is possible, thanks to the very good results obtainable with a relatively small addition of 0.5 to 3.0 %, related to the total formulation amount.

**AEROXIDE® TiO₂ PF 2**
The product AEROXIDE® TiO₂ PF 2 is also produced by flame hydrolysis of titanium tetrachloride. The addition of FeCl₃ gives a AEROXIDE® TiO₂ mixed with 2 % of Fe₂O₃. It is a yellowish white powder and gives excellent heat stability at temperatures >250 °C. The recommended usage level is 0.5–1.5 %, related to the total formulation amount.
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