The influence of the Content and Dispersity of Aluminum Hydroxide on the Properties of Siloxane Sealants

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Abstract. The influence of the content of aluminum hydroxide of various degree of dispersion on the rheological, physical-mechanical and adhesive properties, thermal and fire resistance of siloxane sealants was studied. It was established that the main factor determining the effectiveness of the use of aluminum hydroxide in siloxane sealants is the degree of dispersion. The introduction of aluminum hydroxide makes it possible to vary widely the viscosity of the sealant compositions, while with decreasing of particle size of aluminum hydroxide the viscosity of the compositions increases. The use of aluminum hydroxide with a minimum particle size makes it possible to obtain siloxane sealants with the most optimal level of physical-mechanical and adhesive properties, however, to increase the thermal and fire resistance of sealants, coarse aluminum hydroxide is most preferred.

1. Introduction

The production of siloxane sealants and the expansion of their range in all countries is characterized by a quite rapid growth. The compositions of such sealants, as a rule, are well balanced, which allows to ensure operational properties that satisfy consumers. However, there is fierce competition in this market and the need to improve the properties of siloxane sealants while maintaining or even reducing their cost. In addition, emergence of new ingredients requires exploring possibility of their using and developing siloxane sealants including them.

Presently, aluminum hydroxides are most widely used as flame retardants in vulcanized siloxane rubbers and sealants [1-7]. This is due to their low cost compared to other flame retardants, ease of using and non-toxicity (environmental friendliness) [8-10]. Recently, a large number of various types of aluminum hydroxide have appeared, differing in dispersion, morphology and surface treatment. Accordingly, a study of the effect of aluminum hydroxide content of various the degree of dispersion on the rheological, physical-mechanical and adhesive properties, thermal and fire resistance of siloxane sealants are of both scientific and practical interest.

2. Experimental

Cold curing sealants based on reactive oligomers, including those based on siloxane, are distinguished by the simplicity of processing technology that does not require traditional rubber equipment, as well as the possibility of their use in cases where high vulcanization temperatures are undesirable and
sometimes even unacceptable. The molecular features of low molecular weight siloxane rubbers largely determine the formulation of sealants based on them [11].

In the work, the siloxane oligomer of the brand SKTN «G» was used, zinc oxide was used as a filler. The content of aluminum hydroxide of various dispersion produced by the TK «FM» (Russia), the characteristics of which are shown in table 1, was ranged from 50 to 125 parts by weight per 100 parts by weight of siloxane oligomer. The siloxane oligomer was cured with tetraethoxysilane and dibutyltin dilaurate.

Table 1. Characterization of aluminum hydroxide.

| Brand of aluminum hydroxide | The average particle size, [microns] |
|----------------------------|-------------------------------------|
| TS-302SH                   | 2.3                                 |
| TS-305SH                   | 6.4                                 |
| TS-330SH                   | 37.0                                |
| TS-350SH                   | 57.0                                |

The influence of the content of aluminum hydroxide of various dispersion on the rheological properties of sealants was evaluated. The studies have been carried out with the use of the rotary viscometer «Rheotest». The results are presented in figure 1.

![Figure 1](image)

**Figure 1.** Dependence of the effective viscosity of the sealant compositions on the content of aluminum hydroxide of various brands at a shear rate of $\lg \gamma = 0.43, \left[\gamma, s^{-1}\right]$ and a temperature of $23 \pm 2 ^\circ C$.

With an increase in the content of aluminum hydroxides (figure 1), a regular increase in the viscosity of the composition is observed. The presented data indicate a direct dependence of the viscosity of the compositions on the particle size of aluminum hydroxide. For example, the increase of content of aluminum hydroxide TS-350SH (having the largest particle size (57 microns) of the presented) from 50 to 125 parts by weight increases the viscosity ($\lg \eta$) of the composition in the range from 2.64 to 2.86. And the increase of content of aluminum hydroxide TS-302SH, having a particle size of 2.3 microns, from 50 to 125 parts by weight increases the viscosity ($\lg \eta$) in the range from 2.89 to 3.29. Apparently, with an increase in the degree of dispersion of aluminum hydroxide particles and with an increase in the contact surface, the proportion of physical interactions increases, which leads to an increase in the viscosity of the composition.
It should also be noted that the character of viscosity change observed after a change in the shear rate in the studied systems indicates the presence of a thixotropic effect, which is stronger for compositions filled with aluminum hydroxide with a higher dispersion.

With an increase in the content of aluminum hydroxide, the pot life of the sealants practically does not change and is within 30-40 minutes. Apparently, this reflects the entire range of the presented aluminum hydroxides has a pH in the range from 9.2 to 9.6. Dispersity does not affect the increase in cure rate (decrease in pot life) when using aluminum hydroxides.

**Figure 2.** Influence of the content of aluminum hydroxide of various brands on the tensile strength at break of the siloxane sealants.

An increase in the content of aluminum hydroxide of the brand TS-302SH, TS-305SH, TS-330SH leads to an increase in the tensile strength at break of sealants and is directly dependent on their dispersion (figure 2). This is due to the fact that an increase in the dispersion of aluminum hydroxide contributes to an increase in the contact area of its particles with oligomer macromolecules. As a result, the adsorption interactions are intensified. On the one hand that leads to an increase in the strength of sealants and, on the other hand, to a decrease in elastic properties.

An increase in the degree of filling of the sealants reduces their elongation at break (figure 3). The obtained results correlate with a change in the tensile strength at break (figure 2).

An increase in the content of aluminum hydroxide in sealants based on siloxane oligomer over the entire dosage range increases the value of the hardness of sealants (figure 4). In this case, the highest hardness of sealants is achieved when using aluminum hydroxide of the brand TS-305SH in comparison with other aluminum hydroxides. The smallest hardness values of sealants are characteristic for the composition using coarse aluminum hydroxide (57 microns) of the brand TS-350SH.

**Figure 3.** Influence of the content of aluminum hydroxide of various brands on elongation at break of the siloxane sealants.

Evaluation of the adhesion of sealants to duralumin and steel indicates that the introduction of aluminum hydroxide does not significantly impair the adhesion properties of the sealants. The maximum adhesion values of the sealant to duralumin and steel are characteristic of the brand TS-302SH aluminum hydroxide, while with an increase in its content, the adhesion of the sealant increases. With a content of 100 and 125 parts by weight, the cohesive / adhesive character of the gap was observed (in a ratio of 50/50), which indicates that in that case, the strength of the sealant to the substrates was higher than the strength of the sealant itself. It should be noted that in all other cases the
adhesive nature of the gap was observed. Therefore, when using such sealants, the use of a primer is necessary.

![Figure 4](image.png)

**Figure 4.** Influence of the content of aluminum hydroxide of various brands on the Shore A hardness of the siloxane sealants.

Testing of sealants for resistance to an open flame was carried out by igniting samples on a «MEGA 1» burner with piezo ignition Kovica KS-1005 (Korea). Sealant samples in the form of strips (100x15x2 mm in size) were brought to the burner at an angle of 90 °, burned in the center and kept in an open flame for a certain time, then ignition, residual burning time and self-extinguishing ability were recorded. The test results are presented in table 2.

When siloxane sealants consisting of an aluminum hydroxide of the brand TS-305SH, TS-330SH, TS-350SH from 50 to 125 parts by weight were exposed to an open flame for 10 seconds, they did not ignite and did not burn (table 2). Starting from 15 seconds of exposure to an open flame, all siloxane sealants ignite, however, siloxane sealants containing aluminum hydroxide of the brand TS-305SH, TS-330SH, TS-350SH in an amount of 100-125 parts by weight were self-extinguishing. Exposure of the samples to an open flame for 20 seconds in all cases leads to ignition, retention of residual combustion, and after self-extinguishing, they remain smoldering for some time, except for compositions using of the brand TS-330SH, TS-350SH in an amount of 125 parts by weight. When the samples were exposed to an open flame for 25 seconds, only a siloxane sealant containing aluminum hydroxide of the brand TS-350SH with a dispersion of 57 microns with a content of 125 parts by weight did not ignite and did not burn (table 2), however, its exposure to an open flame for 30 seconds causes the sample to burn until it breaks.

The mechanism of the protective action of aluminum hydroxide from exposure to an open flame is manifested in a combination of a variety of physical-chemical processes. During thermal exposure, aluminum hydroxide releases water vapor, displacing oxygen from the pyrolysis area.

\[ 2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \]

Since this reaction is endothermic, the material is cooled to a temperature below the ignition temperature. Besides, oxides catalyze coke formation processes and help form a protective layer on the surface of a burning polymer [8-12].

The heat resistance of siloxane sealants containing 100 parts by weight aluminum hydroxide dispersion from 2.3 to 57 microns in the temperature range from 22 till 650 °C was determined by thermogravimetric analysis (the analyzer SDT Q 600) at heating rate 10 °C / min, medium – air, air flow rate 100 ml/min. The loss of 20 % of the mass of the sealant containing coarse aluminum hydroxide (brand TS-350SH) in amount 100 parts by weight as a flame retardant, occurs at a higher
temperature (474 °C) than siloxane sealants containing aluminum hydroxide with a smaller particle size (brands TS-302SH, TS-305SH, TS-330SH).

Table 2. Effect of aluminium hydroxide content on fire-resistance of the siloxane sealants.

| Brand of aluminum hydroxide | Content, [parts by weight] | Time of direct exposure of a flame, [seconds] |
|-----------------------------|-----------------------------|---------------------------------------------|
|                             | 10                          | 15                          | 20                          | 25                          |
| TS-302SH                    | 50                         | Flame                        | -                           | -                           |
|                             | 75                         | Flame                        | -                           | -                           |
|                             | 100                        | Self-extinguishes (after 10 s of the flame impact) | Flame | - |
|                             | 125                        | Self-extinguishes (after 8 s of the flame impact) | Flame | - |
| TS-305SH                    | 50                         | Self-extinguishes            | Flame                        | -                           | - |
|                             | 75                         | Self-extinguishes            | Flame                        | -                           | - |
|                             | 100                        | Self-extinguishes            | Flame                        | -                           | - |
|                             | 125                        | Self-extinguishes            | Flame                        | -                           | - |
| TS-330SH                    | 50                         | Self-extinguishes            | Flame                        | -                           | - |
|                             | 75                         | Self-extinguishes (after 7 s of the flame impact) | Flame | - |
|                             | 100                        | Self-extinguishes            | Self-extinguishes (after 10 s of the flame impact) | Flame | - |
|                             | 125                        | Self-extinguishes            | Self-extinguishes            | Self-extinguishes (after 7 s of the flame impact) | - |
| TS-350SH                    | 50                         | Self-extinguishes (after 10 s of the flame impact) | Flame | - |
|                             | 75                         | Self-extinguishes            | Self-extinguishes (after 10 s of the flame impact) | Flame | - |
|                             | 100                        | Self-extinguishes            | Self-extinguishes (after 8 s of the flame impact) | Flame | - |
|                             | 125                        | Self-extinguishes            | Self-extinguishes            | Self-extinguishes            | - |

3. Conclusion
Thus, as a result of the studies, it was found that adding of aluminum hydroxide makes it possible to vary widely the viscosity of the sealant compositions, while with decreasing particle size of aluminum hydroxide the viscosity of the compositions increases. The use of aluminum hydroxide with a minimum particle size makes it possible to obtain siloxane sealants with the most optimal level of physical-mechanical and adhesive properties, however, to increase the thermal and fire resistance of sealants, coarse aluminum hydroxide is most preferred.

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