Study on the Gel Aging of Nano Silica Sol Produced by a Y-shaped Reactor*

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We have developed a new production method for silica sols with a particle size of 3-5 nm using the Y-shaped reactor. Diluted sodium silicate and sulfuric acid were forced to collide with each other at the intersection of the reactor and neutralize at the exit. Silica sols with the appropriate viscosity produced by this method could be used as waste water treatment agents and a retention aids for papermaking. The gel aging phenomena of silica sol were considered in terms of their viscosity and electric conductivity. The objective of this study is to find suitable operation conditions for silica sols and to clarify mechanisms of the aging. [DOI: 10.1380/ejssnt.2009.737]

Keywords: Nano silica sol; Gel aging; Reactor; Viscosity

I. INTRODUCTION

Acid silica sols are produced with sodium silicate and sulfuric acid by their neutralization, which can be described as the following reaction formula:

\[ \text{Na}_2\text{O} \cdot n\text{SiO}_2 + \text{H}_2\text{SO}_4 \rightarrow n\text{SiO}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \]  

(1)

After the neutralization, the process of forming silica particles is shown in Fig. 1. At first, a solution of monomer, Si(OH)\(_4\), is formed, then the monomer polymerizes by condensation to form dimer and higher molecular weight species of silicic acid. Silicic acid has a strong tendency to polymerize. This polymerization followed by addition of monomer to these and linking together of the cyclic polymers to larger three-dimensional molecules. They are considered to be particles which have the average diameter of several nano meters.

Generally, silica sols are produced by a batch system, in which a sodium silicate solution is added to a tank with the appropriate amount (a large amount) of sulfuric acid for around one hour to prevent highly concentrated and localized gelling [1–4]. However, it is impossible to produce silica sols which have the solid concentration of more than 6 wt%. Tokuyama Co., Ltd. has developed a continuous production method by using a newly developed Y-shaped reactor [5]. The reactor has two inlets, in which dilute sodium silicate and sulfuric acid are supplied. The flow rate of each solution is more than 10 m/sec. Two solutions are forced to collide with each other at the intersection of the Y-shaped reactor and neutralize at the exit. Using this method, we can produce homogeneous silica sols continuously. The silica concentration of up to 14-16% is obtained. The produced silica sols gradually increase in the viscosity (aging region) and finally form silica gels. However, the aging characteristics of such highly concentrated silica sols have not been well known. Furthermore, the addition of the appropriate amount of water during aging region can reduce the speed of the gelling.

One of the applications of such nano silica sols is a coagulant for waste water treatment. The coagulant produced with nano silica sols is called an environmental friendly additive, which can become an alternative coagulant for tap water treatment.

In this work, silica sols were produced using a Y-shaped reactor under various conditions. The observations during the aging were conducted by means of two types of viscometer and an electric conductivity meter to investigate the mechanism of the gel aging. The objective of this study is to obtain valuable information which can be used for operating the Y-shaped reactor.

II. EXPERIMENTAL

The SiO\(_2\) concentrations of sodium silica solutions used in this experiment were 280-290 g/L and the molecular ratio of Na\(_2\)O and SiO\(_2\) (=M R) were 3.0-3.2, while the concentrations of sulfuric acid solutions were 200-220 g/L.

Figure 2 shows the experimental apparatus for producing silica sols, which consisted of a sulfuric acid line (A) and a sodium silica line (B). Each line composed of a tank, a pump, and a flow meter.

The flow rate of the sulfuric acid solution was controlled...
FIG. 2: Experimental apparatus.

by an inverter installed in pump A, whereas that of the sodium silica was adjusted by using both valve B1 and B2. The flow rate of each solution was more than 10 m/sec. Both lines were connected to the inlets of the Y-shaped reactor. Produced silica sols were obtained from the outlet of the reactor. silica sols were produced with various flow rate conditions. Here, the excess rate of sulfuric acid and the concentration of SiO₂ were given by the following definitions:

The excess rate of sulfuric acid
\[
\text{excess rate of sulfuric acid} = \frac{\text{H}_2\text{SO}_4 [g/100 ml] \times \text{the flow rate of H}_2\text{SO}_4 [1/min]}{\text{Na}_2\text{O}[g/100 ml] \times \text{the flow rate of Na}_2\text{O} \cdot \text{SiO}_2 [1/min]} \times 62
\]

The theoretical concentration of SiO₂
\[
\text{Theoretical concentration of SiO₂} = \frac{C_{\text{SiO₂}} \times \text{the flow rate of Na}_2\text{O} \cdot \text{SiO}_2 [1/min]}{\text{total amount flow rate of H}_2\text{SO}_4 + \text{Na}_2\text{O} \cdot \text{SiO}_2 [1/min]} \times 98
\]

The produced concentration of SiO₂
\[
\text{produced concentration of SiO₂} = 80.65 \times (\text{specific gravity of produced silica sols} - 1.002)
\]

The aging phenomena were probed in terms of their viscosity and electric conductivity. The viscosity of silica sols was measured using both a vibration viscometry (SV-10, A&D Co. Ltd) and a rheometer (A-300, Elquest Co. Ltd.). The viscosity at the shear rate of 20 s⁻¹ was used for the measurement with the A-300. The electric conductivity was measured by means of an electric conductivity meter (ES-51, Horiba Co. Ltd.). The particle size distribution of silica sols was analyzed by a dynamic light scattering measurement (ELSZ series, Ohtsuka Denshi Co. Ltd.).

III. RESULTS AND DISCUSSION

Figure 3 shows the typical results measured by SV-10, A-300, and ES-51. It is noted that the viscosity obtained by SV-10 gradually increased from the beginning to the end, while those of A300 exhibited nonlinear and significant increases 6 hours after beginning. The electric conductivity of silica sols decreased immediately just before a gel structure was formed.

From the results of the measurement by SV-10, since
FIG. 4: (a) Gel aging model. (from the results of SV-10). (b) Gel aging model. (from the results of A-300).

FIG. 5: Average diameter of silica particles. (Excess rate of sulfuric acid=1.15, concentration of silica particles=15.77 g/100mL.)

The viscosity gradually increased, it is imagined that silica particles in the sol coagulate slowly with each other and finally form clusters as shown in Fig. 4(a). In the case of A-300, because the viscosity exhibited significantly increases, it is supposed that silica particles form network structures as shown in Fig. 4(b).

The results of the dynamic light scattering measurements during the aging are shown in Fig. 5. The average sizes of the silica particles show a sudden increase at around 5 hours.

The viscosity measured by A-300 indicated rapid jump at that time simultaneously. Since the gel transition of the silica sol is considered to suddenly change, and taking into account that the experimental error for SV-10 for more viscous solutions (more than $10^{-1}$ Pa·s), the results by rheometer must be correct. We confirmed that the gel aging of the silica sols can be observed by A-300.

The obtained results by A-300 are schematically shown in Fig. 6. The time at the onset of the sudden increase in the viscosity is considered to coincide with the onset of the sol-gel transition. After the sudden increase, the profile shows a plateau, which agree with the complete gelling.

Figure 7 displays the effect of the excessive rate of sulfuric acid on the aging property measured by A-300. The onset time of the gelling increases with the decrease of the excess rate of sulfuric acid. It should be noted that the aging times depend dramatically on excessive values.

The obtained linear relations can be used to predict onset times.

FIG. 6: Schematic diagram of the aging.

FIG. 7: Effects of the excessive value of sulfuric acid on the onset time of the gelling. (Concentration of silica particles=13.99 g/100mL.)

FIG. 8: The relationship between the onset time of the gelling and the excess rate of sulfuric acid. (Concentration of silica particles=13.99 g/100mL.)

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Figure 9 displays the effect of the concentration of silica particles measured by A-300. The onset time of the gelling increases with the increase of the concentration of silica particles. Since the number of silica particles is big for dense system, particles easily contact with each other and forming network structure. While for the dilute system, the probability of the contact is decreased, however, it is interesting that the sol finally makes a gel formation after a specifically long time (in this case, 24 hours). It should also be noted that the aging times depend dramatically on the concentration.

Figure 10 indicates the effect of agitation measured by ES-51. No significant effect was found for the agitation on the onset time.

Figure 11 shows the effects of the temperature measured by A-300. It is found that the onset times depend strongly on the temperature of the sol. It might be related the temperature dependence on the speed of the Brownian motion of the particles.

IV. CONCLUSIONS

Silica sols were produced continuously by using their newly developed Y-shaped reactor. The silica gel aging properties were observed in terms of their viscosities measured by the two different viscometers, and the electric conductivity. It is expected that the sudden increase in the viscosity might cause the formation of the network structure of silica particles. The results obtained by dynamic light scattering measurements support this model. The onset times of the gelling strongly depend on the concentration of silica, excessive value of sulfuric acid and temperature. These results should be valuable for the operation of the Y-shaped reactor.


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