Effect of Colloidal Silica on the Spreading Pressure of Silicone Fluids

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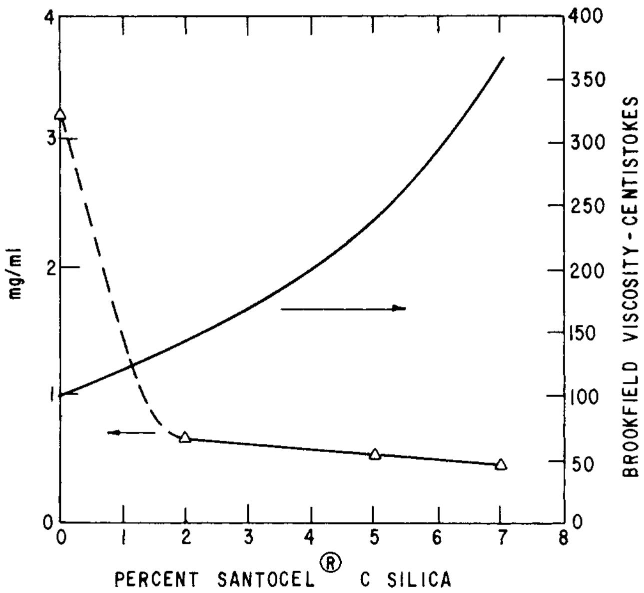

Fig. 1. The amount of silicone fluid antifoam required to suppress the foam generated by 1 ml of 0.5% sodium lauryl sulfate is plotted against the weight percent of Santocel C silica dispersed in the silicone fluid phase of the antifoam. The amount of antifoam is expressed as the milligrams of silicone fluid present in the silicone fluid antifoam emulsion. The formulation of the antifoam emulsion was identical to General Electric Company Antifoam AF-60 except for the variation in the amount of Santocel C. Also plotted (right side) is the viscosity of silicone fluid against the percent of dispersed Santocel C. The silicone fluid Santocel C dispersions were prepared via a Manton-Gaulin homogenizer.

The economic success of many industrial processes are sensitively balanced upon the stability or instability of foam. Thus, the mechanisms of foam stabilization and prevention have been widely studied (Bikerman, 1973, and Ross, 1967).

The purpose of this note is to investigate a well-known phenomenon in antifoam technology: the increase in antifoam effectiveness by inorganic colloidal fillers. An example of this increased effectiveness is illustrated in Figure 1, which plots the amount of silicone fluid required to suppress foam against the amount of colloidal Santocel C silica dispersed in the silicone fluid. As little as 2% silica reduces the amount of antifoam required by about ×6. In some cases of specially treated silica, to be discussed later, a factor of ×10 or more can be achieved.

The addition of inorganic colloidal fillers to antifoams has been the subject of many patents. However, the mechanism by which these fillers increase antifoam effectiveness is a poorly understood area of antifoam technology.

It is generally well accepted that effective antifoams must have a positive spreading pressure on the foaming solution (Ross, 1967). The work reported here concerns the effect of dispersed colloidal silica on the spreading pressure of silicone fluids and the subsequent relationship to antifoam effectiveness. The relationship between the viscosity of silica dispersions in silicone fluids and antifoam effectiveness is also investigated.

EXPERIMENTAL

The work described here is restricted primarily to General Electric Company 100 centistoke silicone fluid SF-96 (100) and Monsanto silica aerogel Santocel C. Santocel C is characterized by a particle size of 0.01 to 0.02 μ and a specific surface area of 130 m^2/g (Corrin, 1953, and Monsanto Technical Bulletin 1C/SCS-257). Dispersions of Santocel C in SF-96 (100) were prepared by several methods: via a Waring blender for 5 m at 17,000 rev./min., via a Manton-Gaulin homogenizer (562 Kg/cm^2), and via a colloid mill, milling for 24 hr. In each case, the silicone fluid used to make the silica dispersion was obtained for comparative measurements. Dispersion viscosities were measured on a Brookfield RVF viscometer. ESR measurements were made on a Jeol Model JESME-X ESR spectrometer. The spin labeled fatty acid was purchased from Syva Corporation, Palo Alto, California.

Spreading pressures were measured by the piston monolayer technique, with a Cenco film balance. A more detailed discussion of the piston monolayer technique is given by Pomerantz et al. (1967). A monolayer of octadecanol was compressed, and then a small drop of silicone fluid was deposited from a fine wire. The Π-A curve upon expansion was then obtained. Typical Π-A data are presented in Figure 2. The spreading pressure (Π_s) was taken to be the extrapolated intercept of the flat portion of the curve. There does not appear to be any precedent for using this extrapolation; however, the spreading pressure thus obtained should correspond to the "initial spreading pressure" as described by Pomerantz et al. (1967). It is the "initial spreading pressure" that should be operative in determining antifoam effectiveness.

CONCLUSIONS

The spreading pressure (Π_s) of commercially available silicone fluid SF-96 (100) was found to be 15.2 to 16.7 dyne/cm at 25°C. The exact value of Π_s for silicone fluids may vary depending upon the concentration of surface active impurities.

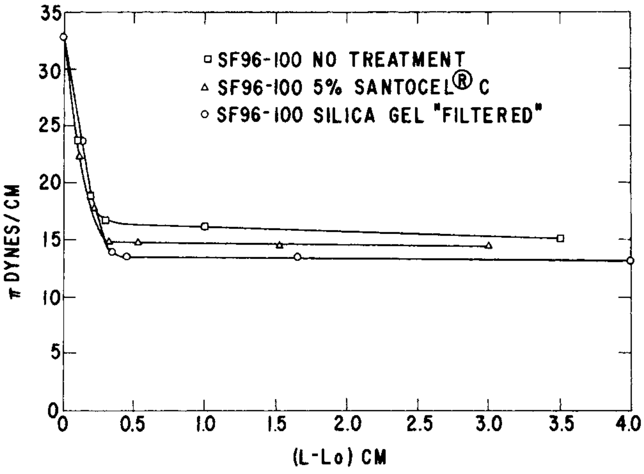

Fig. 2. The surface pressure (Π) of an octadecanol monolayer containing a deposited lens of silicone fluid is plotted against the increase in barrier position (L-L_0). As the monolayer is expanded by increasing the barrier position L, Πdecreases until Π_s (the spreading pressure of the silicone fluid). The Π_s of the silicone fluid is taken to be the extrapolated intercept of the flat portion of each curve. L_0 is the initial barrier position.

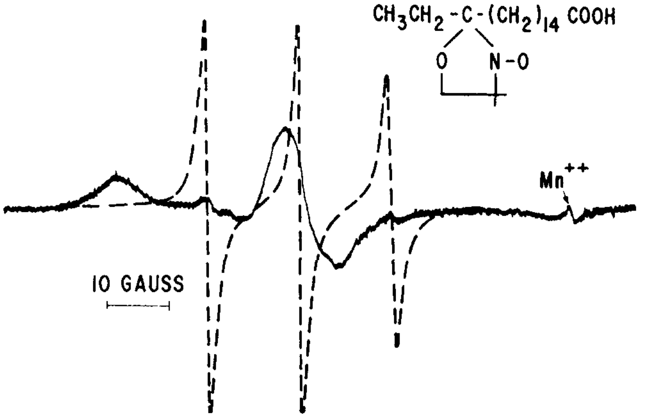

Fig. 3. The ESR spectrum of 2-(14-carboxytetradecyl)-2-ethyl-4, 4-dimethyl-3-oxazolidinyloxyl (spin labeled fatty acid). Dashed spectrum is of 100 p.p.m. spin label dissolved in silicone fluid SF-96 (100). Solid spectrum is of 100 p.p.m. spin label dissolved in silicone fluid SF-96 (100) containing 5% dispersed Santocel C silica. The two spectra indicate that the spin label is strongly adsorbed by the Santocel C. Both samples were purged with nitrogen for 10 min at 60°C to reduce dissolved oxygen. The *g* value for the Mn^{++} marker is 1.981. The unpaired electron on the spin labeled fatty acid is localized near the *N* atom.

The effect of dispersing 5% Santocel C silica, as shown in Figure 2, was to lower Π_s by about 2 dynes/cm. According to Ross (1967), this lower Π_s would not be expected to increase antifoam effectiveness. All other things being equal, a lower spreading pressure would be expected to decrease antifoam effectiveness. The lowering of Π_s by Santocel C was observed regardless of the dispersion preparation method.

Figure 2 also presents the Π-A data for SF-96 (100) equilibrated with coarse (6 to 16 mesh) silica gel. The marked lowering of Π_s by the silica gel suggested that Santocel C silica also lowers Π_s via the adsorption of surface active impurities. In all three cases, presented in Figure 2, the SF-96 (100) was from the same 1 gal. sample, eliminating any uncertainties about the relative level of impurities.

The conclusion that Santocel C reduces Π_s by adsorption of surface active impurities was further supported by the electron spin resonance spectra of a spin labeled fatty acid in SF-96 (100) and in a dispersion of 5% Santocel C in SF-96 (100). These spectra, presented in Figure 3, clearly show that the spin labeled fatty acid is strongly immobilized by the Santocel C. For a more detailed explanation of the spin label method, McConnell and McFarland (1970), and Smith (1970) should be consulted.

The SF-96 (100) equilibrated with coarse mesh silica gel did not show any improved antifoam effectiveness. Therefore, the adsorption or removal of surface active impurities cannot account for the effect of Santocel C in improving antifoam effectiveness.

From Figure 1 it is seen that the viscosity of SF-96 (100) increases with the amount of dispersed silica. Thus, it may be suggested that the increase in viscosity is responsible for the subsequent increase in antifoam effectiveness. However, an antifoam prepared from silica free 350 centistokes silicone fluid was no more effective than antifoam prepared from silica free 100 centistokes silicone fluid.

In summary, the addition of Santocel C silica to silicone fluid SF-96 (100) lowers the spreading pressure about 2 dynes/cm. This lowering is most likely due to the adsorption of surface active impurities, as demonstrated by the effect of coarse mesh silica gel and by electron spin resonance. Santocel C also increases the viscosity of silicone fluids. However, neither the lower spreading pressure, the adsorption of impurities, nor the increase in viscosity can be related to the increase in antifoam effectiveness.

NOTATION

A = area of monolayer film
L = position of barrier on Cenco film balance
L_o = initial position of barrier on Cenco film balance
Π = monolayer film pressure
Π_s = spreading pressure

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The Stability of Nuclei Generated by Contact Nucleation

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Tai et al. (1975) studied contact nucleation of $MgSO_4 \cdot 7H_2O$, $KAl(SO_2)_2 \cdot 12H_2O$, K_2SO_4, and citric acid. In their experiments, the crystal was impacted with a stainless steel rod; the resulting nuclei were swept away from the crystal face by the flowing solution and allowed to develop in a growth chamber. The supersaturation in the chamber was held at the same level as that at which the crystal impact occurred. Their results clearly showed