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Preparation and Properties of Organosilicon Surfactants

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Surface-active polyethenoxy silicic esters were prepared by the reaction of tetraethyl silicate with various polyethenoxy higher alkyl ethers by the use of tetrabutyl titanate as a catalyst. Their properties as surfactant were compared with those of conventional nonionic surfactants. These compounds are soluble in many kinds of organic solvents, and have good dispersing power on such inorganic pigments as titanium oxide in organic media. The dispersing characteristics of these compounds in the inorganic pigments were tested in benzene, carbon tetrachloride, and monochlorobenzene by measuring the sedimentation volume. It was found that the compounds containing a chain of more than six ethenoxy groups were soluble in water. The surface tension of these water-soluble polyethenoxy silicic esters were determined in various concentration regions. In this paper, the preparation and properties of these compounds will be described.

As a part of an investigation of the reaction of the metal-organic compounds with nonionic surfactants, the reactions of silicon tetraethoxide with a number of polyoxyethylene monoalkylethers have been examined.

At the time we undertook this study, there were no details on special surfactants containing metal or metalloid atoms. David *et al.*[1)] have reported on water-soluble long-chain aliphatic orthosilicate esters as surface-active agents. Sowa and Kenny[2)] prepared surface-active complexes of

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1) U. S. Pat. 2476307.
2) U. S. Pat. 2580473.

higher alkylamine by reacting those amines with halogenosilane or titanium tetrahalide. On the other hand, Chales *et al.*³⁾ have reported alkali salts of organosilane compounds as detergents and emulsifing agents. John *et al.*⁴⁾ prepared sililphenoxy alcohol derivatives which were useful as emulsifiers, while Koehler *et al.*⁵⁾ prepared alkanolamine silicate derivatives and reported on the use of these compounds as dispersants. Two of the present authors reported on the preparation of surface-active polyethenoxy titanium esters and their dispersing action on inorganic pigments in organic and aqueous media⁶⁾. Recently, Baily *et al.*⁷⁾ prepared the copolymers of siloxane and alkylene oxide; they described them as useful as stabilizing agents of polyurethan foam.

The present paper is concerned with the compounds belonging to nonionic surfactants derived from organic silicate esters by ester-exchanging reaction with polyoxyethylene higher-alkyl ethers and tetraethyl silicate.

Experimental

1) Preparation

Reagents. Tetraethyl silicate was supplied by the laboratory of the Tama Chemical Co. Purified further by distillation, bp 165°C/760 mmHg. (Found: Si, 13.28%. Calcd for $C_8H_{20}O_4Si$: Si, 13.48%.)

Nonionic Surface-active Agents. The agents employed in this experiment were polyoxyethylene monolauryl ethers ($n=2$, OH value 207.1; $n=4$, OH value 155.0; $n=6$, OH value 125.0; $n=10$, OH value 89.9; $n=21$, OH value 54.5) and polyoxyethylene monocetyl ether ($n=2$, OH value 170.0). They were supplied by the laboratory of the Nihon Surfactant Co. Their chemical formulas corresponded to the following: $HO(CH_2CH_2O)_nC_{12}H_{25}$ and $HO(CH_2CH_2O)_2C_{16}H_{33}$. They were purified as in the previous paper.⁶⁾

Titanium Oxide. The titanium oxide used was No. 820. Rutyl type, supplied by the Ishihara Sangyo Co.; it was stored in dry atmosphere.

Solvents. Carbon tetrachloride and monochlorobenzene were freshly distilled before use.

Analysis of Silicon.⁸⁾ The weighed sample was treated with concentrated sulfuric acid, absolute alcohol, and water in a crucible. The mixture was allowed to attain room temperature and then cautiously heated to dryness; the residue was ignited at about 1000°C and weighed as SiO_2.

Catalyst. *Tetra-n-butoxy Titanium.*⁹⁾ A solution of titanium tetrachloride in *n*-butyl alcohol was diluted with benzene and treated with ammonia. After the removal of the ammonium chloride and the solvent, the tetra-*n*-butoxy titanium was distilled under reduced pressure, bp 174°C/6 mmHg. (Found: Ti, 14.06%. Calcd for $C_{16}H_{36}O_4Ti$: Ti, 14.07%.)

2) Determination

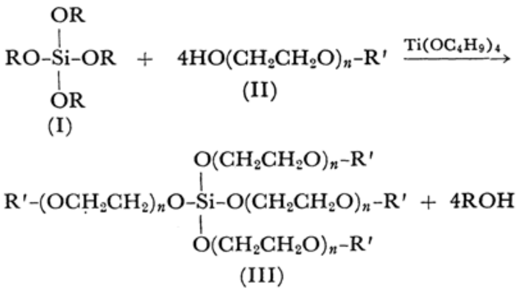
Solubility. Each sample was weighed and dissolved in distilled water; the solution was then allowed to stand in order for its stability to be observed for hydrolysis.

Surface Tension. The surface tension was measured by the drop-weight method, with a tip 0.778 cm in diameter, in a thermo-bath at 25°C. Attention was taken to take 4—5 min for the growth of a drop. The correction of Harkins and Brown¹⁰⁾ was applied.

Cloud Points. The cloud points were determined on dilute solutions of the compounds. The cloud point was taken as the temperature at which a noticeable turbidity first appeared upon the slow heating of a solution in a water bath. Cloud points were also determined on solutions containing sodium chloride solutions.

Dispersion. The settling volume was determined as in a previous paper⁶⁾ by the use of benzene, carbon tetrachloride, and monochlorobenzene as dispersing media.

Synthesis of Compounds. Tetraethyl silicate (I) was allowed to react with a nonionic surfactant (II) in the presence of tetra-*n*-butyl titanate as a catalyst and under non-hydrous conditions; the reaction proceeded, and a low-molecular weight alcohol was thus isolated. The reaction was considered to be as follows:



$$\underset{\text{(I)}}{\mathrm{RO{-}}\overset{\displaystyle\mathrm{OR}}{\underset{\displaystyle\mathrm{OR}}{\mathrm{Si}}}\mathrm{{-}OR}} + \underset{\text{(II)}}{4\mathrm{HO(CH_2CH_2O)}_n\mathrm{{-}R'}} \xrightarrow{\mathrm{Ti(OC_4H_9)_4}}$$

$$\underset{\text{(III)}}{\mathrm{R'{-}(OCH_2CH_2)}_n\mathrm{O{-}}\overset{\displaystyle\mathrm{O(CH_2CH_2O)}_n\mathrm{{-}R'}}{\underset{\displaystyle\mathrm{O(CH_2CH_2O)}_n\mathrm{{-}R'}}{\mathrm{Si}}}\mathrm{{-}O(CH_2CH_2O)}_n\mathrm{{-}R'}} + 4\mathrm{ROH} \qquad (1)$$

$R=C_2H_5$, $n=2$, 4, 6, 10, 21
$R'=C_{12}H_{25}$, $C_{16}H_{33}$

In the case of this reaction, if the catalyst was not used the reaction did not proceed smoothly after several hours of heating. It has been recognized from the related reports that the titanium esters are excellent ester-exchange catalysts¹¹,¹²⁾ for reactions both between an organic ester and an alcohol, and between two organic esters, as is shown in Eqs. (2) and (3). The reaction (1) is one of the ester-exchanging reactions; a catalytic action of the titanium ester on the reaction (1) is considered to be reasonable.

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3) U. S. Pat. 2583322.

4) U. S. Pat. 2584751.

5) J. O. Koehler and H. Lamperey, "Metal-Organic Compounds," Advances in Chemistry, American Chemical Society, New York (1957), p. 217.

6) M. Ochi, T. Yoshino and K. Meguro, This Bulletin, **40**, 983 (1967).

7) Berg. Pat. 618786.

8) D. C. Bradley and D. A. W. Hill, *J. Chem. Soc.*, **1963**, 2106.

9) D. C. Bradley, D. C. Hankock and W. Wardlaw, *ibid.*, **1952**, 2773.

10) W. D. Harkins and F. E. Brown, *J. Am. Chem. Soc.*, **41**, 499 (1919); in "International Critical Tables," Vol. IV, McGraw-Hill, New York (1928), p. 435.

11) J. H. Haslam, "Metal-Organic Compounds," Advances in Chemistry, American Chemical Society, New York (1957), p. 277.

12) U. S. Pat. 2820806.

TABLE 1. STATES AND ANALYTICAL RESULTS OF SURFACE-ACTIVE ORGANOSILICON COMPOUNDS

Compound	State	Si, %	
		Found	Calcd
$Si[O(CH_2CH_2O)_2C_{12}H_{25}]_4$	Slightly yellowish liquid	2.43	2.50
$Si[O(CH_2CH_2O)_4C_{12}H_{25}]_4$	Viscous, slightly yellowish liquid	1.77	1.91
$Si[O(CH_2CH_2O)_6C_{12}H_{25}]_4$	Viscous, slightly yellowish liquid	1.53	1.54
$Si[O(CH_2CH_2O)_{10}C_{12}H_{25}]_4$	White paste	1.19	1.11
$Si[O(CH_2CH_2O)_{21}C_{12}H_{25}]_4$	Waxy white solid	0.61	0.63
$Si[O(CH_2CH_2O)_2C_{16}H_{33}]_4$	Waxy white solid	2.06	2.08

$$R'CO_2R + R''OH \overset{Ti(OR)_4}{\rightleftharpoons} R'CO_2R'' + ROH \qquad (2)$$

$$R'CO_2R + R''CO_2R''' \overset{Ti(OR)_4}{\rightleftharpoons} R'CO_2R''' + R''CO_2R \qquad (3)$$

In the reaction of Eq. (1), after the alcohol formed through the reaction had been removed, the product was obtained as a slightly yellowish liquid or a waxy solid, according to the number of "n" values in formula III. In polyoxyethylene alkylethers, there was some distribution of the chain length of polyethenoxy groups; therefore, the compound of the formula III should be considered to be that of the mean properties.

Preparation of the Tetrapolyethenoxy Lauryl Ether Silicic Ester (n=10). In a four-necked flask, fitted with a stirrer and a reflux condenser equipped with a calcium chloride tube, 62.7 g of polyoxyethylene monolauryl ether ($n=10$), 5.2 g of tetraethyl silicate, and 2 drops of tetrabutyl titanate were placed. The reaction mixture was heated to 120°C for 2 hr. After distillation under reduced pressure at 80°C to remove the ethyl alcohol, a white paste was obtained. Yield, 93.0%.

Found: Si, 1.19%. Calcd for $C_{128}H_{260}O_{44}Si$: Si, 1.11%.

In a similar way, the compounds $Si[O(CH_2CH_2O)_n C_{12}H_{25}]_4$ ($n=2$, 4, 6, 21) and $Si[O(CH_2CH_2O)_2C_{16}H_{33}]_4$ were prepared from tetraethyl silicate with corresponding amounts of polyoxyethylene monoalkyl ethers, in yields of 91—99%. Table 1 gives the appearances and analytical results of the compounds.

Infrared Spectra. The infrared absorption spectra in the 4000—650 cm⁻¹ region were measured with a Hitachi EPI Model-2 spectrophotometer (sodium chloride prism) for the carbon tetrachloride solutions of polyoxyethylene monoalkylether silicic esters, and for the corresponding polyoxyethylene monoalkyl ethers. Before the reaction with tetraethyl silicate, the polyoxyethylene monolauryl ether shows an absorption band (a stretching vibration of the OH-group) at about 3500 cm⁻¹; this absorption decreases when the polyoxyethylene monolauryl ether is reacted with tetraethyl silicate, and a new stretching vibration absorption of the Si-O- appears at 1125 cm⁻¹. The rest of the spectrum is nearly the same as that of the polyoxyethylene monolauryl ether. Similar tendencies were observed for the compounds prepared. Figures 1 and 2 show the infrared spectra of these typical compounds.

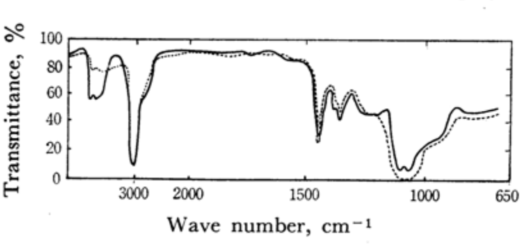

Fig. 1. Infrared spectra of tetrapolyoxyethylene monolauryl ether silicic ester and polyoxyethylene monolauryl ether ($n=2$).
Full line: Starting material
Dotted line: Reaction product

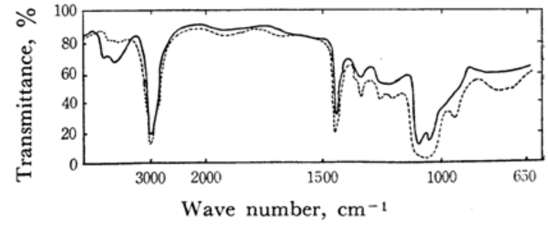

Fig. 2. Infrared spectra of tetra polyoxyethylene monocetyl ether silicic ester and polyoxyethylene monocetyl ether ($n=2$).
Full line: Starting material
Dotted line: Reaction product

Results and Discussion

Solubility. Polyoxyethylene monoalkyl ethers and tetraethyl silicate are soluble in benzene, carbon tetrachloride, and monochlorobenzene. There was no difference among them in solubility in the above organic solvent. However, some differences in solubility in alcohols were observed between tetrapolyethenoxy monoalkyl ether silicic esters and the corresponding nonionic surfactants. The polyoxyethylene monoalkyl ethers $HO(CH_2CH_2O)_nC_{12}H_{25}$, and $HO(CH_2CH_2O)_nC_{16}H_{33}$ are soluble in methyl-, ethyl-, and isopropyl alcohol, irrespective of the "n" values, within the range of 2—21.

However, an alteration in such solubilities of the nonionic surfactants was observed for the compounds $Si[O(CH_2CH_2O)_nC_{12}H_{25}]_4$ and $Si[O(CH_2CH_2O)_nC_{16}H_{33}]_4$; namely, the compounds in which $n>6$ are soluble in water and alcohols, as has been stated above, but the compounds in which $n<6$ are insoluble in such alcohols.

Cloud Points. In order to ascertain the differences in the thermal change of solubility in water,

TABLE 2. CLOUD POINTS OF COMPARABLE NONIONIC SURFACTANTS AND THE CORRESPONDING POLYETHENOXY SILICIC ESTERS

Substance	Concentration %	Cloud point °C
$HO(CH_2CH_2O)_6C_{12}H_{25}$	0.18	50
$Si[O(CH_2CH_2O)_6C_{12}H_{25}]_4$	0.18	42
$HO(CH_2CH_2O)_{10}C_{12}H_{25}$	0.26	87
$Si[O(CH_2CH_2O)_{10}C_{12}H_{25}]_4$	0.26	80

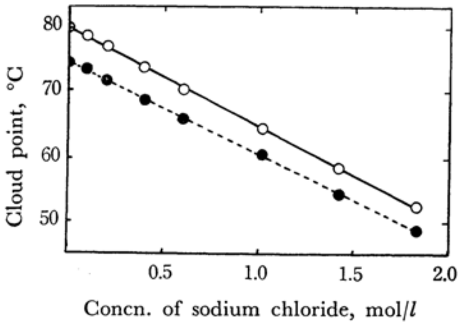

Fig. 3. Effect of sodium chloride on cloud point of 1% solution of the compound.

the cloud points were determined. The could points are given in Table 2.

The change in the cloud point due to the addition of sodium chloride in the solution is shown in Fig. 3. That figure clearly shows that the solubility of the silicic ester surfactant in water is decreased. No difference in the effect on the cloud point of the existence of sodium chloride could be found between $HO(CH_2CH_2O)_{10}C_{12}H_{25}$ and $Si[O(CH_2CH_2O)_{10}C_{12}H_{25}]_4$.

Surface Tension. The water-soluble polyethenoxy silicic esters exhibit surface activity in the aqueous phase. The relations between the surface tension of an aqueous solution of these compounds and the concentration are shown in Figs. 4, 5, and 6.

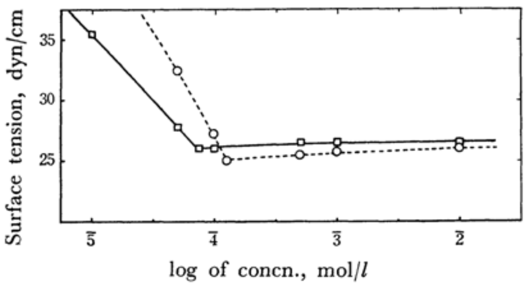

Fig. 4. The surface tension - log concentration curves of tetrapolyoxyethylene monolauryl ether silicic ester and polyoxyethylene monolauryl ether, (n=6); at 25°C.
Full line: Tetrapolyoxyethylene monolauryl ether silicic ester
Dotted line: Polyoxyethylene monolauryl ether

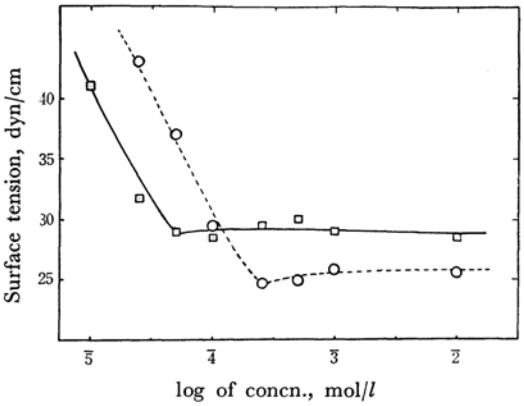

Fig. 5. The surface tension - log concentration curves of tetrapolyoxyethylene monolauryl ether silicic ester and polyoxyethylene monolauryl ether (n=10); at 25°C.
Full line: Tetrapolyoxyethylene monolauryl ether silicic ester
Dotted line: Polyoxyethylene monolauryl ether

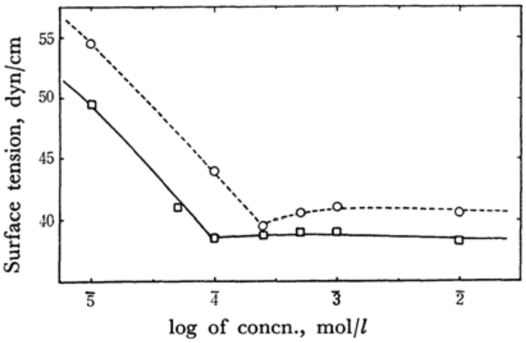

Fig. 6. The surface tension - log concentration curves of tetrapolyoxyethylene monolauryl ether silicic ester and polyoxyethylene monolauryl ether (n=21); at 25°C.
Full line: Tetrapolyoxyethylene monolauryl ether silicic ester
Dotted line: Polyoxyethylene monolauryl ether

TABLE 3. THE CMC VALUES OF AN AQUEOUS SOLUTION OF TETRAPOLYETHENOXY LAURYL ETHER SILICIC ESTERS

Substance	CMC value from the surface tension mol/l
$Si[O(CH_2CH_2O)_6C_{12}H_{25}]_4$	7.16×10^{-5}
$Si[O(CH_2CH_2O)_{10}C_{12}H_{25}]_4$	5.01×10^{-5}
$Si[O(CH_2CH_2O)_{21}C_{12}H_{25}]_4$	9.55×10^{-5}

From these surface tension - log concentration curves, the CMC values were obtained as an inflection of the curves of the surfactants. The values are summarized in Table 3.

The dotted lines in the figures are the curves of the corresponding starting materials. From these data, it is clear that the polyethenoxy silicic

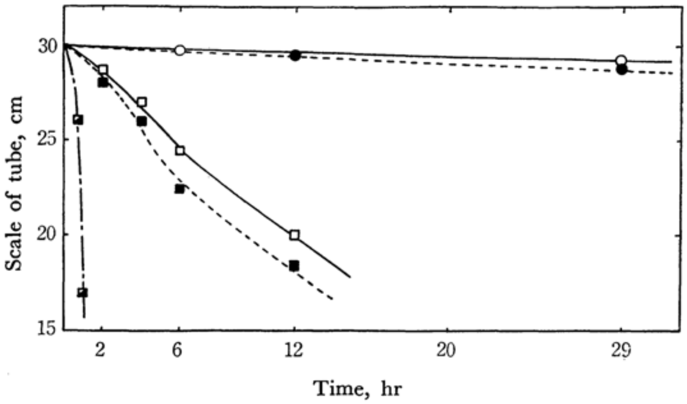

Fig. 7. Effect of the polyethenoxy chain length for dispersion of TiO_2 in benzene solution of $Si[O(CH_2CH_2O)_nC_{12}H_{25}]_4$ (5×10^{-3}mol/*l*).

--●-- *n*, 21; —○— *n*, 10; —□— *n*, 6; --■-- *n* 2;
—-◪-— non additive

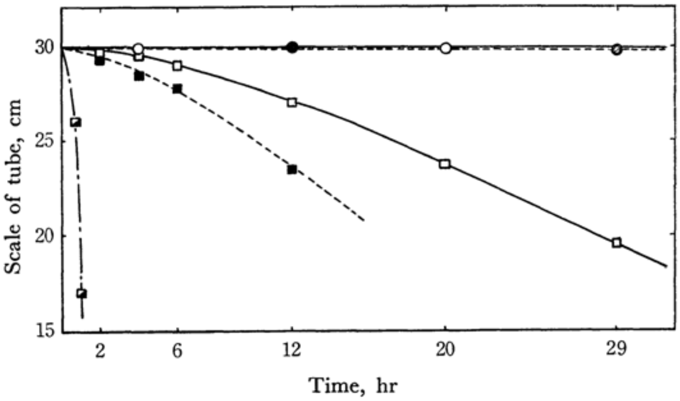

Fig. 8. Effect of the polyethenoxy chain length for dispersion of TiO_2 in carbon tetrachloride solution of $Si[O(CH_2CH_2O)_nC_{12}H_{25}]_4$ (5×10^{-3} mol/*l*).

—○— *n*, 21; --●-- *n*, 10; —□— *n*, 6; --■-- *n*, 2;
—-◪-— non additive

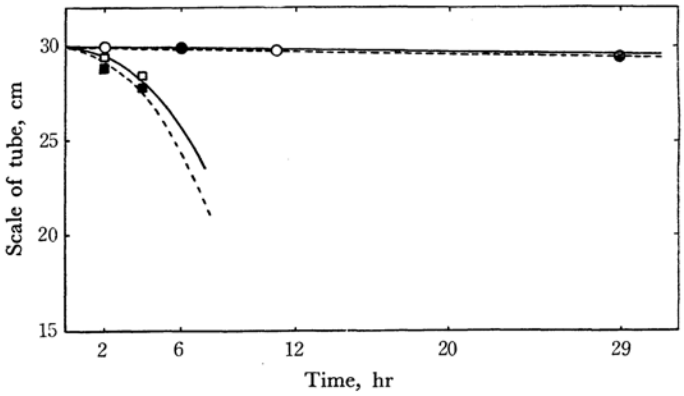

Fig. 9. Effect of the polyethenoxy chain length for dispersion of TiO_2 in monochlorobenzene solution of $Si[O(CH_2CH_2O)_nC_{12}H_{25}]_4$ (5×10^{-3} mol/*l*)

—○— *n*, 21; --●-- *n*, 10; —□— *n*, 6; --■-- *n*, 2 esters have a stronger surface activity than the starting materials in the dilute concentration region. It may be observed that the CMC values of the new surfactants shifted towards a lower concentration region than the CMC value of the corresponding nonionic surface-active agents.

Dispersion. In non-aqueous systems, the polyethenoxy silicic esters exhibit a good dispersing effect on inorganic pigments. Even in aqueous systems, the water-soluble silicic esters containing more than six polyethenoxy groups in a chain exhibit a good dispersing power on inorganic pigments. On the other hand, the dispersing power of the corresponding starting materials is extremely smaller than that of the new surfactants.

In comparison with the dispersing power of the starting materials and new surfactants, the change in the settling volumes of titanium oxide were measured. Figure 7 shows the settling curves in benzene solutions for the analogous surface-active silicic esters in which an alkyl chain of the same length and a different length of a polyethenoxy chain are involved. The settling curves of titanium oxide in polyethenoxy alkylether or tetraethyl silicate and their mixtures were close to the vertical axis in the diagram, and their dispersing powers were extremely smaller than that of tetrapolyethenoxy alkyl ether silicic esters.

When the chain length of polyethenoxy groups in the silicic esters varied under the same conditions, the settling curves obtained varied also. Such tendencies, shown in Figs. 8 and 9 were observed by the use of carbon tetrachloride and monochlorobenzene solutions as the dispersing media.

From these data, it is clear that the polyethenoxy silicic esters have good dispersing power, while polyethenoxy alkylethers or tetraethyl silicate and their mixtures have scarcely any. The degree of dispersing power in such media increases with an increase in the chain length of polyethenoxy groups in this order:

$$-(CH_2CH_2O)_{21}- \approx -(CH_2CH_2O)_{10}- > -(CH_2CH_2O)_6- > -(CH_2CH_2O)_2-$$

In order to examine the effect of the chain length of the alkyl groups on the dispersing power, the settling volumes of titanium oxide in solutions of different kinds of polyethenoxy silicic esters were determined. Figure 10 shows the effect of the chain length of alkyl groups in a polyethenoxy silicic esters on the dispersing power of titanium oxide in a benzene solution. From the settling curves, it was found that the effect of the alkyl chain length in giving good dispersion was in the order:

$$C_{16}H_{33} > C_{12}H_{25}$$

This order is in good agreement with the results

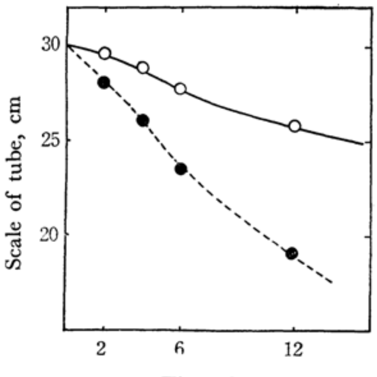

Fig. 10. Effect of the alkyl chain length for dispersion of TiO_2 in benzene solution of $Si[O(CH_2CH_2O)_2\text{-}R]_4$ (5×10^{-3} mol/l).

—○— $R=C_{16}H_{33}$
···●··· $R=C_{12}H_{25}$

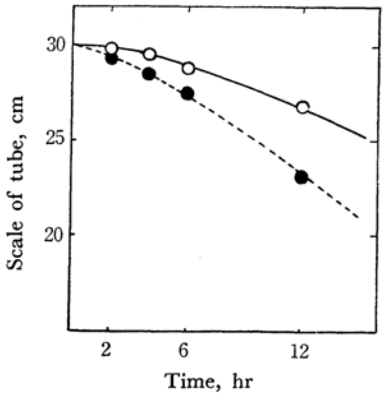

Fig. 11. Effect of the alkyl chain length for dispersion of TiO_2 in carbon tetrachloride solution of $Si[O(CH_2CH_2O)_2\text{-}R]_4$ (5×10^{-3} mol/l).

—○— $R=C_{16}H_{33}$
--●-- $R=C_{12}H_{25}$

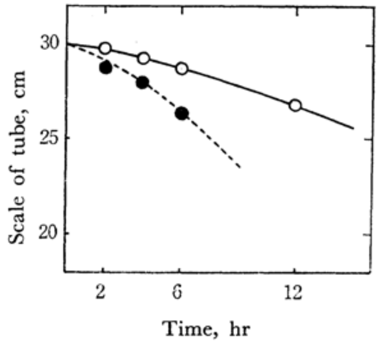

Fig. 12. Effect of the alkyl chain length for dispersion of TiO_2 in monochlorobenzene solution of $Si[O(CH_2CH_2O)_2\text{-}R]_4$ (5×10^{-3} mol/l).

—○— $R=C_{16}H_{33}$
--●-- $R=C_{12}H_{25}$

obtained using carbon tetrachloride and monochlorobenzene solutions as the dispersing media. These results are shown in Figs. 11 and 12 respectively.

In an earlier study, we prepared a series of tetrapolyethenoxy alkyl ether titanium esters. The comparison between tetrapolyethenoxy alkyl ether silicic esters and the corresponding polyethenoxy titanium esters shows the following facts.

Tetrapolyethenoxy titanium esters were easily prepared from the reaction of tetraalkyl titanate with polyethenoxy alkyl ethers; however, in the preparation of the corresponding silicic esters, the existence of such a catalyst as small amounts of tetra-*n*-butyl titanate is indispensable if the reaction is to proceed smoothly.

Furthermore, one of the characteristic properties of tetrapolyethenoxy titanium esters is resistance to hydrolysis; this is in contrast with the usual organotitanium esters, which can be hydrolyzed even in atmospheric moisture. However, it was found that polyethenoxy silicic esters are more stable in hydrolysis than the tetrapolyethenoxy titanium esters; for example, an aqueous solution of the former was stable enough for more than ten days, whereas the stabilities of aqueous solutions of the latter were only a few days on the average. From this fact, the silicic esters were considered to be more desirable than the titanium esters for industrial use.

These findings and other evidence suggest that the polyethenoxy silicic esters have very interesting characteristic properties; further investigations are now in progress.