STUDIES ON ORGANOSOLS (II)

Silver Organosols obtained by a Chemical Method.

By Ituro Yamakita.

In the first paper[1] of this series, some new knowledges about the gold organosols obtained by a chemical method of the author's laboratory were reported. In this paper, concerning the silver organols obtained by the same method, the process of the formation of the sols in various organic dispersing media, and some properties of the sols thus formed—particle size, viscosity, particle charge, stability, and behaviour against coagulating materials—will be described in comparison with those of the hydrosols like the case of gold organosols.

1. Formation of Silver Organosols.

Silver oxide, used as one of the raw materials, was obtained by the double decomposition of sodium or potassium hydroxide and silver nitrate water solutions.

Various organic substances used as the dispersing media for silver organosols were purified by the ordinary method.

Then 1% of silver oxide was mixed thoroughly with 99% of organic substance used as the dispersing media grinding in a porcelain vessel, treated at the temperature $15°\sim20°C$, $50°\sim60°C$, and the change thus produced, was observed.

From the result obtained, we can classify all dispersing media used for the colloidal silver formation test, into three groups (A, B, & C) according to their faculty to formate silver organosols. The detail of the classification is shown in Table 1.

Table 1. Classification of dispersing media.

Group A. The dispersing media belonging to this group produce stable sols.
Linseed oil, Tung oil, Soja bean oil, Cotton seed oil, Beef tallow, Fish oil, Lanolin, Oleic acid, Linoleic acid, Bees wax, Santalol.

Group B. The dispersing media belongings to this group produce unstable sols.
Castor oil, Lard, Cetyl alcohol, Tubaki oil, Olive oil, Turpentine oil, Glycerin, Myristic acid, Palmitic acid, Stearic acid.

Group C. The dispersing media belonging to this group produce no sol.
Capric acid, Acetic acid, Formic acid, Amyl alcohol, Propyl alcohol, Ethylalcohol, Methylalcohol, Benzene, Toluene, Xylene, Nitrobenzene, Anilin, Acetone, Benzoic acid, Carbontetrachloride, Carbonbisulphide, Dioxane, Hexane, Liquidparaffin, Diethyl ether.

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1) This Journal, 17, 83 (1943).

Let us consider the composition and the physico-chemical characters of the classified substances and their sol formation faculty except complicated mixtures of various compounds such as fats and oils. The compounds of group A giving stable sols are high-molecular and unsaturated; the compounds of group B giving unstable sols are also high-molecular but more saturated in comparison with those of group A; the compounds of group C giving no sol are low-melecular or non-polar. From the difference of the properties of the classified compounds, we can deduce that as the favourable conditions to obtain stable silver organosols, the organic compounds to be used as dispersing media are high melecular and at the same time suitably reactive to silver oxide. This deduction in the case of silver organosol formation coincides with that in the case of gold organosol formation.

Next we will consider fats and oils. These substances have, more or less, the faculty to formate silver organosols. Of these, give such drying oils as Linseed oil and Tung oil, the most stable silver organosols. This is the principal difference from the case of gold organosols when the most stable gold organosols are obtained from such non-drying oils as Tubaki oil and Olive oil.

2. Some Properties of Silver Organosols.

(1) Ultramicroscopic observation of silver organosols.

The particle size of the most stable silver organosols produced from soja bean oil and silver oxide was determined by means of an immersion ultramicroscope. The method adopted here is the same as in the case of gold-organosols. If ρ is the density of metallic silver, r is the radius of colloidal silver particles which is presumed to be spherical and π is the ratio of the circumference of a circle to its radius, then $\frac{4}{3}\pi r^3 \rho$ is the weight of one colloidal silver particle. Moreover, if the number of colloidal particles found in the unit volume of the sol is N, the radius of N particles is r on the average and the content of silver in the unit volume of the sol is c, the following relation will hold:

$$\frac{4}{3}\pi r^3 \rho N = c \quad \ldots\ldots\ldots\ldots\ldots(1)$$

Therefore
$$r = \left(\frac{3c}{4\pi\rho N}\right)^{\frac{1}{3}} \quad \ldots\ldots\ldots(2)$$

The numerical values necessary to determine r is shown in Table 2.

This particle size of the stable silver organosol is approximately the same magnitude compared with that of the stable gold organosols.

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Table 2.

Determination of particle size of silver Soja bean oil sol

concentration of the sol	0.03%
specific gravity of the sol at 20°C	0.9335
density of silver at 20°C	$\rho = 10.5$
silver content in the unit volume of the sol	$c = 0.9335 \times 0.0003 = 2.8 \cdot 10^{-4}$
number of particles found in $308\mu^3$ volume of the sol	18.0
(mean value of 80 observations)	
number of particles found in unit volum of the sol	$N = 6.10^{10}$
calculated radius of colloidal silver particle	$r = 22.1 \cdot 10^{-7}$ cm
	$= 22.1 \ \mu.\mu.$

And then, the perceptability of the silver organosol particles by the ultra-microscopic observation shows that these organosols are lyophobe.

(2) Viscosity of Silver Organosols.

The viscosity of silver organosols at 20°C was determined by means of Ostwald's viscosimeter on the next four series.

Series A. Silver oxide was decomposed with oleic acid (silver oxide : oleic acid = 1 : 4); the colloidal silver thus formed was dissolved in benzene, purified by filtering off coarse particles and diluted by adding benzene again to obtain the sols with different concentration. Silver content of the various sols obtained was determined by the ordinary quantitative analysis.

Series B. The preparation of the samples of this series differs from those of series A in the point that as the decomposing agent of silver oxide was used Soja bean oil insted of oleic acid.

Series C. For the samples of this series, as the decomposing agent of silver oxide, oleic acid was used, the colloidal silver formed was dissolved in oleic acid, purified by filtering off coarse particles and diluted by adding oleic acid again to obtain the sols with different content of silver. Other point is the same as in the series A.

Series D. The sample of this series differs from those of series C in the point that as the decomposing agent of silver oxide Soja bean oil was used instead of oliec acid.
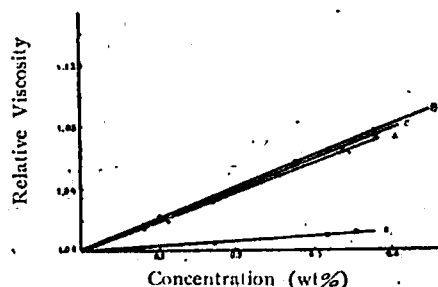

Fig. 1. Relation between viscosity & concentration of silver organosols.

The relation between viscosity increase and concentration of the silver organosols is linear as shown in Fig. 1.

If we now represent the relative viscosity of the sol by η and the total volume of the dispersed particles in the unit volume of the

sol by ϕ, the relation between η and ϕ is given from Fig. 1 as follows:

$$\eta = \eta_0 (1 + k\phi), \ldots \ldots \ldots \ldots (3)$$

where η_0 is the viscosety of dispersing medium and k is a constant. The value of k in equation (3) calculated from Fig. 1 is given in Table 3.

Table 3. Value of K in various cases.

series	volues of K.
A	204
B	216
C	210
D	31

Equation (3) resembles Einstein's viscosity equation[2] which is derived theoretically and presumed to be applicable to most of hydrophobe sols. Einstein's equation is given as follows:

$$\eta = \eta_0 (2 + 2.5\phi), \ldots \ldots \ldots \ldots (4)$$

where η, η_0 and ϕ represent the same as those in equation (3). The relation between η and ϕ in equation (4) is also linear.

If we now compare equation (3) with equation (4), we can find that the value of K, the coefficient of ϕ in equation (3) shown in Table 3, is far larger than 2.5, the coefficient of ϕ in equation (4). Therefore, it indicates that the author's silver organosols are considerably different from the ordinary hydrophobe sols in the enormously large value of K, though the linear relation between η and ϕ shows that the author's silver organosols have some part resembling to the ordinary hydrophobe sols.

Those characters acquired from the viscosity measurement of ths silver organosols agree with those of ths gold organosols.

(3) **Electric charge of colloidal particles and stability of silver organosols.**

When we decompose silver oxide, treating with Soja bean oil, Tubaki oil, Oleic acid, Linolic acid, Stearic acid, or Palmitic acid, and dissolve the colloidal silver particles thus formed in benzene, we have silver benzene sols favourable to compare their stability. Using these benzene sols, the relation between the electric charge of the particles and the stability of the sols was examined in order to know how much the electric charge of the particles might contribute to the stability of the silver organosols.

The apparatus and experimental procedure adopted here are the same as those in the case of gold organosols. The electric charge of sol particles was estimated from the weight increase of platinic electrodes immersed in the sol during the

2) Einstein, *ann. physik.*,[4] **19**, 289 (1906). **34**, 591 (2911).
    F. Eirich, *Kolloid-Z.*, **74**, 276 (1936). **81**, 7 (1937).

application of the fall of potential, 250 volts per centimetre. This experimental result is shown in Table 4.

Table 4. Electric charge of various silver organosol particles.

Decomposing agent of Ag₂O	Dispersing medium	Conc. of sol before experiment	weight incerase of Pt. electrodes	
			⊕	⊖
1. Soja bean oil	Benzen	0.14%	—	—
2. Tubaki oil	„	0.03%	0.1 mg	0.7 mg
3. Oleic acid	„	0.10%	0.6 „	—
4. Linolic acid	„	0.94%	0.15 „	0.1 „
5. Stearic acid..........	„	0.02%	0.30 „	0.40 „
6. Palmitic acid	„	0.01%	0.40 „	1.0 „

⊕: Positive electrode.   ⊖: Negative electrode.
weight increase of electrodes, measured after 5 hours from the beginning.

The stability of the sols was expressed as the concentration change of the sols in the course of time. The results of both stable sols and unstable ones, are shown in Fig. 2.

From Table 4 and Fig. 2, we can recognize that the sols containing particles with electric charge are unstable, while the sols containing particles with smaller electric charge or none, are stable. Therefore we can say that the electric charge of the organosol particles contributes notding to the stability of the sols. This is the marked point different from the case of the ordinary hydrosols in which the electric charge of the colloidal particles is not entirely ignored. This point also coincides with both cases of the author's gold organosols and other silver organosols[3] obtained by treating silver oxide with chlorinated oils.
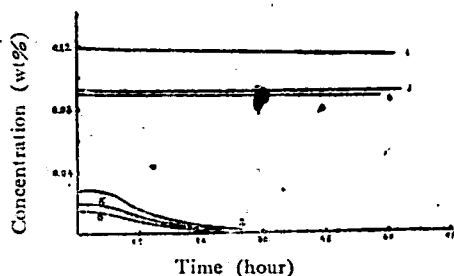

Fig. 2. Stability of silver benzene sols at 20°C, obtained from different decomposing agents of silver oxid.

Decomposing agents
1. Soja bean oil   4. Linolic acid
2. Tubaki oil   5. Stearic acid
3. Oleic acid   6. Palmitic acid

(4) Behaviour of silver organosols against coagulating materials.

The author found that gold organosols dissolved in benzene are coagulated by the addition of small amount of lower fatty acids, inorganic acids and the alcoholic solutions of alkali and various inorganic salts. In order to know the behaviour of these coagulating matters operating in the case of silver organosols, this similar experiment to that adopted in tee case of gold organosols was carried out. Silver

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3) Matumoto and Iwai, *J. Soc. Chem. Ind. Japan*, **43**, 27, 29 (1940).

organosols used here were prepared in the following manner. Silver oxide was decomposed with soja been oil or oleic acid and the colloidal silver thus produced was dissolved in benzene. To these silver benzene sols, various coagulating materials were added. Then the redish brown and transparent sols became bluish brown and untransparent, and the coagulated coarse particles were precipitated. We will call the minimum value of coagulating materials necessary to cause the change the "coagulation value". The coagulation values thus defined of various materials against silver organosols are shown in Table 5.

Table 5. Coagulation value of various substances against silver organosols.

Coagulating agents	Coagulating value (millimol/L)	
	A	B
NaCl 10% water solution	—	—
KCl „	—	—
KI saturated alcoholic solution	7	5
AgNO$_3$ „	30 (unaffected)	30 (unaffected)
HgCl$_2$ „	20 (imperfect)	10 (imperfect)
MgCl$_2$ „	6.4	6.7
CaCl$_2$ „	4.5	3.0
CoCl$_2$ „	4.2	3.3
NiCl$_2$ „	4.9	3.1
AlCl$_3$ „	2.3	2.0
FeCl$_3$ „	7.2	5.3
CuCl$_2$ „	5.6	4.2
NaOH „	23.2	11.6
KOH „	21	10
NH$_4$OH 30% water solution	42.8 (imperfect)	300
HCl „	30 (unaffected)	30 (unaffected)
H$_2$SO$_4$ „	18	9
HNO$_3$ „	25	15
HCOOH „	36	21
CH$_3$COOH „	185 (unaffected)	150 (imperfect)
CH$_3$OH „	—	1164 (unaffected)
C$_2$H$_5$OH „	—	810 „
CH$_3$COCH$_3$ „	—	130 (milky turbid)
distilled water	860 (milky turbid)	—

A: Silver benzene sol obtained by decomposing silver oxide with Soja bean oil.
B: Silver benzene sol obtained by decomposing silver oxide with Oleic acid.

The coagulation values of various coagulating matters in Table 5 are, in general, larger than those of the corresponding gold organosols; moreover, some of them show imperfect coagulation. We can say, therefore, that the films covering silver colloidal particles are more stable than those of gold organosol particles for

coagulating matters.

The mechanism of coagulation of silver organosols is considered to be substantially the same as in the case of gold organosols. The coagulation produced by lower fatty acids may be chiefly due to the selective adsorption of the acid malecules on the surface of colloidal silver particles, and the coagulation produced by alcoholic solutions due to the adsorption of the silver organosol particles on benzene sol particles of alkalis and salts formed with the decrease of their solubility.

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