On the Dispersion of the Hydroxides of Manganese, Iron, Cobalt and of Copper by Autoclaving in the Presence of Aluminium Hydroxide.

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When aluminium hydroxide is subjected to autoclaving, it undergoes imbibition and turns out to be a very stable sol(1). On the contrary, it is well known that ferric hydroxide undergoes dehydration by autoclaving, and turns out to be a compact mass of crystalline structure. If we subject the mixture of these two hydroxides to autoclaving and observe the competition of the two opposing tendencies, i.e., imbibing tendency and dehydrating tendency, we see that the imbibing tendency of aluminium hydroxide predominates and that a rather stable sol is obtained, which contains hydroxides both of aluminium and iron(2).

It is thought that such dispersion might be expected for the hydroxide of other metal, which itself shows dehydrating tendency under autoclaving. Performing the experiment as in the case of Al~Fe hydroxides,

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(1) T. Katsurai and T. Kita, *Bull. Chem. Soc. Japan*, **15**(1940), 458; *Kolloid-Z.*, **95**(1941), 41.

(2) T. Katsurai and T. Kita, *Sci. Pap. Inst. Phys. Chem. Research* (Tokyo), **40**(1942), 70.

some new sols are obtained. In the following, the results are given in each case.

1. Autoclaving of the Hydroxides of Mn, Co, Ni, Cu and of Pb.

The hydroxides are precipitated by adding sodium hydroxide, in a slight excess, to the chlorides of manganese, cobalt, nickel and of copper, and ammonia to the nitrate of lead. In each case, decantation and washing are repeated until the supernatant liquid gives no colouration with phenolphthalein. The hydroxide and the supernatant liquid are then shaken together, and the resulting temporary suspension is removed to a vessel of fused quartz. The vessel is placed in an autoclave of steel and is heated up to 190°C. and is kept one hour at this temperature(3).

By this treatment the hydroxides of manganese, cobalt, and of copper turn out to compact precipitates which settle on the bottom. Their colour is darker than that of the hydroxides which are put to stand at the room temperature. The filtrates obtained by filtering the precipitates are clear and neutral and show no reaction of the metal.

The appearance of the Ni-hydroxide remains unchanged by this treatment. However, the hydroxide can be completely filtered, giving a clear, neutral solution containing no nickel.

The Pb-hydroxide coagulates and settles by this treatment. The supernatant liquid is clear. The precipitate can be filtered, giving a clear, neutral filtrate containing no lead.

Thus by these experiments, we see that the hydroxides show more or less dehydrating tendency.

2. Autoclaving of the Hydroxides of Mn, Fe, Co, Ni, Cu and of Pb in the Presence of Aluminium Hydroxide.

The aluminium hydroxide is precipitated by adding ammonia, in a slight excess, to aluminium chloride. Washing and decantation are repeated until the supernatant liquid shows no colouration with phenolphthalein. The hydroxide is then mixed with each of the hydroxides of manganese, cobalt, nickel, copper and lead (except iron), and is subjected to the 190°–1 hr. treatment. In each experiment the content of the quartz vessel is filtered and the colloidal behaviour of the filtrate is observed.

a. *Al~Mn hydroxides*: As starting materials, 4 g. of aluminium chloride ($AlCl_3 \cdot 6H_2O$) and 3 g. of manganese chloride ($MnCl_2 \cdot 4H_2O$) are used. By autoclaving, a dark brown suspension with some deposit is obtained. The filtrate is a stable sol. By chemical analysis, its composition is found to be

$$Al_2O_3 = 2.00\ \text{mg./c.c.}, \qquad MnO_2 = 0.79\ \text{mg./c.c.},$$
$$Al_2O_3 : MnO_2 = 1 : 0.45\ \text{(mol. ratio)}.$$

b. *Al~Fe hydroxides*: The hydroxides are co-precipitated by adding ammonia to the solution obtained by dissolving 4 g. each of aluminium chloride ($AlCl_3 \cdot 6H_2O$) and ferric chloride ($FeCl_3 \cdot 6H_2O$) together. The

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(3) For the details of the experimental technique, cf. T. Katsurai, *Sci. Pap. Inst. Phys. Chem. Research* (Tokyo), **35**(1939), 191.

remaining procedure is the same as in the other cases. A sol having the following composition is obtained(4).

$$Al_2O_3 = 0.93 \text{ mg./c.c.}, \qquad Fe_2O_3 = 1.08 \text{ mg./c.c.},$$
$$Al_2O_3 : Fe_2O_3 = 1 : 0.75 .$$

c. *Al~Co hydroxides*: As starting materials, 4 g. of aluminium chloride ($AlCl_3 \cdot 6H_2O$) and 3 g. of cobalt chloride ($CoCl_2 \cdot 6H_2O$) are used. Dark blue sol having the following composition is obtained.

$$Al_2O_3 = 1.55 \text{ mg./c.c.}, \qquad CoO = 1.91 \text{ mg./c.c.},$$
$$Al_2O_3 : CoO = 1 : 1.67 .$$

When this sol is shaken, it shows beautiful "schlieren effect".

d. *Al~Ni hydroxides*: No dispersion takes place by the autoclaving. The filtrate is clear and contains neither aluminium nor nickel.

e. *Al~Cu hydroxides*: 4 g. of aluminium chloride ($AlCl_3 \cdot 6H_2O$) and 2.5 g. of cupric chloride ($CuCl_2 \cdot 2H_2O$) are used for the preparation. Dark brown sol having the following composition is obtained.

$$Al_2O_3 = 3.78 \text{ mg./c.c.}, \qquad CuO = 3.88 \text{ mg./c.c.},$$
$$Al_2O_3 : CuO = 1 : 1.31 .$$

This sol also shows "schlieren effect" when it is shaken(5).

f. *Al~Pb hydroxides*: No dispersion takes place by the autoclaving. The filtrate is clear and contains neither aluminium nor lead.

Summary.

The hydroxides of manganese, iron cobalt, nickel, copper and lead show, by autoclaving, more or less dehydrating tendency and undergo contraction of sedimentation volume.

The hydroxides of manganese, iron, cobalt and copper are dispersed by autoclaving in the presence of Al-hydroxide. The sols of the hydroxides of *Al~Co* and of *Al~Cu* show "schlieren effect".

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(4) It was stated in a previous paper that in order to disperse the Al–Fe hydroxides, it was necessary to precipitate the hydroxides of aluminium and iron separately. Cf. (2) p. 70 below. It was, however, found lately that the co-precipitated Al–Fe hydroxides can also be dispersed, when they are fresh, viz., not older than a day after precipitation. In the series of the present investigation, all the hydroxides are subjected to autoclaving within a day after precipitation.

(5) I should like to express my sincere thanks to Mr. K. Kuroda for carrying out the analysis of the sols.