Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. VI. Some Observations on Thermal Transitions of Cobalt Soaps, by Differential Thermal Analysis, Thermogravimetry, and Magnetic Measurement

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Cobalt soaps with different colors, obtained and examined in previous papers[1], are crystalline at room temperatures, but they melt at higher temperatures. In the present paper, their melting behaviors are investigated by differential thermal analysis, thermogravimetry, and the measurement of magnetic susceptibility at various temperatures.

Cobalt soap decomposes at extremely high temperatures. Thermogravimetric analysis is applied also to this process.

Soap which has been cooled from a molten state takes the form of a glassy mass. The characteristics of once-melted soap are examined by reflection spectroscopy, X-ray analysis, and the measurement of magnetic moment.

Experimental

Materials.—Cobalt stearate with different colors were used as in the previous papers[1].

Differential Thermal Analysis.—Soap sample and liquid paraffin, as a reference, were heated simultaneously in coaxial cylinder cells of stainless steel, as Vold has described[2]. Cells were put into holes of a copper block placed at the center of a vertical electric furnace, within an atmosphere of nitrogen. The difference of temperature between sample and reference was measured by a thermocouple of chromel-constantan with two pairs in series. Differential thermo-electric motive force was recorded on the chart of an electric recorder through a D. C. amplifier.

The temperature of the electric furnace was elevated continuously by a program controller at a constant heating rate of 2/3°C/min. The furnace temperature was measured by another thermocouple of chromel-alumel and directly recorded on the same chart as the record of differential temperature. Cooling curves were taken on free cooling.

Thermogravimetry. — An automatic recording thermobalance, with a differential transformer as a detector of the elongation of a spring balance, which will be described elsewhere, was used to record the weight changes during the elevation of the sample temperature at a constant rate of heating of 1°C/min. within an atmosphere of nitrogen. The weight changes by dehydration and by decomposition of cobalt soaps were observed. The sample weight was about 90 mg.

Magnetic Measurement.—Magnetic susceptibilities at various temperatures were measured with Gouy's method*4. Magnetic moments were calculated as in Part IV[1].

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1) H. Kambe, This Bulletin, 34, 1786, 1790, 1794 (1961); 35, 78 (1962); H. Kambe and I. Mita, ibid., 34, 1797 (1961).
2) M. J. Vold, *Anal. Chem.*, 21, 683 (1949).

*4 Magnetic measurements were executed by Mr. H. Honda, at the Resources Research Institute, and by Dr. Y. Matsunaga, at the Department of Chemistry, Faculty of Science, The University of Tokyo.

Reflection Spectroscopy and X-Ray Analysis.—These measurements were carried out as in Parts III and V[1].

Results and Discussion

Differential Thermal Analysis.—Differential thermograms of cobalt stearates are shown in Figs. 1—3. Heating curves at a constant rate of heating and cooling curves at free cooling are shown on opposite sides of the base lines.

Blue anhydrous cobalt stearate (Fig. 1) showed two peaks at 99 and 108°C in the first heating curve, while on cooling two peaks appeared at 89 and 47°C. When cooled soap was heated again, it showed a low-temperature peak at 54C° and two high-temperature peaks at 90 and 100°C. The former of the high-temperature peaks was smaller than in the first heating curve, and the low-temperature peak appeared as a substitute for it.

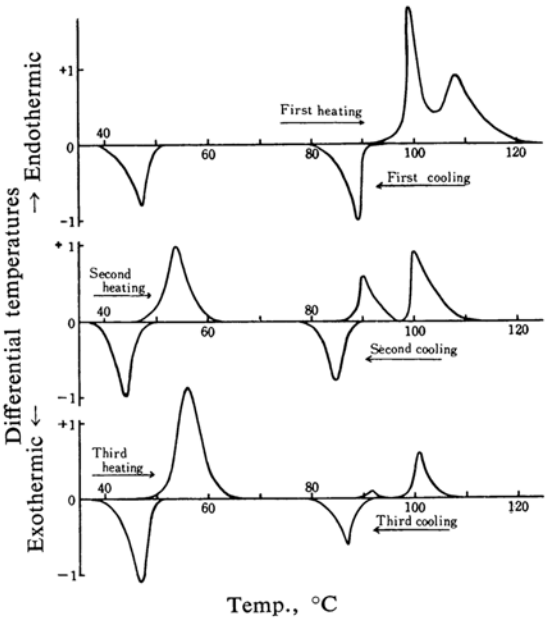

Fig. 1 Differential thermograms of blue cobalt stearate anhydrate. Heating rate: 2/3°C/min.

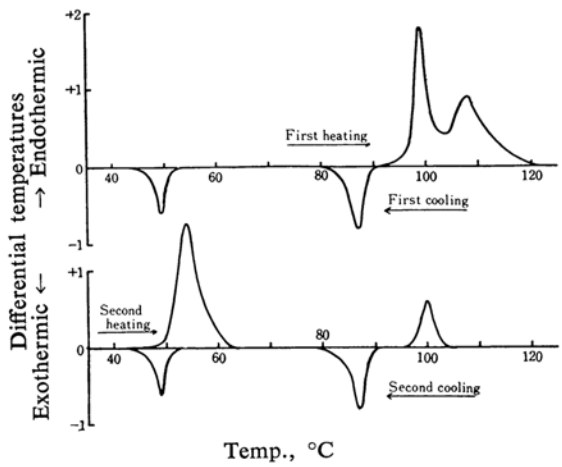

Fig. 2. Differential thermograms of blue cobalt stearate anhydrate. First cooling was done after heating at 120°C for one hour.

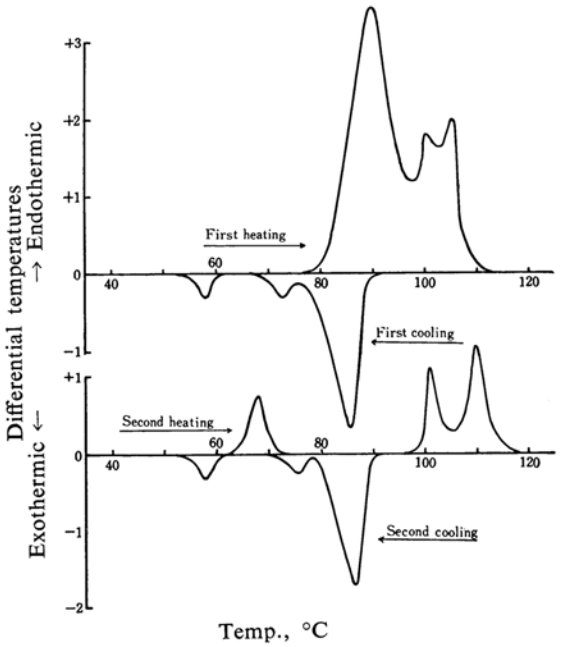

Fig. 3. Differential thermograms of red cobalt stearate dihydrate.

When the twice melted soap was cooled again, two peaks appeared at 85 and 44°C in the cooling curve. The soap generally showed a tendency to be supercooled in cooling curves, and peaks appeared at considerably lower temperatures than in heating curves. The high-temperature peak was not divided into two peaks, as in heating curves.

At the third heating, the low-temperature peak at 46°C was magnified, while the first high-temperature peak almost disappeared. On cooling two peaks appeared at 87 and 47°C.

From these facts, it is concluded that heating has the effect of reducing the high-temperature peaks, especially the lower of them, and extending the low-temperature peak. During heating, the mechanism of the first high-temperature transition might be replaced by that of a low-temperature transition.

When blue cobalt soap was held at 120°C for one hour, this process was advanced considerably, as shown in Fig. 2. In Fig. 2, the first heating and subsequent cooling curves were similar to that in Fig. 1, but in the second heating the low-temperature peak was much

intensified, while the first high-temperature peak disappeared completely, as had been expected.

In the first heating curve, red cobalt stearate dihydrate (Fig. 3) showed a very large peak at 90°C and two high-temperature peaks at 100 and 110°C, as did blue soap. On cooling, a low-temperature peak appeared at 58°C and the high-temperature peaks were displaced to 86°C and 76°C. In the cooling curve of red soap, the high-temperature peak was also divided into two peaks as in heating, in contrast with blue soap. In the second heating curve, a low-temperature peak clearly appeared, while high temperature peaks became smaller although they remained as they were.

In red soap the large peak at 90°C in the first heating curve must correspond to dehydration. This was confirmed by thermogravimetry, as will be discussed below.

Koenig[3] measured visually the melting point of cobalt stearate as 73~75°C. Hattiangdi, Vold and Vold[4] carried out a differential thermal analysis of cobalt soaps by heating at rate of 1.5°C/min. until 150°C, above which decomposition of the soap was feared. They found transition points at 59°C(ΔH=13440 cal./mol.) and at 92°C(probably second-order transition) in cobalt stearate. They also described the visual melting point of cobalt stearate as 80°C. In a free cooling curve, they found only a transition at 57°C. Their sample was perhaps a melted amorphous form, as Vold and Hattiangdi[5] observed only an amorphous halo in a powder X-ray pattern of this soap, as stated in Part V[1]. The peaks obtained by them might correspond to our low-temperatue peak and second high-temperature peak.

Hattiangdi, Vold and Vold[4] have concluded that cobalt soaps are in a mesomorphic state at room temperatures. A revised mechanism of the phase transitions of cobalt soap is proposed as follows:

Crystalline blue anhydrous soap melts at first heating in two stages. The first transition, which may be called premelting, is a phase transition from a crystalline to a plastic mesomorphic state, while the second transition corresponds to true melting. When blue soap is cooled from a melted state, it transforms to an (upper) mesomorphic state with some supercooling, but at a lower temperature a second transition occurs and the soap phase changes to a lower mesomorphic state.

At the second heating, soap transforms from a lower mesomorphic state to an upper mesomorphic state at low temperature transition, as described before. At a higher temperature region, the same two peaks appear as in the first heating. The first of them becomes smaller, however.

It is concluded, therefore, that although the upper transition peak was not apparently divided into two peaks in the first cooling curve, some of soap was transformed from an upper mesomorphic state to a true crystalline form, and it appeared in the second heating curve as a smaller first high-temperature peak. Repeated or prolonged melting suppressed this transition so much that the first high-temperature peak was faded markedly, while the low-temperature peak became eminent.

Crystalline red cobalt stearate shows a large dehydration peak, but thereafter it behaves as an anhydrous soap. The following processes are completely similar to those in the anhydrous blue soap. However, it shows high-temperature peak in the cooling curve, in contrast to blue soap.

Thermogravimetry.—Thermogravimetric curves of blue cobalt stearate anhydrate and red dihydrate are shown in Figs. 4 and 5. In these curves the weight loss (%) observed is plotted

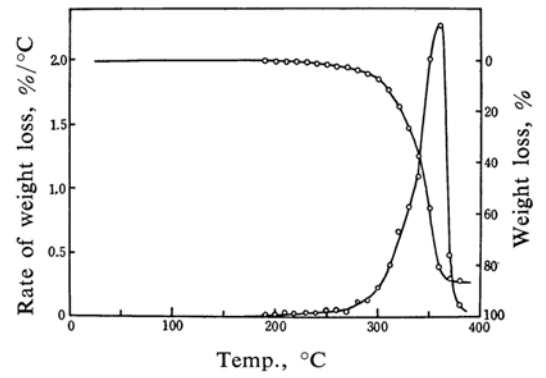

Fig. 4. Thermogravimetric curve of blue cobalt stearate anhydrate.

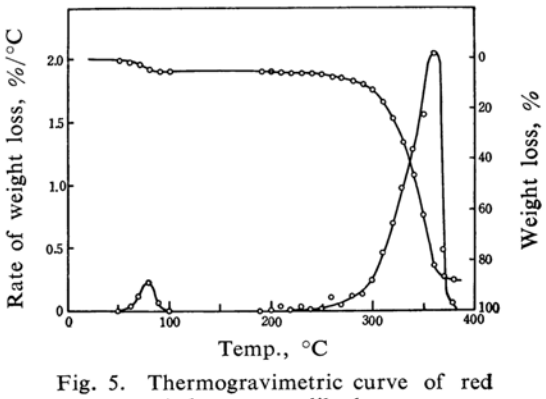

Fig. 5. Thermogravimetric curve of red cobalt stearate dihydrate.

3) A. E. Koenig, *J. Am. Chem. Soc.*, **36**, 931 (1914).
4) G. S. Hattiangdi, M. J. Vold and R. D. Vold, *Ind. Eng. Chem.*, **41**, 2320 (1949).
5) R. D. Vold and G. S. Hattiangdi, ibid., **41**, 2311 (1949).

against temperature. The rate of weight loss (%/°C) was obtained by a graphical differentiation of weight loss curve and is also plotted in the same figure.

Blue soap (Fig. 4) did not show any weight loss at the melting point, but red soap (Fig. 5) showed a weight loss of about 4.4% at about 80°C. Even if somewhat smaller, this is correspondent with the loss of hydrate water from cobalt stearate dihydrate (calcd. 5.46%). This process is also correspondent with the first large peak of differential thermogram of red soap.

Differential thermogravimetric curves of both soaps showed a significant weight loss, which commenced at about 200°C and reached a maximum rate of weight loss at about 360°C. This weight loss is evidently caused by the decomposition of soap. In this process some white crystalline powder was condensed at the cold part of a glass tube, which enveloped an inert atmosphere around the sample. This powder melts at 87.5~88.5°C. This was identified with stearone $(C_{17}H_{35})_2CO$, the melting point of which is 88.5°C. In the sample cell remained a black mass, which was identified as cobalt oxide.

Magnetic Measurement. — The reciprocal molar susceptibility of red cobalt soap was plotted against temperature, as shown in Fig. 6. It was found that the magnetic susceptibility of cobalt soap changed abruptly at the melting point. Below this temperature, Curie's law

$$\chi_M = \frac{C}{T} \qquad (1)$$

where C is a constant, held.

Herron and Pink[6] measured the thermal change of the magnetic susceptibility of cobalt soaps and found that Curie-Weiss' law

$$\chi_M = \frac{C}{T-\theta} \qquad (2)$$

where C and θ are constants, held below 320°K. They obtained Weiss' temperature $-\theta$ as 18.5°K in cobalt stearate. It is difficult to estimate Weiss' temperature from our experiments, which were conducted only above room temperatures.

Properties of Melted Soap.—When cobalt soap was cooled from its melted state, it took a mesomorphic state, as stated above. An X-ray diffraction pattern of melted soap is shown in Fig. 7. It is evident that there is only an amorphous halo, as Vold and Hattiangdi[5] pointed out. The color of melted soap is dark red. Its reflection curve is shown in Fig. 8, where its dominant wavelength is 546c mμ, its purity is 18%, and its brightness is 34.95% (cf. Part III[1]). The color is like that of red soap rather than blue soap. This is because the ground state of the spectral terms is seriously affected by the change of the crystal field on melting. The magnetic moment of melted cobalt stearate, calculated as in Part IV[1], was

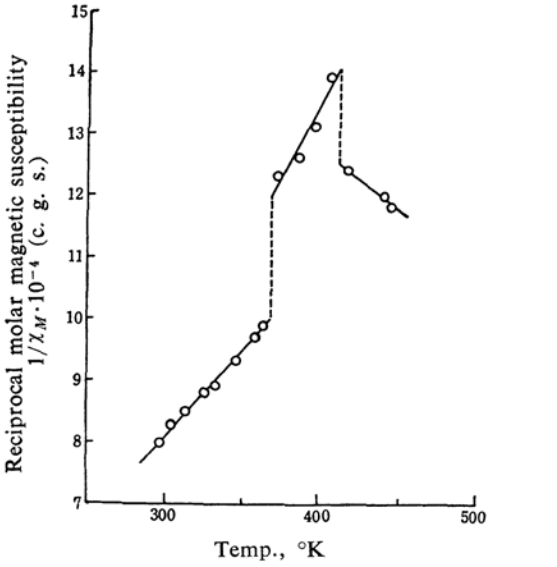

Fig. 6. Temperature dependence of magnetic susceptibility of red cobalt stearate dihydrate.

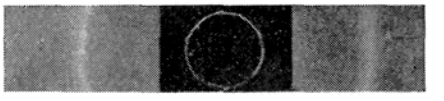

Fig. 7. X-Ray diffraction pattern of melted cobalt stearate.

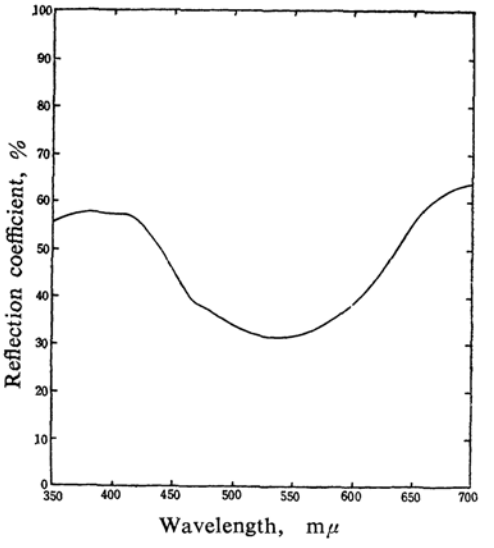

Fig. 8. Reflection curve of cobalt stearate, cooled from melt.

6) R. C. Herron and R. C. Pink, *J. Chem. Soc.*, **1956**, 3948.

4.86 B. M., in which there is a considerable orbital contribution.

Summary

The thermal transitions of red dihydrate and blue anhydrate of cobalt stearate have been measured by differential thermal analysis, thermogravimetry, and magnetic measurement.

Differential thermograms of anhydrous blue soap showed two peaks at high temperatures (about 100°C). When it was heated repeatedly, a new peak appeared at a lower temperature (about 50°C). A low temperature transition is considered to be a transition between mesomorphic phases. The first high-temperature transition corresponds to a transition from a crystalline to an upper mesomorphic state, which disappeared on repeated heating. Red dihydrate soap showed a large peak at 90°C owing to the removal of hydration water. Thereafter it appeared in an anhydrous state.

Thermogravimetric analysis showed the dehydration process in red soap, but not in blue anhydrate. The decomposition of cobalt stearates to stearone and cobalt oxide was found in thermogravimetric curves.

The magnetic susceptibility of cobalt soap obeys Curie-Weiss' law below the melting temperature, but above it the susceptibility decreases abruptly and anomalous behavior is observed.

Melted soap is in an amorphous state, which was certified by X-ray measurement. Its color and magnetic moment show that melted soap is different in nature from red and blue soaps.

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