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# On the Preparation of Cadmium Sulfoselenide by the Wet Processes

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The super-homogeneous coprecipitation method, in which the binary solution reactants made to mix and react in a moment, thus reducing a super-homogeneous precipitate, has been used recently in the preparation of catalysts. The coloring temperature of the cadmium sulfoselenide red pigment can be lowered to 350°C by this method, while, when the usual wet method is used, the temperature is between 450 and 650°C. This is because a very homogenous solid solution can be formed by the super-homogeneous coprecipitation method. This method is also effective in making an anionic solid solution of A(X, Y) with different anions of X and Y. Spectral reflectance measurements and X-ray analysis in the present work have shown that the coloring temperature has been considerably lowered and the transformation of the $\beta$-Cd(Se, S) into the $\alpha$ form has been accelerated by the method.

Cadmium red is a substantial inorganic pigment with a clear tone; it is used in ceramics, glasses, enamels, and resins. This pigment has been considered to be a cadmium sulfoselenide which was a continuous solid solution of cadmium sulfide and cadmium selenide. However, the relation between the compositions and the color has hardly been discussed at all.(1-3) There are various combination of starting materials and processes used in the preparation of cadmium sulfoselenide. The processes are classified into wet and dry methods. In the wet method, the pigment is obtained by sintering the coprecipitate, which has been prepared by treating an aqueous solution of sodium sulfoselenide an aqueous solution of cadmium sulfide; the coloring temperature has been reported to be between 470 and 640°C by Stuckert,(4) between 450 and 650°C by Yamanouchi,(1) between 550 and 650°C by Eroles and Friedberg.(5) In this case, the binary solution is made to mix and react

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1) S. Yamanouchi, *J. Ceram. Assoc. Japan (Yogyo Kyokai Shi)*, **60**, 676 (1952).
2) Milligna, *J. Phys. Chem.*, **38**, 797 (1934).
3) H. Kohl, *Ber. Deut. Keram. Ges.*, **4**, 181 (1935).
4) L. Stuckert, *Glashutte*, **64**, 364 (1934).
5) A. J. Eroles and A. L. Friedberg, *J. Am. Ceram. Soc.*, **48**, 223 (1965).

in a moment, and then a super-homogeneous coprecipitate can be obtained. This is the super-homogeneous coprecipitation method which has been used recently in the preparation of catalysts.[6-8]

The authors will report in this paper the results of an examination of the thermal transformation of the coprecipitate (the $\beta$-Cd(Se, S) into the $\alpha$ form) by spectral reflectance measurements and by X-ray diffraction analysis.[2,9]

### Experimental

**The Preparation of Solutions.**—Table I shows the effect of selenium upon the color. The poorer the selenium content, the more yellowish the color; the richer, the darker.[1] The lattice dimensions, $a_0$ and $c_0$ increase with a rise in the cadmium selenide content. Since the linearity between the lattice dimension and the content is almost complete, the concentration of cadmium sulfide or cadmium selenide in a pigment can be exactly determined by means of the X-ray diffraction patterns.[5,10] E–3 is the best color tone among them; the procedure for obtaining it is follows (the chemicals used in this experiment are commercially-available chemically-pure reagents). A cadmium salt solution (sp. gr. 1.4) is made by dissolving 98.42 g. of cadmium sulfate ($CdSO_4 \cdot 8/3H_2O$) in 102 cc. of distilled water. A sodium sulfoselenide solution is made by dissolving 85.7 g. of sodium sulfide ($Na_2S \cdot 9H_2O$) into 200 cc. of water, and by then dissolving 11.05 g. of metallic selenium into it with heating; the solution is used after filtration (sp. gr. 1.13). When cadmium sulfide is made, of course, metallic selenium is not added. In order to carry out a sudden and homogeneous reaction in a mixer, an intermediate aqueous solution such as a sodium sulfate solution (sp. gr. 1.21) is required.

**The Preparation of Coprecipitates.**—a) The usual method consists of adding a sodium sulfate solution to a cadmium sulfate solution and by then pouring a sulfoselenide solution into it, then obtaining a coprecipitate by stirring, as usual. The reason why a sodium sulfate solution is added is to set up the same conditions as in the following new method. The precipitate is filtered, washed by warm water, and dried at 100°C.

b) In the new method, at first, the double amount of a cadmium sulfate solution mentioned above is put into a 1.8 l. mixer, and then a sodium sulfate solution is slowly added along the wall of the container by means of a separating funnel. The two aqueous solutions easily separate into two layers as a result of the difference in specific gravity. A sodium sulfoselenide solution added by the same method makes the triple layers. The state is shown in Fig. 1. When switched on, the solution suddenly becomes homogeneous, and a precipitate is formed uniformly every part of the solution.

The samples obtained by the a) method (the usual method) are said to form the A-system, and those by the b) method (the new method), the B-system. In order to establish the characteristics of the new coprecipitative method, the authors also made CdS precipitates

TABLE I. EFFECT OF SELENIUM UPON COLOR

Chemical analysis, color measurement and X-ray analysis.

These specimens sintered at 550°C are complete solid solution by X-ray diffraction patterns.

Reactants—$CdSO_4 \cdot 8/3H_2O$ is 40% aq. sol., $Na_2S \cdot 9H_2O$ is 30% aq. sol. and Se is metallic selenium

Chemical analysis of pigments—Cd: EDTA, S: converted to $SO_4$ and estimated as $Ba_2SO_4$, Se: reducted to metallic selenium.

Color measurement—$Y$: Lightness, $P_e$: Excitation purity, $\lambda_d$: Dominant wavelength.

| Sample | Reactants | | | Chemical analysis | | | | |
|---|---|---|---|---|---|---|---|---|
| | $CdSO_4$ | $Na_2S$ g. | Se | Cd | S | Se % | $SO_4$ | Total |
| E-1 | 98.4 | 89.4 | 4.7 | 71.56 | 17.27 | 7.83 | 3.40 | 100.07 |
| E-2 | 98.4 | 87.5 | 7.8 | 69.98 | 15.64 | 10.80 | 2.70 | 99.12 |
| E-3 | 98.4 | 85.7 | 11.0 | 66.83 | 13.70 | 14.39 | 2.50 | 97.42 |
| E-4 | 98.4 | 82.9 | 15.8 | 65.09 | 12.23 | 20.81 | 0.64 | 98.77 |

| Composition | | Color measurement | | | Lattice parameter (Hexagonal) | |
|---|---|---|---|---|---|---|
| CdSe mol. % | CdS | $Y$ % | $P_e$ % | $\lambda_d$ m$\mu$ | $a_0$ Å | $c_0$ |
| 15.5 | 84.5 | 31.9 | 72.0 | 594.8 | 4.16 | 6.77 |
| 22.0 | 78.0 | 25.6 | 68.7 | 606.5 | 4.17 | 6.78 |
| 30.7 | 69.3 | 15.6 | 52.9 | 611.2 | 4.18 | 6.80 |
| 44.7 | 55.3 | 11.2 | 35.9 | 619.2 | 4.19 | 6.81 |

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6) T. Shirasaki, *Catalyzer (Shokubai)*, **6**, 37 (1964).

7) M. Okada, *Report of the Chiba Institute of Technology*, **5**, 18 (1964).

8) L. Gordon, "Precipitation from a Homogeneous Solution," John Wiley & Sons, London (1959).

9) F. Ulrich and W. Zachariasen, *Z. Krist.*, **62**, 260 (1925).

10) K. Hashimoto, *Report of the Chiba Institute of Technology*, **2**, 43 (1962).

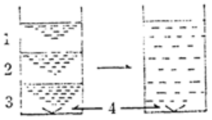

Fig. 1. The illustration of reactor (mixer) for B-system.
1: Sodium sulfoselenide aq. sol. (sp. gr. 1.13) or sodium sulfide aq. sol.
2: Intermediate aq. sol., sodium sulfate aq. sol. (sp. gr. 1.21)
3: Cadmium sulfate aq. sol. (sp. gr. 1.4)
4: Rotor

by these two methods.

**Sintering.**—A dried precipitate (25 g.) is powdered in an agate motor; then it is put into a vitreous quartz Tamman tube (35 mm. in internal diameter) supplied with nitrogen gas (1 l./min.) and heated in the vertical electric furnace, taking care that every part of the sample is equal in temperature. Each sample is heated quickly, kept at the given temperature (350, 400, 450, 500 or 550°C) for 30 min., and then cooled in air. Again it is powdered in the agate motor.

**Measuring Apparatus.**—The Shimadzu Hardy-type photoelectric colorimeter is used for the spectral reflectance measurements. Color measurements are carried out by determining x, y, and z by the 30-division method, and $Y$, $P_e$ and $\lambda_d$, according to the indications of the C. I. E. method.

The Shimadzu X-ray apparatus is used; the characteristic X-ray is $CuK\alpha = 1.539$ Å. MgO is used as the internal standard.

## Results and Discussion

**The Preparation of Samples.**—Precipitates obtained from liquid-liquid reactions are not always homogeneous microscopically in their compositions. This fact has been reported in the field of gravimetric analysis, and attempts have recently been made to get homogeneous precipitates. In the formation of a solid solution of the A(X, Y) type, the diffusion velocities of X and Y across the boundary membranes are different, and so it is impossible that compositions of every particle of precipitate are A(X, Y) exactly. Furthermore the phenomenon of the crystallization of precipitates is not chemical equilibrium but chemical kinetics. The initial precipitate may differ from the following precipitate in composition. By the use of the method in mixing two solutions uniformly during the induction period in the formation of nuclei, a precipitate of the same composition and size may be formed from a supersaturated solution. This is especially very effective in a supersaturated solution of slightly soluble salt, for its induction period is momentary. Thus, the precipitate obtained by the new method (the B-system) may be thought to be highly homogeneous compared with the precipitate formed by the usual coprecipitation method (the A-system). The differences between these two systems will be discussed below.

**The Results of Color Measurement.**—The spectral reflectance curves of the precipitates of cadmium sulfoselenide sintered at the given temperatures are shown in Fig. 2 and Table II. The precipitates of both the A-system and the B-system are amorphous and hardly change at all up to 300°C. The B-system begins to show a reddish tone at 350°C, but the A-system does so at 400°C. Therefore, the B-system is more reddish than the A-system at the same temperature. This may be ascertained from the dominant wavelength. At 500°C the A-system develops the same color as that of B-system sintered at 450°C. This difference is also found in the results of X-ray diffraction analysis.

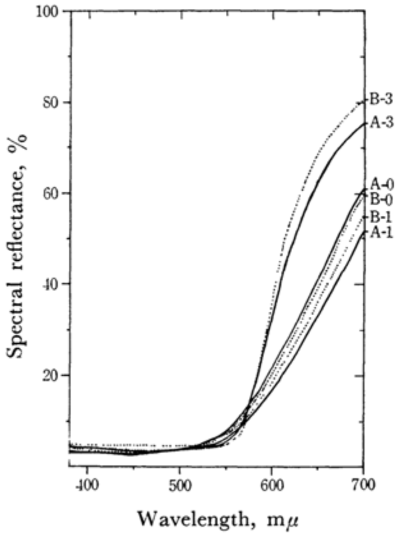

Fig. 2. The spectral reflectance curves of A- and B-system coprecipitates sintered at 350 and 450°C and without heat-treatment.

TABLE II. CHANGE OF COLOR THROUGH SINTERING
A: A-system (usual method)
B: B-system (new method)

| Sample | Sintering temp. °C | Lightness % | Excitation purity % | Dominant wavelength mμ |
|---|---|---|---|---|
| A-0 | | 13.0 | 65.9 | 596.2 |
| A-1 | 350 | 10.6 | 57.7 | 598.3 |
| A-2 | 400 | 12.9 | 60.2 | 603.0 |
| A-3 | 450 | 15.6 | 68.2 | 605.7 |
| A-4 | 500 | 15.7 | 65.0 | 607.0 |
| A-5 | 550 | 16.2 | 65.0 | 609.0 |
| B-0 | | 12.4 | 60.0 | 596.0 |
| B-1 | 350 | 11.6 | 51.7 | 601.9 |
| B-2 | 400 | 12.5 | 58.2 | 606.1 |
| B-3 | 450 | 16.0 | 65.2 | 607.3 |
| B-4 | 500 | 16.0 | 62.3 | 608.0 |
| B-5 | 550 | 16.5 | 60.1 | 608.0 |

**X-Ray Diffraction Patterns.**—The X-ray diffraction patterns of $\alpha$-CdS obtained from cadmium sulfide precipitates of A- and B-systems sintered at 450°C; a typical one is shown in Fig. 3. These patterns show the conversion of the amorphous precipitate of cadmium sulfide into $\alpha$-CdS (the wurtzite structure) by heating, because the broad peak splits into three characteristic peaks, which correspond to (100), (002) and (101) in the wurtzite structure. The thermal transformation of Cd(Se, S) can be studied qualitatively from these peaks, as is shown in Fig. 4. Up to about 300°C no change can be found in these patterns, but at 350°C the spilt peaks in the B-system become observable. This fact shows that the crystallization process corresponds exactly to the coloring process. At 450°C both are transformed into the substance of the wurtzite structure. The A-system develops a color as if it contained a smaller amount of selenium. From this fact, the A-system precipitate may be more inhomogeneous than the B-system and part of the selenium may be lost by the difference between the diffusion velocity of the solid and the missing velocity of the vapor at a low temperature. The diffusion velocity may be faster than the missing velocity of vapor above 500°C; in this case selenium can form a solid solution with CdS. There is no difference in the transformation temperature between the A- and the B-systems in the case of a cadmium sulfide precipitate consisting of only A(X). From this fact, the transition may have no close relation to the defect in the crystalline structure or the particle size of the precipitate, but rather a close relation to the homogeneity of the precipitate. Such a process would be effective in the precipitation of uniform solid solution. It may be possible to contain traces of impurities uniformly in the precipitate.

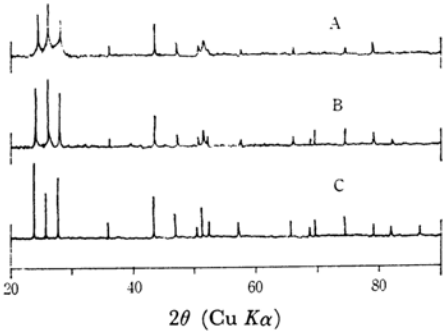

Fig. 3. The X-ray diffraction patterns of $\alpha$-CdS.
A: A-system sintered at 450°C
B: B-system sintered at 450°C
C: Typical one from $\beta$-CdS sintered in $H_2S$ gas at 900°C

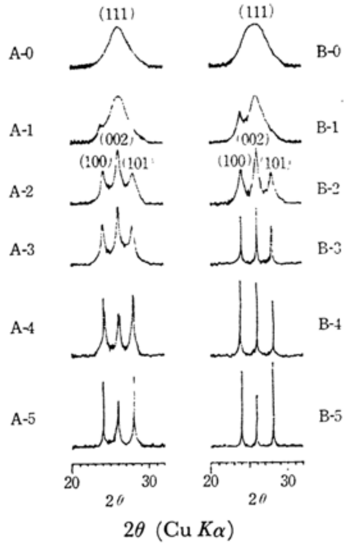

Fig. 4. The thermal transformation of A- and B-system Cd (Se, S) coprecipitates on the X-ray diffraction patterns.
A-0 and B-0: Starting precipitate
A-1 and B-1: Sintered at 350°C
A-3 and B-3: Sintered at 450°C

## Conclusions

1) The optimum temperature of the cadmium sulfoselenide red pigment can be lowered by utilizing the super-homogeneous coprecipitation method.

2) The super-homogeneous coprecipitation method is an important way to obtain the precipitate of a uniform constitution of A(X, Y)-type solid solutions.

3) When selenium is partially substituted for sulfur, the transition to the wurtzite structure occurs at a lower temperature.

4) A precipitate of cadmium sulfoselenide showing the amorphous X-ray diffraction patterns can be transformed, even at 350°C.