962 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(4), 962—964 (1974) [Vol. 47, No. 4

The Effects of the Composition of Raw Cadmium Sulfide on the Characteristics of Cadmium Pigments

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(Received April 6, 1973)

The effects of the S/Cd mol ratios of cadmium sulfide precipitates on the particle size, the hexagonality, and the brightness of cadmium pigments were studied. The precipitates were prepared by mixing an aqueous solution of cadmium nitrate with either sodium sulfide or hydrogen sulfide. Then, cadmium pigments were made of these precipitates by heat-treatment under an atmosphere of oxygen or nitrogen. The characteristics of the pigments were affected by the following three factors; particle size, hexagonality, and brightness. These factors were closely related to the S/Cd mol ratio of the precipitates of the cadmium pigments. We found the minimum points on the curves of the particle size, the hexagonality, and the brightness in relation to the S/Cd mol ratio. From these results, it was concluded that the optimum range of the S/Cd mol ratios of the precipitates for the characteristics of the cadmium pigments was 0.98 ± 0.01.

Cadmium pigments are ordinarily composed of CdS or solid solutions of CdS and either ZnS, CdSe, or HgS. These pigments are mainly formed by two processes, precipitation and calcination. The former process is the precipitation reaction of a metal salt solution with alkali sulfide (selenium is sometimes dissolved in this solution); the latter, the calcination of the precipitates at 500—700 °C in a non-oxidizing atmosphere.

The characteristics of cadmium pigments have been reported in many papers[1-5] and patents.[6] Most of these reports have been concerned with the two processes mentioned above. The effects of the temperature, pH, additions, *etc.* on the pigments have been studied for the precipitation process, and those of the temperature, the atmosphere, the time, additions, *etc.*, for the calcination. However, the characteristics of the precipitated powders and their effects on the final pigments have been little investigated.

We have previously reported that on heat-treatment oxygen and sulfur affected the particle size, the hexagonality, and the color.[7,8] The results showed that the changes in the particle size and hexagonality were very similar to the conditions of heat-treatment. Especially in the heat-treatment, oxygen in an atmosphere distinctly brought about a brighter color than did nitrogen or helium. Therefore, the effects on the pigment characteristics in relation to the amount of cadmium hydroxide and sulfur in precipitates and that of oxygen in an atmosphere were studied.

In this paper, the effects of the S/Cd mol ratio of the CdS precipitates before heat-treatment of the pigment characteristics will be discussed. Some interesting correlations between the S/Cd mol ratios and the pigment characteristics were obtained.

Experimental

Raw Materials. The raw materials were precipitated by the reaction of cadmium sulfate and a sodium sulfide solution of each 1 molar concentration. Precipitates with various S/Cd mol ratios were prepared by the use of the sodium sulfides, dissolved sulfur powder for precipitates including excess sulfur, and mixed sodium hydroxide for those with excess cadmium. After the solution had been stirred for 3 hr at 80 °C, the precipitate was dried at 100 °C, then, it was pulverized to a fine powder. It was considered that all these, including cadmium polysulfides or cadmium hydroxide, were coprecipitated with CdS.

In addition to these materials, other raw materials were prepared by the bubbling of hydrogen sulfide gas. Sulfur or cadmium hydroxide powder was mixed with the suspension after it had been washed to obtain Cd or S excess raw materials. The precipitates prepared by sodium sulfide were classified as Group A, and those prepared by hydrogen sulfide, as Group B.

These raw materials were analyzed by the gravimetric method for sulfur and by the EDTA titration method for cadmium.

Heat-treatment. Each raw material was degassed at 200 °C for an hour under a pressure of 10^{-3} mmHg and then heat-treated for an hour at a constant temperature in pure nitrogen or oxygen gas of an atmospheric pressure. The temperature of the heat-treatment was fixed at 500 °C for Group B, for the precipitates of Group B were stable and no changes in hexagonality occurred at 500 °C, as has previously been reported.[9]

Properties of Products. The particle size was measured by the BET method, from the nitrogen gas adsorption at the temperature of liquid nitrogen, after the raw materials had been pretreated at 200 °C under a pressure of 10^{-3} mmHg.

CdS crystals have two polymorphic forms, *i. e.*, a hexagonal closely-packed structure (wurtzite) and a face-centered cubic (zincblende).

CdS polycrystals usually include both of the forms, and the term 'hexagonality' has been previously used[10,11] to describe the fraction of the hexagonal form in the crystal. We have also used this term 'hexagonality'.

Short and Steward[10] have shown that the 'hexagonality' (H) of CdS polycrystal is related to the ratio (R) between the integrated intensities (I) of the first and second Debye-Sherrer rings:

$$H = 4R/(3R+1.33)$$

where:

$$R = I(100)/I(002+111)$$

As is shown in the previous paper, in this equation the constant value, 1.33, was the lower estimation. From the many experimental results, the most reliable value was 1.70. Therefore, the above equation was modified as follows:

$$H = 4R/(3R+1.70)$$

The X-ray diffraction patterns were recorded by means of a Philips X-ray diffractometer, model PW. As an X-ray radiation source, nickel-filtered copper radiation at 30 kV and 20 mA was used.

The brightness of the specimen was investigated as one pigment characteristic.

Specimens were mixed and kneaded with varnish on Hoover muller* by hand or by four times 25 revolutions under a 150 lb. weight. The spectral reflectance curve of each of these sheets was then measured by means of a spectrophotometer.

The brightness was represented by the slope of the spectral reflectance curve at the 50 percent reflectance point (in arbitrary units), but it agreed well with both the 'excitation purity' from the chromaticity diagram** and with observations. As the slope is proportional to the crystallinity, the brightness represents the purity of the color.[12]

Results and Discussion

Particle Size. The raw materials had particle sizes (surface area diameter) of 10—20 nm for Group A and of 150 nm for Group B. The particle sizes of the heat-treated specimens are shown in Fig. 1.

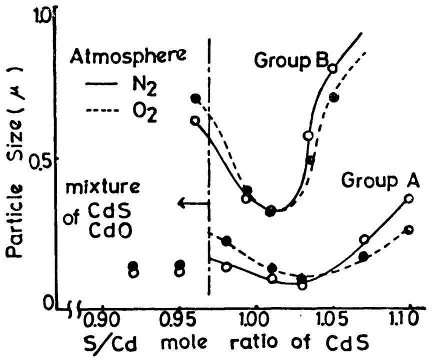

Fig. 1. The correlation between the S/Cd mol ratio of CdS precipitate and particle size of heat-treated specimen.

In Fig. 1, the changes in particle size according to the S/Cd mol ratio of the raw materials describe a curve with a minimum in the range from 1.02 to 1.03. The particle sizes also differed with the atmospheric gas.

It seems to be general that particles grow remarkably on heat-treatment in an excess of either S or Cd. Therefore, it is natural that a miniumm point exists on the curve. Parravano[13] showed that ZnO particles grew by the recombinations of zinc diffused in the crystal with oxygen on the surface. Further, Woodbury[14] and Whelan[15] reported that the diffusion of Cd in the CdS crystal was in proportion to the Cd vapor pressure.

These facts prove that an increase in particle size is promoted by the excess of either S or Cd, and that, because sulfur was more volatile than Cd and was reactive with atmospheric oxygen,*** the position of the minimum point in the curve shifts to a somewhat lower value of the S/Cd mol ratio.

Hexagonality. Changes in the hexagonality of heat-treated specimens of Group A are shown in Fig. 2 in relation to the S/Cd mol ratios of the original specimens. The curve of Group B has been abbreviated to be almost the same as for Group A. The changes in hexagonality showed the same tendency toward particle size.

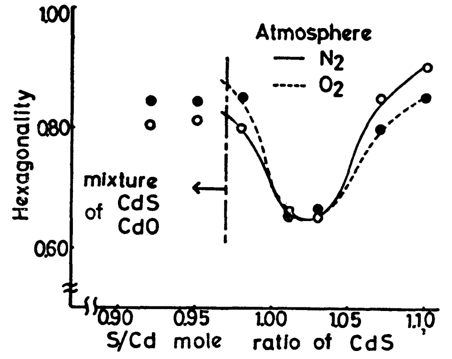

Fig. 2. The correlation between the S/Cd mol ratio of CdS precipitate and hexagonality of heat-treated specimen.

According to Holt and Wilcox,[16] phase transformation to the hexagonal form was accelerated by the quantities of defects. It was supposed that specimens of Group A had more defects than those of Group B, since the particles of the former were fine.

The effect of the oxygen in the atmosphere on the hexagonality was almost the same as that on the particle growth.

Brightness. CdS pigments, prepared under similar conditions, took various hues, brightness, tinting strength, and hiding powers according to the differences in crystal structure, particle size, *etc.*

The correlation with the brightness and the S/Cd mol ratio is shown in Fig. 3 in the case of Group A; the curve is almost the same as Group B.

The changes in brightness showed results similar to those for both particle size and hexagonality, but the minimum point of the curve was less clear compared with the previous two characteristics.

The brightness of heat-treated specimens in an atmosphere of oxygen was higher than that in one of nitrogen. In general, cadmium pigments were pulverized and mixed with vehicles for practical use. As

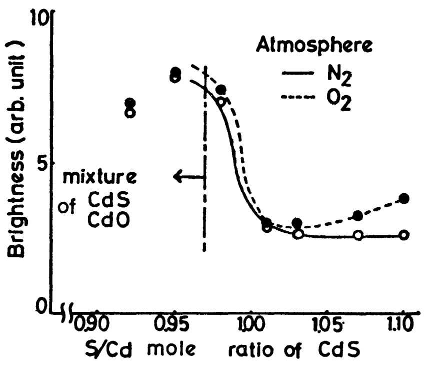

Fig. 3. The correlation between the S/Cd mol ratio of CdS precipipate and the brightness of heat-treated specimen.

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* Japanese Industrial Standard, JIS K5101: Testing methods for pigments.

** Japanese Industrial Standard, JIS Z8701.

*** Observed by the generation of SO_2 gas.

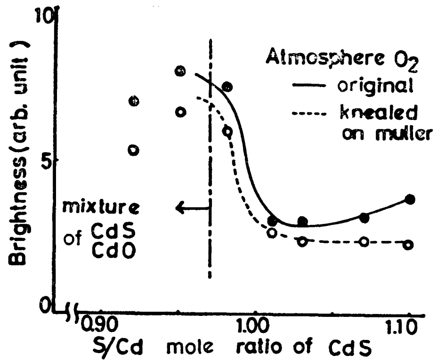

Fig. 4. Effects on brightness by the grinding of heat-treated specimens.

has previously been reported,[12] the brightness decreased upon such treatments, distortion also occurring in a crystal.

As is shown by the dotted lines in Fig. 4, the brightness of the specimens in this study was also reduced by kneading on muller; the reduction was especially remarkable in the specimens with a S/Cd mol ratio of over 1.00 and which has been heat-treated in an atmosphere of nitrogen.

Conclusion. Cadmium pigments with excellent characteristics must have the range in the particle size of 0.1—0.5 μ and as much high hexagonality and brightness as possible.

It has been established in this report that the value of the S/Cd mol ratio of the raw materials has a great effect on the quality of pigments obtained; the optimum value was 0.98±0.01. Under a ratio of 0.97, black cadmium oxide was formed by the decomposition of cadmium hydroxide; over one oxide of 0.99, the products were unsuitable as pigments because of their low brightness.

Further,if oxygen was present in the calcining atmosphere, it caused not only a decrease in the S/Cd mol ratio by the consumption of sulfur, but also an increase in the brightness. However, we could not confirm by any quantitative methods whether or not the oxygen was substituted for sulfur in a crystal.

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