Dry Grinding on a Pigment Mixture. I. The Effect of α-Copper Phthalocyanine as a Lubricant on the Mechanochemical Transformation of Calcium Carbonate

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(Received January 24, 1975)

α-Copper phthalocyanine and calcium carbonate were mixed and ground with a grinder, and then the surface properties of the mixtures were investigated in comparison with the grinding time by means of X-ray diffraction analysis, electron-micrograph observation, and the specific surface area as obtained by the B.E.T. method. In the grinding process, the crystal decays of both α-copper phthalocyanine and calcium carbonate were observed. Particularly, the calcite-aragonite transformation occurred in the case of calcium carbonate. However, the addition of some α-copper phthalocyanine to calcium carbonate interfered with the transformation of calcium carbonate. As a conclusion, it was evident that the surface of calcium carbonate was covered with α-copper phthalocyanine and that the grinding of calcium carbonate was interfered with by the lubricating action of α-copper phthalocyanine.

In some cases, not only are changes in the particle shape and size found in mechanical treatments such as crushing, grinding, and rolling, but also the physical and chemical properties of the particles become different from the original intrinsic properties.[1-5]

Many reports have been published on the mechanochemical changes in inorganic single material[6-8] and in inorganic–inorganic material mixed systems.[9-11] In the field of the paint industry, mixed-type pigments are used to obtain various color pigments. However, few studies have dealt with the grinding of mixtures of an organic pigment and an inorganic one.

In a previous work, we ourselves examined the mechanochemical change in the surface properties of α-copper phthalocyanine–titania, γ-quinacridone–titania mixed systems[12] and α-copper phthalocyanine–alumina mixed systems.[13] In this paper, the grinding process of a mixture of an organic pigment and an inorganic one was investigated by means of X-ray diffraction analysis, the observation of electron micrographs, and also surface-area measurements.

Experimental

The α-copper phthalocyanine (abbrev. α-CuPc) used here was supplied by Dainippon Ink Chemical, Ltd. The calcium carbonate was supplied by the Kokusan Kagaku Co., Ltd. The specific surface areas of α-CuPc and calcium carbonate, as measured by the B.E.T. method, were about 50 m^2/g and 2 m^2/g respectively. These pigments were ground with an Ishikawa-type grinder in a closed chamber at room temperature at the following mixed ratios of weight: α-CuPc *vs.* $CaCO_3$: (1 : 1), (1 : 9) and (1 : 19); these mixtures were abbreviated as follows;

Sample A: a (1 : 1) mixture of α-CuPc and $CaCO_3$
Sample B: a (1 : 9) mixture of α-Cupc and $CaCO_3$
Sample C: a (1 : 19) mixture of α-CuPc and $CaCO_3$

The grinding was done after; 2, 4, 6, 8, and 10 hr.

The X-ray diffractions were measured by using a nickel-filtered copper radiation at 35 kV and 10 mA as the X-ray diffraction source, with a scanning speed of 1/2° per min., a time constant of 2 s, a divergence slit of 1°, and a receiving slit of 0.2 mm. The X-ray diffraction diagrams were recorded by means of an X-ray diffractometer (Geigerflex).

The electron micrographs were taken by means of a Hitachi HU-200-type electron microscope.

The specific surface areas were measured by the B.E.T. method from the nitrogen-gas adsorption at the temperature of liquid nitrogen. The specimens were pretreated under a pressure of 10^{-5} Torr at room temperature for about one hour.

Results and Discussion

The Results for Calcium Carbonate and α-CuPc Alone. Calcium carbonate is well known to have two crystal forms, such as a stable type (calcite) and a metastable type (aragonite) as morphisms at an ordinary temperature and pressure.[14] The X-ray diffraction traces in the grinding process of calcium carbonate are given in Fig. 1. The intensities of all the reflections in the X-ray diffraction diagrams decrease and become weaker during the grinding process. The prominent peak of calcite corresponding to the (104) crystal face decreases more than those of the others. The aragonite peaks are detected for the first time in the specimen ground for 6 hr. After 10 hr grinding, aragonite become the main component of the mixture.

The X-ray diffraction traces of α-CuPc at various stages of the mechanical treatment are given in Fig. 2.

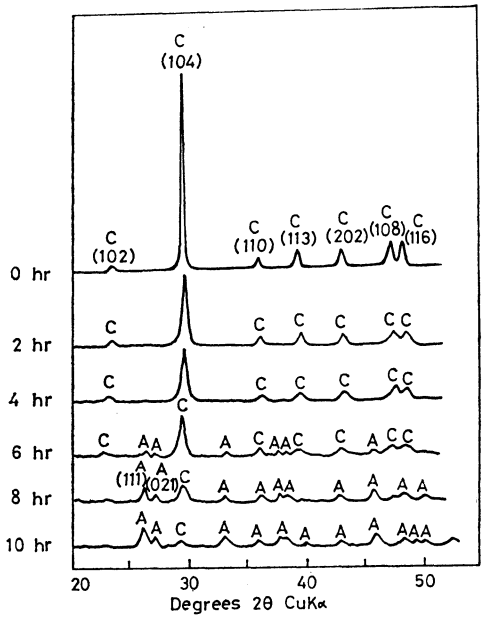


Fig. 1. X-ray diffraction patterns of $CaCO_3$ at different grinding times.

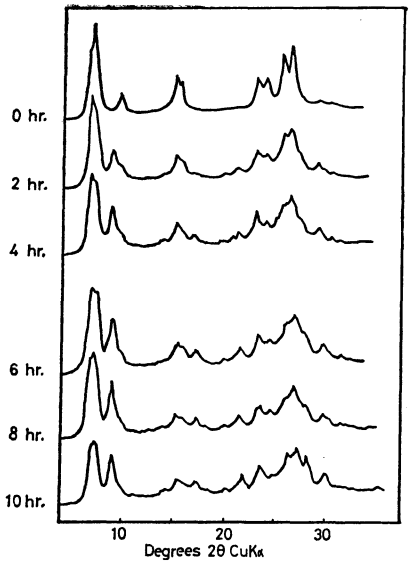


Fig. 2. X-ray diffraction patterns of α-CuPc at different grinding times.

The reflections characteristic of α-CuPc at the (200) and (002) crystal faces near 5°—8° in 2θ and four succesive medium reflections are observed to become broad with the grinding; they become hard to resolve in the specimen ground for 10 hr, much unlike the original situation. The reflection characteristic of β-CuPc corresponding to the $(20\bar{1})$ crystal face is observed in the specimen ground for 2 hr. In general, β-CuPc is known to be transformed to α-CuPc when comminution media are used.[15] However, α-CuPc may be considered to be transformed partially to the β-CuPc by absorbing the grinding energy.

The electron micrographs of the nongrinding specimens and the specimens ground for 10 hr of both calcium carbonate and α-CuPc alone are shown in Fig. 3. The micrograph of the calcium carbonate ground for 10 hr shows it to be finely divided particles. On the other hand, the particles of α-CuPc, compared with the case of calcium carbonate alone, aggregate considerably in the specimen ground for 10 hr. These facts are also confirmed by the specific-surface-area measurements.

The specific surface areas of both calcium carbonate and α-CuPc alone are plotted against the time of grinding in Fig. 4. It can be seen from this figure that the specific surface area of calcium carbonate gradually increases with the treatment, while that of α-CuPc decreases. Two factors may be considered to be the causes of the change in the specific surface area which take place in the process of grinding. One is associated with changes in the crystallite or particle size, the shapes of the particles, an dthe growth of cracks—that is, with primary structural changes. The other factor is related to the formation of secondary particles, which grow as a result of the aggregation or agglomeration of primary particles.[16] In the case of calcium carbonate alone, as has been described above, the particles are divided finely and no formation of secondary particles is observable. On the other hand, the specific surface area of α-CuPc may be considered to decrease with the grinding because of the aggregation.

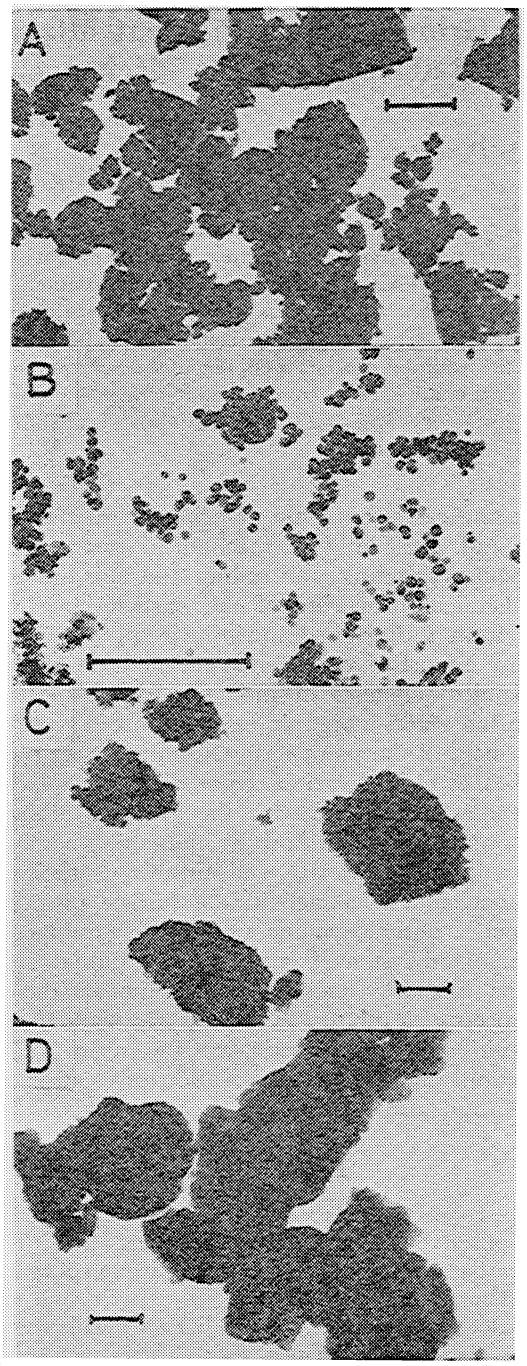


Fig. 3. Electron micrographs of $CaCO_3$ and α-CuPc. The linear dimension on the micrograph represents 1 μ.
A: original $CaCO_3$, B: $CaCO_3$ ground for 10 hr, C: original α-CuPc, D: α-CuPc ground for 10 hr.

The Results for Mixtures of Calcium Carbonate and α-CuPc. As with α-CuPc and calcium carbonate alone, the change in the surface properties of mixtures of several weight ratios of α-CuPc and calcium carbonate during the grinding process are estimated by a method similar to that used above.

The X-ray diffraction patterns of the mixtures (Samples A, B, and C) in the grinding process are given in Fig. 5. The reflections characteristic of α-CuPc in Sample A corresponding to the (200) and (002) crystal

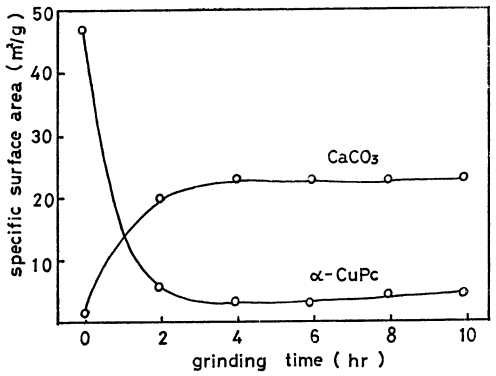


Fig. 4. The change of specific surface areas of α-CuPc and $CaCO_3$ with the time of grinding.

faces become broad, and the medium reflections at higher range become hard to resolve as the grinding proceeds. On the other hand, the (104) reflection of calcium carbonate in the mixtures does not decrease during the treatment more than in the case of calcium carbonate alone.

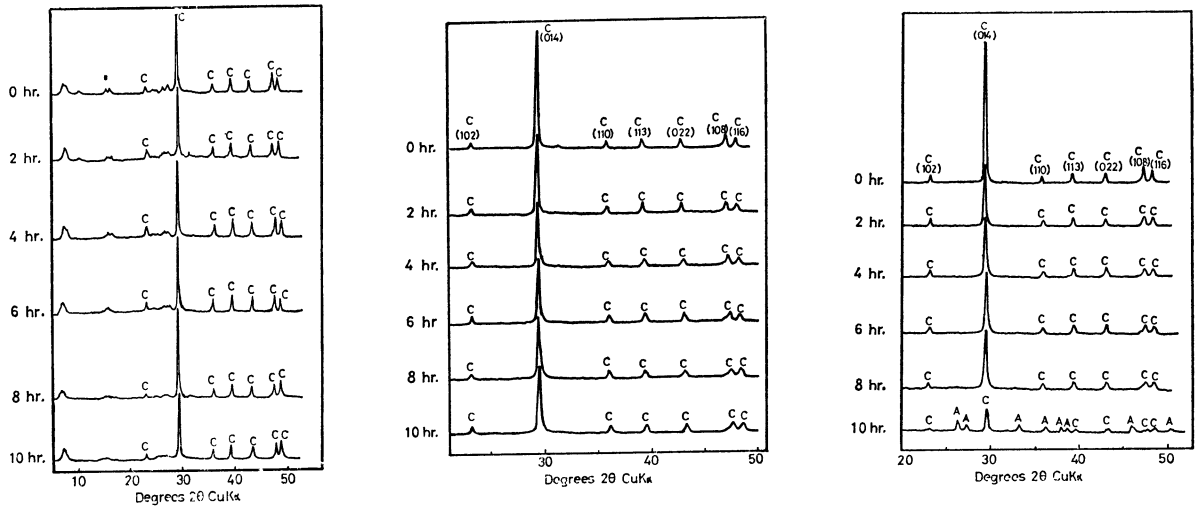
The calcite-aragonite transition is not observed in the specimen ground for 10 hr in Samples A and B; it is detected only in Sample C. The fact that the calcite-aragonite transition does not occur when the calcium carbonate is mixed with α-CuPc suggests that the calcium carbonate may be considered to be covered with α-CuPc; that is, the grinding of calcium carbonate may be interfered with by the lubricating action of α-CuPc. The strength of the lubricating action is also observed to increase with the amount of α-CuPc in the mixture system.

The electron micrographs of the specimens ground for 10 hr are shown in Fig. 6. In the case of Sample A, the particles of the mixture aggregate with each other, and the growth of secondary particles take place in the specimen ground for 10 hr, as in the case of α-CuPc alone. As is to be expected from Fig. 5-a, the calcium carbonate is also observed to be covered with α-CuPc and the grinding of calcium carbonate may be interfered with by the lubricating action of α-CuPc. In the case of Sample B, however, the ground particles of α-CuPc adhere around calcium carbonate particles. As is to be expected from the X-ray diffraction traces, the calcium carbonate in Sample C is ground considerably more than that of the other mixture systems. The electron micrograph of this specimen ground for 10 hr is similar to that of calcium carbonate alone in Fig. 3.

The calcium carbonate in the mixture is hardly ground more than calcium carbonate alone by the lubricating action of α-CuPc, judging from the results of the X-ray diffraction analysis and the observation of the electron micrographs. Consequently, though the specific surface area of calcium carbonate alone increases with grinding, the lubricating action of α-CuPc is expected to prevent an increase in the specific surface area of a mixture. Therefore, it is possible to determine the extent that the lubricating action of α-CuPc prevents the grinding of calcium carbonate by comparing the experimental curve with the theoretical one obtained by evaluating the specific surface areas of both α-CuPc and calcium carbonate alone, as based on the assumption of additivity.

The specific surface areas of mixtures are plotted against the time of grinding in Figs. 7, 8, and 9. It is interesting that the specific surface areas of Sample C gradually increase with the treatment, as with that of calcium carbonate alone, and those of Sample B decrease in the early stage of grinding and afterward gradually increase, while those of Sample A decrease, as with that of α-CuPc alone.

The experimental curves are observed to become lower than the theoretical one. This fact can be explained as follows. As has been described above, if the lubricating action of α-CuPc prevents the grinding of calcium carbonate, the specific surface area of calcium carbonate will not increase as the grinding continuos; that is, as the particle surfaces of calcium carbonate are covered with α-CuPc particles, aggregation is considered to occur. These facts agree with the results of the X-ray diffraction analysis and the electron-micrograph study.



a) sample A b) sample B c) sample C

Fig. 5. X-Ray diffraction patterns of mixtures at different grinding times.

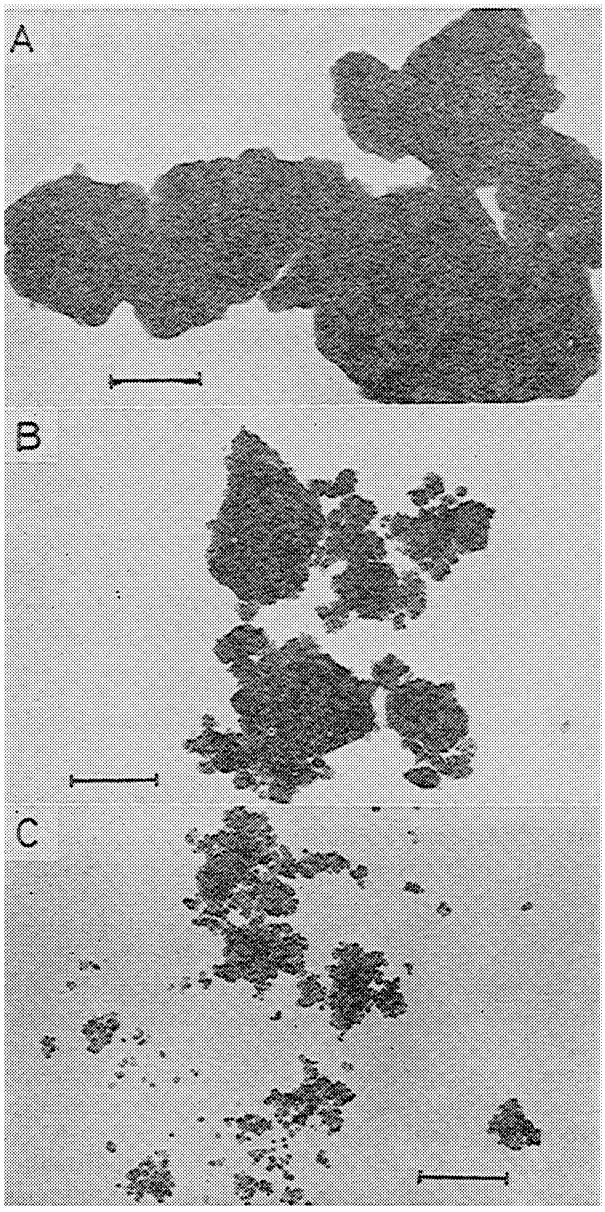


Fig. 6. Electron micrographs of ground mixtures.
The linear dimension on the micrograph represents 1 μ.
A: sample A ground for 10 hr, B: sample B ground for 10 hr, C: sample C ground for 10 hr.

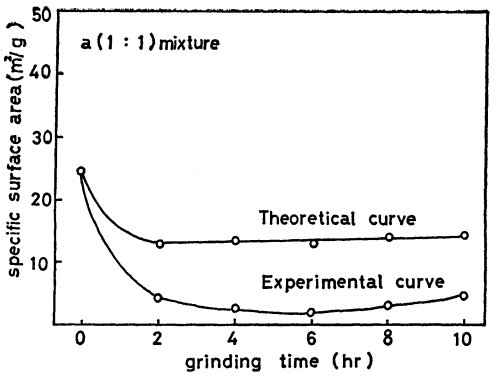


Fig. 7. The change of specific surface areas of sample A with the time of grinding.

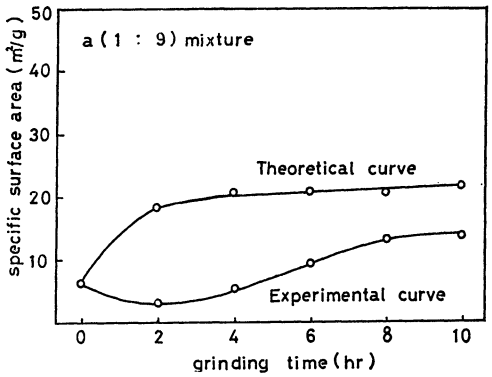


Fig. 8. The change of specific surface areas of sample B with the time of grinding.

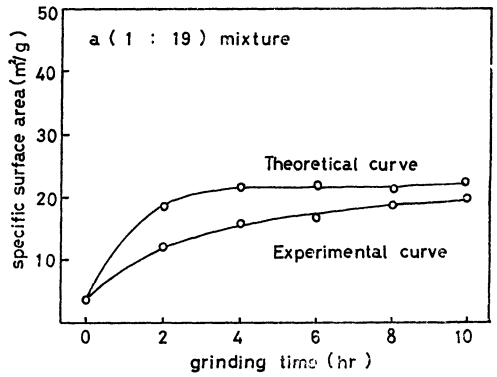


Fig. 9. The change of specific surface areas of sample C with the time of grinding.

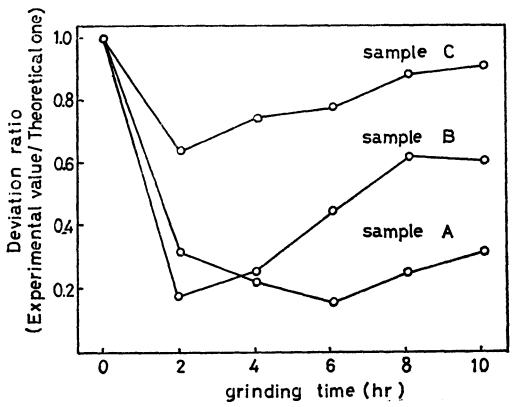


Fig. 10. The change in deviation ratio (Experimental value/Theoretical one) of pigment mixtures with the time of grinding.

The change in the deviation ratios (experimental value/theoretical one) for the mixtures with the time of grinding are shown in Fig. 10. The point at which the deviation ratio equals 1.0 coincides with the value at which the experimental value equals the theoretical one. That is, the lubricating action of α-CuPc is observed in the region in which the deviation ratio becomes lower than 1.0. The lubricating action of α-CuPc is observed in every mixture system, the order of the strength is as follows; Sample A>Sample B>Sample C.

The main conclusions obtained from these results are

as follows: when α-CuPc is mixed with calcium carbonate, the surface of the calcium carbonate is covered with that of α-CuPc, and the grinding of calcium carbonate is interfered with by the lubricating action of α-CuPc.

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