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Microencapsulation of Ultramarine Particles in Water/oil Emulsion and Surface Fractal Dimensionality of the Particles

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ABSTRACT

An approach to the microencapsulation of ultramarine particles in water-in-oil (W/O) emulsion was investigated. The surface shape of the particles was quantitatively characterized via the study of the surface fractal dimensionality. The results showed that there were ultramarine particles in the aqueous beads of W/O emulsion, and that microcapsulizing reactions took place on the surface of the particles, forming a membrane of silica gel capsules which covered the ultramarine particles. As a result, the acid-resistance of the ultramarine was effectively improved. The extent of the acid-resistance of the ultramarine corresponded to the surface fractal dimensionality. Thus the bigger the surface fractal dimensionality of the particles, the better the acid-resistance of the ultramarine. © *1997 Elsevier Science Ltd*

Keywords: ultramarine particle, inorganic pigment, microencapsulation, surface shape, fractal, dimensionality.

INTRODUCTION

Ultramarine is a nontoxic inorganic blue pigment and its application is wide. However, its acid-resistance is poor. It fades to give a grey colour even in environments that are weakly acidic. The formula of blue ultramarine is expressed as $Na_6Al_4Si_6S_4O_{20}$. However, both the colour and the chemical

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composition of different samples of ultramarine vary with differences in the proportions of the raw materials and with the production conditions. X-ray diffraction studies have shown that whatever their colours and components are, ultramarine samples have the same crystal lattice. Ultramarine, which has a cage–cavity structure, is an aluminosilicate containing sodium polysulphide.[1,2] The coloration of ultramarine is attributed to its particular crystal lattice and the location of the sodium polysulphide in the cavity. Its poor acid-resistance also results from this structure. For this reason, it is impossible to raise the acid-resistance of ultramarine by changing its interior construction.

Microencapsulation of ultramarine particles in an acid-resistant membrane is an effective method of improving the acid-resistance of ultramarine. After microencapsulation some changes to the surface shape of the particles, which is one of the factors that affects the acid-resistance of ultramarine, take place. Although the surface shape of the particles can be observed by electron microscopy, and the acid-resistance can be determined through measuring colour difference, the relationship between the surface shape and the acid-resistance has not been quantitatively characterized. In recent years, fractal theory has played an important role in the study of geometrical shapes of solid surfaces.[3,4] The surface fractal dimensionality of particles can quantitatively characterize the surface shape of solid particles. In this paper the microcapsulizing mechanism of microencapsulation of particles of ultramarine, and the relationship between the acid-resistance of ultramarine and the surface fractal dimensionality of its particles, are discussed.

EXPERIMENTAL

Microencapsulation and photomicroscopy of particles

Microencapsulation was realized in three steps. The first of these was the preparation of the liquid/liquid emulsion. An aqueous solution of Na_2SiO_3 was added to a solution of petroleum or petroleum ether containing the emulsifier Span 80. The mixture was fully stirred to form a water-in-oil (W/O) emulsion (a liquid/liquid emulsion). Secondly, the powdered ultramarine was dispersed with a small amount of an aqueous solution of Na_2SiO_3 to form a suspending liquid. The above liquid was added to the emulsion made in the first step and the mixture fully stirred to form a W/O emulsion containing particles of ultramarine (a solid/liquid/liquid emulsion). Finally, an aqueous solution of NH_4Cl was added to the above solid/liquid/liquid emulsion and the newly formed mixture stirred. After de-emulsification, the solid settled to the bottom of the vessel. This solid was separated from the liquids, washed

with water, filtered and dried. Observations were made with an OLYMPUS CH-2 microscope at specific stages in the process described above and photographic records were taken simultaneously.

Acid-resistance experiments and colour difference measurement

The original powder and microcapsulized samples (0.5 g each) were individually mixed with a mixture of TiO_2 (0.3 g) and an alkyd paint (3.0 g), respectively. The above mixtures were ground and deposited on slides, allowed to settle for 30 min, dried at 110°C and cooled to room temperature. Half of each of these samples (together with the slide) was soaked into a sulphuric acid solution of 1 mol dm^{-3} at 50°C. After a specific period of time, they were taken out, washed with water and dried in air. The value of the colour difference between the soaked and the unsoaked section of each sample (ΔE) was measured with a JFY-ABI colorimeter.

Surface shape of ultramarine particles, and fractal dimensionality aspects

Observation of the surface shape of the ultramarine particles was made with a PHILIPS EM400ST transmission electromicroscope and photomicrographs were taken simultaneously. Computerized procedures for pattern recognition were employed. The surface fractal dimensionality D was then determined; data relevant to this will be reported separately.

RESULTS AND DISCUSSION

Microencapsulation of ultramarine particles

Microencapsulation of the ultramarine particles was achieved through reaction in a W/O emulsion which contained ultramarine particles in their Na_2SiO_3 aqueous solution beads. These beads acted as "microreactors" in the microcapsulizing reaction in the W/O emulsion.[5,6] For this purpose, a suitable W/O emulsion of solid/liquid/liquid must first be prepared.

Ultramarine is an inorganic substance and its particles are hydrophilic. In the W/O emulsion, ultramarine particles may be in the aqueous beads. However, the density of ultramarine is obviously higher than that of the oil. Thus, it is difficult to acquire a W/O emulsion containing ultramarine particles in their aqueous beads in one step. Therefore the emulsion was prepared in stages, as described above. The viscosity of the system increased along with the formation of the liquid/liquid emulsion in the first step. Then ultramarine, dispersed in a solution of Na_2SiO_3 beforehand, was added to this

emulsion. After fully stirring ultramarine particles entered the beads in the W/O emulsion. By this time, the "microreactors" were formed. The photomicrographs of the liquid/liquid emulsion and solid/liquid/liquid emulsion are given in Fig. 1. When an aqueous solution of NH_4Cl was added to the emulsion, the former penetrated through the oil phase into the beads. Then NH_4Cl reacted with Na_2SiO_3 to form silica gel membrane on the surface of the ultramarine particles in the "microreactors", and the particles were capsulized. This reaction did not occur in the oil phase.

Such a capsulizing method is superior to that of direct reaction in a suspending liquid containing ultramarine particles, Na_2SiO_3 and NH_4Cl, for most of the silica gel formed during the reaction in the emulsion was on the surface of the ultramarine particles as the component of the membrane. However, a lot of silica gel formed during the reaction in the suspending liquid was free and did not form capsules on the ultramarine particles. The free silica gel is not only useless to the strengthening of the acid-resistance of ultramarine, but also reduces the saturation of the ultramarine.

Colour difference, acid-resistance, surface shape and fractal dimensionality

The original sample and three microcapsulized ultramarine samples (the amounts of the reactants were the same and their concentrations were different in the preparations) were soaked in acid at the same time. In 3 min the original sample faded to greyish white, but the colour of the others did not alter significantly. After the samples had been soaked for 40 min, values of colour difference (ΔE) between the soaked part and the unsoaked part of each sample were measured. The results are listed in Table 1. The lesser the value of ΔE, the better the acid-resistance of the sample, and vice versa. Sample No.3 has the best acid-resistance and the original sample has the worst.

Figure 2 gives the transmission electron microscopy (TEM) photographs of a particle of the original sample (a) and a particle of a microcapsulized

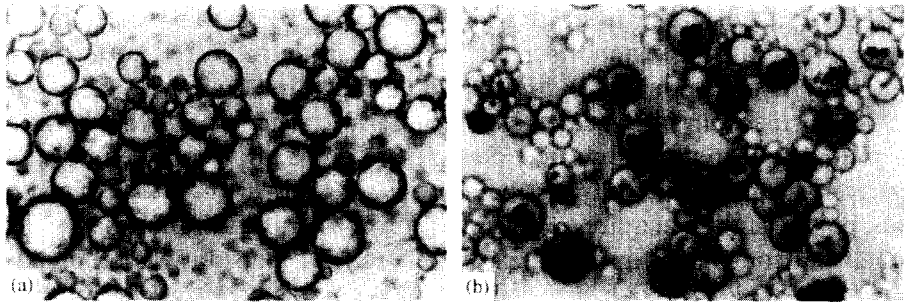

Fig. 1. Microphotographs of emulsions. (a) Liquid/liquid emulsion. (b) Solid/liquid/liquid emulsion.

sample (b). Other TEM photographs of the original and the microcapsulized samples were taken. It can be seen from these photographs that the particles of the microcapsulized samples have membranes covering their surface, and that these membrane are composed of silica gel formed during the reaction between NH_4^+ and SiO_3^{2-}. These membranes prevent the samples from being attacked by acid. The microcapsulized ultramarine showed good acid-resistance. However, the particles of original sample have no membrane and showed poor acid-resistance.

From the TEM photographs mentioned above it can be seen that the surface of the ultramarine particles is not regularly two-dimensional, but quasi-tri-dimensional and complex. Also, parts of their surface are similar to the whole, i.e. this kind of surface has the property of self-similarity and can be considered as a fractal surface. Its shape can be quantitatively characterized with surface fractal dimensionality (D). The surface dimensionalities of the original and the microcapsulized samples are also listed in Table 1.

TABLE 1
Colour Difference (ΔE) and Surface Dimensionality (D)

Samples	*Original*	*Microencapsulation*		
		No. 1	*No. 2*	*No. 3*
ΔE/NBS	18.255	11.871	2.067	1.618
D	2.277	2.316	2.370	2.385

Fig. 2. TEM photographs of particles. (a) Original sample. (b) Microcapsulized sample.

It can be inferred that the bigger the D value of a sample, the better its acid-resistance. This conclusion can be explained as follows: The process of formation of surface shape is a growing process involving fractals. During microcapsulizing the growth of fractals of silica gel particles on the surface of ultramarine particles leads to the growth of silica gel villi sticking out like branches. These villi criss-cross with each other to form a membrane, which increases the degree of roughness and complexity of the surface. The more the villi are formed on the surface of the ultramarine particles, the higher the degree of criss-crossing; the larger the D value (which reflects the complex nature of the surface shape), the better the acid-resistance of the ultramarine. That is, the acid-resistance of the microcapsulized ultramarine with silica gel increases with the increase of the fractal dimensionality of the surface of the corresponding ultramarine particles.

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