September, 1983] Bull. Chem. Soc. Jpn., 56, 2569—2571 (1983)

Surface Treatment of Inorganic Pigments by N^ε-Acyllysine

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(Received February 2, 1983)

Inorganic pigments(calcium carbonate, iron oxide, and titanium dioxide) were treated with N^ε-lauroyl-L-lysine, which is almost insoluble in both polar and nonpolar solvents. Two methods were employed for the treatment: (1) grinding of various weight proportional mixtures of pigment and the *N*-acyllysine; (2) adsorption of the *N*-acyllysine from its calcium ethylate solution on pigment. In method(1), the sufficient hydrophobic treatment was made when the weight percent of the *N*-acyllysine in the mixture was above about 30%. On the other hand, in method(2), although the amount adsorbed of the *N*-acyllysine was about in the range of 10^{-6} mol/g, the treated pigment showed a hydrophobicity. The critical surface tension of the treated samples estimated by using various mixtures of methanol and water was in the range from 23 to 39 dyn/cm.†

The surface treatment of solids[1—3], especially pigments, by surface active agents, polymers, and coupling agents are very important for preparing a good dispersion in the paint and printing industries. However, the above methods are not always suitable due to the detachment of the treating agents from the pigments in suspensions.

In general, it is known that amino acids and their derivatives[4,5] show surface activities for modifying wettability of solids. Especially, N^ε-Acyllysine is an interesting material because it is insoluble in both ordinary polar and nonpolar solvents due to its strong hydrogen bonding within the molecules. If the *N*-acyllysine could be applied to treat surface of pigments, a strong coating would be expected without detaching the *N*-acyllysine from the treated surfaces.

In this work, surface treatment of inorganic pigments by an *N*-acyllysine such as N^ε-lauroyl-L-lysine is described.

Experimental

Materials. The pigments used in this study were calcium carbonate (calcite) supplied by Kokusan Chemicals Co., Ltd., and iron oxide (R-110-A) and titanium dioxide (rutile) supplied by Titan Kogyo Co., Ltd.

N^ε-Lauroyl-L-lysine prepared from lauric acid and L-lysine[6] was kindly supplied by Ajinomoto Co., Ltd. This structural formula is shown as follows:

$$n\text{-}C_{11}H_{23}CONH(CH_2)_4CH(NH_2)COOH.$$

Calcium ethylate[7] was prepared by heating calcium chloride and ethyl alcohol together until calcium chloride completely dissolved.

Apparatus and Procedure. Two methods were employed for the surface treatment of pigments by N^ε-lauroyl-L-lysine.

(1) The Coating by Grinding: Calcium carbonate and N^ε-lauroyl-L-lysine were ground together in various proportions (total weight, 20 g) by a grinder (Type AOA of Ishikawa Kojo Co.). The various proportions of calcium carbonate to N^ε-lauroyl-L-lysine were as follows: sample No. 1, 1:10; No. 2, 1:5; No. 3, 1:3; No. 4, 1:2; No. 5, 1:1; No. 6, 2:1; No. 7, 3:1; No. 8, 5:1; No. 9, 10:1. The change of crystal form of the ground samples was measured by X-ray diffraction consisting of a Geigerflex diffractometer with nickel filtered copper radiation. The specific surface areas of the ground samples were measured by a Sorptograph Model ADS-1B (Shimadzu Seisakusho Co., Ltd.). To measure the sedimentation volume of the ground samples, water was added to 1 g of the ground sample in a 30 ml graduated cylinder to adjust a total volume of 30 ml.

(2) The Coating by Adsorption of N^ε*-Lauroyl-L-lysine from Its Calcium Ethylate Solution*: One gram of pigment was placed in a L-shaped test tube and N^ε-lauroyl-L-lysine solution of calcium ethylate was added. Then the L-shaped test tube was shaken at 25 °C. After at leat 2 h, having reached adsorption equilibrium, the sample was separated by centrifuging and dried *in vacuo*. The amount of N^ε-lauroyl-L-lysine adsorbed was determined from the difference of the concentrations of N^ε-lauroyl-L-lysine before and after the adsorption, by means of an UV spectrophotometer (Type ESP-3T of Hitachi).

The critical surface tension of the pigment coated with N^ε-lauroyl-L-lysine was estimated by using various mixtures of methyl alcohol and water at 20 °C.[8]

Results and Discussion

(1) The Coating by Grinding. The intensities of all the reflections of calcium carbonate alone in the X-ray diffraction diagrams decreased and became weaker during the grinding process. Similarly, all the reflections of N^ε-lauroyl-L-lysine alone decreased with the grinding time. Further, although the X-ray diffraction measurement was carried out on the ground samples of calcium carbonate and N^ε-lauroyl-L-lysine, the change of crystal forms of the ground samples was difficult to estimate due to a remarkable difference of their intensities. Since the original crystal forms of calcium carbonate and N^ε-lauroyl-L-lysine were not changed by up to 1 h grinding, the grinding time was taken as 1 h to study an effect of coating without considering any crystal transformation.

The specific surface areas of all the ground samples are plotted against the weight percent of N^ε-lauroyl-L-lysine, as shown in Fig. 1. The specific surface areas of the ground samples had a minimum value and increased gradually with an increase of content of N^ε-lauroyl-L-lysine in the mixture; finally they reached the value of N^ε-lauroyl-L-lysine alone. This might be interpreted by assuming that the grinding of calcium carbonate is interfered with by the addition of N^ε-lauroyl-L-lysine and the calcium carbonate becomes

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† 1 dyn $=10^{-5}$ N.

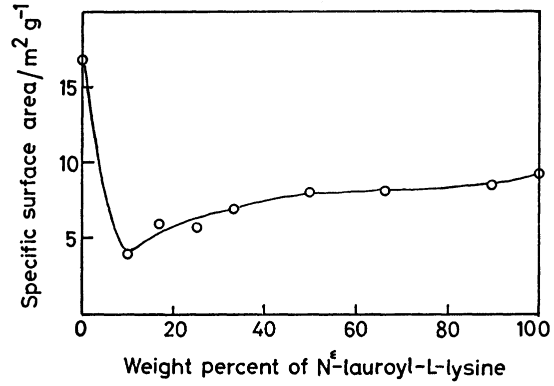

Fig. 1. Specific surface areas of ground samples as a function of weight percent of N^{ε}-lauroyl-L-lysine.

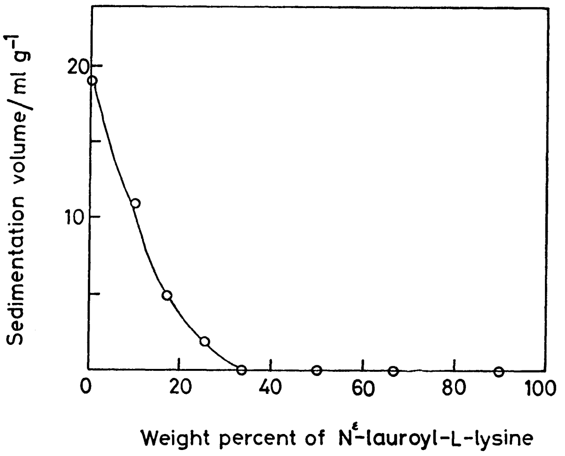

Fig. 2. Sedimentation volumes of ground samples as a function of weight percent of N^{ε}-lauroyl-L-lysine.

covered with N^{ε}-lauroyl-L-lysine with an increase of the amount of N^{ε}-lauroyl-L-lysine.

Figure 2 gives the sedimentation volume of all the ground samples in water *vs.* the weight percent of N^{ε}-lauroyl-L-lysine in the mixtures. Calcium carbonate alone completely sedimented, while N^{ε}-lauroyl-L-lysine formed a compact layer at the air/water interface. In the mixtures from No. 1 to No. 6, the particles were attached to the air/water interface like N^{ε}-lauroyl-L-lysine alone. The sedimentation of particles was observed distinctly in mixture No. 7, and further the volume ratio of the floating particles to the sedimented ones was nearly unity in mixture No. 9. Here, all the sedimented particles were confirmed to be calcium carbonate by the X-ray diffraction measurement. Thus, the above results indicate that when the weight percent of N^{ε}-lauroyl-L-lysine in the mixture is above about 30%, the efficient coating for calcium carbonate can be obtained which will show a strong hydrophobicity like N^{ε}-lauroyl-L-lysine alone.

(2) The Coating by Adsorption of N^{ε}*-Lauroyl-L-lysine from Its Calcium Ethylate Solution.* Figure 3 shows the adsorption isotherms of N^{ε}-lauroyl-L-lysine on pigments at 25 °C. It can be seen from Fig. 3 that, except for iron oxide, the amount of N^{ε}-lauroyl-L-lysine adsorbed increases with an increase of the concentration of N^{ε}-lauroyl-L-lysine. In the case of calcium carbonate, the adsorption isotherm follows a Langmuir type. Also, Fig. 3 gives the adsorption isotherms of N^{ε}-lauroyl-L-lysine on each pigment by the addition of water(5 vol%) into the solution. In all cases, the amount of N^{ε}-lauroyl-L-lysine adsorbed was enhanced compared with that for no addition of water. This result can be explained as a lowering of the solubility of N^{ε}-lauroyl-L-lysine in calcium ethylate solution by the addition of water. Further, the area occupied per molecule of N^{ε}-lauroyl-L-lysine on the pigment at the equilibrium concentration of 3 mmol dm^{-3} is obtained and their values are listed in Table 1. It is found that the area occupied for calcium carbonate is smaller than that for the other pigments, indicating that N^{ε}-lauroyl-L-lysine molecules on calcium carbonate are much more "collapsed" than that for the others. This difference might be interpreted by the acid-base property of pigments.

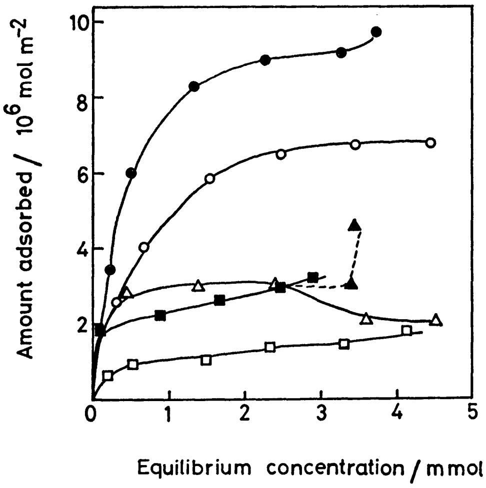

Fig. 3. Adsorption isotherms of N^{ε}-lauroyl-L-lysine on pigments: no addition of water; ○ $CaCO_3$, △ α-Fe_2O_3, □ TiO_2, addition of water (5 vol%); ● $CaCO_3$, ▲ α-Fe_2O_3, ■ TiO_2.

Table 1. The area occupied per N^{ε}-lauroyl-L-lysine molecule on pigments

Pigment	Area occupied/Å^2 (I)	Area occupied/Å^2 (II)
Calcium carbonate	24.6	18.0
Iron oxide	67.0	53.2
Titanium dioxide	125.8	51.9

(II) lists the values obtained by the addition of water.

Generally, it is known[9] that calcium carbonate is a basic pigment, while the others(iron oxide and titanium dioxide) are neutral or acidic. As the pH of the N^{ε}-lauroyl-L-lysine solution in this study ranges between 4.5—5.0, it is anticipated that the adsorption capacity of N^{ε}-lauroyl-L-lysine on calcium carbonate can be enhanced by the acid-basic interaction.

(3) Wettability of the Pigment Coated by N^{ε}*-Lauroyl-L-lysine.* The results of wettability experiments for the pigment coated by the adsorption of N^{ε}-lauroyl-L-lysine are given in Fig. 4. The critical surface

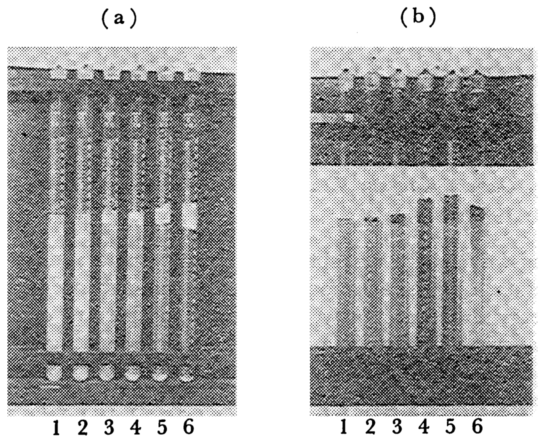

Fig. 4. Results of wettability experiments in aqueous methanol solutions: (a) calcium carbonate, (b) iron oxide; surface tension(dyn/cm), 1=23, 2=30, 3=39, 4=50, 5=60, 6=71.

tension of the pigment coated by N^{ε}-lauroyl-L-lysine was determined by using a series of aqueous methanol solutions. The pigment coated by N^{ε}-lauroyl-L-lysine became completely wet in solutions with surface tension below its critical surface tension. The critical surface tension of calcium carbonate coated with N^{ε}-lauroyl-L-lysine (No. 1—6) by grinding and by the adsorption had almost the same value, ranging between 30 and 39 dyn/cm. Also, the critical surface tension of iron oxide coated with N^{ε}-lauroyl-L-lysine by the adsorption was in the range between 23 and 30 dyn/cm.

Although the wettability of calcium carbonate coated with N^{ε}-lauroyl-L-lysine is not so different for the two methods, there is an extraordinary difference of the amount of N^{ε}-lauroyl-L-lysine required to render the surface hydrophobic sufficiently; the amount required by grinding is about 1.3 mmol/g, while that by the adsorption ranges as low as 10^{-3} mmol/g.

It is very important to elucidate how strong the attachment of N^{ε}-lauroyl-L-lysine is against organic solvents, to determine the stability of coating. So, the following test was carried out to estimate the strength of coating of N^{ε}-lauroyl-L-lysine on the pigment; the iron oxide coated with N^{ε}-lauroyl-L-lysine by the adsorption was treated in toluene at its boiling point for 10 min and then the sample was dried in a vacuum oven to eliminate toluene. The critical surface tension of the treated sample was then determined by the previous method. If N^{ε}-lauroyl-L-lysine is removed from the coated sample by the above treatment, the critical surface tension of the treated sample would show a higher value compared with that for the untreated sample. In this experiment, the critical surface tension of the treated sample showed almost the same value as that without the treatment. This result shows that the attachment of N^{ε}-lauroyl-L-lysine on the iron oxide is strong enough against the toluene treatment.

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