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PREPARATION OF RED ORGANIC PIGMENT WITH SILICA GEL AS CORE

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Red organic pigment with silica gel as core was prepared by deriving the surface silanols of silica gel to the structure similar to azo dyestuff, such as Sudan I. The surface silanols were esterified with phenylmethanol, and the introduced phenyl group was nitrated, reduced, diazotized and coupled with 2-naphthol as shown in Fig. 1. The prepared pigment showed approximately same color as Sudan I.

Generally, organic pigments are excellent in color but do not have good resistance to solvent, water, heat and light. To overcome these defects, organic pigment with silica gel as core was prepared by synthesizing the organic dye on silica gel surface. The merits of this pigment preparation are to be able to regulate particle size and hiding power by selecting size and kind of used core oxides or hydroxides.

The pigment was prepared by esterification, nitration, reduction, diazotization and coupling as follows:

Esterification Four kinds of methods[1)] were reported as the esterification method of the surface silanols of silica gel by alcohol treating, but in this experiment the reflux method was used in a similar manner to the previous reports[2,3)]: 50 g of silica gel (Wako pure chemical industries' Wakogel C-200) was added to the mixture of 100 g of phenylmethanol and 200 g of tetradecane, and was refluxed under stirring for 5 hours. Then the contents were filtered, washed with benzene and acetone and vacuum dried (50°C), and was called as esterified sample.

Nitration 40 g of the esterified sample was added slowly in mixed acid (mixed solution of 100 ml conc. nitric acid and 100 ml conc. sulfuric acid), and was stirred for 20 minutes at 60°C. Then the contents were immediately cooled by adding into a lot of water, and was filtered, washed with water (untill the filtrate became approximately neutral) and acetone, and vacuum dried (50°C). The product was called as nitrated sample.

Reduction 35 g of the nitrated sample was added in mixed solution of 300 ml of 1 mol/l-tin(II) chloride-conc. hydrochloric acid solution and 50 ml of methanol, and was refluxed for 10 minutes under stirring. Then the content was filtered, washed and dried in a similar manner as nitration. The product was called as reduced sample.

Diazotization and coupling

Diazotization was carried out as follows: 30 g of the reduced sample was dispersed into 250 ml of 2 mol/l-hydrochloric acid, and 50 ml of 2 mol/l-sodium nitrite aqueous

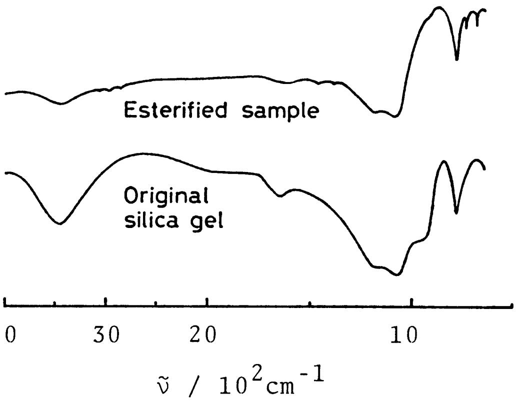

Fig. 2 IR spectrum of esterified sample

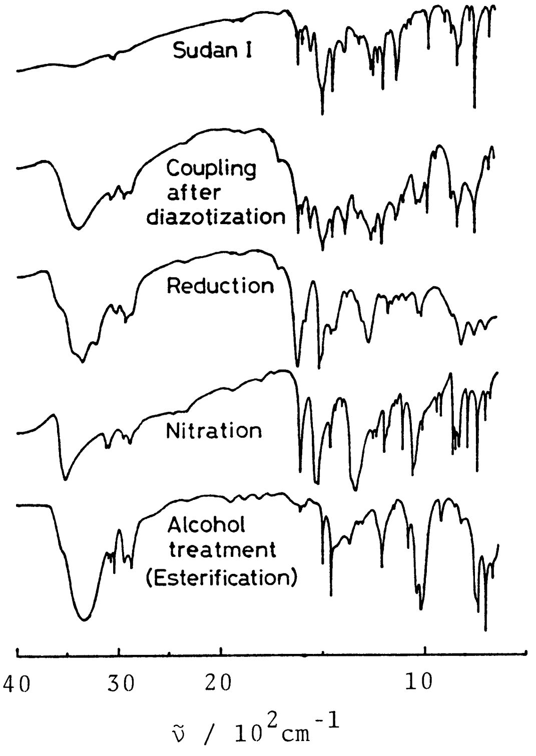

Fig. 3 IR spectra of the surface groups on silica gel

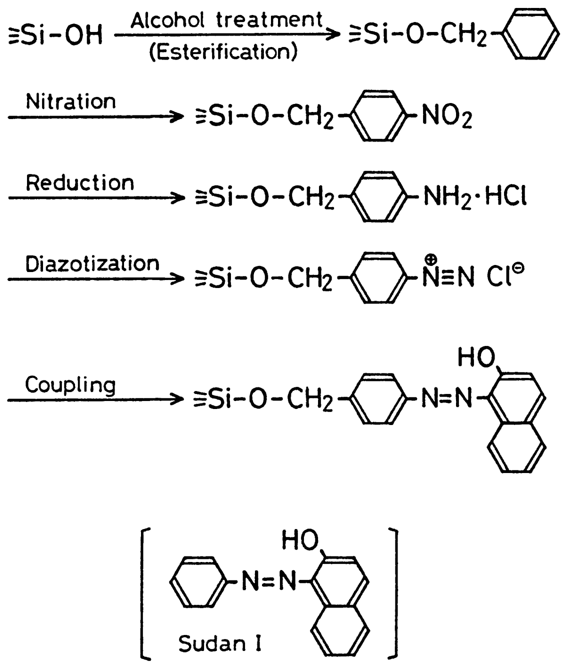

Fig. 1 Preparation process

solution was slowly added (keeping the temperature under 10°C). Separately, 28.8 g of 2-naphthol was dissolved in 250 ml of 2 mol/l-sodium hydroxide aqueous solution, and was cooled to 5°C, then coupling was carried out by adding slowly the diazotized suspension under stirring under 10°C and maintaining the condition for 10 minutes. During the coupling procedure it is necessary to keep the suspension under weak alkaline condition, because 2-naphthol might be freed in acid condition and silica gel might be dissolved in strong alkaline condition. The alkalinity of the suspension was adjusted with dilute hydrochloric acid, if necessary. After these treatment the organic matters, which were not bonded to silica gel, were dissolved by adding 200 ml of acetone to this suspension and the suspension was filtered and washed well with water (untill the filtrate became approximately neutral) and with acetone, and vacuum dried at 50°C. The product was called as pigmented sample.

As the result of IR spectra, the esterified sample exhibits the 3030, 2960-2850, 1500-1350, 750 and 700 cm^{-1} bands which are attributed to the aromatic nucleus or methylene chain, respectively, and the strength of a 950 cm^{-1} band corresponding to the surface silanols of silica gel4) decreased, as shown in Fig. 2. So we presume that the surface silanols were esterified.

The occupied area of surface alkoxy group calculated from carbon content (Table 1) was 3.67×10^{-19} m^2. This value agreed with the occupied area of a molecule of benzene adsorbed on silica at 20°C.5) So it was presumed that the surface alkoxy groups of the esterified sample were distributed vertically on silica gel, and the surface of silica gel was coated completely. This sample showed organophilic and hydrophobic property.

For the identification of the surface groups of the nitrated, reduced and pigmented samples, IR spectra were measured on alcohols which were prepared by

Table 1 Results of ultimate analysis

	Carbon (%)	Nitrogen (%)
Esterified sample	11.66	——
Nitrated sample	7.04	1.02
Reduced sample	2.59	0.13
Pigmented sample	2.67	0.15

strongly hydrolyzing the samples of each stage. The results were shown in Fig. 3. The nitrated sample was found to exhibit bands at both 1520 and 1340 cm^{-1} and 870 cm^{-1} positions, the former two bands are due to aromatic nitro group and the latest one to C-N stretching vibration. In the reduced sample, the bands of nitro group disappeared and the bands due to asymmetric and symmetric N-H stretching, N-H bending and C-N stretching vibration of aromatic primary amine newly appeared in 3450, 3350, 1620 and 1280 cm^{-1} positions. The absorption pattern of the pigmented sample showed the same pattern to Sudan I, with exception of the bands due to methylene chain and primary alcohol.

As the results, alkoxy group introduced onto silica gel by esterification was derived finally to the structure similar to Sudan I, azo dyestuff, as shown in Fig. 1. But Table 1 showed that the amount of surface groups decreased with each treatments and hydrolysis took placed on this occasion. However the color of the pigmented sample prepared by this experiment showed approximately same color as Sudan I.

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