Preparation of Iron phthalocyanine derivatives and their adsorption properties on cotton

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1. INTRODUCTION

Recently, metal complexed phthalocyanine(MPc) derivatives have been investigated with a great attention. In addition to blue or green colorants for LCD color filter, enzyme-like catalytic functions of MPc derivatives those contain carboxylic acid groups could be applied as odor-removing systems and antibactericidal systems[1-3]. In this study, four kinds of phthalocyanine derivatives were synthesized and evaluated their properties.

2. EXPERIMENT

2.1 Materials

Trimellitic anhydride, Pyromellitic dianhydride, 4-nitrophthalimide, Urea, Ferric chloride, Ammonium molybdate, 2-Nitrotoluene, sodium hydroxide, c-HCl were used for this study.

2.2 Milling for exhaustion

Four synthesized MPc derivatives were prepared for application to cotton fiber by means of a WSD-13 sand mill (Woo seong co., Korea). MPc derivatives as well as the dispersing agents UL-NA(Borregaard, Norway) and Reax-85A (Westvaco, USA) were stirred in water at room temperature for 1hr and then circulated in the mill at room temperature for 3hr.

2.3 Exhaustion and soaping procedure

Traditional dyeing method was employed as exhaustion treatment of MPc on cotton fiber. Treatment was carried out under follow condition; 2% o.w.f. of MPc concentration, 90℃X60min, NaCl 25g/l, Na_2CO_3 45g/l. After exhaustion, treated cotton fiber was washed by 60℃ hot water containing 4g/l soaping agent.

2.4 Measurement of adsorption properties

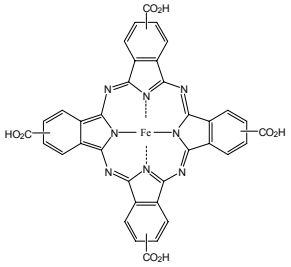
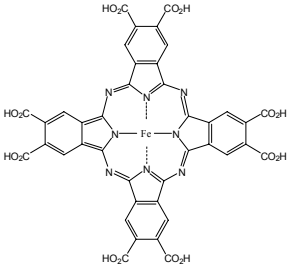
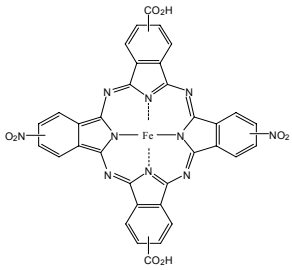
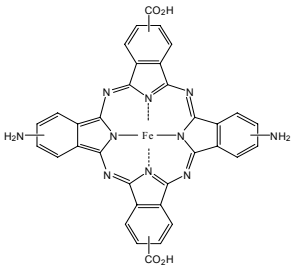
The adsorption properties of cotton treared by MPc were evaluated by K/S values measured with a CCM(X-rate 8000, USA).

3. RESULT & DISCUSSION

3.1 Synthesis of Iron phthalocyanine derivatives

Four kinds of MPc derivatives were synthesized in this study(table 1). Three derivatives, such as tetracarboxylic iron phthalocyanine, octacarboxylic iron phthalocyanine, dinitro dicarboxylic iron phthalocyanine were synthesized by the following procedures.

Table 1. Chemical structure of synthesized MPc

Tetracarboxylic lron phthalocyanine	Octacarboxylic lron phthalocyanine
	
Dinitro dicarboxylic lron phthalocyanine	**Diamino dicarboxylic lron phthalocyanine**
	

The mixture of reagents and solvent(2-nitrotoluene) was stirred uniformly, heated up to 190~195℃ and maintained for 5 hours. The color of reaction mixture gradually deepened and finally a greenish solid was obtained. From the reaction mixture, solvent was distilled off by a reduced pressure, then precipitates were filtered and washed with methyl alcohol. After filtration, the wet cake was added into 5% aqueous sodium hydroxide solution and hydrolyzed for 24 hours with a

refluxing. After cooling to room temperature, c-HCl was added into the above solution within temperature of around 30℃, then further stirring was carried out for 1 hour at room temperature. After filtration, the solid was subsequently washed with plenty of hot water until free from salt in the product. Filter cake was dried in oven at 90℃ for 16 hours. As reagents used above, trimellitic anhydride, 4-nitrophthalimide, urea, ferric chloride, ammonium molybdate were used for dinitro dicarboxylic iron phthalocyanine. Tetracarboxylic iron phthalocyanine and octacarboxylic iron phthalocyanine were prepared from trimellitic anhydride, urea, ferric chloride, ammonium molybdate and pyromellitic dianhydride, urea, ferric chloride, ammonium molybdate as starting materials, respectively.

Diamino dicarboxylic phthalocyanine was prepared starting from dinitro dicarboxylic phthalocyanine analogue. Dinitro dicarboxylic phthalocyanine was dispersed in water and sodium sulfide nonahydrate was gradually added. The suspension was heated up to between 70 and 75℃ with stirring for 10 hours. After cooling to room temperature, c-HCl was added and pH was controlled to between 1 and 2 then further stirring carried out for 1 hour without heating. After filtration, the solid was washed with plenty of hot water until free from salt in the product.

Structural analysis was carried out by a Mass and an Elemental Analysis for prepared phthalocyanines. Improved affinity of phthalocyanines synthesized to the polymers containing hydroxyl groups was observed.

3.2 Analysis of particle size

Average particle sizes of MPc were below 300nm after milling.

3.3 Adsorption properties on cotton

K/S values of MPc on cotton fiber were given in Fig. 1. By comparing of K/S values, octacarboxylic lron phthalocyanine had the highest value as 15.5 while the lowest values was shown on dinitro dicarboxylic lron phthalocyanine as 1.5. It may be ascribable to the number of carboxyl groups.

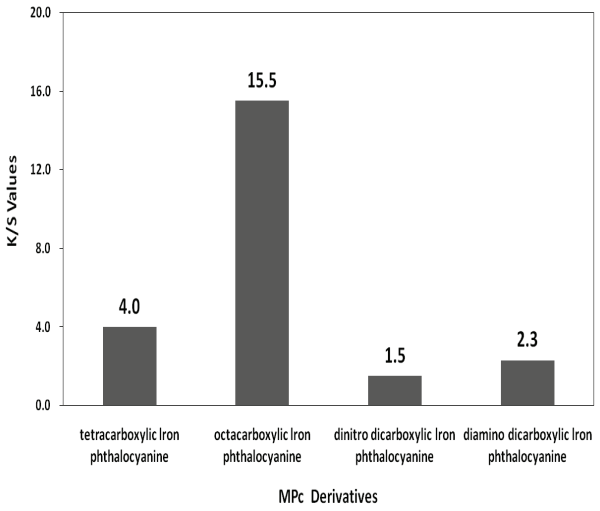


Fig. 1. K/S Values of MPc on cotton fiber

4. CONCLUSION

Four Iron phthalocyanine derivatives were synthesized and analyzed by a MASS and an Elemental Analysis. After milling of MPc, average particle sizes were below 300nm. Synthesized MPc derivatives were adsorbed on cotton fiber by traditional dyeing method.

The K/S value of octacarboxylic lron phthalocyanine was greatest in comparison with other MPc for the exhaustion on cotton fiber.

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