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### Removal of ethanethiol by mordant-dyed cotton and wool fabrics

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The objective of the study presented in this thesis is to elucidate the removal mechanism of ethanethiol for copper mordant-dyed cotton and wool fabrics by investigating the removal rate for the some sample fabrics.

In the first of this thesis, Chapter 2, the characterizations of mordant-dyed cotton and wool sample fabrics were described. Various mordant-dyed cotton and wool fabrics were prepared by using C. I. Direct Red 28 (Congo red) as a model dye and a copper salt. The dye and the copper uptakes were measured, and the copper states in the fibers were analyzed spectroscopically. It was found that two types of copper ions exist, i.e., the copper ions coordinated to the dye molecule (dye type) and bound electrostatically to carboxyl groups of the fibers (carboxyl type). The former was mainly supported in cotton fabrics while the latter was in wool fabrics. By spectroscopic approach, the presence of the coordination for copper and dye was confirmed. In the followed Chapters 3 to 5, removal of ethanethiol by fabric samples were experimentally investigated. In Chapter 3, the effects of the differences in the kind of fibers on the removal behavior of ethanethiol were examined using the copper mordant-dyed cotton and wool fabrics. The residual concentration curves of ethanethiol with time, and the apparent removal rate evaluated from the semilogarithmic plots for the curves were obtained. The results showed that there was no simple relationship between the removability and the copper uptake, and the moisture of the sample fabric around (humidity) may affect the removal rate. Post-mordant dyed cotton fabrics exhibited fast-slow type of the apparent rate, while wool fabrics showed slow-fast type. The rate property depended on the kind of fiber species. The slow-fast type was a specific behavior that was observed for the first experiment for the mordant dyed wool fabrics. To elucidate the ethanethiol removal mechanism, it is necessary to understand the adsorption of ethanethiol and/or the diethyl disulfide. Therefore, in Chapter 4, the removal processes of ethanethiol with the formation of diethyl disulfide by the mordant-dyed fabrics were examined by gas chromatography with flame photometric detection. The amount adsorbed to the fabrics was estimated by subtracting the amounts of ethanethiol and diethyl disulfide in gas phase from the amount of initial injection. Removal properties were discussed with considering the transition of these three amounts in the system. The removal rate tendency for fast-slow and slow-fast types for the samples dyed with Congo red was found to exhibit similar behaviors for the

other four direct dyes. From the repeat removal experiments or the experiments using the fabrics adsorbed diethyl disulfide, the stable adsorption of ethanethiol to dye type copper was shown to be involved in the reaction rate. In Chapter 5, initial removal rates for the mordant-dyed fabrics were examined. The initial removal rates were analyzed by using the Langmuir-Hinshelwood (L-H) model, which was a typical heterogeneous catalytic model. The L-H model explained the removal rates for the cotton sample fabrics. For the wool samples dyed with the direct dyes, it was found that the kinetics of the L-H model fitted to the results of the second run for removal, while dyed with the basic dye, the model explained the rates for the first run. The parameters of the formation rate constant of diethyl disulfide and the adsorption equilibrium constant of ethanethiol showed that the dependence of the chemical structure of the dyes for the initial rate was larger for the wool than for the cotton. Most of unpleasant odors in daily life are considered to be complex odors. From a practical point of view, the removal behaviors for ethanethiol and ammonia alone, and their complex (mixed) odor were investigated in Chapter 6. Furthermore, the relationship between the removal properties of each of the surface reflection spectrum of a sample fabric before and after removal reaction was investigated. The formation of copper ammine complex in the fabrics was confirmed in the atmosphere including ammonia from surface reflection spectra. It was obtained some interesting findings that the catalytic activity of copper to ethanethiol not affected, or improved under the complex odor of ammonia and ethanethiol.

In this thesis, the deodorization mechanism for ethanethiol by mordant dyed fabrics was discussed. Focusing on the oxidation product of the ethanethiol and their adsorption on the fabric as well as the reduction of the ethanethiol, it was possible to show that the adsorption had a function of modifying the deodorizing performance. Certain results have obtained to take in consideration the principles of deodorant fiber in accordance with the intended use. I expect that the fundamental findings in the present work will be some help to pursuit of comfort for the odor issue of living spaces.