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Color Variations of Cotton Dyed with Reactive Cu-complex Azo Dyes by Histidine, and Testing Methods for Color Fastness to Perspiration

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ABSTRACT

The adsorption of histidine (His) on cellophane films dyed with five reactive Cu-complex azo dyes, CI Reactive Red 23, CI Reactive Violet 5, and 1:1 and 1:2 Cu-complex azo dyes, from aqueous His was estimated as a function of immersing time. During the incomplete abstraction of copper on immersion, the dyed films adsorbed His to a larger extent than the amount of adsorption on the undyed film. On immersing the dyed fabrics in aqueous His, the rates of color variations of Cu-complex azo dyes on cotton fabrics were faster than those on cellophane, although the order of the rates of the dyes on both the samples was similar to each other except for monochlorotriazinyl dyes examined. Although the Cu-complex azo dyes examined are not suitable for the dying of cotton materials subject to perspiration, the ISO and JIS methods for color fastness to perspiration are too mild to assess the reactive dyeings investigated. © 1997 Elsevier Science Ltd. All rights reserved

Keywords: reactive dyes, Cu-complex azo dyes, perspiration, histidine.

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INTRODUCTION

The test methods for the color fastness to perspiration[1,2] examine the color variations of the test fabrics and of the staining of adjacent cloths after the test fabrics were dipped into acidic and alkaline 'artificial' perspiration containing histidine (His), and then kept in contact with the adjacent cloths for a given time. The test methods were originally aimed at examining the color variations of direct Cu-complex azo dyes by artificial perspiration; the staining of adjacent cloths in contact with the wet test fabrics may be a secondary examination. A mild test may be applied to the direct-dyed cotton fabrics, since the perspiration test for such fabrics causes dye bleeding under severe conditions. A more severe perspiration test, however, should be made to assess the performance of reactive dyeings, since reactive-dyed cotton fabrics may be used under much more severe conditions than direct-dyed fabrics. Thus, the staining test of adjacent cloths in the present testing methods[1,2] may not be pertinent to reactive dyeings.

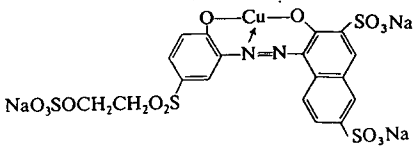
On immersing cotton fabrics dyed with reactive Cu-complex azo dyes in aqueous His, on the other hand, color variations are observed, depending upon the dye and on the conditions under which the fabrics are immersed.[3–5] When the immersed fabrics are irradiated, further color variations may occur, due to light fading and also, probably, to the coordination to and/or the abstraction of the copper atoms by the action of heat when the time of immersion is not sufficiently long.

In this present paper, the specific features of the color variations of reactive cotton dyeings are examined, since such color variations of Cu-complex reactive azo dyes on cellulose by His may be very relevant to the perspiration test assessments. The adsorption of His on cellophane dyed with some Cu-complex azo dyes on the abstraction of copper atom is initially examined and cotton dyed with five Cu-complex azo dyes were then immersed in His and the color variations of the fabrics measured with respect to the values of the color differences after washing and drying. The color variations of the immersed fabrics were also examined by the action of heat. On the basis of the present and previous results,[3–5] problems on testing methods for the color fastness to perspiration are discussed.

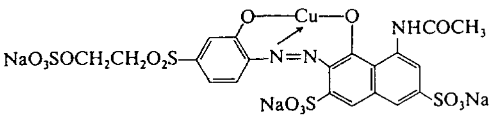
EXPERIMENTAL

Three vinylsulfonyl (VS) reactive dyes, supplied by DyStar Japan Ltd, and two monochlorotriazinyl (MCT) dyes, supplied by Nippon Kayaku Co. Ltd, were used. The chemical structures of the dyes used are as follows:

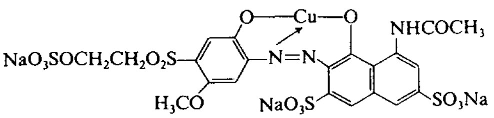
1) CI Reactive Red 23, CI 16202



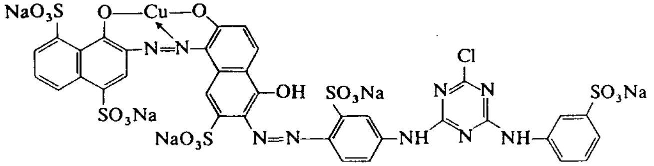
2) CI Reactive Violet 5, CI 18907



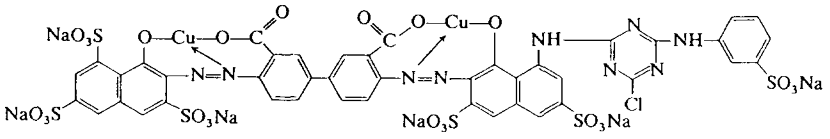
3) A VS 1:1 Cu-complex monoazo dye (Blue-Cu)



4) A MCT 1:1 Cu-complex disazo dye (Blue-1Cu)



5) A MCT 2:1 Cu-complex disazo dye (Blue-2Cu)



Cotton fabrics were dyed by the usual all-in method (liquor ratio, 30:1; temperature, 50 and 80°C for VS and MCT dyes, respectively; dye, 1.0% o.w.f.; Na_2SO_4, 50 g dm^{-3}; Na_2CO_3, 20 and 10 g dm^{-3} for VS and MCT dyes, respectively). Chemicals used were of reagent grade and used as received. The dyed fabrics were immersed in aqueous His of a given concentration for a definite time, and then centrifuged for 60 s by a centrifuge equipped with a washing machine (Toshiba ASD-550N). The centrifuged fabrics were set in a sample holder of a glass vessel for exposure of JIS L0888[4] under conditions of RH 100% (which were made by adding some water at the bottom of the glass vessel), and the glass vessel was kept in a dryer in the dark at a given temperature.

The absorption spectra of the dyed cellophane were measured by a Ubest V-560 spectrophotometer (Jasco Corp.) by the method previously reported.[3–5]

The adsorption of His on dyed cellophane was estimated by the differences in absorbance between the adsorbed and original dyed films at 212 nm.[3,4] The fabrics to which a prescribed treatment was given were immediately washed with water to remove buffer and dried before the spectral measurements were taken. The reflection spectra of the sample fabrics were measured using the same photometer equipped with a reflection system. Color differences between the original dyed fabrics and of a sample after the corresponding treatment were calculated from the spectra by a computer program.

RESULTS AND DISCUSSION

Adsorption and desorption of His

The adsorption of His on cellulose occurs rapidly, while the abstraction of copper atoms from Cu-complex azo dyes on cellulose proceeds slowly for many normally used dyes. Since the additional adsorption of His was shown to result from the coordination of His to the copper atoms in the dyes on cellophane,[4] the adsorption of His changes with time on cellophane dyed with Cu-complex dyes, with high rates of abstraction of copper. The facts that the amounts of additional adsorption were proportional to those of the ordinary adsorption on cellulose, which were dependent upon the pH of aqueous His, and to the concentrations of dye on cellulose, may imply a 1:1 complex formation between dye and His.[4]

The adsorption of His on cellophane dyed with various dyes, on immersing in aqueous His of 0.020 mol dm^{-3} (+ NaCl 0.05 mol dm^{-3}) at pH 7.56, was examined as shown in Fig. 1. In the case of Blue-2Cu, whose copper atom was abstracted very rapidly by His, no additional adsorption of His was observed, the adsorption being the same as that on undyed film.

The adsorption of His on the film dyed with Blue-1Cu and CI Reactive Violet 5 was smaller than that in the case of Blue-Cu and larger than that in the case of undyed film. The adsorption of His on cellophane dyed with Blue-1Cu was decreased with time of immersion and then remained constant for some time. The copper atoms of Blue-1Cu were gradually abstracted accompanied by a slow decomposition of the dye.[5] This adsorption behavior may be explained by the fact that the abstraction of copper atoms and the decomposition of Blue-1Cu proceeded from the surface of the dyed film. Since the copper atoms of CI Reactive Violet 5 are abstracted rapidly from the beginning of immersion, compared with the case of Blue-Cu and CI Reactive Red 23,[5] the adsorption of His on cellophane dyed with CI Reactive Violet 5 is smaller than that of the film dyed with Blue-Cu. Since the additional adsorption of His due to coordination and the abstraction of

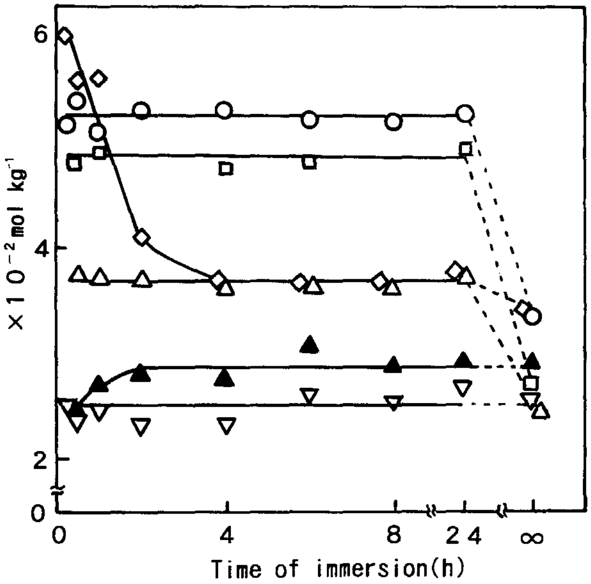


Fig. 1. Absorption of histidine on cellophane and on the films dyed with reactive dyes from aqueous histidine of 0.020 mol dm^{-3} (+ NaCl 0.050 mol dm^{-3}) at pH 7.56 and 25°C. The adsorption of histidine from the same solution on the corresponding dyed films from which the copper atoms of the dyes were abstracted by immersing them in aqueous EDTA of 0.050 mol dm^{-3} (+ NaCl 0.050 mol dm^{-3}) at pH 12.00 for 6 h was plotted at infinite time.

	—	*CI Reactive Red 23*	*CI Reactive Violet 5*	*Blue-Cu*[22]	*Blue-1Cu*	*Blue-2Cu*
Conc. of dyes on cellophane ($\times 10^{-2}$ mol kg^{-1})	0	1.12	1.00	1.14	1.35	0.60
Symbols	▲	○	△	□	◇	▽

copper may proceed simultaneously, the additional adsorption of His decreases during the initial time of immersion in the case of Blue-1Cu.

With CI Reactive Violet 5, an intermediate amount of adsorption was observed from the beginning. The adsorption of His on cellophane dyed with Blue-Cu[3,4] and CI Reactive Red 23 was larger than that on the film dyed with Blue-1Cu and CI Reactive Violet 5, since the former two dyes have smaller rates of color variations than those for the latter two dyes.

On the other hand, the copper atoms in the dyes could be almost abstracted by immersing the dyed films in aqueous EDTA at pH 12 for 6 h. The adsorption of His on the Cu-abstracted films, which is shown in Fig. 1 at the abscissa of infinite time, was nearly the same as that on the undyed films. Since the copper abstraction from CI Reactive Red 23 on cellulose might be incomplete because of the low rate compared with the other cases, the adsorption of His was still a little larger than that of the other cases. Even in case of Blue-Cu, where no abstraction of copper was observed on immersing in aqueous His, EDTA abstracted the copper atom to give no additional adsorption of His.

For all the dyes examined, it was confirmed that His adsorbed on dyed and undyed films was desorbed almost instantly by immersing them in water at room temperature.

Color variations by His

Color variations by the immersion in aqueous His

On immersing the dyed cellulose films in an aqueous weakly alkaline His, the absorption spectra of Cu-complex azo dyes on cellulose varied quickly initially, and then more slowly with the time of immersion.[3–5] The main band became broad and a red shift of λ_{max} occurred. These spectral variations have been confirmed to be due to the coordination of His to the copper atom in the dyes and/or the abstraction of copper atoms followed by the dissociation of hydroxyl groups. The attainment of the complete abstraction took a long time for usual dyes. The rates of color variations were increased with an increase in His concentration, pH, and ionic strength. After the abstraction, even though incomplete, on re-immersing the dyed film in buffer solution at different pHs, spectral variations were observed depending upon the pH, probably due to the dissociation of hydroxyl, or carboxyl groups.

In order to examine the spectral variations for Cu-complex azo dyes on cotton fabrics, the color differences between the dyed fabrics immersed in aqueous His at pH 9.0 and the original ones were estimated (Fig. 2). When leaving the immersed fabrics for 2 weeks as they were after centrifuging the fabrics treated under given conditions without washing, spectral variations were observed. In the case of a treatment at pH 8, the same reflection spectrum

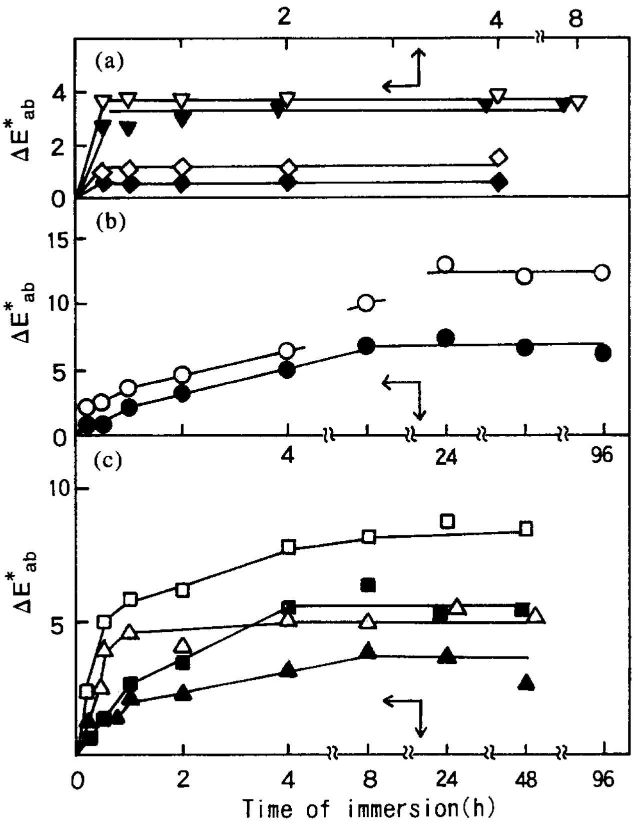


Fig. 2. Relationships between color variations, ΔE^*_{ab} of cotton fabrics dyed with Cu-complex azo dyes, (a) Blue-1Cu (◇, ◆), and Blue-2Cu (▽, ▼), (b) CI Reactive Red 23 (○, ●) and (c) CI reactive Violet 5 (△, ▲), and Blue-Cu (□, ■), and the time of immersion in aqueous histidine of 0.0050 (open symbols) and 0.02 mol dm^{-3} (closed symbols) (+ NaCl 0.050 mol dm^{-3}) at pH 9.00. Spectral measurements of the immersed samples were made after washing and drying.

as that on the washed fabrics was obtained after one week, whilst no complete variation in the spectra was attained in case of pH 9 even after leaving them for 2 weeks. Thus, the pH value on the fabrics changed gradually from 8 or 9 to become weakly acid when the fabrics were allowed to remain at room temperature for a long period. The color variations of MCT dyes occurred quickly although they were small at pH 9 [Fig. 2(a)], while those for the three VS dyes occurred quickly initially and then more slowly [Fig. 2(b) and (c)]. On immersing the dyed fabrics in aqueous His, some differences in the color variation behavior were noticed, with no dependence of the rates or of the final color changes on the His concentration unlike the case of dyed films.[5] By prolonged immersion, in addition to color variations, the dyed fabrics appeared to become pale.

The order of the rates of color variations for dyed fabrics was as follows: Blue-2Cu ≈ Blue-1Cu > > Blue-Cu ≈ Violet 5 > > Red 23. The rates of color variations for cotton fabrics were faster than those for cellophane. The spectral variations and the order of the rates for two kinds of cellulose sample, films and fabrics, were essentially similar to each other, except for the MCT dyes examined.

Color variation by heating after the immersion in aqueous His

After the cotton fabrics dyed with Blue-Cu were immersed in aqueous His of 0.005 and 0.02 mol dm^{-3} at different pHs for 15 and 30 min, color variations were observed under the conditions of 60°C and RH 100% as a function of time (Fig. 3). Heating of the dyed fabrics at 60°C after the immersion in the His solution at pH 5.6, 7.6, and 9.0 resulted in a gradual increase in the color change, and its rates, with an increase in the pH of aqueous His, a promotion of color change due to the coordination to the copper atom and/or the abstraction, although the color variations caused by the immersion were different. The longer heating gave no further change in color, since the immersed fabrics were practically dry despite the environment at RH 100%. Although immersion of the dyed fabrics in aqueous His for a shorter time gave color variations less than those for the longer immersion, the heat treatment of the immersed fabrics seemed to result in the same variations as those by the long immersion (cf. Figs 2, 3 and 4).

In the JIS testing method for color fastness to light and perspiration,[6] an estimation of the color variations of dyes on cotton fabrics only by light is mediated after immersing the fabrics in the artificial perspiration containing His for 30 min. On irradiating after immersing the dyed fabrics in aqueous His, since the heat effects result from light absorption, no distinction can be made between the light and heat effects. The color variation of the immersed fabrics by bodily temperature may be much slower than those by the heat of light absorption, although the ISO and JIS methods[1,2] examine this.

Comments on the testing method for color fastness to perspiration

Inevitable structural modification of Cu-complex azo dyes by His

As far as the perspiration color fastness of reactive dyeings is concerned, only Cu-complex azo dyes have a possibility of showing the color variations due to the His coordination to copper atoms followed by the abstraction. The rates of color variations depend upon the His concentration and on the temperature and pH of the solution as well as the time of immersion.[3–5]

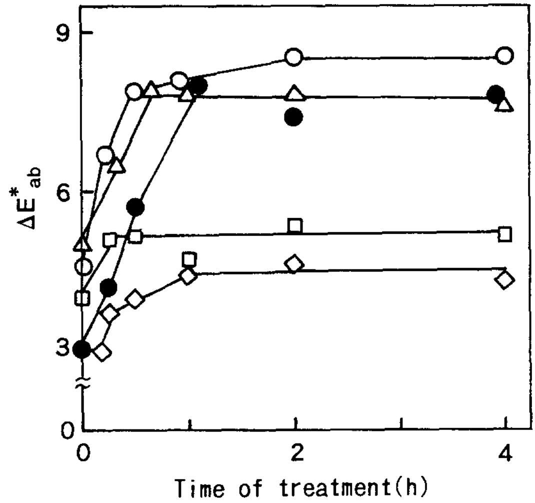


Fig. 3. Color variations, ΔE^*_{ab}, of cotton fabrics with time, which were dyed with Cu-complex azo dyes, Blue-Cu, and immersed in aqueous histidine of 0.02 or 0.0050 mol dm^{-3} (+ NaCl 0.050 mol dm^{-3}), by the heat treatment at 60°C.

Conc. of His	0.020 mol dm^{-3}				0.0050 mol dm^{-3}
pH of aq. His	5.6	7.6	9.0	9.0	7.6
Time of immersion (min)	30	30	30	15	30
Symbols	□	△	○	●	◇

Cu-complex azo dyes are subject to color variations by the ligand exchange of the oxo group for the His ligand, forming free hydroxyl groups, and/or subsequent abstraction of the copper atoms by His when the dyed fabrics are 'sweaty'. The color changes of Cu-complex azo dyes are not a matter of degree, although this depends upon the conditions under which the dyeings are exposed to perspiration.

Their hydroxyl groups, and in rare cases carboxyl groups, show acid dissociation behavior with pH, although the values of pK_a depend on the structure of the dyes. The extent of color variations by the dissociation of hydroxyl groups may depend not only on the pH of substrate in which the dye exists, but also on the dye itself. The dissociation of the carboxyl groups for Blue-2Cu, for example, occurs in the acidic region, and that of hydroxyl groups in a more strongly alkaline region. The abstraction of copper atoms

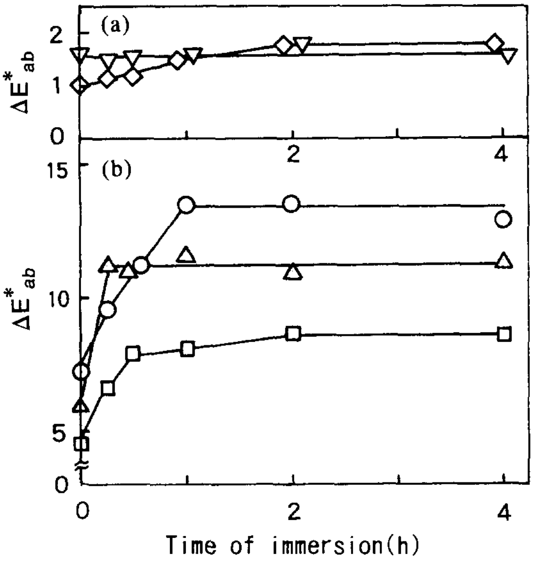


Fig. 4. Color variations, ΔE^*_{ab}, of cotton fabrics with time, which were dyed with Cu-complex azo dyes, (a) Blue-1Cu (◇), and Blue-2Cu (▽), and (b) CI Reactive Red 23 (○), CI Reactive Violet 5 (△), and Blue-Cu (□), and were immersed in aqueous histidine of 0.02 mol dm^{-3} + NaCl 0.050 mol dm^{-3} at pH 9.00, by the heat treatment at 60°C.

by His, although it occurs very easily, results in little color change in the neutral region. In the case of Blue-Cu, although no copper atoms are abstracted by His, large color variations are observed on immersion in aqueous His, since the pK$_a$ for the free hydroxyl group formed by the ligand exchange exists in the neutral region. Although the latter dye suffered a smaller intramolecular modification than the former dye, the latter showed a larger change in color than the former. Thus, the extent of structural modification does not correspond to that of color change.

The reflection spectra of wet fabrics after dipping in weakly alkaline aqueous His should be measured to obtain the maximum color difference, although the color variation of dry specimens after immersing in aqueous His is estimated in the ISO and JIS methods.[1,2] Since the pH in the cotton fabrics seemed to become weakly acidic medium by drying and storage, as mentioned in a previous section, the Cu-complex azo dyes examined in this study should show smaller color differences on dry fabrics than on wet ones. Moreover, in order to obtain a larger color difference under the definite conditions, a much longer time of immersion than that of the present methods is necessary depending upon the conditions of His solution.

Unrestrained modification by His

Since the adsorption of His on cellulose occurs rapidly, but the color variations due to the coordination of His to the copper atom in Cu-complex azo dyes followed by the abstraction of the copper atom occur slowly, the complete color variation may be attained by further sweating. The abstraction of the copper atom may advance further by repeated perspiration, but it may be minimized by frequent washing immediately after the sweating, since His adsorbed on cellulose can be easily desorbed by washing.

Once Cu-complex dyes undergo structural modification, it is completely irreversible and unrestrained. The original structure can only be reformed using chemical reactions. The dyes which exist nearer the surface of the fabrics undergoes preferential modification, and this may proceed after every 'sweating'; there may therefore be a heterogeneous distribution of a mixture of the original and modified dyes in the fabrics.

Significance of testing methods for color fastness to perspiration

In a series of previous papers,[3–5] we have elucidated the potential properties of color variations for Cu-complex azo dyes on immersing reactive dyeings in aqueous His. If such colour variations were considered severe, their dyeings should not be used for garments worn in an environment subject to perspiration. From this view point, and to make the product properties clear, cotton dyeings should be produced which obviate this problem. If this was to be effected, no perspiration testing method would be necessary, but in order to make assurance doubly sure by measuring the color fastness to perspiration, testing methods may be required.

The ISO and JIS methods, however, estimate the magnitude of color variations under the defined conditions using the gray scale, and no potential color variation for the individual dye. The color variations brought about by alkaline artificial perspiration should be almost always larger than those by acidic conditions. Estimation of the color differences of dry specimens after the dipping may lower the test values in both acid and alkaline regions, since color variations may occur due to the pH-change in the fabrics during drying. It may be possible to compare the rates of variation between the two conditions, because the color differences may be estimated under the same conditions.

As previously noted, however, the ISO and JIS methods may be too mild to assess the color fastness of heavy duty wear such as reactive dyeings. Since the staining of adjacent materials may be out of the question for the usual tests, the methods may be insufficient to fully assess the perspiration colorfastness of fabrics with such high wet fastness. The present testing methods should be modified, depending upon what properties of the test specimen dyed with reactive Cu-complex azo dyes are required to be examined.

We have, unfortunately, found neither Cu-complex azo dyes whose cotton dyeings are suitable for wear under conditions which are likely to be 'sweaty', nor a testing method which can discriminate between suitable and unsuitable cotton dyeings for wear. Since even CI Reactive Red 23, which had the least rate of color variation, showed a considerably large initial color variation, it may be concluded that there is no respectable difference in the color variations of the dyes examined in this present study.

Moreover, the present study showed that, after immersing the cotton fabrics dyed with Cu-complex azo dyes in aqueous His for even a short time, the heat treatment gave similar color variations to those of a more prolonged immersion. Since the heat was usually generated by light absorption, by which the accompanied simultaneous fading was accelerated by the presence of His on fabrics, the joint effects of light and perspiration should be taken into consideration.

SUMMARY

The color variation behavior of Cu-complex azo dyes on cotton fabrics on immersing in an aqueous His was similar to that on dyed cellophane, although the rates of variations on fabrics were usually faster than those on cellophane.

Since the dyed fabrics previously immersed in aqueous His for a short time showed further color variations on heating the wet fabrics, the JIS L0888 method for the color fastness to light and perspiration may examine the total effects of His on Cu-complex dyes on cellulose. However, the ISO and JIS methods for the color fastness to perspiration may be too mild to assess the effect of His on reactive Cu-complex azo dyes on cotton fabrics.

ACKNOWLEDGEMENTS

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