Dyes and Pigments **23** (1993) 135–147

Structure Reactivity Correlations of Azo Reactive Dyes Based on H-acid. IV. Investigations into the Light Fastness in the Dry State, in the Wet State, and in Presence of Perspiration*

Karl Bredereck‡ & Christian Schumacher

Institut für Textil-und Faserchemie, Universität Stuttgart,
Pfaffenwaldring 55, 70550 Stuttgart, Germany

(Received 10 May 1993; accepted 9 June 1993)

ABSTRACT

In this paper we report on substituent effects on the light fading of azo reactive dyes based on H-acid on cellulose in the dry state, in the wet state, and in the presence of perspiration. Dyes containing strongly electron donating substituents tend to always fade oxidatively, while dyes with strongly electron withdrawing substituents prefer a reductive degradation pathway. In the dry state, a reductive fading mechanism prevails. In the presence of water, the fading becomes oxidative, while the fading of dyes containing electron donor substituents greatly enhanced. In the presence of artificial alkaline perspiration, the reductive fading is greatly accelerated. Thus, dyes containing an electron withdrawing substitution pattern have poor fastness properties to perspiration and light, while they fade reductively. The amino acid histidine, which is a component of perspiration, is concluded to be responsible for the enhanced reductive light fading in the presence of perspiration.

1 INTRODUCTION

The fading of dyed textiles by chlorinated water, peroxide-washing, and the combined action of perspiration and light is an important problem in the

---

*This paper forms part of the PhD thesis by C. Schumacher, University of Stuttgart, Germany.

‡To whom correspondence should be addressed.

Dyes and Pigments 0143-7208/93/$06·00
Printed in Great Britain

dyestuff industry.[1] In this series of papers, we discuss structure reactivity correlations of closely related azo reactive dyes based on the H-acid monoazo chromophore with respect to the above mentioned fastness requirements. In part I[2] we reported on dye selection and synthesis, their general characterization in terms of aggregation, pK_a values, and dyeing behaviour etc. In parts II[3] and III[4] we covered the fastness to chlorine or hypochlorite, respectively, and the fastness to peroxide treatment. In this paper the light fading of the dyes on cellulose is investigated with special emphasis on the influence of water and perspiration on the fading rate.

Much work has been done previously with respect to the light fading of dyes (see review articles by Giles and McKay,[5] Bentley *et al.*,[6] Evans and Stapleton,[7] Kramer,[8] Baumgarte and Wegerle[9] and Allan[10]).

The photochemical degradation of azo dyes can occur either by photooxidation or photoreduction. Under aerobic conditions, the photooxidative pathway was found to proceed by reaction of singlet oxygen with the hydrazone form of azo dyes via an 'ene'-type of reaction.[11] On the other hand, a reductive mechanism prevails under anaerobic conditions. The reductive cleavage of the azo bond involves hydrazyl radicals and yields aromatic amines.[12,13] On the fibre, a reductive fading of dyestuffs has been reported on protein substrates such as wool or gelatine,[14–16] while on oxidative degradation was found for other non-protein fibres such as cellulose or polyethylene-terephthalate.[17,18]

According to Sramek,[19] who conducted a statistical screening on the light fastness of commercial dyes, the light fastness is in most cases significantly lower when the exposed samples are wet, and only in few cases equal to the value in the dry state. Datyner *et al.*[20] gave some explanation for the lower wet fastness to light.

Presently, very little is known about the effect of perspiration on light fading despite its industrial importance. It is not yet clear whether perspiration-light fading differs from the fading caused by water and light. However, there are indications that the perspiration-light fastness often differs from the light fastness in the wet state.[21] It is difficult to directly compare these two fastness gradings, since the irradiation exposure times and wet/dry-cycles of the perspiration-fastness assessments (e.g. JIS L0888 and Krucker[22]) differ from the wet-light fastness, which makes any comparison intrinsically unreliable.

Human sweat not only contains water, but salt, amino acids, and also lactic acid.[23,24] The common perspiration fastness testing solutions (e.g. DIN 54020 or JIS L0848) contain mixtures of the above mentioned compounds. In Japan, different perspiration testing solutions are used.

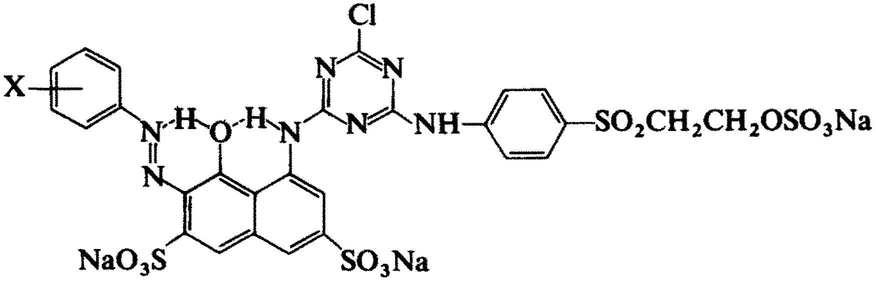
In Japan, some procedures for perspiration-light assessments have been defined (e.g. JIS L0888) but in Germany no DIN testing procedure has yet been released. Fresh perspiration is acidic, but it turns alkaline due to bacterial action.[25,26] Therefore, two perspiration tests (pH 5·5 and pH 8·0) are commonly used.

Artificial perspiration always contains various amounts of histidine, which is responsible for demetallizing copper complex azo dyes, leading to a change of shade.[25] The demetallized copper free dye has a lower stability to light, and thus fades more rapidly. It has also been reported that the light fastness of metal free dyes is in many cases also adversely affected by the presence of perspiration, for reasons which are not known.[21,27] Only a few other papers on the combined fastness to perspiration and light have been published, e.g. by Inoko *et al.*,[28] Kurihara[29] and Oe.[30]

2 EXPERIMENTAL

2.1 Dyes and dyeings

The dyes used for our investigations were monoazo reactive dyes based on H-acids, having the structures shown below:

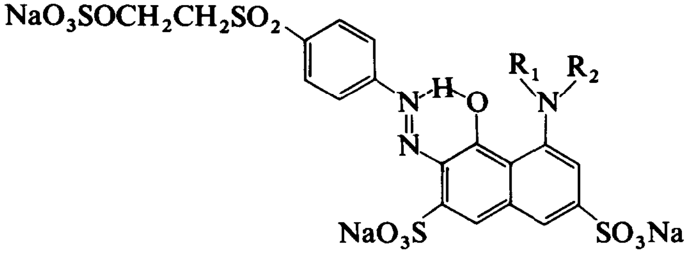


X = *p*-OCH$_3$ (**1**), *p*-CH$_3$ (**2**), H (**3**), *p*-Cl (**4**), *p*-NO$_2$ (**5**),
o-OCH$_3$ (**6**), *o*-CH$_3$ (**7**), *o*-Cl (**8**), *o*-NO$_2$ (**9**),
o-SO$_3$H (**10**), *o*-sec-C$_4$H$_9$ (**11**), *o*-COOH (**12**)

Dyes **1–12** contain bifunctional reactive groups, namely a vinylsulphonyl and a monochlorotriazinyl anchor, both attached on the side of the coupling component in a conjugated manner. The preparation, purification and characterization of dyestuffs **1–12**, as well as their dyeing behaviour were described in part I[2] in this series of papers.

Dyes **13–17** are monofunctional vinylsulphonyl reactive dyes with the anchor located on the side of the diazo component, with modification of the substituents on the N-atom of the H-acid moiety. The synthesis and characterization of the dyes **13–17** is described in Ref. 31.

The dyeing procedure (exhaust process, approximately 1% o.w.f dyestuff



$NR_1R_2 = NH_2$ (13), $NHCH_3$ (14), $N(CH_3)_2$ (15), $NHCOCH_3$ (16), NCH_3COCH_3 (17)

on cellulose) on cellulose film (®Cellophane) and cotton fabric was described in part II.[3]

2.2 Irradiation experiments

Pieces of dyed cellulose film (1 × 4·5 cm each, 6 pieces per dye) were attached to a plastic strip (13·5 × 4·5 cm) by means of an adhesive. This strip was then mounted on a ®Xenotest 150 S (Heraeus, Hanau, Germany) and irradiated for 60–72 h (wet, perspiration) or 120 h (dry), respectively. After discrete time periods (every 10–12 h for the wet/perspiration irradiation and 24 h for the dry irradiation) one exposed sample per dye was removed and the irradiation was continued.

The amount of faded dye was estimated by measuring the absorbance with a Lambda 2 UV-VIS spectrometer (Perkin Elmer, Überlingen, Germany). Inaccuracies due to the sometimes occurring slightly unlevel dyeing of the cellulose films were taken into account by measuring every sample before and after the irradiation. We also observed an unlevel fading in case of the perspiration-light series, which was compensated by measuring at different spots of the cellulose film.

By means of pseudo-first order kinetic evaluation, the kinetic rate constants k were obtained ($\ln E/E_0$ of the films plotted versus the time; k is the initial slope).

The irradiation was conducted dry (a), wet (b) and in the presence of artificial (alkaline) perspiration (c). The perspiration solution was prepared according to DIN 54020. It contains 0·5 g/litre of L-histidine, 5 g/litre of NaCl, 5 g/litre of $Na_2HPO_4 \times 12H_2O$, NaOH until pH 8·0. In all cases, the perspiration solution was freshly prepared before use. In the case of (b) and (c) the reservoir of the ®Xenotest equipment was filled with demineralized water (b) and the perspiration solution (c), respectively. The wet/dry cycles for (b) and (c) were identical. They were programmed on the ®Xenotest as follows: 1 min sprinkling under irradiation followed by 29 min of dry irradiation.

The irradiation of cotton fabric was performed by attaching pieces of 13·5 × 4·5 cm of dyed samples on the ®Xenotest equipment. The conditions during the irradiation were as described above. Instead of obtaining rate constants, we only measured the percentage of fading which we obtained from reflection measurements (via Kubelka-Munk function, see part 3).

Investigations into the mechanism of the perspiration-light fading were performed with samples of dyestuff **16** dyed on cellulose film. The samples for the irradiation were prepared as described above. However, the wet/dry sprinkling programme was modified for experimental reasons. Every 6 h, testing solutions with varying histidine content (0–10 g/litre of histidine, without salt and alkali) were manually sprinkled onto the samples until they were completely wet, and the samples containing different histidine concentrations were then further exposed to light. A separate determination of the histidine content of the cellulose film was not undertaken.

3 RESULTS AND DISCUSSION

Table 1 contains the obtained rate constants of the reactive dyes **1**–**17** on cellulose film for the light fading in the dry state, in the wet state, and the perspiration-light fading. Figure 1 shows the Hammett-plots for the para-substituted dyes **1**–**5**. Figure 2 illustrates the influence of water (k_{wet}/k_{dry}) and perspiration (k_{persp}/k_{dry}) on the fading as a function of Hammett σ constant, while k_{persp}/k_{wet} separates the influence of perspiration components from the effect that arises from the presence of water in perspiration.

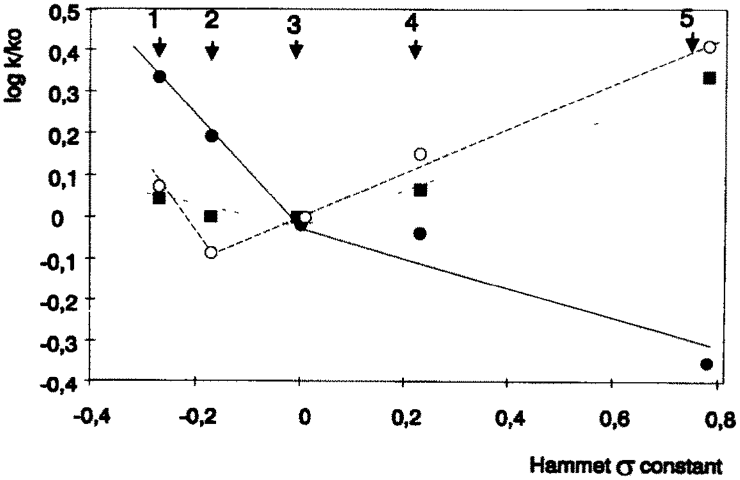


Fig. 1. Hammett-plot for the light fading of dyes **1**–**5** in the dry state (■), in the wet state (●), and in presence of artificial alkaline perspiration (○).

TABLE 1

Light Fading of Dyes **1**–**17** on Cellulose Film. Pseudo-first Order Rate Constants of the Photochemical Fading in the Dry State (k_{dry}, 66% Relative Humidity), in the Wet State (k_{wet}), and in Presence of Perspiration (k_{persp}); Cycles of 29 min of Dry Irradiation and 1 min of Sprinkling with Water or Artificial Alkaline Perspiration According to DIN 54020, 37°C

Dye	$k \times 10^3$ (h^{-1})		
	k_{dry}	k_{wet}	k_{persp}
1	1·26	12·0	11·3
2	1·14	8·69	7·8
3	1·15	5·57	9·5
4	1·33	5·19	13·5
5	2·49	2·49	24·5
6	1·48	13·2	12·0
7	1·30	10·7	10·5
8	37	67	84·5
9	5·13	8·08	44
10	1·06	3·01	15·5
11	20·5	20·9	23·5
12	1·70	6·13	5·15
13	2·57	30·5	31·5
14	2·94	52	61
15	11·00	50	96
16	2·35	3·26	16
17	3·03	4·57	17

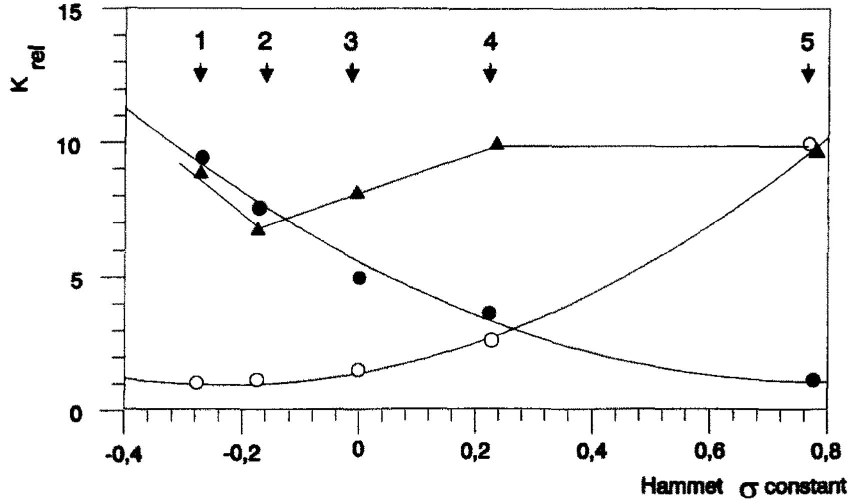


Fig. 2. Influence of water and perspiration on the light fading of dyes **1**–**5**, relative fading rates k_{wet}/k_{dry} (●), k_{persp}/k_{wet} (○), k_{persp}/k_{dry} (▲).

3.1 Light fading in the dry state

The substituent effect of the para-substituted dyes **1**–**5** on the light fading in the dry state is small as far as absolute numbers are concerned (Table 1), but it is clear that electron withdrawing substituents increase the fading rate. This observation is underlined by the Hammett-plot (Fig. 1, dry series) which contains relative figures and mainly a positive ρ value. Furthermore, one may draw two separate straight lines in the Hammett-plot with a negative slope for dyes with electron donating substituents ($\rho = -0{\cdot}231$, **1**–**3**) and a larger positive slope for dyes with electron withdrawing substituents ($\rho = +0{\cdot}425$, **3**–**5**). According to the usual interpretation in the literature,[14–18] a positive slope in the Hammett-plot is very likely due to photoreduction, while a negative slope is due to photooxidation. On the basis of this interpretation, the fading of the H-acid type of dyes is mainly reductive in the dry state, with an oxidative contribution for electron donating substituted dyes (**1**, **2**).

An alternative interpretation for the two separate straight lines in the Hammett plots was given by Hempel *et al.*,[32] using azo hydrazone tautomerism. Here, however, this explanation seems to be unlikely, since there is no indication of any significant azo content.[2] Instead, we suggest that here a change of the fading mechanism within the series may explain the curved Hammett-plot.

Also, the observed reductive fading (e.g. **5** fades faster than **1**, see Kuramoto and Kitao[33] who reported on a fast fading of NO_2-substituted dyes) contradicts the well established empirical rule suggesting an oxidative fading on cellulosic fibres (see above). Apparently, not only the substrate, but also the nature of the dye is important as well, and, at least in case of the H-acid type of azo dyes, a reductive fading on cellulose is conceivable.

As far as the ortho-substituted dyes (**6**–**12**) are concerned, dyes **8** and **11** have extremely low light fastness properties in comparison with the other dyes (Table 1). A significant decrease in the light stability due to ortho-chlorine substituents has been reported by Wegmann.[34] The reason for this, however, is not yet understood. The light fading of dye **11** (*o*-s-C_4H_9) is, in contrast to all other dyes, not much affected neither by water or perspiration, which makes a special degradation pathway probable.

3.2 Light fading in the wet state

The fading rate is in most cases much faster when the exposed samples are wet rather than dry (Table 1). The difference between the wet and the dry series is most striking for dyes with electron donating substituents. Dyes **1** and **6** fade approximately 10 times faster and dyes **2** and **7** fade eight times faster when wet (Table 1). The impact of water on the fading rate decreases with increasing electron withdrawing power of the substituents (see Fig. 2, k_{wet}/k_{dry}). For dyes **5**, **9**, **16** and **17** no significant difference was evident.

The substituent effect in the wet series is reversed if one refers to the dry series. According to the Hammett-plot in Fig. 1, we now observe a dominant oxidative fading, which is implied in the large ρ-value ($\rho = -1{\cdot}30$ for **1–3**), with reductive participation ($\rho = -0{\cdot}363$ for **3–5**). Again, there are two separate straight lines.

Apparently, the presence of water leads to a change of mechanism from a reductive fading to an oxidative fading. The reason for the change of mechanism, or the enhanced oxidative fading, may be the higher oxygen availability in the cellulose, which is essential for any oxidative fading due to the swelling in the presence of water. There is no significant effect of water if the dye fades reductively, due to its electronic state (e.g. **5**, **9**, **16**, **17**).

The light stability of dyes **13–15** is greatly decreased in the presence of water, whilst **16** and **17** are only marginally affected. This effect is due to the absence of any electron withdrawing substituents on the N-atom of the H-acid coupling component (**13–15**), and these dyestuffs are thus susceptible to oxidative fading. We must state, therefore, that electron withdrawing substituents (acyl or heterocycles such as triazinyl) at this position are essential for any reasonable light fastness.

During the wet irradiation experiments, we recognized that the quality of the applied water (for sprinkling of the samples) has a great effect on the fading rate obtained. In fact, we found that any traces of copper ions in the water led to a change in shade and a lower fading rate.[31] Apparently, some dyes, especially those with ortho substituents (e.g. **10**, *o*-SO_3H), very efficiently absorb metal ions from the water upon extensive sprinking (every half hour for 2 days), forming metal azo dye complexes. The UV-VIS spectrum of the thus obtained sample is identical to the copper complex of the azo dye.[31] These metallized dyes are then more stable to light. Due to the metal absorbing property (see Shukla and Sakharande[35]) of some dyes, we used demineralized water in all further examinations. Also, the metal ion absorbing properties of the dyes make it understandable why poor reproducibility of the wet light-fastness measurements is often encountered, since the quality of the applied water plays an important role.[21]

3.3 Light fading in the presence of perspiration

Upon the addition of perspiration components to the sprinkling solution, the substituent effect is reversed once again. Dyes with a high electron density in the chromophore are only marginally affected (**1**, **2**, **6**, **7**, **13** and **14**, see Table 1 and k_{persp}/k_{wet} in Fig. 2), which means that the perspiration components make no large difference. For these dyes the oxidative fading mechanism is maintained. However, with increasing electron withdrawing character of the overall substitution pattern, the perspiration-light fading of dyes is very significantly increased (**4**, **5**, **9**, **10**, **16** and **17**, see Table 1 and $k_{\text{persp}}/k_{\text{wet}}$ in Fig. 2). We observed a change of mechanism toward reductive degradation (see the Hammett-plot in Fig. 1, $\rho = +0{\cdot}500$ for perspiration-light).

The light fading in the presence of perspiration seems to be comparable to the dry state if one considers the Hammett-plots, which are almost congruent (Fig. 1). In both cases we suggest a dominant reductive fading mechanism. However, the Hammett-plot contains only relative numbers. The absolute fading rates vary significantly. The perspiration-light fading is much faster than the fading in the dry state ($k_{\text{persp}}/k_{\text{dry}}$ in Fig. 2, and Table 1).

Figure 2 reveals that the negative effect of perspiration on the light fastness ($k_{\text{persp}}/k_{\text{dry}}$) is partly due to water, for dyes fading in an oxidative manner (**1**, **2**, see $k_{\text{wet}}/k_{\text{dry}}$), but also due to the presence of perspiration components for dyes being sensitive to reductive degradation (**5**, see $k_{\text{persp}}/k_{\text{wet}}$). The same holds true for **6**, **7**, **12**, **13**, **14** and, respectively **9**, **10**, **16** and **17**.

3.4 Light fading on cotton fabric

Table 2 shows the fading on dyed cotton fabric (percentage of fading after 48 h exposure). In principle, the substitution dependence on the fading obtained is similar to the results for cellulose film. Therefore, further detailed discussion is not necessary. It should be mentioned, however, that differences in the light fastness between the "Cellophane and the cotton series may arise from differences in the dye aggregation[2] or dye distribution[36] in cellulose (e.g. compare the wet-light fastness of **12** with **1–4**, Tables 1 and 2).

3.5 Investigations into the mechanism of perspiration-light fading

The crucial question resulting from the above results is: why do perspiration components so drastically enhance the reductive photochemical degradation of the dyes? Some indications of the answer may already be documented in the literature.

Thus, Okada *et al.*[37,38] found that the presence of hydrogen donating substrates (reducing agents) such as mandelic acid favoured a reductive photofading. Baumann[39] reported that the histidine content of wool decreases significantly with the action of ultraviolet light, while other amino acids are protected. Cumming *et al.*[15] recognized a change in the photofading mechanism towards reductive fading in the presence of histidine (for azo dyes based on R-acid, on methylethylcellulose).

TABLE 2

Light Fading of Dyes **1**–**13**, **16** on Cotton Fabric. Dye Degradation (%) by Light after 48 h of Exposure; see Table 1 for Experimental Conditions

Dye	*Dye fading (%)*		
	Dry	*Wet*	*Perspiration*
1	32	71	66
2	37	67	72
3	21	51	52
4	21	45	55
5	40	33	88
6	53	86	79
7	34	78	77
8	73	97	97
9	49	46	92
10	36	43	77
11	82	94	91
12	27	74	52
13	40	95	84
16	20	25	76

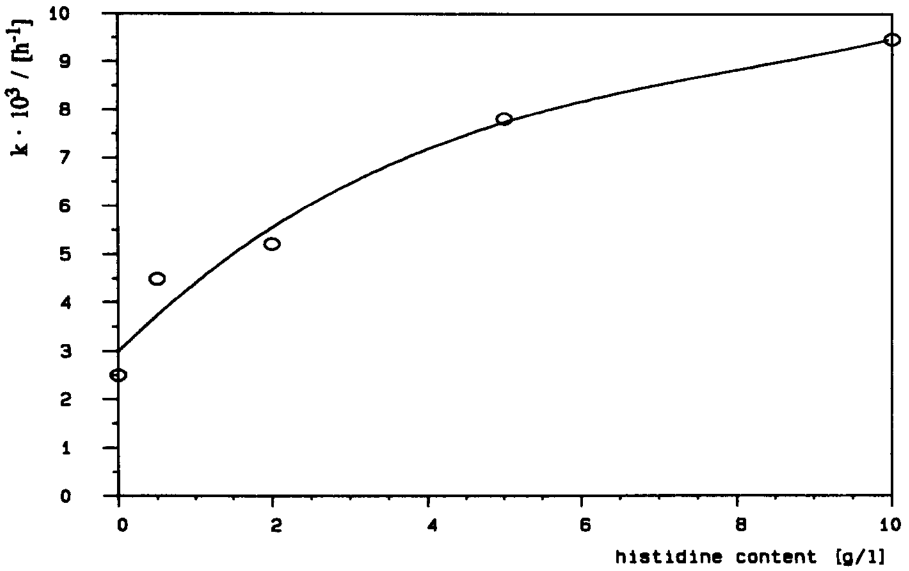


Fig. 3. Light fading curve of dye **16** on cellulose film as a function of the histidine concentration.

Considering these results, we anticipated also the involvement of histidine in the perspiration-light fading. In Fig. 3, the rate constant of the photofading of the H-acid dye **16** on cellulose film is plotted versus the histidine content (without salt and alkali). It is evident, therefore, that histidine participates in the photofading and greatly accelerates the fading velocity.

It must be stated, however, that the fading rate for comparable histidine contents is much lower than under the perspiration-light conditions which were applied in Section 3.3 (Table 1). We checked for the influence of salt, which proved to be small. Instead, the reason for this effect is very likely the modified sprinkling programme (here sprinkling every 6 h) or the changed wet/dry-cycles. On average, the samples are longer in the wet state when the technique in Section 3.3 is applied. Also, this observation emphasizes the importance of the wet/dry-time programme for the fastness obtained to perspiration and light.

4 CONCLUSIONS

The inference to be drawn from the above results is that substituent effects on the fading by light and water on the one hand, and by light and perspiration on the other hand, are mutually exclusive. This means, that if one stabilizes a dye towards one fastness criterion, the other one automatically becomes worse. Dyes containing electron withdrawing substituents have a reasonable light fastness in the dry and wet state, but a very poor perspiration-light fastness under the conditions applied in this work. The wet light-fastness is similar to the light-fastness in the dry state for such dyes, indicating that water has no significant impact on the fading.

Conversely, dyes containing electron donating substituents suffer from poor wet-light fastness properties. For these dyes, the fastness to perspiration-light is similar to the wet light-fastness, and the wet light-fastness is much worse than the light-fastness in the dry state.

Thus, the effect of perspiration can be due to water alone for dyes with electron donating substituents, but can also be due to sweat components, like histidine, for other dyes with electron withdrawing substituents.

Furthermore, by the introduction of ortho substituents, the photostability is not improved as in the case of bleaching fastness (hypochlorite[2] and peroxide[3]); the light fastness becomes even worse (see Tables 1 and 2).

The crucial question arises how to make molecules more stable to light. Based on the H-acid azo chromophore, this task seems to be impossible. New chromophores which are more stable to light would be one answer. Furthermore, one could apply singlet oxygen quenchers, radical scavengers, or excited dyestuff trappers for depressing any one of the critical degradation routes. Some approaches towards these directions have been described before (see Oda and Kitao,[40] Kuramoto,[41] Neevel *et al.*[42] and Rath and Brielmeier[43]).

ACKNOWLEDGEMENTS

C.S. expresses his gratitude to the Stipendienfonds der Chemischen Industrie, Frankfurt am Main, for financial support. We specially thank Dr H. Tappe and Dr W. Russ of the Hoechst AG, Frankfurt am Main, for their fruitful suggestions during the work.

REFERENCES

1. Abeta, S., Yoshida, T. & Imada, K., *Am. Dyest. Rep.*, **73/7** (1984) 26.
2. Bredereck, K. & Schumacher, C., *Dyes and Pigments*, **21** (1993) 23.
3. Bredereck, K. & Schumacher, C., *Dyes and Pigments*, **21** (1993) 45.
4. Bredereck, K. & Schumacher, C., *Dyes and Pigments*, **22** (1993) 121.
5. Giles, C. H. & McKay, R. B., *Text. Res. J.*, **33** (1963) 527.
6. Bentley, P., McKellar, J. F. & Phillips, G. O., *Rev. Prog. Color.*, **5** (1974) 33.
7. Evans, N. A. & Stapleton, I. W., In *The Chemistry of Synthetic Dyes*, Vol. VIII, ed. K. Venkatarman. Academic Press, New York, 1978, p. 221.
8. Kramer, H., *Chimia*, **40** (1986) 160.
9. Baumgarte, U. & Wegerle, D., *Melliand, Textilber.*, **67** (1986) 567.
10. Allan, N. S., *Rev. Prog. Color.*, **17** (1987) 61.
11. Griffiths, J. & Hawkins, C., *J. Chem. Soc. Perkin II*, **1977**, 747.
12. Van Beek, H. C. A. & Heertjes, P. M., *J. Soc. Dyers Colour.*, **79** (1963) 661.
13. Van Beek, H. C. A., Heertjes, P. M., Houtepen, C. & Retzloff, D., *J. Soc. Dyers Colour.*, **87** (1971) 87.
14. Kienle, R. H., Stearns, E. I. & van der Meulen, P. A., *J. Phys. Ch*em., **50** (1946) 363.
15. Cumming, J. W., Giles, C. H. & McEachern, A. E., *J. Soc. Dyers Colour.*, **72** (1956) 373.
16. Giles, C. H., Shah, C. D. & Watts, W. E., *J. Soc. Dyers Colour.*, **88** (1972) 433.
17. Shah, C. D. & Srinivasan, R., *J. Appl. Chem. Biotechnol.*, **27** (1977) 429.
18. Chipalkatti, R. H., Desai, N. F., Giles, C. H. & Macaulay, N. J., *J. Soc. Dyers Colour.*, **70** (1954) 487.
19. Sramek, J., *Textil, Prague*, **27** (1972) 10, 328.
20. Datyner, A., Nicholls, C. H. & Pailthorpe, M. T., *J. Soc. Dyers Colour.*, **93** (1977) 213.
21. Hoechst, AG, Personal communication, 1992.
22. Krucker, W., *Textilveredlung*, **21** (1986) 295.
23. Robinson, H., *Physiol. Rev.*, **34** (1954) 202.
24. Heir, S. W., Cornbleet, T. & Bergheim, O., *J. Biol. Chem.*, **166** (1946) 327.

25. Perspiration Fastness Subcommittee, *J. Soc. Dyers Colour.*, **68** (1952) 392; **70** (1954) 63.
26. Gudewil, S., *Textilveredlung*, **23** (1988) 265.
27. Achwal, W. B. & Habbu, V. G., *Man-Made Textiles in India*, **29** (1986) 286.
28. Inoko, T., Nakabayashi, T. & Miyake, K., *Senshoku Kogyo*, **35** (1987) 165 (Jap.); via *CA*, **107** (1987), 60548h and WTA 1987/7332.
29. Kurihara, H., *Tochigi-ken Sen'i Kogyo Shikenjo Kenkyu Hokoku*, **1976**, 31; via *CA*, **89** (1978) 181132a; idem *Sen'i Kako*, **29** (1977), 500 (Jap.); via *CA*, **89** (1978) 25904y.
30. Oe, S., *Kenkyu Hokoku—Gigu-ken Sen'i Shikenjo*, **1** (1978), 1 (Jap.); via *CA*, **93** (1980) 48394d.
31. Schumacher, C., PhD thesis, Universität Stuttgart, Germany, 1992.
32. Hempel, R., Viola, H., Morgenstern, J. & Mayer, R., *Z. Polymerforsch. Faserforsch. Textiltechnik*, **29** (1978) 190.
33. Kuramoto, N. & Kitao, T., *J. Soc. Dyers Colour.*, **96** (1980) 529.
34. Wegmann, J., *J. Soc. Dyers Colour.*, **76** (1960) 205.
35. Shukla, S. R. & Sakharande, V. D., *Dyes and Pigments*, **17** (1991), 11; **17** (1991) 101; idem, *Am. Dyest. Rep.*, **7** (1991) 38.
36. Kissa, E., *Text. Res. J.*, **41** (1971) 715.
37. Okada, Y., Motomora, H. & Morita, Z., *Dyes and Pigments*, **16** (1991) 205.
38. Okada, Y. & Morita, Z., *Dyes and Pigments*, **18** (1992) 259.
39. Baumann, H., *J. Soc. Dyers Colour.*, **90** (1974) 125.
40. Oda, H. & Kitao, T., *J. Soc. Dyers Colour.*, **101** (1985) 177; **103** (1987) 205.
41. Kuramoto, N., *J. Soc. Dyers Colour.*, **103** (1987) 319.
42. Neevel, J. G., van Beek, H. C. A. & van de Graaf, B., *J. Soc. Dyers Colour.*, **107** (1991) 110.
43. Rath, H. & Brielmeier, H. J., *Melliand. Textilber.*, **42** (1961) 911.