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The light stability of azo dyes and dyeings V. The impact of the atmosphere on the light stability of dyeings with heterobifunctional reactive azo dyes

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Abstract

Two heterobifunctional reactive azo dyes (A(MCT-VS), (B(MCT-VS)) as well as their partly and fully hydrolysed derivatives and their "naked chromophores" have been used in preparing cellulosic dyeings. Reactive (RC) and substantive (N) dyeing procedures have been used, respectively. Two sets of dyeings (5 pieces each) have been produced as members of the A group and those of the B group. All dyeings have been exposed to light of Xenotest 450 equipment for 96 h in open and in closed air as well as in closed oxygen and closed nitrogen atmospheres, respectively. Similar exposures have been performed also in the presence of artificial perspiration prepared according to Japanese standard (pH = 3.5). The light stability of all dyeings of the A group exceeded that of the respective values of the members of the B group under exposure to light in open air atmosphere in the absence of perspiration. In the presence of perspiration, however, all members of the B group proved to be more stable to light than the respective members of the A group. It could be concluded that the members of the A group proved to be less sensitive to oxidative photofading than those of the B group whereas the sensitivity to reductive photofading was definitely higher in A dyeings. The observed rather contradictory behaviour between the A and B groups of similar chemical structure might be attributed to the Hammett effect of the electron donating methoxy substituent in the B structures.

Keywords: Photofading; Reactive azo dyes; Effect of atmosphere; Cotton; Light stability; Effect of perspiration

1. Introduction

Studies on the light stability of cotton fabrics dyed with heterobifunctional reactive azo dyes as well as with their partly and fully deactivated derivatives, respectively, have been published earlier [1–4]. Similar studies have been performed also in the presence of perspiration [5–15]. The rate and extent of the photofading induced by exposure to light depend not only on the substrate and on the characteristics of the dyes but also on the quality of incident light as well as on the environmental conditions. The earlier studies mentioned have been performed mainly in open air.

Among many other studies on the subject matter those published by Okada and co-workers have to be mentioned [5–13].

Light induced oxidative degradation of vinyl sulphonyl (VS) reactive azo dye was dominant in the presence of dry air, whereas reductive mechanisms occurred in air free system under the impact of DL-mandelic

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acid [5]. Major influence could be attributed to the oxidisability of the chromophore of the studied VS reactive dyes in the photofading process.

Photodegradation of wet VS reactive dyeing occurred under the action of light induced singlet oxygen [6].

The rate of photooxidation exceeded in wet dyeing than that in the dry one. The higher was the dye content of the dyeing the faster was the photofading [7].

Oxidative photofading could not be modified under aerobic wet conditions by the addition of DL-mandelic acid [8].

The type of the photochemical reaction – oxidative or reductive – is highly dependent on several conditions (temperature, pH, moisture, presence or absence of oxygen, dye concentration as well as on the chemical and physical characteristics of the substrate) under which the light exposure of the dyeing was performed [9].

The photofading of VS dyeing becomes reductive under anaerobic conditions and its rate increases with the decreasing pH value. The rate of the oxidative photofading of VS dyeings increases, however, under aerobic conditions with the increasing pH value. Dominant was the dependence of the rate of photofading on the pH if wet VS dyeing had been exposed to light [10].

No photofading could be observed on monochlorotriazine (MCT) reactive cellophane azo dyeings if exposure had been performed in oxygen free water. If DL-mandelic acid was added to the former system, reductive photofading occurred [11].

Some MCT reactive azo dyeings underwent reductive photofading in aerated water while some others showed oxidative fading under identical conditions. Consequently the type of photofading of such dyeings is sensitively dependent not only on the circumstances of exposure but also on the chemical structure of the MCT reactive azo dye [12].

The rate of photofading of MCT reactive azo dyed cotton fabric and cellophane film, respectively, could be represented by two kinetic sections. The rate was markedly higher in the first section than in the second one for both systems. The rate of fading was fairly constant or continuously decreasing in the second section [13].

The type of substituents in the reactive azo dye molecule has strong influence on the chemical characteristics of photofading under light exposure. Electron donating substituents bring about oxidative photofading whereas electron withdrawing ones promote reductive photofading. Reductive fading mechanism prevails in the dry state, it becomes, however, oxidative in the presence of water. In the presence of artificial alkaline and acidic perspirations, respectively, the reductive fading is greatly accelerated [14].

Dyeing with the earlier studied two heterobifunctional reactive azo dyes and with their deactivated derivatives were exposed to light in the presence and absence of artificial perspiration, respectively, in the present work in open and closed air as well as in closed oxygen and closed nitrogen atmospheres, respectively [1–4].

2. Experimental

2.1. Materials

2.1.1. Dyes

The dyes used are shown in Table 1.

The performed reactive dyeing has been denoted by the lower index of RC while the non-reactive one has been denoted by the lower index of N.

2.1.2. Substrate

Plain woven scoured, bleached and mercerised cotton fabric:

– Yarn density:	Warp: 288/10 cm; weft: 256/10 cm
– Surface density:	108 g m^{-2}
– Tensile strength:	Warp: 265[N/5 cm]; weft: 235 [N/5 cm]
– Elongation at break:	Warp: 8.25%; weft: 13.91%
– Yarn fineness:	Warp: 20 tex; weft: 20 tex
– Equilibrium moisture regain at 65% rh.:	7.33%
– Water retention:	44.74%
– Degree of polymerization (DP):	1795 ± 50

2.1.3. The composition of the artificial perspiration

The composition of the artificial perspiration has been disclosed in Table 2.

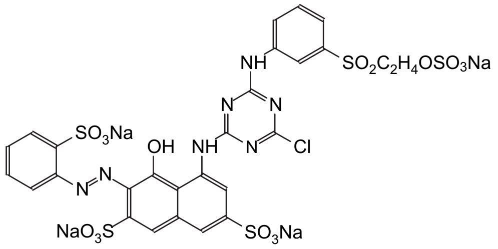
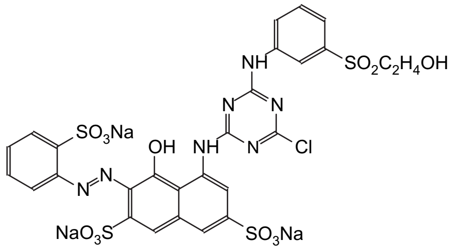
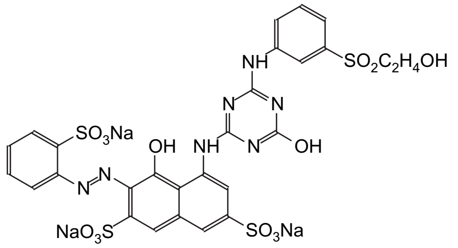
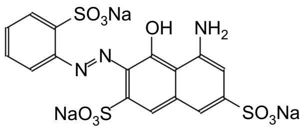
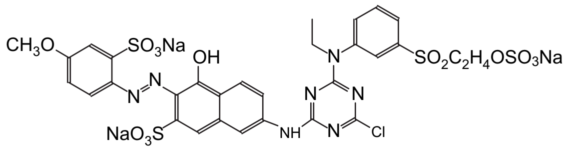
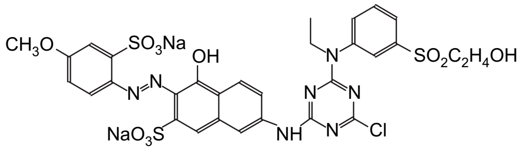
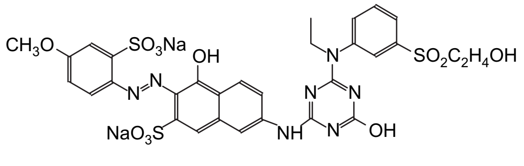
2.2. Dyeing procedures

The dye-to-fibre ratio was 3:100, using a fibre-to-liquor ratio 1:50. The dyeing system was continuously stirred during the whole procedure in a Multi-Dye equipment.

2.2.1. RC-procedure

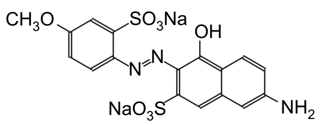
At the beginning of the procedure the dyeing system contained distilled water, dyestuff, 5 g substrate and 50 g l^{-1} Na_2SO_4 at ambient temperature. The temperature of the bath was raised to 60 °C within 10 min and was kept at that level for a further 10 min. After the addition of 20 g l^{-1} K_2CO_3 the system was kept at 60 °C for a further 60 min. The dyed sample was washed subsequently for 5 min at ambient temperature followed by rinsing in 0.3% aqueous acetic acid solution at 50 °C for 5 min, followed by hot rinsing at 90 °C as many times as necessary to obtain a colourless washing liquor. The sample was then air-dried at room temperature.

Table 1
Dyes used for dyeing

No	Formula	Abbreviation	Explanation
1		A(MCT-VS)	Heterobifunctional reactive azo dye
2		A(MCT-VH)	A(MCT-VS) with hydrolysed VS group
3		A(MHT-VH)	A(MCT-VS) with hydrolysed MCT and VS groups
4		A(Chr)	A chromophore A(MCT-VS) without MCT and VS groups
5		B(MCT-VS)	Heterobifunctional reactive azo dye
6		B(MCT-VH)	B(MCT-VS) with hydrolysed VS group
7		B(MHT-VH)	B(MCT-VS) with hydrolysed MCT and VS groups

(*continued on next page*)

Table 1 (*continued*)

No	Formula	Abbreviation	Explanation
8		B(Chr)	A chromophore B(MCT-VS) without MCT and VS groups

The RC-dyeing procedure was considered as completed if an extraction of the dyed sample in *N*,*N*-dimethylformamide (liquor ratio of 1:50) for 5 min at boiling temperature, did not cause dissolution of traces of dye in the liquor.

2.2.2. N-procedure

This procedure was distinguished from the RC one by the following: no K_2CO_3 was added to the dye bath within the procedure which lasted for 80 min and finally the dyed fabric was not washed prior to drying. It was padded to a liquor pick-up of 100% and dried at room temperature in open air. The dye pick-up of the N-dyed samples exceeded that of the RC dyeings by approximately 50%.

2.3. Exposure to light

Dyeings were exposed to light for 96 h in a Xenotest 450 equipment at black panel temperature of 40 °C and of rh. 45%. Exposures in closed atmospheres were performed in sealed quartz cuvette delivered by Original-Hanau as an accessory of Xenotest.

2.4. Colour measurement

Colour coordinates of dyeings before and after exposure for different periods were established by Datacolor colour measuring instrument. The data enabled the calculation of the colour difference (ΔE^*_{ab}) between the samples before and after the exposure to be made.

Table 2
The composition of the artificial perspiration (JIS L 0848 Japanese standard)

Component	g/l
Lactic acid	5
NaCl	5
$Na_2HPO_4 \cdot 12H_2O$	5
DL-aspartic acid	0.5
Glucose, anhydrous	5
Histidine	0.5
Sodium D-pantothenate	5
	Filled up with distilled water 1000 ml Acetic acid to adjust the pH = 3.5

3. Results and discussion

3.1. Photofading of A dyeings

The data obtained in open air atmosphere were taken to be the standard for comparison with data obtained in further systems (Fig. 1). The order of sequence of the dyeings demonstrated in the *x*-axis follows decreasing binding strength between the dye molecule and the substrate.

Oxidative photofading might be assumed in the oxygen containing system. The observed differences in the rate of photofading might be attributed to the following factors: difference in the oxygen concentration in atmosphere and retained moisture in the closed atmosphere.

Higher rate of photofading in closed air as compared with that in open air might be explained with the presence of moisture for the full time of exposure in the first system. The same impact of moisture combined with that of the highest oxygen concentration explains the highest rate of photofading in closed oxygen.

The rate of photofading shows for all the studied dyeings the following increasing order of sequence: open air < closed air < closed oxygen. The rate of photofading in closed nitrogen was equal to or less than that in open air for the first three dyeing [A(MCT-VS)$_{RC}$, A(MCT-VH)$_{RC}$, A(MCT-VS)$_{N}$], whereas it exceeded that in the last two dyeings [A(MHT-VH)$_{N}$, A(Chr)$_{N}$].

The light sensitivity of the studied dyeings increased with the decreasing binding force between dye and

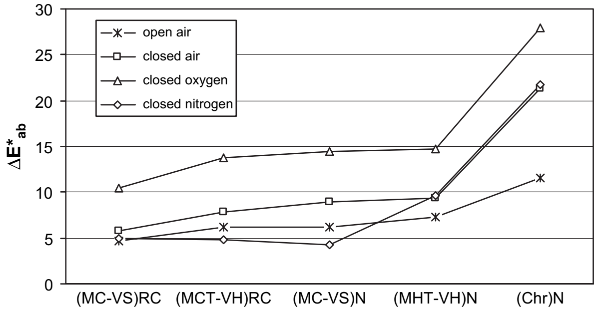


Fig. 1. The photofading of the dyeings of A group after exposure to light in dry state in the absence of perspiration.

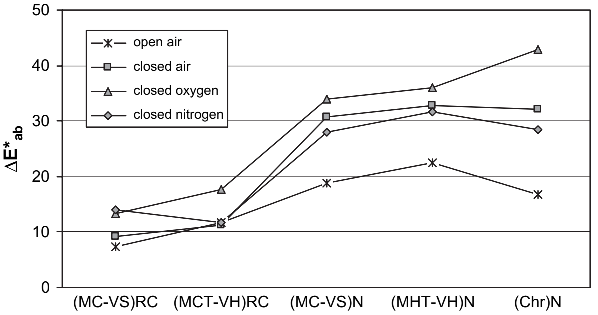


Fig. 2. The photofading of the dyeings of A group after exposure to light in wet state in the presence of perspiration.

substrate. The highest rate of photofading could be observed in N-dyeing of the chromophore in all the studied atmospheres. Main role in light stability of dyeing can be attributed to the covalent bond between the MCT group of the dye and the substrate. The only exception from the latter statement is the behaviour of A(MCT-VS)$_N$ dyeing in closed nitrogen atmosphere where no oxidative photofading can be assumed.

The sequence of order of the increasing rate of photofading in the presence of perspiration was the following for the dyeings of A group: open air < closed nitrogen < closed air < closed oxygen (Fig. 2).

The main impact on photofading might be attributed to the artificial perspiration as long as moisture had been present in the system. The concentration of oxygen in the atmosphere also plays a role but only of secondary importance in that series of photofading.

The sensitivity towards photofading increases among the members of A group in the following order of sequence in all atmospheres: A(MCT-VS)$_{RC}$ < A(MCT-VH)$_{RC}$ < A(MCT-VS)$_N$ < A(MHT-VH)$_N$.

Resistance to photofading decreases with the increasing rate of hydrolysis of MCT-type dye–fibre bonds while the VS-type reactive bond remains stable also in the presence of acidic perspiration. The missing of VS-type bonds brought about the increasing sensitivity of A(MCT-VH) dyeing and the missing protection by covalent bonds in the A(MCT-VS)$_N$ and A(MHT-VH)$_N$ dyeings, might explain their higher rate of photofading.

Table 3
Acceleration quotients of photofading brought about by perspiration in A dyeings in the studied atmospheres

Dyeing	Acceleration quotients and atmospheres			
	Open air	Closed air	Closed oxygen	Closed nitrogen
A(MC-VS)$_{RC}$	1.6	1.6	1.3	2.9
A(MCT-VH)$_{RC}$	1.9	1.4	1.3	2.4
A(MC-VS)$_N$	3.0	3.5	2.3	6.7
A(MH-VH)$_N$	3.1	3.5	2.4	3.3
A(Chr)$_N$	1.4	1.5	1.5	1.3

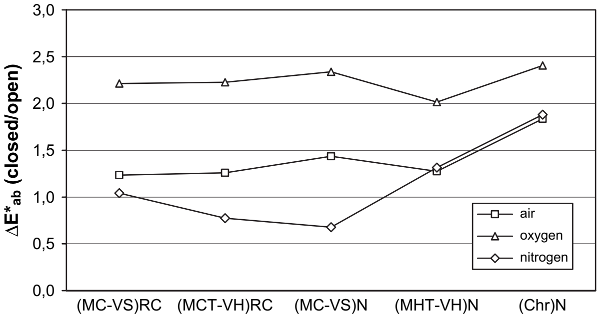


Fig. 3. The impact of the quality of atmosphere on the rate of photofading of A dyeings in the absence of perspiration in relation to the respective values obtained in open air.

Slight deviation occurred from that rule in closed nitrogen atmosphere in the photofading of A(MCT-VH)$_{RC}$ dyeing. The role of oxygen widely exceeded that of perspiration in the photofading of A chromophore and dyeing.

Perspiration accelerated the photofading in all studied atmospheres for all A dyeings (Table 3). The acceleration for N-dyeings significantly exceeded that in RC dyeings. The higher was the rate of photofading in the absence of perspiration the lower was the acceleration brought about by the presence of perspiration.

The acceleration in photofading has been controlled by the rate of splitting of the MCT-type covalent bond in RC dyeings. The originally already high rate of photofading in Chr$_N$ dyeings could only be less markedly accelerated in the presence of perspiration (Figs. 3 and 4).

3.2. Photofading of B dyeings

The data obtained in open air atmosphere were taken to be the standard for comparison with data obtained in further systems (Fig. 5). The order of sequence of the dyeings demonstrated in the *x*-axis follows decreasing binding strength between the dye molecule and the substrate.

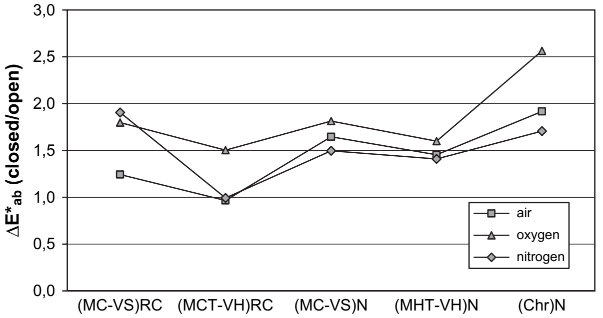


Fig. 4. The impact of the quality of atmosphere on the rate of photofading of A dyeings in the presence of perspiration in relation to the respective values obtained in open air.

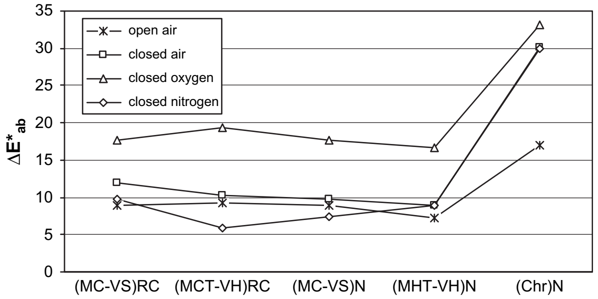


Fig. 5. The photofading of the dyeings of B group after exposure to light in dry state in the absence of perspiration.

Table 4
Acceleration quotients of photofading brought about by perspiration in B dyeings in studied atmospheres

Dyeing	Acceleration quotients and atmospheres			
	Open air	Closed air	Closed oxygen	Closed nitrogen
$B(MC\text{-}VS)_{RC}$	0.70	0.82	0.96	1.10
$B(MCT\text{-}VH)_{RC}$	0.87	1.11	0.95	1.27
$B(MC\text{-}VS)_N$	1.53	2.39	1.53	3.35
$B(MH\text{-}VH)_N$	2.15	2.74	1.78	2.78
$B(Chr)_N$	0.95	1.14	1.36	1.17

No differences in the rate of photofading could be attributed to covalent dye–fibre bonds among the first four members of the B dyeings if exposed to light in open air.

Markedly higher rate characterised, however, the photofading of B chromophore N-dyeing in the same system.

No protective impact of covalent bond occurred under similar exposure to light neither in closed air nor in closed oxygen atmosphere. The increased moisture content of the closed air atmosphere generated slight increase of photofading in RC dyeings but no similar detectable impact could be observed on N-dyeings. Very significant deterioration of light stability occurred in closed air atmosphere for $B(Chr)_N$-dyeing. The high oxygen content (closed oxygen) generated twofold higher rate of photofading for both B_{RC}- and for B_N dyeings as compared with the respective rates obtained in open air. Identical increase in the rate of photofading of $B(Chr)_N$-dyeing occurred if the respective rates in closed oxygen and in open air were compared, however, the increase relative to that obtained in closed air was nearly negligible. It can be concluded that the dominant type of reactive bonds between B dye and cellulose did not protect the B dyeings against photofading in the studied atmospheres. (It could earlier be observed [2] that VS reactive bond was dominant in B dyeings whereas MCT bond was the same in A_{RC} dyeings, consequently MCT dye–fibre bonds decelerate the photofading of MCT_{RC} dyeings while VS_{RC} bonds did not do the same.).

The general impact of the presence of perspiration has been the deceleration of photofading in B_{RC} dyeings (Fig. 6). The impact of perspiration was, however, very significantly accelerating in the photofading of the studied B_N dyeings in the three oxygen containing atmospheres.

In closed oxygen atmosphere the protecting action of perspiration was just detectable (Table 4).

Definite acceleration was brought about by perspiration in the studied N-dyeings. The only exception was B chromophore N-dyeing in which, however, the rate of photofading was very high already also in the absence of perspiration (Figs. 7 and 8).

Comparing the ratio of photofading between of respective A and B dyeing the following can be concluded:

All the A dyeings show lower rate of photofading in the absence of perspiration than that of the respective B dyeing, whereas the rate of photofading of B dyeings was markedly lower than that of respective A dyeings in the presence of perspiration.

Consequently perspiration has a marked acceleration impact on the photofading of A dyeings while protective or much less accelerating effect could be demonstrated in photofading of B dyeings.

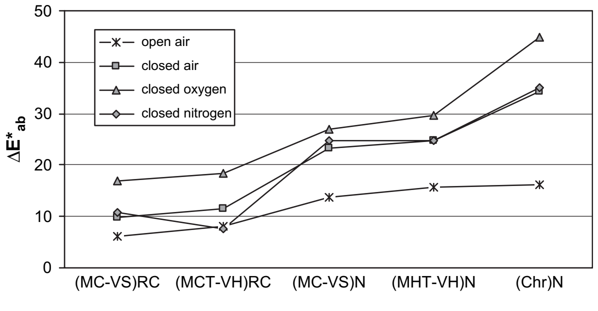


Fig. 6. The photofading of the dyeings of B group after exposure to light in wet state in the presence of perspiration.

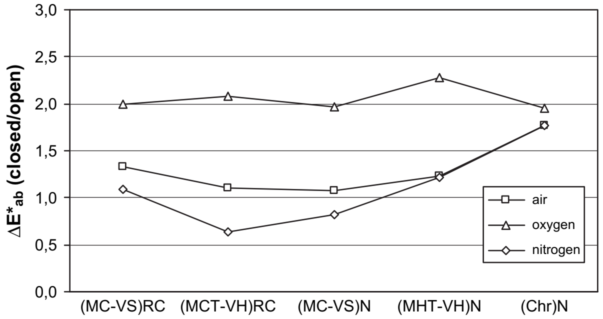


Fig. 7. The impact of the quality of atmosphere on the rate of photofading of B dyeings in the absence of perspiration in relation to the respective values obtained in open air.

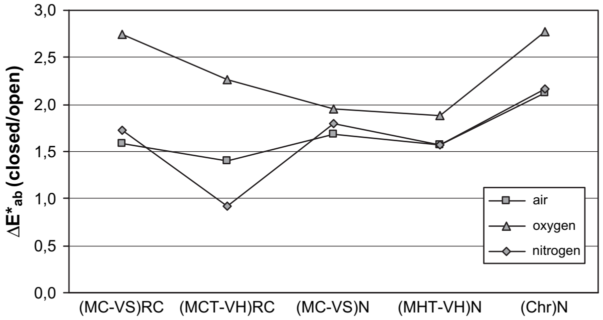


Fig. 8. The impact of the quality of atmosphere on the rate of photofading of B dyeings in the presence of perspiration in relation to the respective values obtained in open air.

It can be concluded that all the dyeings of A group are not too much sensitive to photooxidation they are, however, rather sensitive to reduction. The dyeings of B group are, however, very sensitive to photooxidation and not really sensitive to photoreduction. The result what could be observed on these considerations is that the reducing impact of perspiration counterbalanced the oxidising effect of atmosphere and resulted in accelerated photoreductive fading for A dyeings.

The rapid photofading of B dyeings under the impact of oxygen in the atmosphere could partly be compensated by the reducing effect of perspiration resulting in decelerated photofading.

This difference in reactivity might be attributed to electron donating impact of methoxy substituent (Hammet's σ value -0.27 [16]) in all members of the B group.

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