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# The Light Stability of Azo Dyes and Azo Dyeings. III. The Effect of Artificial Perspiration on the Light Stability of Reactive and Non-Reactive Derivatives of Two Selected Azo Chromophores in Aqueous Solution

P. Aranyosi,[a] Zs. Csepregi,[a] I. Rusznák,[a]* L. Töke[b] & A. Víg[b]

[a]Department of Organic Chemical Technology, T.U. Budapest H-1521, Budapest, PO Box 91 Hungary
[b]Organic Chemical Technology Research Group of Hungarian Academy of Sciences, Hungary

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*ABSTRACT*

*The light stability of two series of azo dyes has been studied in aqueous solution. The first chromophore (A(Chr)) is the coupling product of diazotized ortanilic acid and H-acid, and the second (B(Chr)) is that of diazotized p-anisidine-2-sulfonic acid and J-acid. Bifunctional and monofunctional reactive, as well as non-reactive derivatives, respectively have been exposed to light in aqueous solution. The light stability of the members in the 'A'-group, except A(Chr) and A(DCT) exceeded that of the corresponding members of the 'B'-group. The light stability of the heterobifunctional reactive members of both groups (MCT-VS) could be improved by partial (MHT-VS and MCT-VH) or total (MHT-VH) hydrolysis of the reactive groups. The presence of artificial perspiration in the dye solution very significantly deteriorates the light stability of all the dyes studied. The perspiration induced a decrease in the light stability of the 'A'-group significantly, exceeding that of the 'B'-group; $t_{50}$ values, however, are very close to each other subsequent to perspiration-light exposure of all the studied 14 dissolved dyes.* © *1998 Elsevier Science Ltd*

*Keywords*: dissolved azo dyes, lightfastness, perspiration–light stability, additive effect.

## INTRODUCTION

A full elucidation of the chemical and physical details pertinent to the photofading process would be of value in attaining an improvement in the

*Corresponding author.

generally medium light fastness of azo reactive dyes. The effect of certain additives which deteriorate light stability has been published earlier [1–4]. Human perspiration is one of such additives and this can be simulated by a mixture of appropriately selected chemicals. The artificial perspiration in the present work was prepared according to the Japanese standard [5].

In the possible mechanisms of the photofading process three main modes, viz., radical, reductive and oxidative, need to be considered. Photofading, however, often follows mixed mechanism pathways. As Egerton and Morgan noted [6] photofading is much more the characteristic of a fibre–dye system than that of the dye alone. The type of photofading mechanism may vary with the nature of the fibre, and it may also be different according to the applied conditions of the dyeing procedure and those of the exposure [6, 7]. The structure of azo dyes, i.e. the nature of their diazo and coupling components, as well as their substituent groups, determine the light stability of dyed systems on an identical substrate.

The light stability of dyeings with the monoazodyes $R_1-N=N-R_2$ ($R_1$; the substituted aromatic residue of the diazo component; $R_2$, $-OH$ and/or $-NH_2$ substituted phenyl or naphthyl residue of the coupling component) is generally not dependent on $R_1$ while it is in close correlation with $R_2$ [6].

The presence of too many electron withdrawing substituents in the dye molecule can significantly lower the light stability due to deformation of the azo bond. Intermolecular H-bonds bring about aggregation of the dye molecules, thus improving the light stability [3].

In addition to the above mentioned three types of mechanism of photofading, photoisomerization may also occur.

Van Beek and Heertjies [1] and van Beek [8] observed that the photoreduction of selected monoazo-dyes in aqueous solution was significantly accelerated by the addition of acetic acid, tartaric acid, succinic acid, malonic acid, mandelic acid, acetone or methanol. The rate of photofading was increased by compounds containing CH–OH groups due to the proton donating ability of this group. Compounds containing a carbonyl or phenyl group in an $\alpha$-position to the proton donating group showed an identical effect. Dissolved oxygen decelerated the very high rate of photofading of such a system. These authors assumed that the dissolved oxygen oxidised the initially reduced photofading products. In the presence of dissolved oxygen peroxy compounds could also be detected among the photofading products.

Intermediary hydrazyl radicals and hydrazo components have also been observed in photoreduced azo compounds [1, 8]. Due to the instability of the radicals, either hydrazo compounds occur in the system or the starting azo compound is regenerated (Fig. 1).

Reducing agents produced by photoactivation of appropriate aliphatic or aromatic compounds have been used to study the photofading of azo dyes in

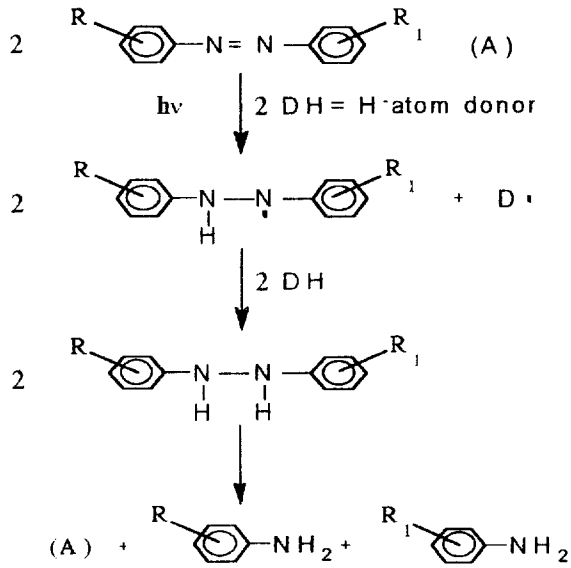



**Fig. 1.** Reductive mechanism of the photofading of azo–dyes [1, 4].

aqueous solution in the absence and presence of dissolved oxygen [2, 9]. Photoactivated sodium–mandelate solution was found to be one of the most suitable reducing agents for azo dyes and for their selected mixtures. All the studied reactions, in which the azo dyes as well as the dissolved oxygen were considered as oxidizing agents could be described as redox reactions with the photoactivated reducing agent. Dissolved oxygen present in the system reacted more rapidly with the reducing agent, thus inhibiting and postponing the reaction of the azo dyes. The rate of photofading of the dissolved dye is controlled by the equilibrium constant of the redox reaction.

The oxidation mechanism of photofading might be attributed to the action of singlet oxygen in the system. Such a mechanism has been suggested by Kuramoto and Kitao [3], as shown in Fig. 2. Amino-compound additives usually inhibit oxidative photofading.

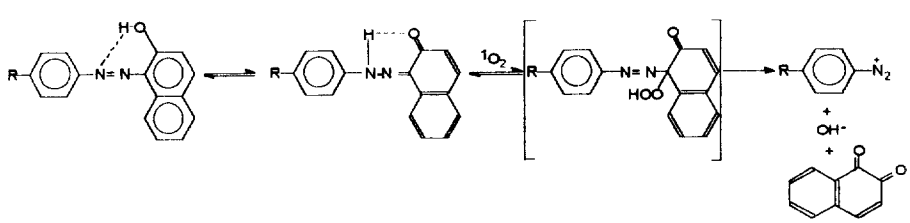



**Fig. 2.** Oxidative photofading of azo–dyes.

The action of dissolved sodium mandelate or of oxygen on a monochlorotriazinyl azo reactive dyed system has been studied by Okada *et al.* [10]. A reductive photofading mechanism was demonstrated in the presence of sodium mandelate whereas oxidative photofading occurred in the presence of oxygen. If the azo form was predominant in the azo-hydrazone tautomeric equilibrium of the azo reactive dye bound to cellophane under exposure of the system an improved light stability was attained in the presence of oxygen compared to a system containing predominantly the hydrazone form of the dyes.

A preferred oxidative mechanism generated by singlet oxygen has been assumed by Okada *et al.* [10–12] in studying the photofading of wet sulphato-ethyl sulphonyl-(vinylsulphonyl-) azo reactive dyed cellulose samples. The rate of photofading was controlled by the sensitivity of the dye to oxidation. The photofading of that dye-component in the dye-mixture which is more sensitive to oxidation was the more rapid. Components which are less sensitive to oxidation may act in such systems as photosensitizers and in certain cases a self-photosensitising effect of certain dyes was also demonstrated.

Sirbiladze *et al.* [13, 14] have demonstrated that stable free radicals were generated under the exposure of some azo reactive dyed cellulose samples to light. The proportion of radical photofading cannot be neglected beside other mechanisms.

We have recently studied (unpublished work) the light stability of dyeings produced with the dyes used in this present work. The role both of chemical modification of the dye molecule and of the type of the dye–fibre bond on the light stability of the dyeing was apparent.

In this study, differently substituted azo reactive dyes have been exposed in aqueous solution to light in order to find a correlation between their structure and the rate of photofading. The action of artificial perspiration on the rate of photofading was the subject of a further part of this study.

## EXPERIMENTAL

### Materials

Fourteen dyes were studied, eight belonging to a group derived from the coupling of diazotized orthanilic acid with H-acid ('A'-group) and six derived from the coupling of diazotized *p*-anisidine-2-sulfonic acid with J-acid ('B'-group). The 'A'-group consists of three hetero-bifunctional reactive dyes, three monofunctional reactive dyes and two non-reactive dyes whereas the 'B'-group consists of one hetero-bifunctional dye, three monofunctional reactive dyes and two non-reactive dyes.

The structure of the dyes and other relevant data are set out in Table 1. Artificial perspiration solution [5] was used in the second part of the experiments; the composition of the artificial perspiration is shown in Table 2.

## Methods

*Dye solutions*
$5\times10^{-5}$ mol dye was dissolved in 1000 $cm^3$ distilled water in the first part of the study. The same concentration of dyes was used in the artificial perspiration solution for the second part of the study.

*Exposure*
The optical system shown in Fig. 3 was used for the exposure. A high pressure mercury vapour lamp (TUNGSRAM HPLG 250) was the light source and the distance between the optical lens and the sample was 300 mm.

*Evaluation of photofading*
Absorption data were recorded on an HP UV-VIS 8452A Diode-Array Spectrophotometer.

Exposure and spectrophotometric measurement were performed in the same sealed quartz cuvette. The change in absorbance at max was determined, where

- $A_0$ the initial absorbance prior to exposure
- $A_t$ absorbance after $t$ min of exposure
- $A_{sc}$ absorbance of the solvent and the cuvette
- $A\%$ optical density

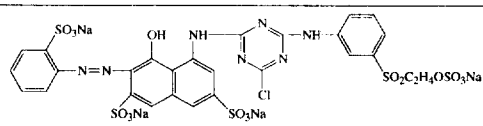
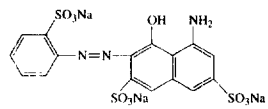
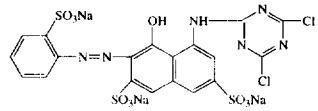
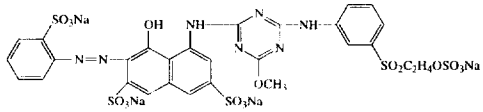
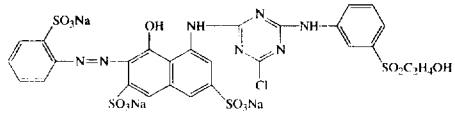
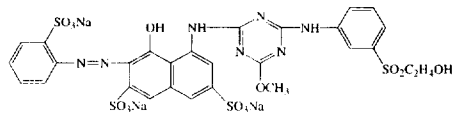
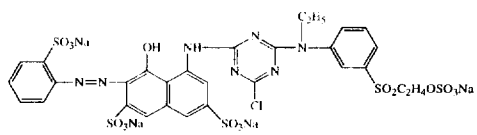
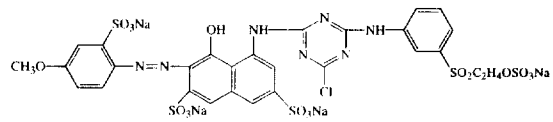
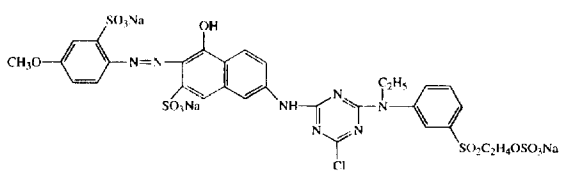
$$A\% = \frac{A_t - A_{sc}}{A_0 - A_{sc}} \times 100$$

Absorbance was plotted against the time of exposure and the curves were constructed with the help of regression analysis. Two characteristic points of the obtained kinetic curves were used for the evaluation: $t_{50}$ (time of exposure needed for 50% drop in the initial optical density) and $t_{20}$ (time of exposure needed for 80% drop in the initial optical density). A third point ($t_e$) could also be calculated representing that time of exposure which was needed for retaining $100/e = 36.79\%$ of the initial optical density.

## Results and discussion

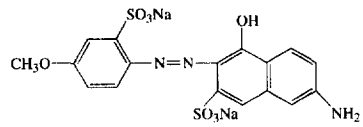
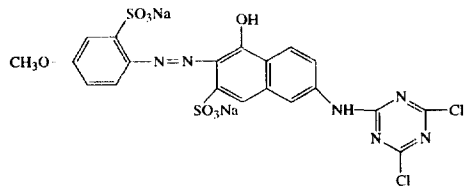
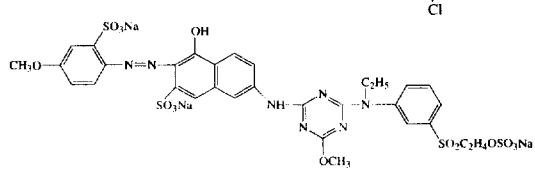
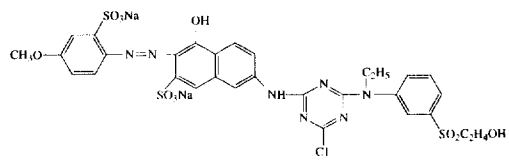
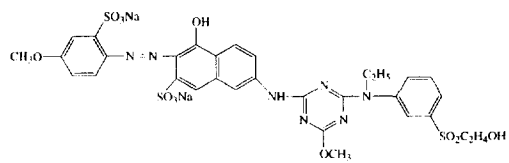
Data pertaining to the kinetics of the photofading of members of 'A'-group in aqueous solution are shown in Table 3 and in Fig. 4. Similar data are given in Table 4 and in Fig. 4 for the photofading of the 'B'-group dyes.

**TABLE 1**
Dyes

| *Code* | *Structure* | *Absorption peak (nm)* | *Molecular mass* |
|---|---|---|---|
| A(MCT-VS) |  | 510 | 982.87 |
| A(Chr) |  | 526 | 501.97 |
| A(DCT) |  | 512 | 649.91 |
| A(MHT-VS) |  | 534 | 978.92 |
| A(MCT-VH) |  | 534 | 880.93 |
| A(MHT-VH) |  | 534 | 876.98 |
| A(MCT-VS)$_{Et}$ |  | 512 | 1010.90 |
| A(MCT-VS)$_{Met}$ |  | 534 | 984.85 |
| B(MCT-VS) |  | 502 | 937.96 |

(*continued*)

**TABLE 1—*contd***

| *Code* | *Structure* | *Absorption peak (nm)* | *Molecular mass* |
|---|---|---|---|
| B(CHR) |  | 494 | 453.03 |
| B(DCT) |  | 502 | 599.97 |
| B(MHT-VS) |  | 502 | 934.01 |
| B(MCT-VH) |  | 502 | 836.03 |
| B(MHT-VH) |  | 502 | 832.07 |

Based on the data in Tables 3 and 4, and Fig. 4, the following general observations can be formulated (the term 'deactivated' used in the following text refers to methanolysis in the case of the MCT reactive group and hydrolysis in the case of the VS reactive group):

—The basic chromophore of the 'B'-group (B(Chr)) is significantly more stable to light in aqueous solution than that of 'A'-group [A(Chr)].

—Similar tendency occurs in the comparison of the dichlorotriazinyl members [A(DCT), B(DCT)] but the difference is somewhat smaller in favour of the 'B'-group member.

—The light stability of A(MCT-VS) and $A(MCT\text{-}VS)_{Met}$ is slightly exceeded by that of $A(MCT\text{-}VS)_{Et}$.

—The light stability of the monofunctional dye with deactivated chlorotriazinyl group [A(MHT-VS)] is better than that of the member with deactivated

**TABLE 2**
Artificial Perspiration Solution [5]

| *Component* | *Structure* | *Concentration* ($g\ l^{-1}$) |
|---|---|---|
| Disodium hydrogen phosphate | $Na_2HPO_4 \cdot 12H_2O$ | 5 |
| Sodium chloride | NaCl | 5 |
| Sodium D-pantothenate | $C_9H_{16}NO_5Na$ | 5 |
| Glucose (anhydrous) | $C_6H_{12}O_6$ | 5 |
| Lactic acid (85 %) | $CH_3CHOHCO_2H$ | 5 |
| L-Histidine monohydrochloride monohydrate | $C_6H_9N_302HCl \cdot H_2O$ | 0.5 |
| DL-Aspartic acid | $HOOCCH_2CH(NH_2)COOH$ | 0.5 |
| Acetic acid | $CH_3COOH$ | ([a]) |

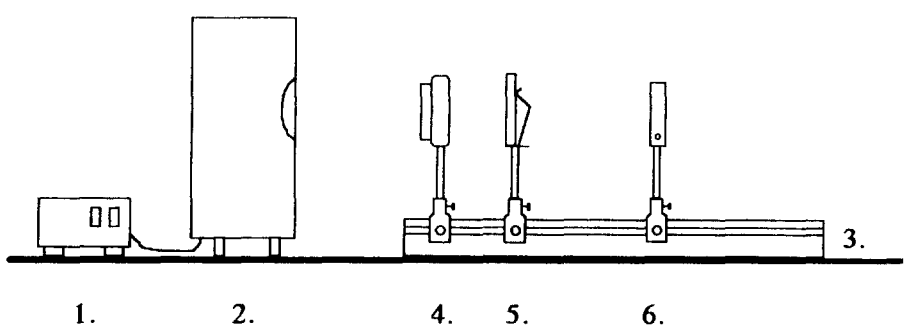
[a] The final pH of the solution was adjusted to 3.5 by the acetic acid component.

VS group [A(MCT-VH)]. The third monofunctional 'A'-dye, the dichlorotriazinyl derivative [A(DCT)] shows the poorest light stability among the monofunctional reactive members.

—The 'A'-group member with both deactivated reactive groups [A(MHT-VH)] has nearly the same light stability as A(MHT-VS).

—The light stability of the monofunctional B(MCT-VH) dye is much greater than that of the other three reactive members of the 'B'-group [B(MCT-VS), B(MHT-VS), B(DCT)]; there is no difference in the light stability of the latter three dyes.

—The best light stability was observed in the aqueous solution of the 'B'-group member with two deactivated reactive groups B(MHT-VH).




1. 250 W mercury lamp power supply
2. 250 W high pressure mercury vapour lamp
3. Standard triangular optical bench
4. Quartz lens
5. Filter cell
6. Cuvette holder

**Fig. 3.** System used for light exposure of liquids.

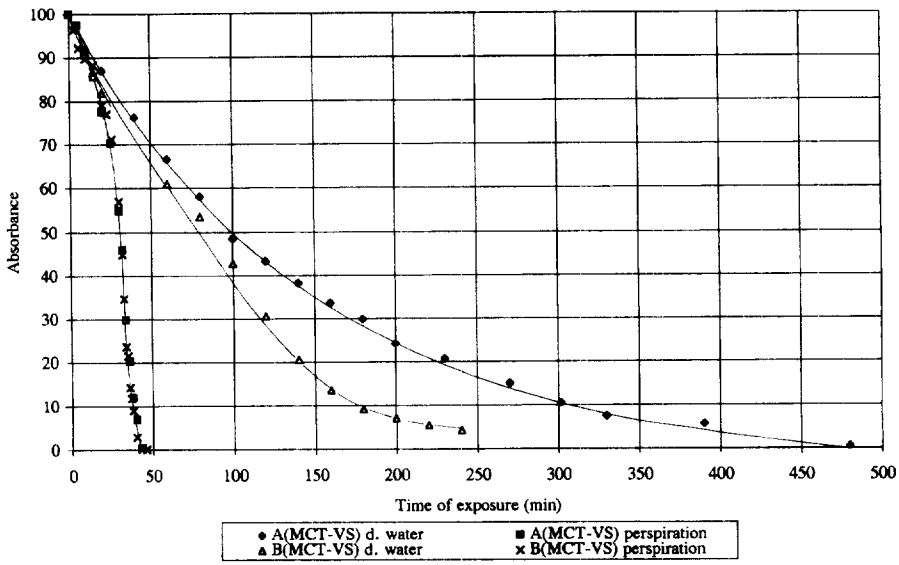



**Fig. 4.** Kinetics of photofading of A(MCT-VS) and B(MCT-VS) dyes in distilled water and in artificial perspiration.

—Among the four hetero-bifunctional reactive members of the two dye groups A(MCT-VS)$_{Et}$ excels in light stability; the worst light stability was for B(MCT-VS).

—Between the dichlorotriazinyl monofunctional reactive members of the compared two groups, the light stability of B(DCT) is markedly better than that of A(DCT).

—Very significantly better light stabilities could be observed in the aqueous solution of the monofunctional reactive members of the 'A'-group [A(MCT-VH), A(MHT-VS)] than in that of the corresponding two members of the 'B'-group.

—Significantly better was the light stability of the 'A'-group member with two deactivated reactive groups than that of the 'B'-group member.

**TABLE 3**
Kinetics of Photofading of 'A'-group Dyes Exposed to Light in Aqueous Solution

| *Code* | $t_{50}$ *(min)* | $t_{20}$ *(min)* | $t_e$ *(min) (36.7879%)* | $(r^2)$ |
|---|---|---|---|---|
| A(MCT-VS) | 104.8 | 200.2 | 136.8 | 95.96% |
| A(Chr) | 30.3 | 71.2 | 44.0 | 95.26% |
| A(DCT) | 45.6 | 83.0 | 58.1 | 87.96% |
| A(MHT-VS) | 222.5 | 515.2 | 320.5 | 99.68% |
| A(MCT-VH) | 196.8 | 438.6 | 277.8 | 99.59% |
| A(MHT-VH) | 210.7 | 484.2 | 302.3 | 99.88% |
| A(MCT-VS)$_{Et}$ | 125.6 | 284.7 | 178.9 | 99.61% |
| A(MCT-VS)$_{Met}$ | 102.7 | 216.5 | 140.8 | 95.69% |

**TABLE 4**
Kinetics of Photofading of 'B'-group Dyes Exposed to Light in Aqueous Solution

| *Code* | $t_{50}$ *(min)* | $t_{20}$ *(min)* | $t_e$ *(min) (36.7879%)* | $(r^2)$ |
|---|---|---|---|---|
| B(MCT-VS) | 67.9 | 133.3 | 89.8 | 97.44% |
| B(Chr) | 63.0 | 122.9 | 83.1 | 93.74% |
| B(DCT) | 67.4 | 143.0 | 92.7 | 96.41% |
| B(MHT-VS) | 69.5 | 135.8 | 91.7 | 91.23% |
| B(MCT-VH) | 94.6 | 194.4 | 127.9 | 94.50% |
| B(MHT-VH) | 133.7 | 297.9 | 188.7 | 98.76% |

—The reliability of the discussed data is in most of the cases very good ($r^2 > 95\%$) and in further cases good ($r^2 > 85\%$).

Dyes dissolved in artificial perspiration solution were exposed to light, removing samples at intervals identical with those applied in the first set of experiments. The photofading of the 'A'-group members is set out in Table 5 and that of the 'B'-group members in Table 6.

Observations in photofading of the dissolved dyes in artificial perspiration are as follows:

—The light stability of the chromophore of 'B'-group (B(Chr)) is significantly deteriorated by the presence of artificial perspiration, whereas little drop occurs only under similar conditions in the already poorer light stability

**TABLE 5**
Data For the Photofading Kinetics of the 'A'-group Members in Artificial Perspiration Solution

| *Code* | $t_{50}$ *(min)* | $t_{20}$ *(min)* | $t_e$ *(min) (36.7879%)* | $(r^2)$ |
|---|---|---|---|---|
| A(MCT-VS) | 31.2 | 35.4 | 33.8 | 87.02% |
| A(Chr) | 23.6 | 27.9 | 25.4 | 99.88% |
| A(DCT) | 27.1 | 30.7 | 29.5 | 73.86% |
| A(MHT-VS) | 29.5 | 36.0 | 32.0 | 98.09% |
| A(MCT-VH) | 35.9 | 42.3 | 41.0 | 86.71% |
| A(MHT-VH) | 26.1 | 31.2 | 28.3 | 99.94% |
| $A(MCT\text{-}VS)_{Et}$ | 30.0 | 34.3 | 32.4 | 95.93% |
| $A(MCT\text{-}VS)_{Met}$ | 32.1 | 39.9 | 36.3 | 92.44% |

**TABLE 6**
Data For the Photofading Kinetics of the 'B'-group Members in Artificial Perspiration Solution

| Code | $t_{50}$ *(min)* | $t_{20}$ *(min)* | $t_e$ *(min) (36.7879%)* | $(r^2)$ |
|---|---|---|---|---|
| B(MCT-VS) | 30.9 | 34.9 | 33.6 | 95.25% |
| B(Chr) | 25.8 | 31.2 | 29.5 | 92.54% |
| B(DCT) | 22.5 | 25.7 | 24.3 | 99.05% |
| B(MHT-VS) | 26.1 | 30.9 | 29.4 | 87.77% |
| B(MCT-VH) | 28.2 | 32.8 | 30.2 | 94.99% |
| B(MHT-VH) | 29.7 | 37.9 | 33.4 | 89.94% |

of the 'A' chromophore. The observed two values are nearly equal to each other.

—Although the change in light sensitivity caused by artificial perspiration is much higher on dissolved 'A'-group members than on the 'B'-group members, the obtained $t_{50}$ values do not vary too much among the 14 dyes studied. The mean value of $t_{50}$ in the 'A'-group is 29.4 and that of in the 'B'-group 27.2. The highest $t_{so}$ value was found with A(MCT-VH) (35.9) whereas the worst belonged to B(DCT) (22.5).

## CONCLUSIONS

### Light stability in aqueous solution

Although the chromophore of the 'B'-group [B(Chr)] is significantly more stable to light than that of the 'A'-group, the opposite is true for their derivatives carrying active and/or deactivated reactive groups. Consequently, in the case of the 'A'-group the introduction of reactive groups in active or deactivated form has a light stability improving effect. In the case of the 'B'-group, however such improvement occurred only if both types of reactive groups had been built into the dye molecule and either both or at least the VS group was deactivated. Consequently, light stability improvement in the 'B'-group might be expected under the chosen experimental conditions, from the presence of deactivated VS group in the molecule. The light stability improving effect of partial or complete deactivation occurs also among the hetero-bifunctional reactive members of the 'A'-group.

The reactive hetero-bifunctional members of 'A'-group show markedly poorer light stability than the above mentioned deactivated derivatives. It is noteworthy, that similar $C_2H_5$ substitution on the NH-group in the bridge between the two reactive groups existing in the B(MCT-VS) system resulted, with the 'A'-chromophore [A(MCT-VS]$_{Et}$), in better light stability than those of the A(MCT-VS) or A(MCT-VS)$_{Met}$ systems.

The hetero-bifunctional reactive member of the 'B'-group has equally poor light stability to the chromophore [B(Chr)] of the group. A marked improvement was achieved in this only if either both, or the VS group, had been deactivated prior to exposure. Consequently, the presence of the deactivated VS group (–$SO_2$–$CH_2$–$CH_2$–OH) improves the light stability of the 'B'-group chromophore derivatives in aqueous solution. In contrast with expectations, the dichlorotriazinyl reactive group in the dye molecule [A(DCT), B(DCT)] did not markedly improve the light stability compared to those derivatives containing two reactive groups in appropriately deactivated form.

**Light stability in aqueous artificial perspiration solution**

All fourteen members of the two dye groups practically lost their light stability in the presence of artificial perspiration in aqueous solution. The loss in the case of the 'A'-group members was markedly higher than that for the 'B'-group member. The $t_{50}$ mean values however are nearly identical after exposure in the presence of artificial perspiration, which implies that the increase of photofading in aqueous solution due to the presence of artificial perspiration was at least twice as high in the case of 'A'-group members than within the 'B'-group. An induction period occurred in the kinetic curves of the photofading in the presence of artificial perspiration, whereas no such period was observed on the kinetic curves of photofading in aqueous solutions without additives. It might be assumed therefore, that an interaction between artificial perspiration and the dissolved $O_2$ in the solution is responsible for the formation of the induction period. Further studies to resolve this phenomenon are being carried out.

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