

# Catalytic bleach: Most valuable applications for smart oxidation chemistry

Josef J. Dannacher

*Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland*

Available online 20 March 2006

## Abstract

The extraordinary interest of the chemical industry in oxidation catalysts is described. Regarding the use of such substances in catalytic bleaching, the washing process is employed to illustrate the pertinent phenomena and to quantify the current state of the art. Bleaching of stains, an essentially heterogeneous process, and of migrating dyes, basically a homogeneous oxidation reaction, are both discussed in quantitative terms. Likewise, the extent of damage to fibers and dyes, i.e. concomitant adverse effects inherent to any laundry bleaching system, is indicated. The essentials of the corresponding screening procedures are reviewed. With regard to chemical structures, results for complexes of diverse sorts of chelating agents are reported. These comprise 1,4,7-trimethyl-1,4,7-triazacyclononane-, salene-, saltrene- and terpyridine-type ligands and manganese, in different oxidation states, as the heavy metal cation. A qualitative model is presented to characterize the role of a bleach catalyst in activating hydrogen peroxide, i.e. at present the standard latent oxidant incorporated in modern detergent formulations. Relying on diverse experimental methods, critical aspects of catalytic bleaching have been studied. The ensemble of the corresponding results renders it possible to properly assess the technology per se and to indicate most promising routes for future pertinent research.

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*Keywords:* Bleach catalysts; Mechanistic aspects; Detergents; Benefit–Damage balance

## 1. Introduction

The present study deals with the use of oxidation catalysts in bleaching processes. It is laundry bleaching that will serve as a model to illustrate the most important phenomena, to characterize the current state of the art and to allude to promising directions for further improvement. Laundry bleaching is particularly suited for this purpose, as this application has been absorbing a good deal of the pertinent research activities [1], and because it involves two types of potential application of catalytic oxidation, a homogeneous reaction referred to as DTI (dye transfer inhibition) and a heterogeneous reaction called stain bleaching. Regarding the most crucial boundary conditions, laundry bleaching comprises an aqueous alkaline medium,  $\text{H}_2\text{O}_2$  as the oxidant and a multitude of substrates.

The interest of the chemical industry in oxidation catalysts goes far beyond their use in bleaching processes. Oxidations represent the most important class of chemical reactions, omnipresent in nature as well as in the laboratory of the chemist. The manufacturing of a great deal of chemicals involves an

oxidation step. With respect to yield, chemical rate and selectivity, oxidations often proceed in an unsatisfactory manner. The method of choice to remove such deficiencies is catalysis. Correspondingly improved production processes are of utmost importance to the chemical industry particularly in a period of time of tough competition and alarming price erosion.

In view of this central role of oxidation reactions in chemistry, it is not surprising that oxidation catalysts developed for a particular reaction can often be used in further processes, too. By the same token, it occurs that pertinent research efforts fail with respect to the original target reaction but accidentally furnish oxidation catalysts for another – sometimes much more important – process. This favorable situation explains the unusually big elbow-room which extensive research in the field of catalytic oxidation often enjoys in chemical companies. Moreover, the shared interest in fundamental aspects of the most important class of chemical reactions paves the way for fruitful collaborations between industrial and academic research groups. Typically, the latter strive for most detailed mechanistic insight into the catalysis of very specific oxidation reactions. Novel compounds developed in such a context may prove extremely valuable for other applications. It seems desirable that such substances be tested with a view to catalysis of alter-

*E-mail address:* [josef.dannacher@unibas.ch](mailto:josef.dannacher@unibas.ch).

native processes, such as bleaching. Successfully managing such co-operations requires long-term commitment, competent and open-minded scientists on both sides, mutual respect and fairness.

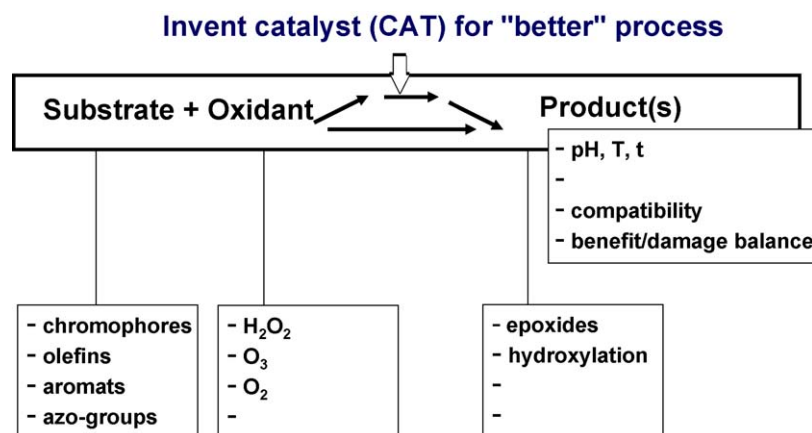
In the present context, bleaching means oxidative destruction of chromophores, i.e. chemical degradation of molecular moieties responsible for absorbing visible electromagnetic radiation. This increases the total reflectance of the substrate and lets it appear brighter. Bleaching is an essential component of various cleaning and refinement processes. Hydrogen peroxide has been employed for bleaching purposes for over a century [2]. Peroxide-based laundry bleaching, originally invented and still in widespread use in Europe, was first introduced in 1907 [3]. At that time, detergent manufacturers began to incorporate substantial amounts of sodium-perborate (SPB) in their powder products. SPB provides for both, adequate storage stability and quick release of hydrogen peroxide on dissolution. Excellent bleaching results are obtained with such detergents provided that clothes are washed close to the boil ( $T \approx 95^\circ\text{C}$ ) [3]. However, a clear trend to much lower wash temperatures has been observed for quite some time [4]. Particularly in Europe, this is a consequence of the increasing use of modern fibers and fabrics and of the ongoing efforts to save energy. As a result, the typical wash temperature in Europe is now at  $T = 40^\circ\text{C}$ . Moreover, on a global scale, washing at ambient temperatures ( $T \approx 20^\circ\text{C}$ ) dominates [4].

At  $T = 40^\circ\text{C}$  the bleaching power of hydrogen peroxide is unsatisfactory. This problem has been partially solved by introducing so-called activators, with *N,N,N',N'*-tetraacetyethylene diamine (TAED) as the best-known representative [5]. On perhydrolysis these activators generate peracids on a stoichiometric basis. Note that one mole of TAED is capable of generating two moles of peracetic acid. Referring to the total mass of the detergent, activated formulations of high-quality contain 12–15% of SPB and some 5% of TAED. This means that about one half of the available hydrogen peroxide can be transformed into peracetic acid, i.e. into a chemically more reactive species. In this way, TAED helps to improve the insufficient bleaching performance of SPB at  $T = 40^\circ\text{C}$ . However, at even lower temperatures this type of activation of SPB becomes ineffective.

For quite some time, chemists have been trying to solve the problem of inefficient low temperature laundry bleaching by means of catalysis. The corresponding research focused on heavy metal cations and, in particular, on their coordination compounds [6]. Some 10 years ago, in the course of pioneering pertinent work, mono- and, especially, bi-nuclear manganese complexes of 1,4,7-trimethyl-1,4,7-triazacyclononane (TMTACN) have been demonstrated to be highly active bleach catalysts [7]. Incorporating as little as 0.05% of such a catalyst into a SPB-containing detergent powder provides as much bleaching power at  $T = 40^\circ\text{C}$  as do 5% of TAED. Moreover, these bleach catalysts prove effective even at  $T = 20^\circ\text{C}$ . Unfortunately, dramatic damage to fibers and dyes sometimes accompanies the use of these Mn-TMTACN-type catalysts [8]. In pertinent terms, the quoted manganese complexes show a poor benefit–damage balance. Therefore, detergent producers have been reluctant to use such catalysts in their laundry products. However, there is no scientific evidence that such adverse effects are an inherent drawback of bleach catalysts in general. On the contrary, more recently developed novel coordination compounds significantly improve low temperature laundry bleaching without causing more damage than the established standard technology [9,10].

The author's research group has been active in the field of catalytic bleach for quite some time. Based on a comprehensive strategy, numerous compounds have been tested and derivatives of selected classes of ligands have been synthesized. To be able to assess these compounds in a quantitative way, reliable in-house screening procedures for various applications have been established [11]. Also, diverse mechanistic aspects have been studied in order to gain more fundamental insight into the activation of hydrogen peroxide [12]. A large part of the work of the author's group has concerned manganese complexes of salen- [13], saltren- [14], TMTACN- [8,15,16] and terpyridine-type [10,17] ligands.

Apart from providing for improved bleaching performance of hydrogen peroxide, a suitable oxidation catalyst must meet a whole range of additional application-specific requirements. Some of them form part of the quoted benefit–damage balance of the process in question and further ones concern the compatibility with the entire set of boundary conditions. Cross fertilization



Scheme 1. The objective of catalytic bleach (see text).

in the sense alluded to at the outset of this article must not be neglected. By means of example, vain efforts to invent bleach catalysts for laundry application may give birth to catalysts useful in hard surface cleaning or in hair bleaching.

## 2. Results and discussion

### 2.1. The objective of catalytic bleach

Quite generally, searching for bleach catalysts aims at improving the following process (cf. Scheme 1). Reacting with a suitable oxidant, a light-absorbing substrate must be degraded into colorless products, without violating a set of process-specific boundary conditions. Typically, the chromophores to be destroyed consist of extended conjugated  $\pi$ -systems, made up of moieties such as olefins, aromats and azo-groups. With respect to the oxidant,  $H_2O_2$  and its derivatives, as well as  $O_3$  and  $O_2$  are particularly favored [3]. The chemical nature of the generated products is of minor importance, as long as they are colorless. An important feature of any bleaching process is its specific set of boundary conditions, symbolized by the bold box in Scheme 1. Referring to laundry bleaching, i.e. the model system of the present article, the most obvious restrictions concern pH, temperature ( $T$ ) and process-time ( $t$ ). Though somewhat less evident, but at least of equal importance are compatibility with the other system components and proper consideration of the benefit–damage balance when evaluating specific bleach systems. At low temperatures, bleaching of the kind described suffers from low reaction rates as a consequence of the high activation energies of the corresponding oxidation reactions. The method of choice to remove this deficiency consists in opening alternative reaction pathways by means of catalysis. Consequently, pertinent research is thus concerned with inventing a catalyst that renders it possible to run the target process in a more favorable way (cf. Scheme 1).

Some particularly promising applications for bleach catalysts are listed in Table 1. The bleach system is a chief constituent of many detergents, which in their turn contribute considerably

Table 1

Areas of application for catalytic bleach

|                                    |              |
|------------------------------------|--------------|
| Detergents                         | Hair         |
| Pretreatments                      | Skin         |
| Pulp and paper                     | Teeth        |
| Advanced oxidation processes (AOP) | Purification |

See text.

to cleanliness in today's world. With respect to aesthetics and hygiene, washing and cleaning are cornerstones of a modern way of life [4]. In the textile industry, a variety of refinement processes requires proper pretreatment of the fibers and fabrics [18]. Hydrogen peroxide-based bleaching of pulp and paper is driven by many environmental issues [19]. Similarly, the use of hydrogen peroxide in conjunction with metal complex catalysts, UV radiation and ozone in so-called advanced oxidation processes (AOP) [20] is a growing technology to eliminate diverse pollutants and to improve the biodegradability of effluents. Hair bleaching accompanies or precedes hair dyeing [21]. Hydrogen peroxide is used to whiten skin and teeth [22]. Hydrogen peroxide is frequently used to purify diverse chemicals and materials in order to meet the requirements of the corresponding customers and consumers. In all these areas of application, there are specific deficiencies to be removed by suitable catalysts.

### 2.2. Bleach catalysts in laundry application

A symbolic representation of the washing process is given in Fig. 1. Nowadays, a typical wash-load contains white as well as colored fabrics. Before laundering, we find two sorts of dirt on both kinds of fabric, as indicated on the left-hand side of Fig. 1. Soils are removed from the textiles by surfactants, a major component of modern detergents. Adhering much more tightly to the fibers, stains cannot be eliminated in this way. To get rid of them, they must be bleached, i.e. chemically degraded on the fiber. Whether or not the corresponding fragments remain on the textiles is considered immaterial, provided that they are colorless, i.e. do not absorb light. Ideally, the washing process

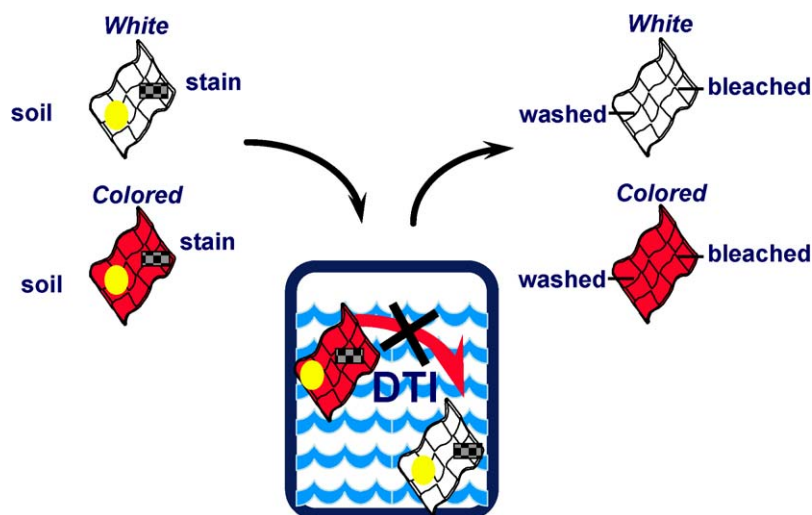


Fig. 1. Symbolic representation of the washing process (see text).

furnishes the outcome depicted on the right-hand side of Fig. 1: white is white again, colored is colored again, soils have been removed and stains have been bleached away. However, when laundering in the way described, an additional problem is created. Dyestuff coming off the colored fabrics may discolor the white textiles. This latter problem can be solved by bleaching the migrating dyes in the wash liquor. Being an important constituent of a modern detergent the role of the bleach system is thus at least 2-fold. It is responsible for dye-transfer-inhibition (DTI) and for the “disappearance” of stains.

In its nature laundering is a typical recycling-process. Therefore, the quality of any specific washing system must be assessed based on its benefit–damage balance. With respect to bleaching, speed and extent of chromophore destruction characterize the desired performance, whereas the concomitant degradation of fibers and the fading of the colored textiles represent the most important adverse effects to be avoided. With a view to inventing novel bleach catalysts, it is imperative to define a reliable set of parameters which makes it possible to quantify the effects and to estimate the practical value of a specific product candidate. To this end, suitable screening procedures must be established and the corresponding results must be interpreted in relation to the performance of the current state of the art.

### 2.3. Dye transfer inhibition

Regarding DTI by catalytic oxidation in the wash liquor, considered to be an essentially homogeneous reaction, the performance of a specific substance is expressed in terms of its DTI-efficiency  $a$  (cf. Fig. 2a). In the present context it seems sufficient to recall the basic meaning of this measure of quality. Readers interested in a detailed description of the entire experimental set-up and of the exact evaluation procedure are referred to the pertinent literature [23]. First, for a given set of experimental conditions and in the absence of the catalyst, the extent of discoloration of a white cotton fabric is ascertained by determining its CIE-luminance [24] values before ( $Y(W)$ ) and after ( $Y(A)$ ) the treatment. Symbolically, the corresponding reference swatch is depicted in Fig. 2a. Then, the experiment is repeated with the only difference that a small quantity of the catalyst to be tested is added. Again, the extent of the discoloration is characterized by determining the corresponding CIE-luminance ( $Y(E)$ ). Qualitatively, two extreme outcomes of such a test are conceivable. If  $Y(E) = Y(A)$ , the white fabric is equally discolored in both cases, i.e. adding the catalyst does not at all improve the situation. Such a catalyst is useless (cf. Fig. 2a) and, according to Eq. (1), assigned an  $a$ -value of 0%. On the other hand, if adding the catalyst completely inhibits discoloration of the white fabric,  $Y(E) = Y(W)$  and  $a$  equals 100%. The performance of such a catalyst is perfect (cf. Fig. 2a). As a rule of thumb, catalysts with  $a \geq 80\%$  furnish excellent results, when applied in practice. It is illusive to hope for an oxidation catalyst that will provide high  $a$ -values for any dyestuff conceivable. DTI by catalytic bleaching may fail for two reasons. First, some dyes are extremely oxidation resistant. Second, there are dyes that exhaust so rapidly on cotton that catalytic oxidation may not be fast enough to provide the required degree of protection. Notice

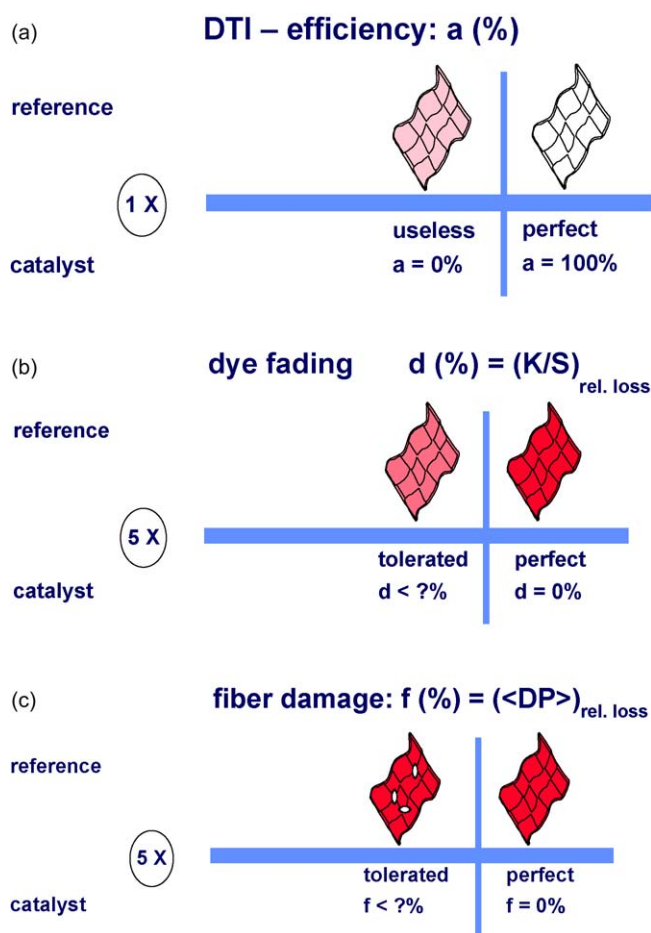


Fig. 2. (a) quantifying DTI-performance. The DTI-performance of a bleach catalyst is expressed as a percentage termed DTI-efficiency  $a$  (see text). (b) Quantifying dye-fading. The extent of dye-fading  $d$  is expressed as relative loss of dyestuff derived from the Kubelka–Munk function (see text). (c) Quantifying fiber damage. The extent of fiber damage  $f$  is expressed as relative reduction of the average degree of polymerization of the cotton fibers (see text).

that a useful DTI-system must be especially active during the initial phase of a washing cycle as it is in this period where the concentration of migrating dyes in the wash liquor is highest:

$$a = \frac{Y(E) - Y(A)}{Y(W) - Y(A)} \times 100\% \quad (1)$$

Referring to a proper set of dyes, high  $a$ -values are necessary but not sufficient to turn an oxidation catalyst into a good DTI-additive for detergents. An adequate evaluation of a possible product must also include its damage potential. In the present context two types of adverse effect, namely dye-fading and fiber damage, are well to the fore. To quantify these degradation processes, a carefully selected set of six differently dyed cotton swatches (vide infra) is subject to five consecutive washing cycles with the system in question. The extent of dye-fading (cf. Fig. 2b) is expressed in terms of the dye-fading parameter  $d$ . A reference value  $d_{\text{ref}}$  is first determined in the absence of the catalyst, by measuring the reflectance spectra  $\beta(\lambda)$  [25] of the swatches before and after the complete treatment. These spectra are subsequently transformed into  $(K(\lambda)/S(\lambda))$  functions according to the Kubelka–Munk theory [26] (cf. Eq.

(2).  $K(\lambda)$  denotes the Kubelka–Munk absorption constant,  $S(\lambda)$  the Kubelka–Munk scattering constant.

$$\frac{K(\lambda)}{S(\lambda)} = \frac{[1 - \beta(\lambda)]^2}{2 \times \beta(\lambda)} \quad (2)$$

In the present context it is sufficient to notice that the quotient  $K(\lambda)/S(\lambda)$  is directly proportional to the number of dyestuff molecules on the fiber, presuming that the assumptions of the Kubelka–Munk theory hold strictly true [26]. In this sense,  $d_{\text{ref}}$  evaluated at  $\lambda = \lambda_{\text{max}}$  according to Eq. (3), represents the relative amount of degraded dye due to the treatment with the catalyst-free system. Ideally,  $d_{\text{ref}} = 0$ . In practice, however, even the catalyst-free system will give rise to some dye-fading, as symbolically depicted by the different grey scale of the test swatch before and after the treatment, respectively. To qualify as a useful reference system,  $d_{\text{ref}}$  must not exceed  $d_{\text{tol}}$ . The latter percentage, an upper bound for the tolerable extent of dye-fading, can be inferred from the current state of the art technology. The experiment is then repeated with the only difference that the catalyst has been added to the detergent. Normally, but not necessarily so, the corresponding dye-fading parameter  $d_{\text{cat}}$  exceeds  $d_{\text{ref}}$ . Note that insignificant catalyst-induced dye-fading ( $d_{\text{cat}} - d_{\text{ref}}$ ) is tolerated provided that the total benefit–damage balance of the bleach additive is advantageous:

$$d = \frac{[K(\lambda_{\text{max}})/S(\lambda_{\text{max}})]_{\text{before}} - [K(\lambda_{\text{max}})/S(\lambda_{\text{max}})]_{\text{after}}}{[K(\lambda_{\text{max}})/S(\lambda_{\text{max}})]_{\text{before}}} \times 100\% \quad (3)$$

An analogous approach is used to determine fiber damage as indicated in Fig. 2c. The assessment is based on measuring the average degree of polymerization (DP) of the cotton fibers [27]. Evaluation takes place before and after five consecutive washing cycles, first without and then with the catalyst, respectively. The relative loss is expressed as a percentage  $f$ , computed according to Eq. (4). The evaluation closely resembles the dye-fading assessment. Some damage ( $f_{\text{ref}}$ ) will be ascertained even for the catalyst-free system. Again, how much catalyst-induced fiber degradation ( $f_{\text{cat}} - f_{\text{ref}}$ ) is tolerated, depends on the overall performance of the substance in question in relation to the state of the art technology.

$$f = \frac{\text{DP}_{\text{before}} - \text{DP}_{\text{after}}}{\text{DP}_{\text{before}}} \times 100\% \quad (4)$$

To characterize the current state of the art of DTI by catalytic oxidation, selected results for a particularly promising substance are summarized in Figs. 3–5. Notice that the 14 dyestuffs, labeled according to their color index (CI) notation, constitute a carefully selected representative test set for the target process. Data for the entire set render it possible to predict the performance of a DTI-catalyst in practice. Commencing with the DTI-efficiency  $a$ , the compound in question, the saltren-Mn(III) complex **1** [9] (c.f. Scheme 2), performs as follows. At reasonable catalyst concentrations, we find excellent performance with respect to six dyes (cf. top six dyes in Fig. 3), and rather poor  $a$ -values regarding another five (cf. bottom five dyes in Fig. 3). Respecting the

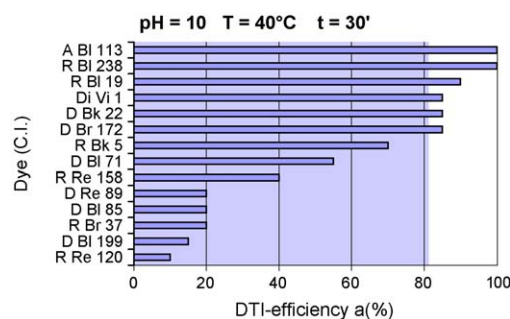


Fig. 3. DTI-efficiency  $a$  of catalyst **1**. The 14 test dyes, labeled according to their CI notation, constitute a carefully selected representative set to determine the DTI-performance of a bleach catalyst, as described in detail in [9] (see text).

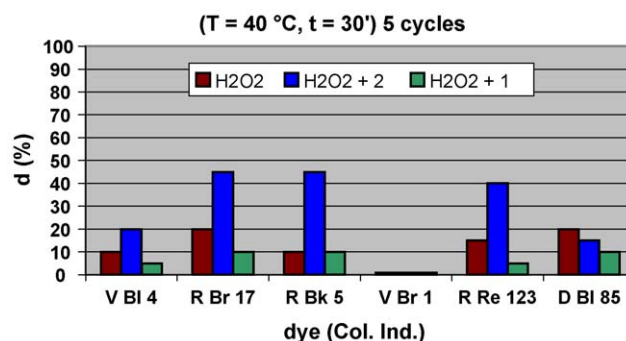


Fig. 4. Dye-fading  $d$  due to catalysts **1** or **2**. The six differently dyed cotton test swatches, labeled according to their CI notation, constitute a carefully selected representative set to determine the extent of dye-fading due to a bleach catalyst (see text).

remaining three, the effects of catalyst **1** are significant but not quite at the desired level [9]. As well as any alternative technology, DTI by catalytic oxidation is dyestuff-specific. In terms of dye-fading and fiber degradation, the evaluation of **1** yields the results given in Figs. 4 and 5 [9]. The outcome is obtained by subjecting the aforesaid sextet of differently dyed cotton swatches to five consecutive cycles with the washing systems indicated. This renders it possible to reliably characterize the damage potential of any bleach catalyst in keeping with an efficient screening process. The proper way of interpreting such data ought to be based on the ensemble rather than on the individual swatches. More-

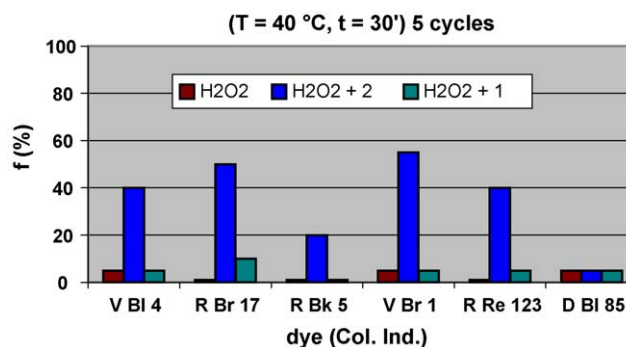
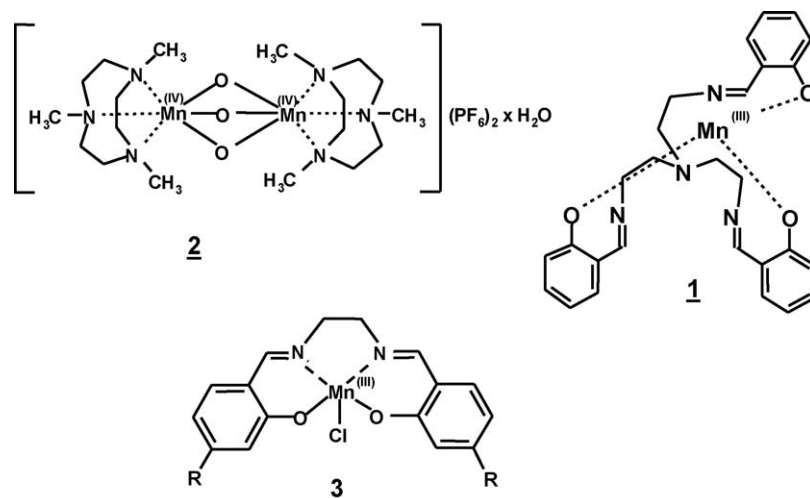


Fig. 5. Fiber damage  $f$  due to catalysts **1** or **2**. The six differently dyed cotton test swatches, labeled according to their CI notation, constitute a carefully selected representative set to determine the extent of fiber damage due to a bleach catalyst (see text).



Scheme 2. Examples of manganese bleach catalysts.

over, the damage detected must always be evaluated in relation to suitable reference systems. In the present context the reference system of choice is the catalyst-free peroxide-containing system which is practically inactive regarding DTI-protection, i.e. is characterized by  $a \approx 0\%$  for the entire set of the 14 test dyes. According to Fig. 4, dye-fading for this reference system is  $0 \leq d_{\text{ref}} \leq 20\%$  on an individual basis. It is very gratifying to notice that adding catalyst **1** is not a source of additional fading as  $d_{\text{cat}} \leq d_{\text{ref}}$  in all the cases. Conversely, making use of catalyst **2** results in unacceptably big dye-fading. On an average, the components of the test set suffer dye-fading of 12.5% (reference system), 9% (**1**) and of 28% (**2**), respectively.

With regard to fiber damage a similar ranking is encountered. Our reference system gives rise to  $f_{\text{ref}} \leq 5\%$  on an individual basis. Adding catalyst **1** increases this percentage only slightly while the use of catalyst **2** gives rise to dramatic fiber damage of up to  $f_{\text{cat}} \leq 55\%$ . This latter increase is certainly not acceptable. Considering the average fiber damage per component of the test set, the ranking closely resembles the situation encountered for dye-fading, with 2.5% (reference system), 3% (**1**) and 35% (**2**), respectively. It must be emphasized that fiber damage is dye-dependent, in as much as all the data in Fig. 5 refer to one and the same kind of cotton fabric! In which manner fiber degradation is mediated by the colorants is poorly understood at present. Based on the performance and damage data presented, catalyst **1** is rightly considered a very promising DTI-additive. Its benefit–damage balance is very attractive as it does hardly increase the adverse affects of the corresponding reference sys-

tem and yet provides a high degree of protection against a series of important colorants.

#### 2.4. Selectivity of DTI by catalytic oxidation

With these application results in mind it is interesting to address the question of selectivity of DTI by catalytic oxidation. Carried to extremes, the technology is expected to solve the following task: any specific colorant must be degraded rapidly when dissolved or dispersed in the wash liquor, but not be affected at all when forming part of a dyed fabric. While striving for a perfect solution in this sense is bound to fail, sufficient selectivity can indeed be achieved. This is demonstrated by the data for the degradation of Reactive Black 5 (R Bk 5) as shown in Table 2. The widespread use of R Bk 5 in the textile industry makes it a particularly suitable model dye for studies concerning laundry bleaching as well as waste water treatment by means of advanced oxidation processes (AOP).

The entries in Table 2 contain degradation data for two different oxidation catalysts, i.e. **2** and **3** (cf. Scheme 2) and for the catalyst free reference system containing hydrogen peroxide only [28]. Approximately the same absolute quantity of R Bk 5 is present either as a homogeneous solution (20  $\mu\text{mol}$ ) or in form of a dyed cotton fabric (18  $\mu\text{mol}$ ). Note that bleaching data in solution refer to one single cycle, whereas bleaching of the fabric is the result of five consecutive treatments with the system in question. As to the experiments in solution, which mimic the essential part of the DTI-process, we notice that the reference

Table 2  
Oxidative degradation of Reactive Black 5, in homogeneous solution and in form of a dyed cotton swatch

|                                      | Dissolved dye |          |                        | Dyed fabric |          |                        |
|--------------------------------------|---------------|----------|------------------------|-------------|----------|------------------------|
| R Bk 5 offered ( $\mu\text{mol}$ )   | 20            | 20       | 20                     | 18.2        | 18.2     | 18.2                   |
| R Bk 5 destroyed ( $\mu\text{mol}$ ) | 12.4          | 19.2     | 0                      | 9           | 2.5      | 2.2                    |
| R Bk 5 destroyed (%)                 | 62            | 95       | 0                      | 49          | 14       | 12                     |
| Catalyst                             | <b>2</b>      | <b>3</b> | $\text{H}_2\text{O}_2$ | <b>2</b>    | <b>3</b> | $\text{H}_2\text{O}_2$ |
| Number of consecutive washing cycles | 1             | 1        | 1                      | 5           | 5        | 5                      |

See text.

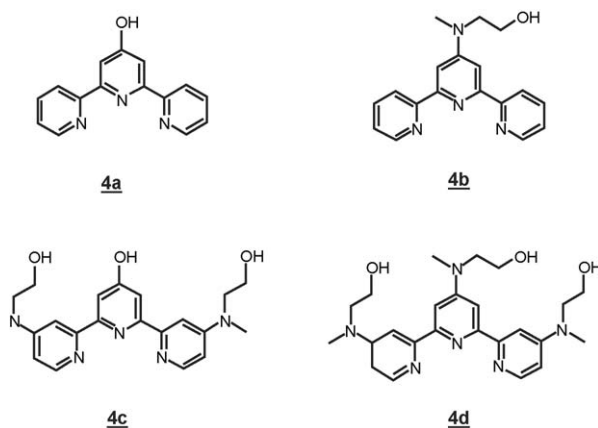
system is not giving rise to any dye degradation at all. On the other hand, catalyst **2** helps to eliminate 62% of the originally available R Bk 5 while catalyst **3** achieves 95%. With respect to treating the dyed swatches, which is a model for dye-fading, already the reference system brings about 12% of dye-fading. Catalyst-induced dye-fading is 37% (i.e. 49–12%) for **2** and a trifling 2% (i.e. 14–12%) for **3**. Supposing that each of the five consecutive washing cycles contributes equally to the total fading, some 7.5% is obtained for **2** and as little as 0.4% for **3** per cycle. With respect to these data, **3** is rightly considered to be a promising DTI-additive.

A first order analysis of these DTI-data reveals a few interesting aspects. Obviously, there are completely inactive ( $a=0$ ) bleaching systems which nevertheless cause some damage ( $d_{\text{ref}} > 0$ ) as, e.g. hydrogen peroxide itself, which is unable to degrade R Bk 5 in homogeneous solution and yet it causes some dye-fading on the test swatches. There are bleaching systems of medium activity and dramatic damage potential, as, e.g. **2** when used as a DTI-additive. However, there are also bleaching systems with excellent performance and hardly any catalyst-induced damage, as, e.g. **1**. Therefore, it is certainly incorrect to claim that large effects are necessarily tied to high damage.

### 2.5. Stain bleaching

Useful alternative technologies [29] are available to substitute or to complement DTI by oxidative degradation. On the contrary, this is not the case for low temperature stain bleaching, where practically all the hopes to solve the problem rest on novel oxidation chemistry. Proper evaluation of the corresponding substances relies on analogous test criteria as outlined for DTI. Regarding dye-fading and fiber damage exactly the same procedures can be used, whereas to quantify the actual stain bleaching effects, a suitable set of test stains must be defined. This selection is similarly problematic as choosing an adequate range of test dyes for the DTI-screening. However, in the present context it is sufficient to consider bleach effects on tea-stained cotton. This is by far the most widely used test material to identify promising bleach boosters for laundry application. Usually, there is some fluctuation of the results depending on the specific quality of the tea and on the details of the staining procedure employed. Suitable test material can be prepared in-house or bought from external sources. Among the more widely used sorts we find BC-1 tea-stained cotton available commercially [30]. More recently, researchers in the field have often worked with this material with a view to making bleach data more comparable. Preferably, bleach effects are expressed in terms of change of luminance  $\Delta Y$  [24] relative to a suitable reference system.

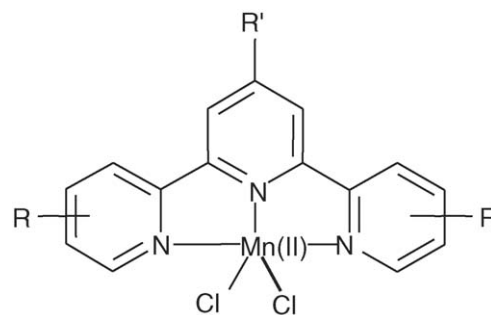
With respect to European laundering conditions TAED-activated formulations represent the state of the art technology at  $T=40^\circ\text{C}$  [5]. At this temperature, the use of TAED significantly ameliorates stain bleaching by hydrogen peroxide. This benefit is not questioned. However, when the temperature is lowered to some  $20^\circ\text{C}$ , this activator approach may fail completely [9]. On the other hand, it is fair to say that the degree of damage due to the use of TAED is accepted by the consumers. As a consequence, any catalytic system which improves bleaching at ambient tem-



Scheme 3. Structure of selected terpyridine ligands (see text).

perature and does not give rise to increased dye-fading or fiber damage will be considered promising. Such progress can indeed be achieved. When laundering at ambient temperature, making use of catalyst **1** provides a noteworthy increase of  $\Delta Y \approx 2.5$  [9] as compared with a TAED-activated formulation. Thereby the concomitant level of damage is not increased relative to the hydrogen peroxide-containing reference system and, thus, even below the one of the TAED-activated product. To sum it up, hardly any catalyst-induced adverse effects paired with clearly improved performance turn catalyst **1** into a promising detergent additive for improved stain bleaching at ambient temperatures.

More recently, a family of terpyridine derivatives has been synthesized with a view to devising more powerful low temperature bleach catalysts [31]. Depending on the specific substitution pattern of the ligand (cf. Scheme 3), some of the corresponding 1:1 manganese(II) complexes [32], denoted as *ligand*-MnCl<sub>2</sub> (cf. Schemes 3 and 4) yield very promising effects. In particular, catalyst **4c**-MnCl<sub>2</sub>, which is a complex of high specific activity, makes it possible to significantly improve the bleaching power of a SPB-containing detergents. Notably, this holds true for ambient temperatures where again an increase of  $\Delta Y \approx 2.5$  can be achieved [10] as compared to a TAED-activated system. Since catalyst-induced adverse effects are comparably low [10], also **4c**-MnCl<sub>2</sub> is rightly considered a promising bleach additive. Striving for a consistent protocol to optimize the substitution pattern, the subgroup **4a**-MnCl<sub>2</sub>–**4d**-MnCl<sub>2</sub> of a larger set of terpyridine manganese complexes was extensively studied



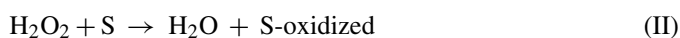
Scheme 4. Structure of terpyridine manganese complexes used as bleach catalysts (see text).

with respect to particularly important aspects such as catalytic bleach activity, damage potential, adsorption on textiles, complex stability, disproportionation of  $\text{H}_2\text{O}_2$ , rate of oxidation of selected substrates, estimates for catalytic turnover numbers [10,17]. Selected results will be discussed in Section 2.8.

### 2.6. A qualitative model

The application data presented demonstrate that adding a tiny quantity of a suitable manganese complex results in significantly improved bleaching effects, with a concomitant level of damage equivalent to the one of the established standard technology. The degree of improvement depends strongly on the specific chemical structure of the compound in question. In which way exactly a particular substitution pattern results in improved bleaching, remains a challenging question. However, it is to be expected that other derivatives of the already identified promising ligand classes will make it possible to attain still better results in the future. Alternatively, such an additional improvement may also come from novel chelates and, even more likely, from completely different approaches of hydrogen peroxide activation. In order to efficiently do research in this field, it is crucial to be aware of the current level of understanding of the mechanism of hydrogen peroxide bleaching. This provides a very helpful guideline for any intuition-based trial and error strategy.

Even in the absence of a bleachable substrate, the thermodynamically unstable hydrogen peroxide molecule dismutates to water and oxygen according to reaction (I). The rate of this disproportionation varies strongly according to the specific reaction conditions. The relative stoichiometrical amount of the evolved oxygen is referred to as the active oxygen content of hydrogen peroxide. However, once formed as a final product of reaction (I), such a dioxygen molecule ( ${}^3\sum_g^-$ ) does not possess any kind of extraordinary chemical reactivity. In particular, ground state molecular oxygen itself is a useless low temperature bleaching agent. In the context of bleaching, the term active oxygen refers to the fact that one of the two oxygen atoms in hydrogen peroxide is potentially available for substrate (S) oxidation according to net reaction (II). Therefore, at first sight, when striving for high bleaching power (I) is considered an undesirable side reaction because it deprives the bleaching system of its most precious component by generating bleach-inactive molecular oxygen:



While a comprehensive description of reaction (I) is still lacking, the following simple model is fully compatible with what is known by experience in the field of bleaching. In the course of the spontaneous disproportionation of hydrogen peroxide (cf. Fig. 6), an ensemble of active oxo-species is generated. Their nature and their relative abundance are determined by the process conditions, symbolically represented by the large brackets in Fig. 6. The individual species – some of them very short-lived and/or highly reactive – are interrelated by a complex set

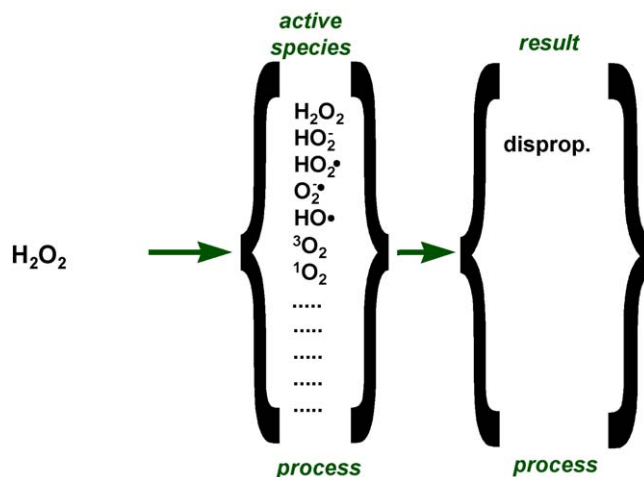


Fig. 6. A qualitative model for hydrogen peroxide bleaching. Decomposition of hydrogen peroxide in the absence of a substrate and of a catalyst. In this case, the only result observed is *disproportionation* according to reaction (I).

of parallel/consecutive reactions, involving, e.g. the transfer of a hydrogen atom, of a proton or of an electron, or participation in chain reactions. In the absence of a bleachable substrate (S), all these species are finally deactivated according to net reaction (I), which consists of several coupled reaction pathways all ending up in dioxygen and water. The net result observed is disproportionation.

Within the multitude of substances known to catalyze reaction (I), enzymes termed catalase are by far the most efficient representatives (cf. Fig. 7). In the field of bleaching, reaction (I) is commonly referred to as catalase-type degradation of hydrogen peroxide implying unproductive annihilation of the initially available active oxygen. The use of any catalysts changes the process conditions and, consequently, the relative abundance of the constituents of the ensemble. Commonly, catalases are believed to accelerate exclusively reaction (I) and not to influence reaction (II) [33]. Enzymes active in catalyzing (II) are termed peroxidases. However, it must be emphasized that reaction (II) is of course substrate-specific and that in a few instances catalases have indeed been shown to effectively catalyze the oxidation of substrates such as lower aliphatic alcohols [34]. This means that catalases can show peroxidase-type activity. Conversely, the author is unaware of any peroxidase-type bleach catalyst that is completely inactive regarding reaction (I). Therefore, with respect to bleaching, the difference between catalase- and peroxidase-type catalysts is probably more of a gradual than of a principal nature. In other words, with respect to a specific substrate, any kind of hydrogen peroxide activating compound may simultaneously catalyze (I) and (II). However, when the relative level of activation differs considerably, it is justified to speak of a catalase- or of a peroxidase-type catalyst, respectively. In terms of our model, the two kinds of catalytic activity give rise to different compositions of the quoted ensemble of active species. Catalase-like action may predominantly generate intermediates that are too short-lived or not sufficiently reactive for bleaching, while peroxidase-like action results in intermediates capable of substrate oxidation. Both types of intermediates are



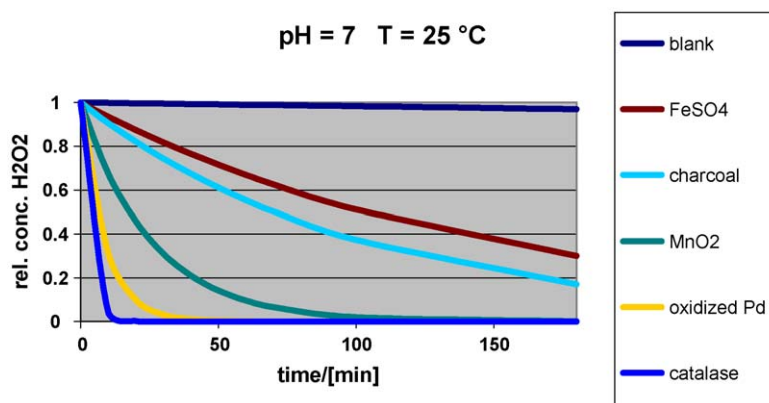


Fig. 7. Catalase-type activity of diverse materials. Catalyst concentrations are  $20 \mu\text{M}$   $\text{FeSO}_4$ ,  $20 \mu\text{M}$   $\text{MnO}_2$ , 0.05% charcoal Darco 6–60 (100–325 mesh), 0.001% oxidized Pd (as Pd) 2% on aluminosilicate (<200 mesh), 0.00005% catalase, Bovine liver catalase containing 11,000 units/mg.

interrelated so that the entire ensemble can still decay according to net reaction (I) when no substrate is present.

It must be emphasized that in the course of any hydrogen peroxide-based bleaching (I) and not (II) is the dominant reaction. In practice, a huge excess of oxidant is normally used to facilitate efficient bleaching [3]. At the end of a successful bleaching process the lion's share of the active oxygen consumed is found in the ambient atmosphere, i.e. not in the decomposition products (S-oxidized) of the degraded chromophores. This holds true for laundry bleaching at the boil as well as for activated or catalyzed low temperature bleach. In this context it is illustrative to recall pertinent application data (vide 2.8) which represent typical relative amounts of catalyst, substrate and oxidant. Referring to bleaching of Morin, a frequently used test dye for first stage screening of potential laundry bleach catalysts (vide 2.8), the proportion is 1:16:1000. At  $T = 40^\circ\text{C}$ , particularly active catalysts, such as TMTACN- or terpyridine-manganese complexes, are capable of completely discoloring the corresponding Morin solutions on the time scale of minutes with practically no hydrogen peroxide left at the end of the process (vide 2.8). Therefore, even when the decomposition of each Morin molecule required several equivalents of hydrogen peroxide, some 90% of the originally available active oxygen ends up as gaseous dioxygen. Consequently, it seems recommendable to pay more attention to the catalase-type activity, when searching for bleach catalysts. Experimentally, reaction (I) is much easier to follow than (II). The determination of the kinetics of oxygen evolution in the course of reaction (I) and of the stability of the catalyst with respect to this very process may favorably complement the extensive study of the actual target reaction (II).

In the absence of a catalyst and of a substrate (I) is the only decay channel available to  $\text{H}_2\text{O}_2$ . In the field of bleaching this reaction pathway is referred to as *disproportionation* (cf. Fig. 6). When a bleachable substrate S is added to the system, two further processes must be considered. In practice, suitable test material makes it possible to split the overall result into these three components. In conformity with the pertinent terminology, the two additional processes are called *bleaching* and *damage*, respectively (cf. Fig. 8). High-quality bleaching requires primarily promoting the former process component and suppressing

the latter to the best possible. Moreover, as long as the intricate coupling of (I) and (II) is disregarded, *disproportionation* must be considered obstructive to efficient bleaching and thus be blocked, too. For a laundering temperature close to the boil, this can be achieved inasmuch as superb stain removal is obtained and the level of concomitant damage is acceptably low. However, with respect to the *disproportionation* only very limited process control is attained, because most of the originally available active oxygen ends up unused in the gas phase. The more the temperature is lowered, the smaller the effects due to each of the three process components. Below some  $50^\circ\text{C}$ , only little hydrogen peroxide disproportionates, bleaching effects fade away and most of the initially available active oxygen is found as unreacted  $\text{H}_2\text{O}_2$  in the drain. This situation has instigated the extensive search for bleach catalysts in order to achieve at low temperature what is possible at the boil. Also, if such an approach simultaneously improved the overall efficiency of the target process with respect to the initially available active oxygen, it would constitute a major breakthrough.

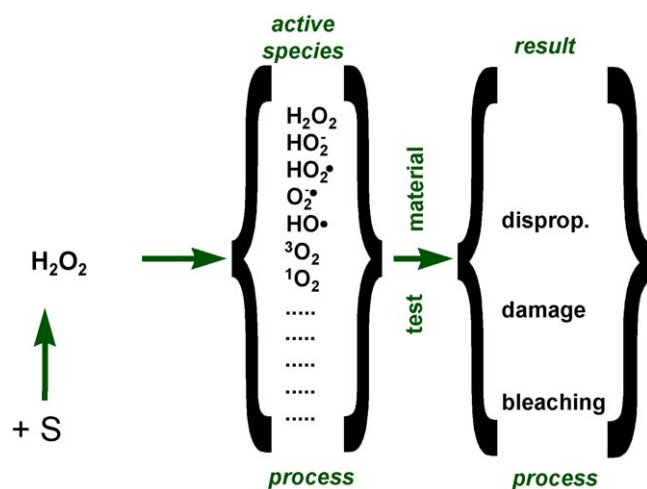


Fig. 8. A qualitative model for hydrogen peroxide bleaching. Decomposition of hydrogen peroxide in the presence of a substrate (S). Suitable test material makes it possible to split the net result into the three components: *disproportionation*, *bleaching* and *damage* (see text).

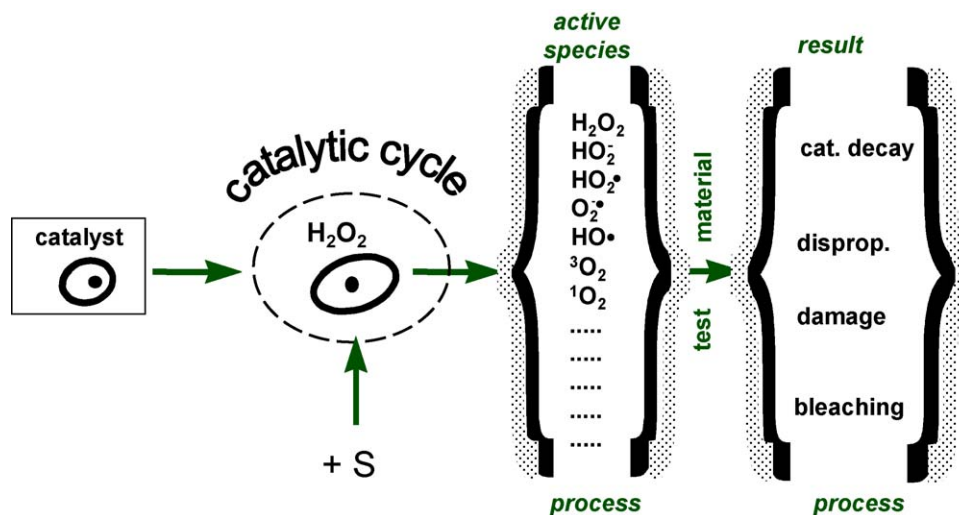


Fig. 9. A qualitative model for hydrogen peroxide bleaching. Decomposition of hydrogen peroxide in the presence of a substrate (S) and of a catalyst. Suitable test material makes it possible to split the net result into the four components: *disproportionation*, *bleaching*, *damage* and *catalyst decay*.

Fig. 9 describes the situation when a catalyst enters the scene. On the left side, a chelate, composed of a heavy metal cation and of an organic ligand, is symbolized. The interaction of such a complex with the oxidant in the course of a catalytic cycle, i.e. a dramatic change of the process conditions represented by the additional pair of brackets in Fig. 9, changes the ensemble of intermediates. The net-effect of introducing a catalyst, i.e. the way *disproportionation*, *bleaching* and *damage* are altered can only be evaluated at the end of the corresponding test procedure. Furthermore, as indicated in Fig. 9, an additional aspect must be considered, namely *catalyst decay*. Typically, the more active in catalyzing (II), the higher the risk that such a complex is degraded by some of the active species itself helps to generate. To sum it up in terms of the major elements of Fig. 9, our ability to describe the chemistry involved decreases when moving from left to right. At the outset, the situation is fairly well defined, since the structures of catalyst and oxidant are known and even the substrate can be adequately characterized. Regarding the center part of Fig. 9, where our ensemble is positioned, we merely dispose of a qualitative model. At last, we are forced to evaluate a specific bleach system based on the phenomena relevant to practice. It is true that we are able to quantify these phenomena and to reliably assess the performance of catalyst candidates. However, we are not able to relate these results in a straightforward way to well-defined physical and chemical properties of a catalyst. This means we must content ourselves with defining the objective of pertinent research in phenomenological terms as follows: channel as much as possible of the available active oxygen towards *bleaching* and reduce *disproportionation*, *damage* and *catalyst decay* to the best possible.

### 2.7. The question of the bleach-active species

To probe at least the principal aspects of the proposed ensemble of intermediates, a conceivable crucial role of selected species has been investigated. In comparison with the washing tests reported on so far, a simplified experimental set-up was

used for this purpose. The essential components of this test system comprise a buffered aqueous solution as the medium (pH 10.5), hydrogen peroxide (6.5 mM) as the oxidant and an in-house standardized tea-stained cotton fabric as the yardstick to quantify the bleaching effects [35]. This material is prepared in such a way that in the medium quoted a 60-min treatment at  $T = 60^\circ\text{C}$  eliminates  $\approx 90\%$  of the initial staining. Again, the Kubelka–Munk function (2), this time integrated over the entire visible range of the electromagnetic spectrum [36], was used as a measure proportional to the amount of stain on the fabric. The extent of bleaching observed with this simplified test system correlates closely with the outcome of the typical screening procedures relied on in practice.

Hydrogen peroxide-based bleaching has repeatedly been associated with radicals. In particular, the hydroxyl radical  $\bullet\text{OH}$ , known to be generated under specific conditions (e.g. Fenton reaction [37]) has been attributed a role. Another conceivable protagonist, the perhydroxyl radical  $\bullet\text{OOH}$  is less frequently mentioned in the pertinent literature. Both of these radicals are an important component of a set of chemical reaction equations developed to model a radical mechanism of hydrogen peroxide bleaching (cf. Scheme 5) [38]. According to this model, the transfer of an electron from an arbitrary donor (D) to hydrogen peroxide induces a radical chain reaction which ultimately results in the disproportionation according to net reaction (I). Then, the intermediate steady-state concentration of  $\bullet\text{OH}$  and of  $\bullet\text{OOH}$  is potentially available for reacting with a substrate,



Scheme 5. A radical chain model for  $\text{H}_2\text{O}_2$  decomposition. Conceivable donors, D are  $\text{M}^{n+}$  cations in diverse oxidation states and  $\text{HOO}^-$  (see text).

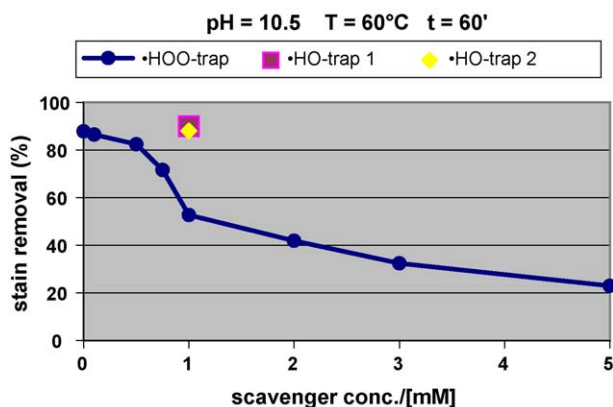


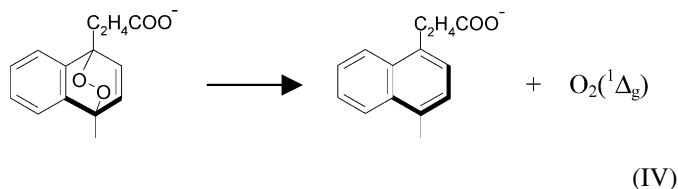
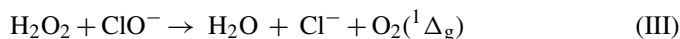
Fig. 10. Quenching of the bleaching effect on tea-stained cotton as a function of the scavenger concentration (see text).

i.e. for bleaching. Specific candidates for the role of the donor D are metal cations and the perhydroxyl anion.

The relevance of this model for laundry bleaching was experimentally confirmed in the author's laboratory. To this end, studying the impact of radical-specific scavengers on the stain bleach effect was adopted as a straightforward strategy. Regarding  $\bullet\text{OH}$ -specific scavengers, which can be used in an alkaline medium and which are kinetically well characterized, two suitable substances were identified. Both of them, potassium hexacyanoferrate(II) [39], termed  $\bullet\text{HO}$ -trap 1 in Fig. 10, and 4-nitroso-*N,N*-dimethylaniline [40], termed  $\bullet\text{HO}$ -trap 2 in Fig. 10, react with  $\bullet\text{OH}$  radicals close to or at the diffusion controlled limit ( $k_s \geq 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ ), while the reaction with  $\text{H}_2\text{O}_2$  and with  $\bullet\text{O}_2^-$  is  $k_s \leq 3 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$  [41]. Note that the latter species, termed superoxide, is the conjugate base of  $\bullet\text{OOH}$ . At pH 10.5 the acid  $\bullet\text{OOH}$  ( $\text{pK}_a = 4.8$ ) [42] is completely deprotonated, i.e. present as  $\bullet\text{O}_2^-$  only. Adding either of the two scavengers ( $c_s = 1 \text{ mM}$ ) to the test system did not at all decrease the bleaching effect. This contradicts the hypothesis that the  $\bullet\text{OH}$  radical is the dominant bleach-active species. As to the analogous experiments for the  $\bullet\text{OOH}$  radical, present in form of its conjugate base  $\bullet\text{O}_2^-$ , hydroquinone was selected as a useful scavenger. The literature value for its bimolecular rate constant with  $\bullet\text{O}_2^-$  at neutral pH is  $k_s \approx 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$  [42]. The dependence of the bleaching effect as a function of the hydroquinone concentration is depicted in Fig. 10. Notice that the test fabric is highly wash-resistant in as much as no stain removal is observed in the absence of hydrogen peroxide. Conversely, when working with  $6.5 \text{ mM} \cdot \text{H}_2\text{O}_2$  nearly 90% of the stain is bleached. As shown in Fig. 10, this bleaching effect decreases gradually with increasing concentration of hydroquinone. This provides strong evidence that superoxide plays a dominant role regarding the bleaching activity of the postulated ensemble. In other words the mysterious active oxygen of the bleachers, alias "oxygen in statu nascendi", may translate as superoxide for chemists.

Another conceivable candidate for the role of a bleach-active species in laundry bleaching is molecular oxygen in its  $^1\Delta_g$  state, often simply referred to as *singlet oxygen* in the pertinent literature. Although thermodynamically accessible when  $\text{H}_2\text{O}_2$  disproportionates according to (I) [43], hardly any elec-

tronically excited oxygen molecules are detected in the case of the uncatalyzed decomposition of hydrogen peroxide [44]. Conversely, in the presence of a catalyst, such as  $\text{MoO}_4^{2-}$  [45] the formation of  $\text{O}_2(^1\Delta_g)$  was unambiguously demonstrated. Moreover, the generation of singlet oxygen in the course of various decay reactions of organic derivatives of  $\text{H}_2\text{O}_2$ , particularly peracids, is an experimental fact [44]. Quite generally, the extent of  $\text{O}_2(^1\Delta_g)$  generation in the course of peroxide decomposition depends strongly on the detailed reaction conditions. Furthermore, photochemically produced singlet oxygen is believed to bring about stain bleaching in an ancient process called lawn bleaching [3]. Therefore, it is tempting to check for a conceivable role of this electronically excited species in the present context, too. This time an alternative experimental strategy was adopted aiming at producing instead of quenching a bleach effect. Two reliable sources of singlet oxygen were used. The first concerns the classical bimolecular reaction (III) [46], the second one the unimolecular decay of an endoperoxide according to (IV) [47]. Although, in both cases, trapping experiments confirmed quantitative generation of  $\text{O}_2(^1\Delta_g)$  in our simplified test system, no singlet oxygen induced stain bleaching was observed. The most likely reason for this failure is the short life-time of  $\text{O}_2(^1\Delta_g)$  in the condensed medium in question.



These findings for the uncatalyzed hydrogen peroxide-based stain bleaching are in accord with the radical reaction model shown in Scheme 5 and with the proposed ensemble of intermediates according to our model. They are also compatible with the experimental fact that the initial stock of active oxygen is predominantly depleted by disproportionation and to a much lesser extent by stain oxidation let alone by degradation of fibers and dyes. In general, each species of the ensemble will contribute to each of the three process components, i.e. to *disproportionation*, *bleaching* and *damage*. However, at least for the specific testing conditions used, by far the most substantial contribution to *bleaching* originates in  $\bullet\text{O}_2^-$ . Evidently, this species is enough reactive to bring about the desired effect, but still sufficiently selective to avoid an unacceptable level of *damage*. On the other hand, the  $\bullet\text{OH}$  radical, i.e. the active species of diverse advanced oxidation processes (AOP), is known to react very unspecifically with organic materials often resulting in complete mineralization of the latter [48]. Also, in the field of bleaching,  $\bullet\text{OH}$  radicals are mostly blamed for causing *damage* rather than praised for producing bleaching effects [49]. Thus, a significant contribution of  $\bullet\text{OH}$  radicals to the observed bleaching effects seems incompatible with the concomitant low level of *damage*. In other words, practical pertinent experience is in support of data which indicate no essential role of  $\bullet\text{OH}$  radicals in our test system.

On lowering the temperature, the thermal induction of the chain reaction becomes less and less efficient and the active oxygen available remains more and more unused in the wash liquor. A bleach catalyst's foremost role is to reinitiate this chain reaction. Redox-active transition metal cations are known to be useful in this sense. Complexed by an organic ligand, they are prevented from precipitating as oxides/hydroxides, as they would otherwise do in an aqueous alkaline oxidative environment. This catalyst stability is particularly important in laundry applications, because such precipitates can deteriorate the entire process dramatically. They can decompose  $\text{H}_2\text{O}_2$  in a catalase-type reaction [50] with a corresponding loss of active oxygen and/or they can adsorb on the fabrics as disturbing incrustations [4]. Apart from reinitiating the bleach-relevant chain reaction, a bleach catalyst may open alternative reaction pathways, as, e.g. in the case of  $\text{MoO}_4^{2-}$  (vide supra) [45] which increases the production of singlet oxygen considerably. Such an additional reaction channel may favor or impede bleaching depending on the species generated. Moreover, parts of the ligand may interact directly with the ensemble of intermediates. Especially, aromatic amines and phenols, owing to their particularly rich oxidation chemistry [51], are likely to be engaged in such an interaction. In this context it is interesting to note that the excellent performance of highly DTI-active salene-type manganese complexes (**3**) is not reduced when up to 90% of the chelate is substituted by an equivalent quantity of free ligand [52].

The presented model for laundry bleaching makes it possible to interpret some of the practical aspects in chemical terms. Referring to the four process components defined, this applies most to *complex stability* and to *disproportionation*, and somewhat less so to *bleaching*. Even more problematic in this respect is *damage*. This is particularly disturbing, inasmuch as *damage* may indeed be the decisive process component. While consumers may be more or less annoyed by inefficient bleaching they are very much concerned about permanent damage to their fabrics, as the example of TMTACN has demonstrated. Dye-fading is a degradation process of utmost importance, particularly to dyestuff producers. Dyes decay by a multitude of mechanisms, some dyes more easily others hardly at all. A whole series of fastness tests forms part of any reliable colorant screening. Thereby the influence of the substrate is also considered. Fastness with respect to washing and bleaching varies widely in the domain of colorants. This is already reflected by dye-fading data obtained for laundry bleaching with hydrogen peroxide only. Whereas the degree of dye degradation caused by peroxide-based bleaching, on an average as well as individually, is on a tolerable level, the relative differences can span a whole order of magnitude (cf. Fig. 4). Typically, under these conditions, vat dyes fade least, reactive dyes somewhat more and direct dyes most. Moreover, the extent of dye-fading increases with increasing temperature. However, as stated previously, even a treatment with SPB-containing detergents at the boil does not give rise to unacceptably high dye-fading. With TAED-activated formulations, dye-fading increases but not above the usual level of tolerance. On the contrary, the use of a catalyst may yield an unacceptable level of dye-fading (cf. Fig. 4).

Turning our attention to fiber damage reveals a critical role of the dyestuff. Quite generally, white cotton fabrics suffer hardly from any fiber degradation at all [15], when subject to laundry bleaching with hydrogen peroxide only. Most interestingly, this holds also true for TAED-activated as well as for catalysts-containing detergents. Even with TMTACN-type Mn complexes, there is no significant degree of fiber damage in the case of white cotton [15,16]! Undoubtedly, it is the dyed and the stained fiber that may be dramatically damaged when specific oxidation catalysts are present. This problem can be so serious that the corresponding bleach booster cannot be commercialized. A frequently encountered explanation for the massive fiber degradation which may indeed accompany the use of such a bleach catalyst invokes the hypothesis of metal deposition on the fabrics. Some dyestuffs are suspected of supporting such a process, due to their ability to coordinatively bind metal cations. The more a dyestuff is able to complex positively charged ions, the higher the local concentration of metallic centers on the fiber. Accordingly, by analogy to Fenton-type chemistry, these metallic centers are considered potential sources of locally produced aggressive radicals which react very unspecifically with almost any other substance available.

To test this hypothesis the metal content of diverse cotton fabrics was determined. However, no evidence in favor of this argumentation was found. Mn-TMTACN-type [16] as well as Mn-terpyridine-type chelates [10] were studied under conditions where the former catalyst causes massive and the latter only moderate fiber degradation. However, all the treated fabrics, white as well as stained ones, contained 0.5–1 ppm of Mn. This concentration remained constant after up to 10 washing cycles. In other words, no progressive accumulation of Mn was observed. Identical results were obtained from different experimental techniques, such as X-ray fluorescence, ICP-MS and radiochemical methods [16]. The latter technique revealed that there is a dynamic equilibrium between the Mn adsorbed and the Mn in the wash liquor, and that the metal content is distributed evenly on the treated fabrics [16]. Typical Mn content of white cotton before treatment was also about 0.5 ppm, while the tea-stained material employed to quantify the bleach effects contained about 10 times as much Mn before the first treatment (cf. Fig. 11).

On the detergent market, the appearance of **2** as a bleach additive prompted two types of response. First, people have been impressed by the great low temperature bleaching power of the corresponding products. Second, increased dye-fading and, even more disquieting, massive fiber damage was sometimes detected [8]. Amazingly, the latter type of damage was particularly big in the case of vat-dyed cotton, a class of dyestuffs considered to be particularly stable. Another rather special property of many vat dyes is their marked absorption in the near-infra-red (NIR) [53]. This makes them the colorants of choice as camouflage in military applications. In an extensive comparative study on a series of vat-dyed cotton swatches, the damage after 10 washing cycles with a TAED-activated and with a catalyst **2**-containing detergent formulation, respectively, has been determined at equal levels of stain-bleaching at  $T=40^\circ\text{C}$  [15]. In broad outline, the results show an acceptable level of average dye-fading

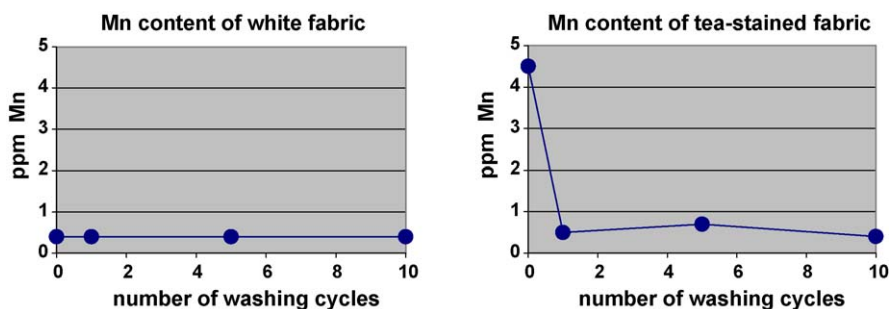


Fig. 11. Manganese content of white and of tea-stained cotton, before and after up to a 10-fold treatment with a Mn-TMTACN-type [16] catalyst-containing detergent formulation. The catalyst concentration in the wash liquor was 5  $\mu$ M. Fiber damage  $f$  of the catalyst-free reference system and of the catalyst-containing system after 10 washing cycles.

( $d \approx 10\%$ ) and very little fiber damage fading ( $f \approx 4.5\%$ ) in case of TAED-activation (cf. Fig. 12). Relative to this well established standard technology, the catalytic system causes clearly increased average dye-fading ( $d \approx 15\%$ ) and, most notably, and order of magnitude more fiber damage ( $f \approx 45\%$ )! Interestingly, most substantial fiber damage ( $f_{\text{cat}} \geq 40\%$ ) is observed for those vat-dyes that give rise to both, a significant NIR-absorption and a clearly detectable EPR-signal [15] CI Vat Black 30 (**5**) (cf. Scheme 6) is one of the strongest NIR absorber in the entire vat dye range, and V Bk 30 dyed cotton gives rise to a very strong EPR-signal (cf. Fig. 13). It is this dye that induced the highest degree of fiber damage ( $f_{\text{cat}} = 73\%$ ) in our study [15]. It must be noted that neither the NIR-absorption nor the EPR-signal of V Bk 30 dyed cotton is compatible with the well-established structure of this dye (cf. Scheme 6). However, it has been known for quite some time that **5** is chemically modified in the

course of the vat dyeing process. A definitive explanation for this structural change involved a phthaloylceramidon ( $\text{PCO}/\text{H}^\bullet$ ), i.e. a paramagnetic free radical (**5a**) (cf. Scheme 7), stemming from a 1,1'-dianthrimide, i.e. a structural subunit present in **5**. It was concluded that  $(\text{PCO}/\text{H})^\bullet$  and its  $\pi$ -dimer  $(\text{PCO}/\text{H})_2$  (**5b**) are in equilibrium [53]. The latter, thought to be formed by overlapping the  $\pi$ -orbitals of the face-to-face stacked radicals, is a closed-shell diamagnetic species responsible for the NIR absorption, whereas the paramagnetic (**5a**) gives rise to the EPR-signal.

It is tempting to blame persistent free  $\pi$ -radicals for their complicity in massive fiber degradation. Their presence as such is not the origin of the adverse phenomena, as the corresponding data for TAED-activated bleaching show (cf. Fig. 12). In the light of the present model, persistent  $\pi$ -radicals on the fiber seem to increase the effective range, in terms of both time and space,

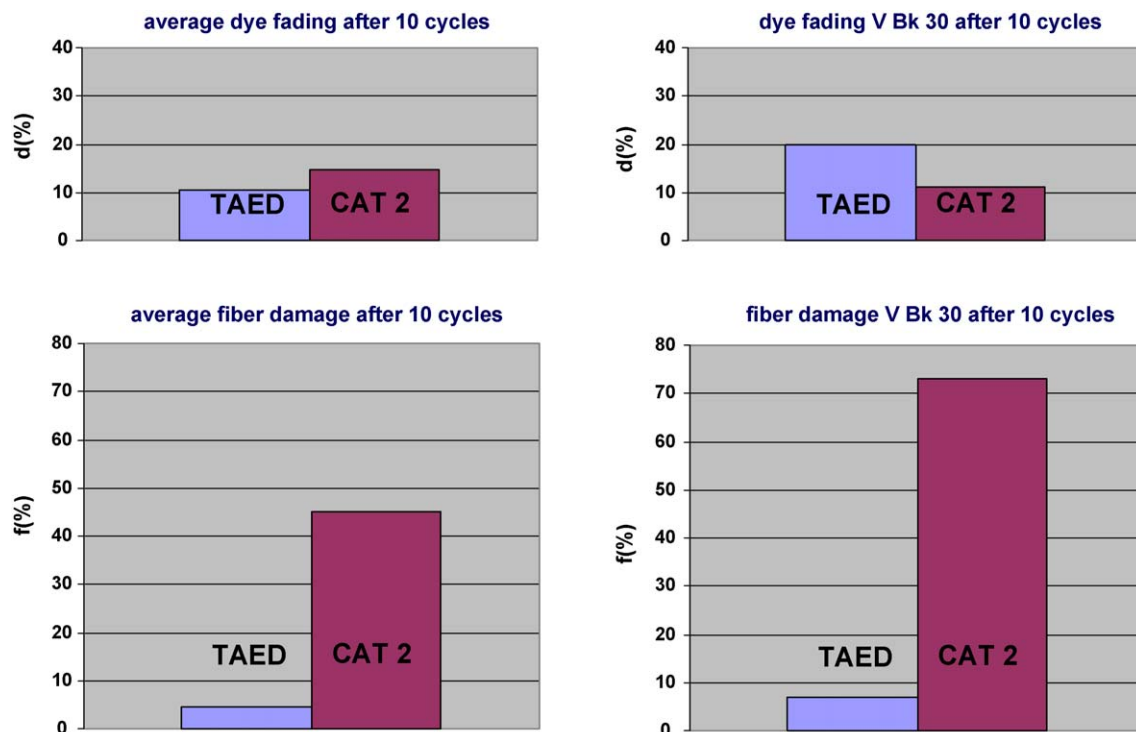


Fig. 12. Dye-fading  $d$  and fiber damage  $f$  of vat dyes. Average values for a series of eight vat dyes and specific values for V Bk 30, i.e. **5**, after 10 washing cycles with a TAED-activated and with a catalyst **2**-containing detergent formulation of equal bleaching performance, respectively, at  $T = 40^\circ\text{C}$ .

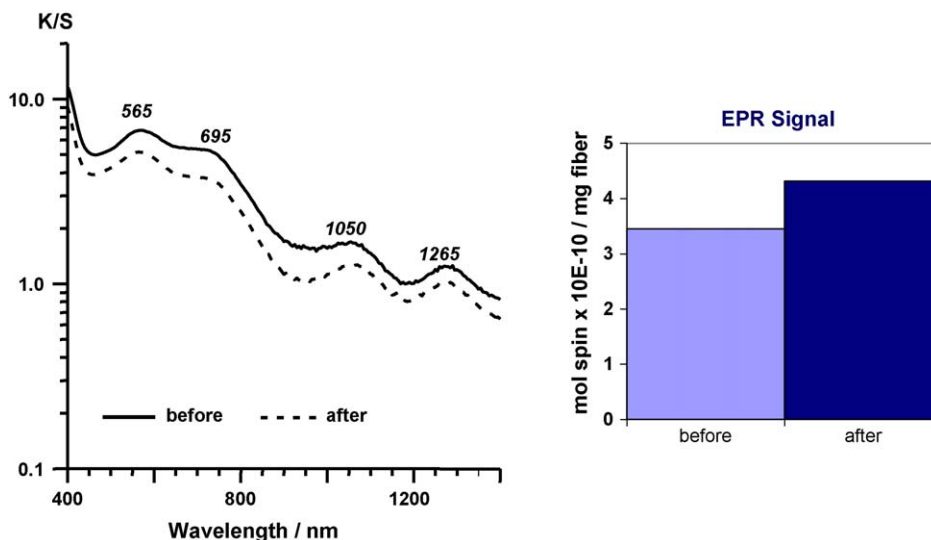


Fig. 13. Kubelka–Munk absorption spectrum (VIS/NIR) and EPR signal of a V Bk 30 dyed cotton swatch, before and after 10 washing cycles (see text).

of aggressive primary constituents generated in the course of the catalytic activation of  $\text{H}_2\text{O}_2$  by **2**. It is interesting to note that this massive dye-mediated fiber degradation takes place without significant fading of the colorant. On an average  $d_{\text{cat}} \approx 1\%$  for V Bk 30 dyed cotton per washing cycle (cf. Fig. 12). If the process boosted was a desired one, the stability of the mediator would be remarkable. Moreover, this reduction of the dye content of the fiber is accompanied by a significant increase of the EPR signal. After 10 washing cycles the relative amount of persistent radicals has increased by some 20%. Qualitatively, similar behavior has been observed for catalytic bleach of other vat dyes with hydrogen peroxide in the presence of **2**. One of them, V Br 1, is an important constituent of the set of dyes used to assess the damage potential of bleach catalysts (vide supra). It must be emphasized that the situation described is a peculiarity of the use of **2**, not of bleach catalysts in general. This can be deduced from numerous screening results, particularly from damage data on V Br 1, for

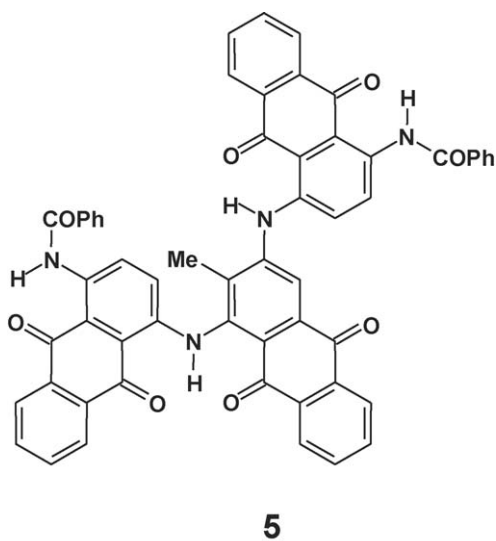
diverse other families of oxidation catalysts such as **1**, **3** and **4**. Referring to our qualitative model, the initial composition of the ensemble is catalyst-specific. It may contain especially aggressive species which are not necessary for efficient bleaching but which may cause dramatic damage, particularly when kept alive for an extended period of time by a correspondingly favorable environment.

## 2.8. Mapping application data into chemistry

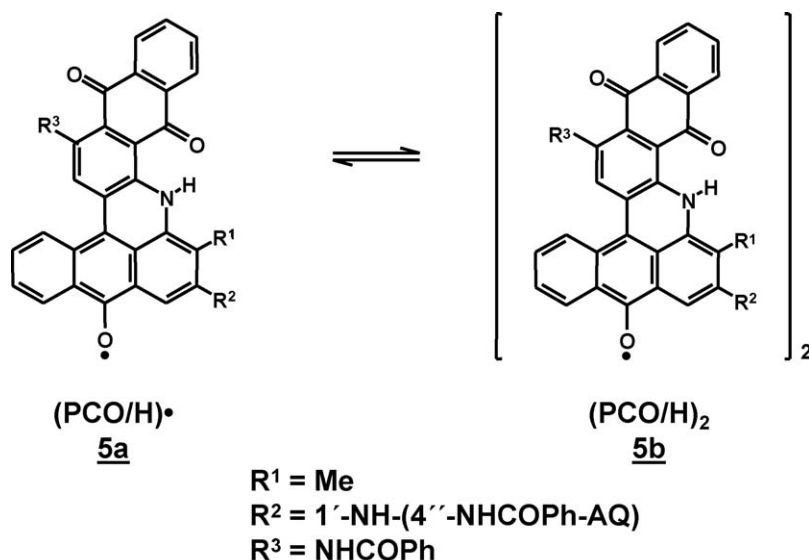
It is interesting to study to what extent the four process components (cf. Fig. 9) can be related to the chemical properties of bleach catalysts. By the same token, it is tempting to probe the degree of predictive power obtainable from the corresponding application data. To this end the behavior of a group of manganese terpyridine complexes (cf. Schemes 3 and 4) is discussed in this section.

Numerous researchers have studied the activation of hydrogen peroxide by transition metal cations. The pertinent patent literature claims such cations as bleach catalysts for various applications. When added directly in form of a salt, it is often difficult to reproduce the claimed effects. With respect to laundry bleaching, this is not amazing as such “naked” cations are readily oxidized and precipitated in the alkaline oxidative environment. Colloidal oxides/hydroxides of heavy metals can be highly active in decomposing hydrogen peroxide [50]. The time development of such a system is difficult to predict. In laundry application, heavy metal cations are considered a source of diverse problems rather than a bleach promoting agent. To prevent them from inducing adverse effects, detergents contain chelating agents, such as EDTA or DEQUEST. The corresponding complexes are believed to be catalytically inactive. However, a transition metal cation as the actual source of activation and a suitable ligand for its proper stabilization still form the basis of most contemporary strategies to invent better bleach catalysts.

Chemical substitution of the terpyridine (TERPY) moiety is required, to attain the desired degree of stabilization, as shown



Scheme 6. Chemical structure of CI Vat Black 30 **5**.



Scheme 7. Equilibrium between the paramagnetic phthaloyl-ceramidonyl radical (PCO/H) $\cdot$  **5a** and its diamagnetic dimer (PCO/H) $_2$  **5b**.

by the following observation. In an aqueous borax buffer solution (pH 10) with 8.6 mM  $\text{H}_2\text{O}_2$  and at  $T = 40^\circ\text{C}$ , the TERPY-MnCl $_2$  complex largely decays within the process time of 30 min, while ligand-substituted derivatives such as **4a**-MnCl $_2$  (cf. Schemes 3 and 4) survive under these conditions without detriment [31]. In the present context, complex stability with respect to reaction (II), i.e. parallel to catalytically bleaching a substrate, is clearly more relevant. Also, such a determination makes it possible to estimate turn-over numbers. The corresponding experimental data for catalyst **4a**-MnCl $_2$ –**4d**-MnCl $_2$  ( $C_{\text{cat}} = 10\ \mu\text{M}$ ) are depicted in Fig. 14 [10]. The conditions are as indicated in the Figure caption. Three consecutive bleach cycles are shown. At the beginning of each cycle proper aliquots of the model substrate Morin, i.e. (2',3,4',5,7-pentahydroxyflavone) and of the oxidant  $\text{H}_2\text{O}_2$  are added to achieve the starting concentration of 160  $\mu\text{M}$  and 10 mM, respectively. Evidently,

the catalytic activity of catalyst **4a**-MnCl $_2$ , **4c**-MnCl $_2$  and **4d**-MnCl $_2$  is hardly affected, since the respective rate of bleaching is nearly the same for all the three cycles. On the other hand, catalyst **4b**-MnCl $_2$  fatigues, as the corresponding decay function reveals. Except for **4b**-MnCl $_2$ , it may thus be concluded that these complexes do not suffer significant *catalyst decay* in the course of bleaching.

Regarding *disproportionation*, our quartet of substituted pyridines separates into two pairs (cf. Fig. 15). The triply substituted ligands **4c**-MnCl $_2$  and **4d**-MnCl $_2$  decompose  $\text{H}_2\text{O}_2$  much more rapidly than the mono substituted **4a**-MnCl $_2$  and **4b**-MnCl $_2$ . In the light of its very poor stability, the behavior of the TERPY-MnCl $_2$  complex is easy to understand. Its catalase-type activity is most probably due to the Mn $^{2+}$  ions freed by the decaying chelate. In relation to the preceding remarks on the fate of “naked” ions in an oxidative alkaline medium, the

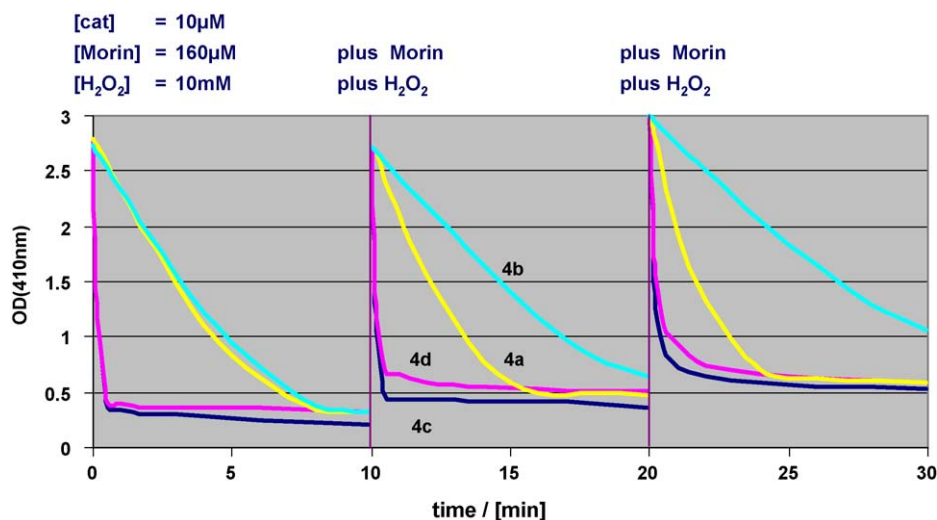


Fig. 14. Repeated bleaching of Morin in homogeneous solution, followed by its absorption at 410 nm and catalyst stability. At  $t = 0$ , the concentration are 160  $\mu\text{M}$  Morin, 10  $\mu\text{M}$  catalyst and 10 mM  $\text{H}_2\text{O}_2$  in 10 mM carbonate buffer (pH 10) at  $T = 23^\circ\text{C}$ . To re-attain the starting concentrations, addition of proper aliquots of Morin and of  $\text{H}_2\text{O}_2$  was repeated after 10 and 20 min.

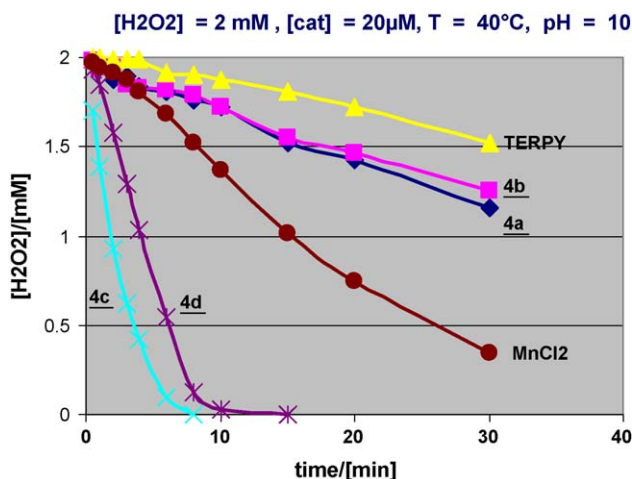


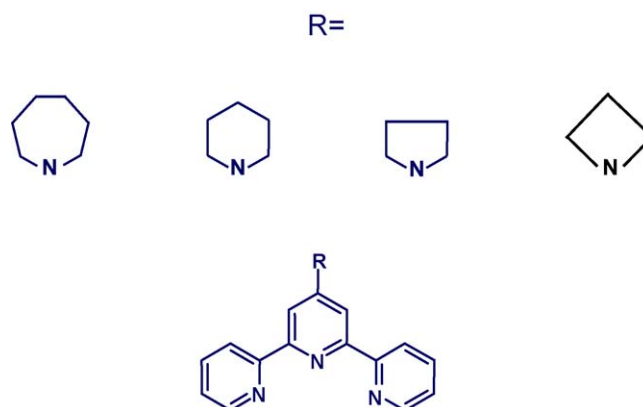
Fig. 15. Disproportionation of  $\text{H}_2\text{O}_2$  in the presence of diverse terpyridine-Mn complexes or of  $\text{MnCl}_2$ . The concentrations are  $20 \mu\text{M}$  catalyst and  $2 \text{ mM}$   $\text{H}_2\text{O}_2$  in  $10 \text{ mM}$  carbonate buffer (pH 10) at  $T = 40^\circ\text{C}$ .

difference relative to the much more efficient  $\text{MnCl}_2$  is not surprising.

To characterize the same set of compounds with respect to *bleaching* we refer again to the oxidation of Morin in homogeneous solution (cf. Fig. 14). Disregarding the quoted stability problem of **4b**- $\text{MnCl}_2$ , the relative ranking of the two pairs of terpyridine complexes found with respect to *disproportionation* is also evident regarding *bleaching*. The two strongly catalase-active substances **4c**- $\text{MnCl}_2$  and **4d**- $\text{MnCl}_2$  are also the better bleach catalysts for Morin degradation. TERPY- $\text{MnCl}_2$  and  $\text{MnCl}_2$  do not catalyze the oxidation of Morin. Data on Morin have proven to be good indicators for stain bleaching activity. In the case of the terpyridine complexes **4a**- $\text{MnCl}_2$ –**4d**- $\text{MnCl}_2$ , the relative ranking derived from stain bleaching figures is in accord with these Morin results [10].

Mapping *damage*, i.e. possibly the decisive component process, into the chemical structure of a catalyst is as laborious as rewarding. Evidently, this requires extensive comparative studies and at least some mechanistic investigations. Referring to laundry bleaching adequate test material is available to probe the damage potential of a specific catalyst. As to our quartet **4a**- $\text{MnCl}_2$ –**4d**- $\text{MnCl}_2$  of terpyridine chelates, their adverse effects are acceptably small and, in relative terms, tend to reproduce their respective activity with respect to *bleaching*.

In view of the multiple role of a bleach catalyst in a most complicated process, it is illusive to hope for a comprehensive structure–activity–relationship (SAR). However, if high-quality application data are available, models for the fine-tuning of a lead structure may be possible. By means of example, 4'-substituted terpyridine ligands with closely related substituents, such as a series of homologue cyclic aliphatic amines (cf. Scheme 8), show an excellent linear correlation between stain bleaching effects, expressed as  $\Delta Y$  and the gas phase basicity [54] of the nitrogen lone pair of the corresponding cyclic amine (cf. Fig. 16). It is tempting to extrapolate the experimental data available for pyrrolidine ( $n=5$ ), piperidine ( $n=6$ ) and azepane ( $n=7$ ) [31] as the 4'-substituent to ring-size four. This implies  $\Delta Y \approx 7.5$  for the corresponding 4'-azetidide ( $n=4$ )



Scheme 8. Selected 4'-substituted terpyridine ligands. The substituents are aliphatic cyclic amines of variable ring size.

substituted terpyridine ligand. It would be very interesting to check this prediction by experiment. With a view to identifying conceivable reasons for this interesting correlation, it is useful to recall that the s-character of the nitrogen lone pair electrons in cyclic amines increases with decreasing ring size [54]. This influences the electronic coupling of these substituents with the terpyridine moiety.

### 2.9. Routes to better bleach catalysts

Obviously, as a damage promoting element, a persistent radicals-containing surface or interface is undesired. On the other hand, an adverse effect is often the start of a superior alternative technology. More lately, a variety of tools has become available to build and to analyze novel solid state materials with most interesting physical and chemical properties [55]. Various heterogeneous catalysts to disproportionate excess  $\text{H}_2\text{O}_2$  as well as organic peroxides are known (cf. Fig. 7). So far, most of the corresponding research has focused on the catalase-type activity of such surfaces. However, in the light of the model for catalytic bleaching put forward in the present paper, a more extensive study of the activity of such surfaces seems very

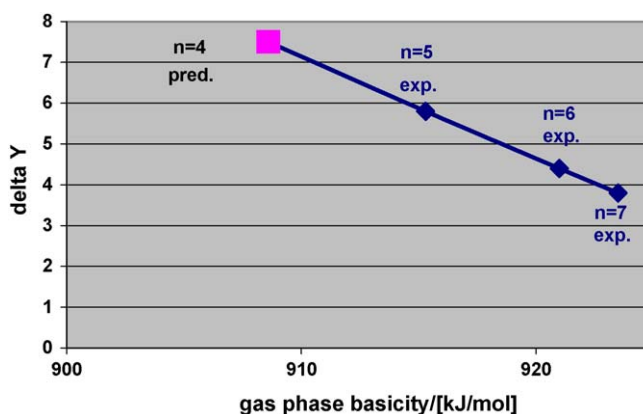


Fig. 16. Luminance change  $\Delta Y$  for catalytically bleaching a tea-stained cotton fabric as a function of the gas phase basicity of a homologous series of 4'-substituted terpyridine-Mn complexes. The values for ring size seven, six and five are experimental. The data point for ring size four is obtained by linear extrapolation.



promising. In the recent past, diverse techniques for chemically modifying suitable high specific surface substances have been developed [56]. Materials with wide cavities and channels have been functionalized and equipped with rather complicated chemical groups, as bulky as porphyrins [57]. It is likely that properly constructed surfaces are capable of inducing the system of chain reactions considered responsible for bleaching (vide supra). Furthermore, subtle modifications may equally well allow for fine-tuning of the corresponding properties as does chemical derivatization of the ligand in the case of metal-complex-type catalysts as discussed. Such solid state catalysts can be much more cost-competitive. At the same time, their use may render it possible to solve stability problems in an elegant way and to penetrate important market segments such as liquid formulations in the field of laundry and cleaning products. While better performing chelates may still be invented, the author considers the solid state approach to be the much more promising strategy. In times when speed and cost of novel product developments are decisive, the transfer of properly modified technologies from other domains is the method of choice.

When in an unsaturated molecule all of the hydrogen atoms are replaced by fluorine, the ionization energies corresponding to  $\sigma$ -electrons are shifted much further to higher energies than those corresponding to  $\pi$ -electrons. Quite some time ago, this phenomenon, termed the perfluoro-effect [58], has been discovered by photoelectron spectroscopists. Surprisingly, its chemical implications have hardly been exploited so far. Recalling that oligopyridines, such as the discussed terpyridines, own some of their highly interesting chemical properties to the fact that they function simultaneously as a soft  $\sigma$ -base and as a soft  $\pi$ -acid [59], perfluorination of such ligands is expected to dramatically alter the electronic properties and especially the catalytic behavior of the corresponding metal complexes. Also, it is recalled that due to the very similar Van der Waals radii of hydrogen and fluorine stereochemical aspects are only slightly affected by such a modification. If perfluorination is favorable or rather disadvantageous to catalytic bleaching must be checked by experiment. However, it would be very interesting in general to look into the consequences of ligand perfluorination in the context of chelate-based activation of hydrogen peroxide.

### 3. Conclusions

The net performance of chelate-type bleach catalysts depends strongly on the detailed chemical structure of the ligand. Reliable application tests are available to properly evaluate the quality of specific bleach boosters for laundry application. This makes it possible to base the fine-tuning of a ligand structure on SAR inferred from a proper set of screening data. However, the chemist's intuition is still paramount when novel substitution patterns and, even more so, when novel lead structures are to be devised. Nowadays, it is likely that such compounds are primarily invented in the course of academic research programs, rather than in industry. The evaluation procedures discussed facilitate easy pre-screening of such novel chemicals with respect to their capacity of  $H_2O_2$  activation. In this context it is particularly advantageous that diverse catalysts with an attractive

benefit damage balance are accessible for quick comparative tests. Preliminary in-house identification of potentially useful compounds should hence be easy. In case of promising results, it is recommended that potential partners for later stage R&D work are actively approached. Such an approach can considerably speed up the development of novel bleach catalysts without too much risk regarding intellectual property. In a time of intense inter-sectorial and interdisciplinary collaboration, the transfer of technologies and ideas from one area to another is favored very much. With respect to bleaching, the author considers the many facets of the field of solid surfaces as particularly promising.

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