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Fingerprints of bleach systems

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Abstract

Bleach catalysts represent cost-effective, environmentally friendly bleach systems allowing a perfect stain removal at low temperature. However, the detergent industry still hesitates to use this technology in a broader range of consumer products as it always bears an unpredictable risk of product failure. Bleach components act in the laundry process by way of chemical reactions. Whereas their main task should be the oxidation of colored food stains, side reactions with dyed fabrics and cotton fibers cannot be excluded.

In this comparative study bleach performance, dye fading and fiber damage of eight different bleach systems are examined. The selection covers activators, transition metal complexes designed for peroxide and aerial bleaching, as well as oxygen transfer agents. Multi-cycle washing tests are performed under real life conditions following recently developed dye and fiber damage test protocols. The results indicate that each bleach system has its characteristic performance and damage profile. Whereas the reactivity can be controlled by the usage concentration, the selectivity seems to be an intrinsic property. Bleach catalysts are not necessarily more aggressive than common bleach systems but their performance and damage profiles might be different. A better understanding of the reaction mechanisms is needed to minimize product failures.

Keywords: Bleach system; Bleach catalyst; Stain; Dye damage; Fabric damage

1. Bleach in laundry and cleaning processes

1.1. The bleach market

Bleach systems are essential components of laundry and cleaning products, from an economical as well as an ecological point of view. Year by year, enormous quantities of hypochlorite bleaches are released into the environment through the washing process. In addition, over 750,000 t of bleaching agents based on active oxygen are consumed worldwide. With a share of 85% peroxide derivatives (percarbonate and perborate) account for most of this, while bleach activators contribute to about 15% [1]. The consumption of hydrogen peroxide as well as organic and inorganic peracids is of minor importance.

The market for bleach activators has stabilized at a high level and is growing only moderately. Its value is estimated to be about 320 mio €, of which in total over 98% are accounted for by tetraacetylethylene diamine (TAED) and nonanoyloxybenzenesulfonate sodium (NOBS). TAED is an indispensable ingredient of European powder detergents, whereas NOBS has been dominating the North American market for almost 15 years. In Japan, two NOBS-related compounds, lauroyloxybenzenesulfonate sodium (LOBS) and decanoyloxybenzoic acid (DOBA), are in use additionally. Only two bleach catalysts are used to a minor extent in laundry and cleaning applications. Pentaamine acetato cobalt(III) nitrate (PAAN) and $[Mn_2(\mu\text{-}O)_3L_2][PF_6]_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) (Mn-TACN) are used in machine dishwashing detergents.

On a global basis about 30% of all detergents contain a built-in bleach system. For several reasons the remaining market cannot be reached with current technology. In Europe, there is a general trend for energy saving, e.g., shorter washing cycles. Furthermore, in many countries the washing is done at ambient temperature. Under both conditions TAED and NOBS are not very effective. In parallel, liquid detergents are gaining in importance. In such formulations, current bleach systems are not storage stable. New packaging systems (dual chamber bottles) and bleach technologies have to be developed to enter the liquids market successfully [2].

Besides performance especially cost of a bleach system is a key success factor for product commercialization. In the rural areas of Asia and Africa, most of the washing is still done by hand, using bar soaps or simple washing powders. The addition of persalt/activator systems would increase the price of such detergents by up to 50% and would thus put it out of reach for the average consumer. In these regions, bleach systems

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must be based on natural resources such as light and oxygen. A breakthrough is therefore achievable with catalyst technology only.

Based on actual market prices for persalts (approximately 0.60 €/kg) and activators (approximately 3.00 €/kg) it can be estimated that the sales price for new bleach systems (catalysts) should not exceed 200 €/kg in order to be competitive. If suitable systems would be available, the theoretical market for active oxygen based bleach systems can be estimated at around 1000 million € for laundry and cleaning applications. Even bigger markets exist in textile and pulp and paper industries.

1.2. Recent development in bleach technology

In the last 30 years, there were three breakthroughs in bleach technology. At the end of the 1970s, a bleach activator was used commercially for the first time. In combination with perborate, it allowed to reduce the washing temperature from 90 °C to 60 °C with an acceptable loss of stain removal and disinfection performance. In view of the oil crisis, this was a major step towards significant energy saving. As a consequence a few years later all European heavy-duty powder detergents contained TAED.

In 1994 Mn-TACN was introduced in laundry powders, allowing to substitute 5% TAED by only 0.05% of the catalyst and still receiving a better stain removal performance. Unfortunately, the catalyst proved to be aggressive to certain dyed fabrics and had to be withdrawn from the market. Nevertheless, this molecule initiated a push to develop alternative bleach catalysts. The latest breakthrough was made at the beginning of the new millennium when aerial bleaching systems were described in the patent literature. Although not yet commercialized such systems might be the bleach systems of the future.

Catalysts have many advantages over bleach activators, which have to be used in stoichiometric quantities. Catalyst are highly volume efficient needing less space in concentrated detergent powders and tablets. Furthermore, their lower activation energy allows a perfect stain removal at 20–40 °C, enabling further energy savings, i.e. an especially important aspect in times of increasing oil prices. Last but not least, catalyst technology is Green Chemistry and reduces the environmental pollution. In principle, the currently used 750,000 t of oxygen based bleach products could be substituted by only 1500 t of appropriate aerial bleaching catalysts.

1.3. Bleach – a chemical reaction

How do bleach components differ from other detergent ingredients? Builder (zeolite, citric acid, etc.) remove water hardness by ion exchange, whereas surfactants form micelles, lower the surface tension and support the removal of particulate and oily stains. The bleach system, however, acts via aggressive oxidation chemistry. Its main task is the removal of colored food stains. Unfortunately, the bleach system is not able to differentiate between unwanted food residues and certain synthetic textile dyes. Very often the bleach system attacks both in parallel leading to color fading which becomes visible after a few washing cycles. In the worst case, the bleach system may also react with the cellulose moieties of cotton fibers leading to significant damage and destruction of the garment.

The industry has spent several hundred million Euros within the last 10 years for R&D efforts on new bleach systems. However, keeping in mind the high financial risk if a product fails because of damaging properties, none of the many described systems has been commercialized at present. Ongoing research is focused on even more selective bleach systems targeting colored stains without harming colors and fibers.

1.4. Stains more than chromophores

Stains not only consist of colored chromophores but have proven to be exceptional complex mixtures. Anthocyanidines are the color giving components of red wine grapes. During the fermentation process and aging of the wine additional condensation, polymerization and oxidation reactions take place forming new colored complexes [3].

Carotenes, nature's most widespread pigments are major components of red, orange and yellow fruits, root crops and vegetables. In principle, carotenes are easy to oxidize because of the large number of conjugated double bonds. In food preparation, however, they are very often solubilized in oils and fats (e.g., spaghetti sauce) and therefore protected against hydrophilic bleach systems such as peracetic acid.

The light harvesting components in green plants are the third major group of natural chromophores. In food processing steps, especially during thermal treatment, chlorophylls are not very stable, resulting in color change or color loss. Exchange of the Mg-ion by Cu-ion stabilizes the chromophore. Cu-chlorophyll is 1 of about 500 food additives that are allowed in Europe. For better visual appearance and improved shelf life of food preparations a large number of natural and synthetic dyes, preservatives and antioxidants are used. Some of these compounds are found in stains later on, making the oxidation of the basic chromophore more difficult. Bleaching of model dyes in solution may give a first indication of the performance of a bleach system, but only washing trials using stained fabric can give a final conclusion.

1.5. Bleach systems

In this comparative study bleach performance, dye fading and fiber damage of eight different bleach systems are examined (Fig. 1). TAED (**1**) is used as standard bleach activator [4]. Under alkaline conditions in the presence of perborate it generates bleach active peracetic acid (**2**). This can be used, e.g., to activate *N*-methyl-3,4-dihydroisiquinolinium-tosylate (**3**) to form the oxaziridine (**4**) in situ [5]. Sugar based ketone 1,2:4,5-di-*O*-isopropyliden-D-erythro-2,3-hexodiulo-2,6-pyranose (**5**) reacts with potassium peroxomonosulfate to yield dioxirane (**6**) in the washing liquor [6]. After oxygen transfer reactions the precursors (**3**) and (**5**) are formed back and thus act as metal-free catalysts.

$[Mn_2(\mu\text{-}O)_3L_2][PF_6]_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) (Mn-TACN) (**7**) (Fig. 2) is used as an example of an aggressive bleach catalyst [7]. Instead of the preformed complex (**7**) the ligand salt 1,4,7-trimethyl-1,4,7-triazacyclononane

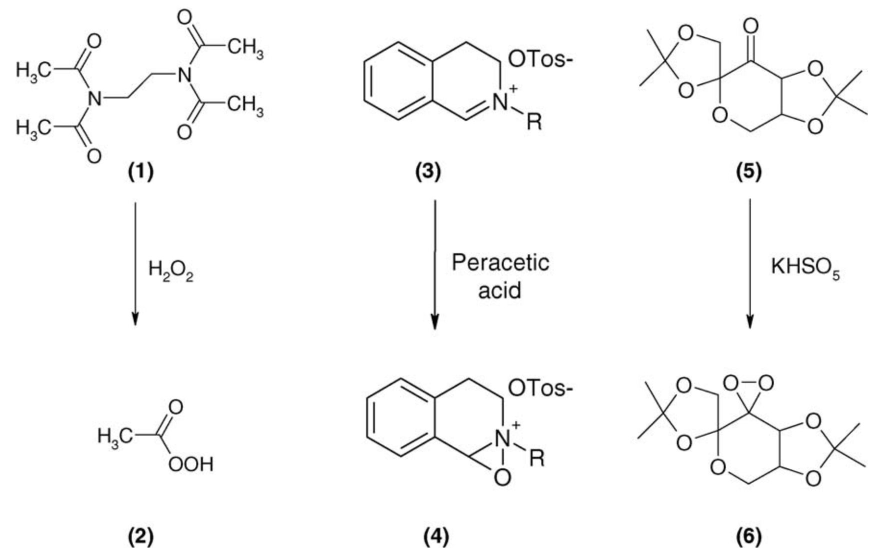

Fig. 1. Generation of bleach active species from activator and oxygen transfer agents.

hydrogensulfate (TACN-salt) (**8**) often can be used in oxidation and bleach reactions [8] as it forms the metal containing complex (**7**) in situ in the washing liquor in the presence of manganese ions. Manganese–Salen complexes such as Mn–Salen (R = alkylamino) (**9**) are known to be good bleaching agents in combination with a persalt or hydrogen peroxide [9]. The recently described manganese complex 1,8-diethyl-1,4,8,11-tetraazacyclotetradecane-manganese(II) chloride (Mn-Clm) (**10**) can be used in peroxide bleaching reactions but also under aerial bleaching conditions in which oxygen from air is used to bleach a stain [10].

2. Experimental

Wash tests were performed under the conditions described in Ref. [11]:

- washing machines: Miele W927, fuzzy logic system disabled;
- 40 °C cotton program without pre-wash;
- main wash time: 50 min (time at high temperature);
- main wash suds level: 12 l;
- water hardness: 15° dH;
- ballast load including one cloth of WfK SBL fabric as a soil donor;
- one wash cycle including two stain swatches (four replications);
- 20 wash cycles including the AISE dye set of 40 monitors;
- 50 wash cycles including the fiber damage monitors.

A 6 g/l EN 60456 reference detergent A* base powder (WfK Testmaterialien GmbH) and 1 g/l sodium perborate tetrahydrate (Degussa AG) were used as base detergent. The catalysts were

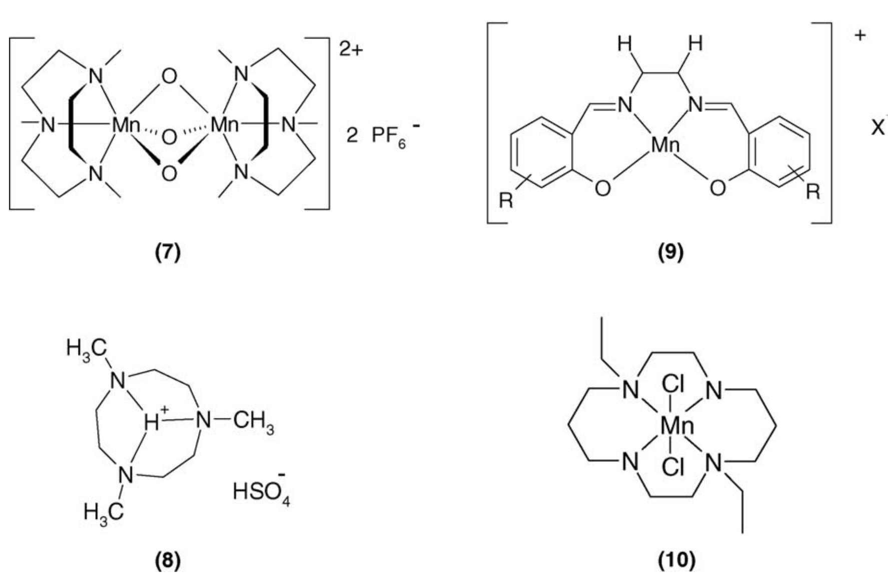

Fig. 2. Bleach catalysts.

dosed at concentrations of 10 mg/l in peroxide bleaching and 4 mg/l in aerial bleaching reactions.

Stain monitors were purchased from EMPA (CH), the dye monitors (AISE Dye Set) from UMIST, Department of Textiles (Manchester). Textiles for fiber damage (ISO 2267 cotton cloth (WfK 11A) from WfK Testmaterialen GmbH) was repeatedly pre-bleached to reach a certain initial degree of fabric damage.

Stain removal was measured after a single wash cycle, color measurements after 20 cycles. CIELab L^*, a^*, b^* measurements were taken with a spectrophotometer (Datacolor Elrepho 3000) with UV cut-off at 420 nm. Based on the measurements, ΔE (CIELab) = delta E values of the washed fabrics, relative to the unwashed fabrics, were calculated according to ISO 105-J03.

Fiber damage measurements were done after 50 cycles at 40 °C according to [12]. The chemical wear of the standard cotton was determined using the Cuen method. The tensile strength loss (TSL) of the ISO 2267 cotton was determined after conditioning of the strips from the standard cotton cloths at 20 °C and 65% RH for at least 18 h. TSL in percentages, was calculated as the difference between the tensile strength of the unwashed cotton and the washed cotton, divided by the average tensile strength of the unwashed cotton, multiplied by 100%.

3. Results and discussion

3.1. Bleach performance

The bleach results strongly depend on the washing conditions, the bleach active species and the type of stain. As natural stains are complex mixtures of chromophores, food ingredients and additives the oxidation reaction is very complex and can be influenced in many ways, positively and negatively. For performance evaluation commercially available stain swatches are used, pieces of white cotton cloths with 15 spots of various natural stains. Not all of these stains are bleachable. The color giving component of mud, clay and dirty motor oil (DMO) are insoluble pigments and withstand oxidation. In part, they are removed by the surfactant system.

500 mg/l TAED are used as reference standard to simulate a European heavy duty powder detergent with high bleach content (Fig. 3). In peroxide bleaching reactions at 40 °C 10 mg/l Mn-Clm give in general a similar stain removal as TAED. However, on three stains significant differences emerge. Whereas red wine is much better oxidized by TAED, the catalyst clearly is superior on more hydrophobic stains, such as curry and tomato. Moving from peroxide to aerial bleaching this trend becomes more obvious. Under aerial bleaching conditions there is enough oxygen dissolved in the washing liquor to react with the catalyst to achieve a good bleach performance. Even a concentration of 4 mg/l Mn-Clm shows good stain removal except on tea and red wine stains. As aerial bleaching systems normally act by formation of (free or localized) radicals, which react with triplet oxygen to form peroxides, radical scavenging polyphenolic compounds might inhibit the necessary reaction step.

Instead of a preformed metal complex in many cases the free organic ligand in form of its salt can be used in bleach reactions. There are enough metal ions available in the wash liquor to form

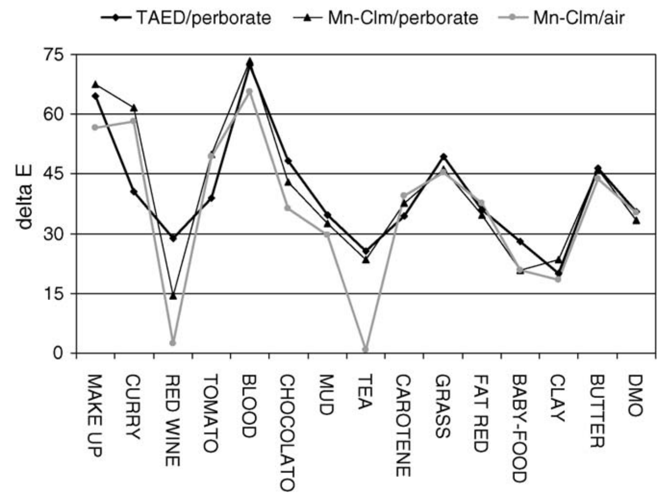

Fig. 3. Bleach performance profiles of TAED and Mn-Clm under peroxide and aerial bleaching conditions at 40 °C.

the complex in situ, brought in either by the tap water or as part of the stain. It is therefore not surprising that TACN-salt and Mn-TACN show a comparable stain removal profile (Fig. 4). As some of the ligand salt is lost in side reactions, its performance is slightly inferior to that of the preformed complex. Detergent formulations based on the ligand are sensitive with regard to the choice of builder system and complexing agents as well as the load and composition of soil.

In general, when moving from activator to catalyst technology a shift in the selectivity of bleachable stains is observed. Peracetic acid, generated from TAED, oxidizes red wine stains excellently. This performance cannot be matched by bleach catalysts. When moving from catalytic peroxide to aerial bleaching this trend becomes even more obvious. Tea and red wine stains very often withstand their complete removal in aerial bleaching processes. On the other hand, hydrophilic peracetic acid is not in favor to penetrate into oily and fatty stains. Metal complexes remove such colored stains more easily. A challenge for all bleach systems remains grass stain, not because of stability

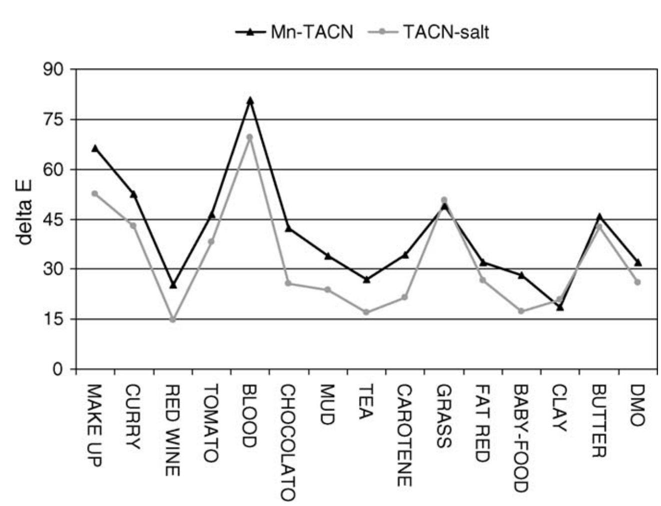

Fig. 4. Bleach performance profiles of Mn-TACN and TACN-salt under peroxide bleaching conditions at 40 °C.

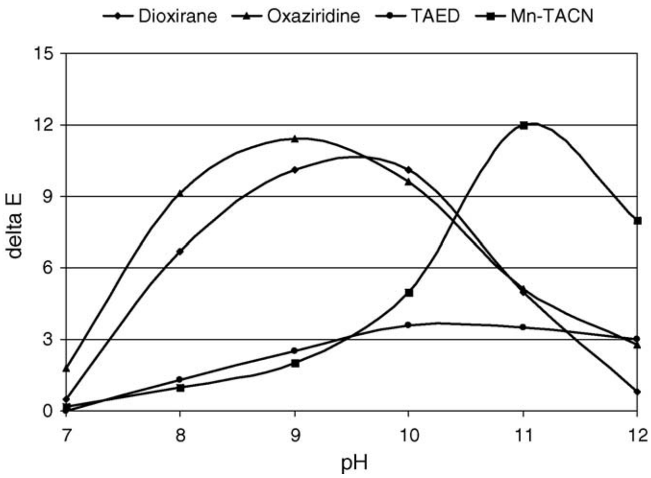

Fig. 5. Tea stain removal at 40 °C, pH dependence of various bleach systems.

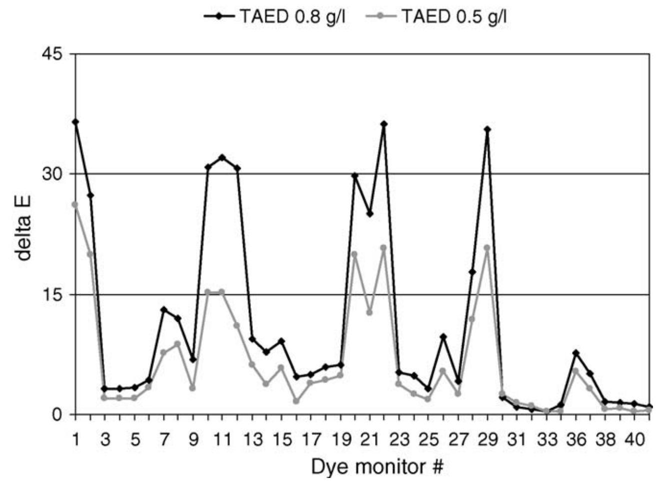

Fig. 6. Dye damage profiles of TAED after 20 washing cycles at 40 °C, AISE dye set.

of the chlorophylls but due to the lipophilic cellular components which protect the chromophore.

A further factor influencing the stain removal performance is the pH of the washing liquor, usually 9.5–10.5 with powder formulations and 7.5–8.5 with liquid detergents. This does not necessarily match exactly with the pH optimum of the individual bleach systems. Bleach activators generally are not very effective below pH 8, as there are not enough perhydroxyl anions available for a fast perhydrolysis reaction. Therefore, TAED removes tea stains best at pH 9.5–10.5. As shown in Fig. 5, the catalyst Mn-TACN is more reactive but has its narrow optimum around pH 11. Broad maxima are found for dioxirane (**6**) and oxaziridine (**4**) between pH 8 and 10. At least in case of dioxirane generating systems, the precursor ketone can be tailored to the desired pH by modifying the substituents.

3.2. Dye damage

A standard method for the detection of color damaging properties of bleach systems was recently proposed in the Color Damage Profile test (CDP test) protocol [11]. The AISE dye set is recommended as dye monitor [13]. This is a selection of 40 of the most important chromophores covering Sulfur, Vat, Direct, Azoic and Reactive dyes on cotton. In addition various Acid, Basic and Disperse dyes on synthetic fibers are included. Please note: the dyeings are numbered 1–41, dyeing 34 is missing. The bleaching results (color damage) of the CDP test are evaluated after 20 wash cycles as delta *E*. Delta *E* values higher than 10 are generally not acceptable for consumers.

Following the CDP test protocol, Fig. 6 shows the bleaching results for two different TAED concentrations after 20 washing cycles at 40 °C. Not surprisingly, the higher the activator concentration the higher the fading of selected dyes. Even at a concentration of 500 mg/l TAED which is common when modern European heavy duty compact powders and tablets are used, approximately 25% of all dyes are severely damaged. Especially sensitive to TAED are both Sulphur black dyes (dyes #1 and 2) and the Direct black dyes #10–12, where no major influence of the used after-treatment agent can be seen. Two shades of Reactive black #20 and 21, Reactive orange #22 and the Trichromatic mixture #29 also proved to be sensitive.

Although used only in catalytic amounts the highly reactive Mn-TACN attacks a large number of dyes (Fig. 7). The severe damaging properties are seen by the extremely high delta *E* values. Vat blue dye #5, Direct black dye #10 and 11, Reactive red and black dyes as well as the Trichromatic mixtures #27 and 29 do not withstand the bleach catalyst. On the other hand, Reactive orange dye #22 is not damaged at all under these conditions. Therefore, the color damage profile of Mn-TACN is very different to that of the bleach activator TAED.

More gentle than the preformed complex is the TACN ligand itself. After 20 wash cycles, no significant damage is observed. From their different damage profiles it can be conclude that Mn-TACN and TACN-salt act in this case via two different bleach mechanisms.

Very gentle to dyed fabric is the Mn-Clm complex in peroxide as well as in aerial bleach reactions (Fig. 8). When used in combination with persalts only Reactive violet (#26) appears

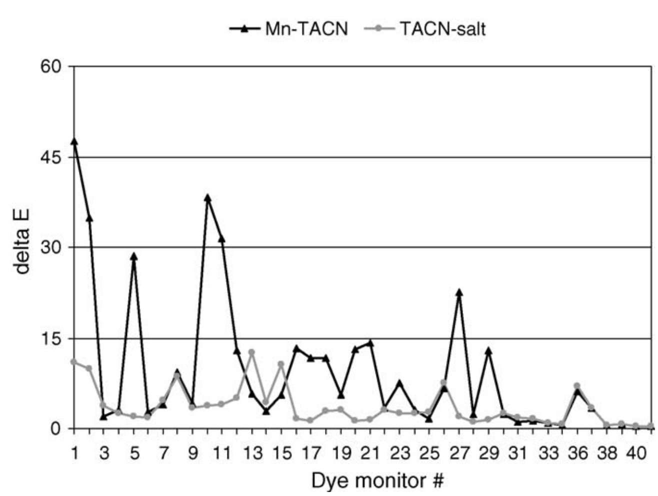

Fig. 7. Dye damage profiles of Mn-TACN and TACN-salt after 20 washing cycles at 40 °C, AISE dye set.

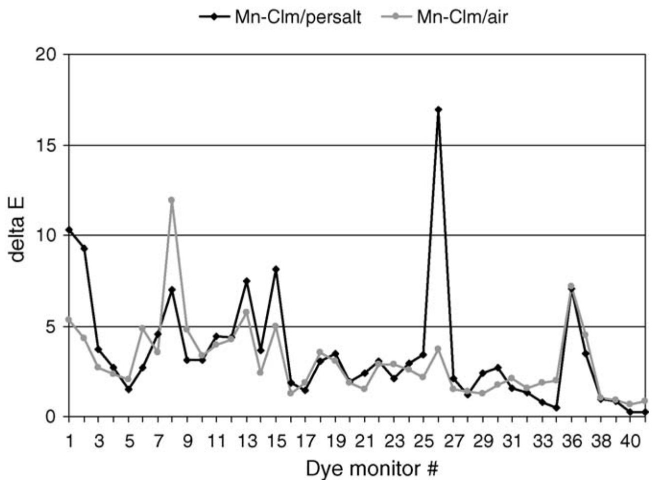

Fig. 8. Dye damage profiles of Mn-Clm under peroxide and aerial bleaching conditions after 20 washing cycles at 40 °C, AISE dye set.

to be sensitive, whereas in presence of air Direct yellow dye #8 is attacked to a certain extent. Under these conditions even sensitive Sulphur black dyes #1 and 2 are quite stable. This is really surprising as sulphur dyes are known as not being stable to oxidation.

Fig. 9 clearly shows that each bleach system has a characteristic color damage profile. TAED, Mn-TACN, Mn-Clm and Mn–Salen complexes leave their specific fingerprints on the AISE dye set. None of the profiles matches another one.

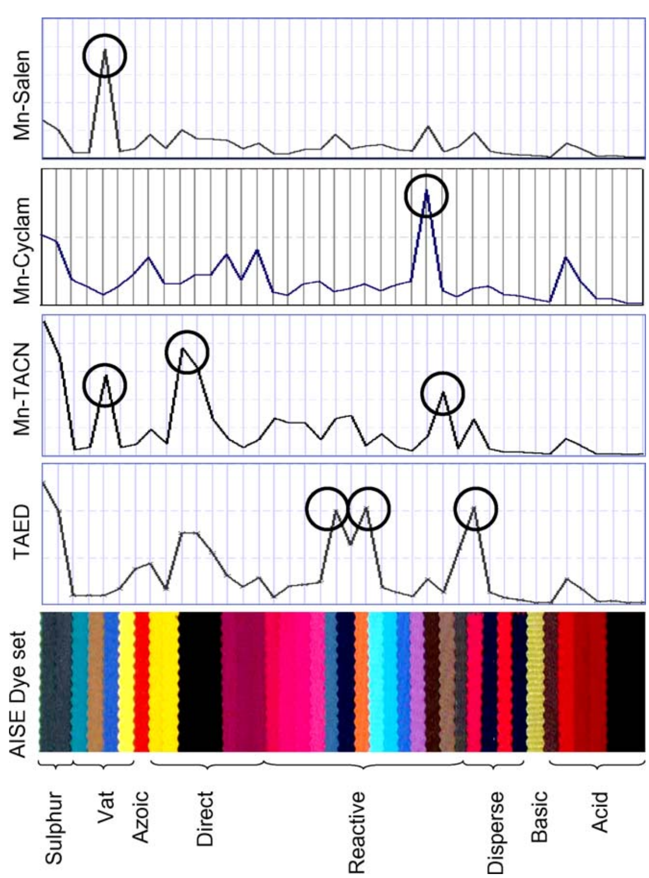

Fig. 9. Dye damage profiles of bleach catalysts on AISE dye set.

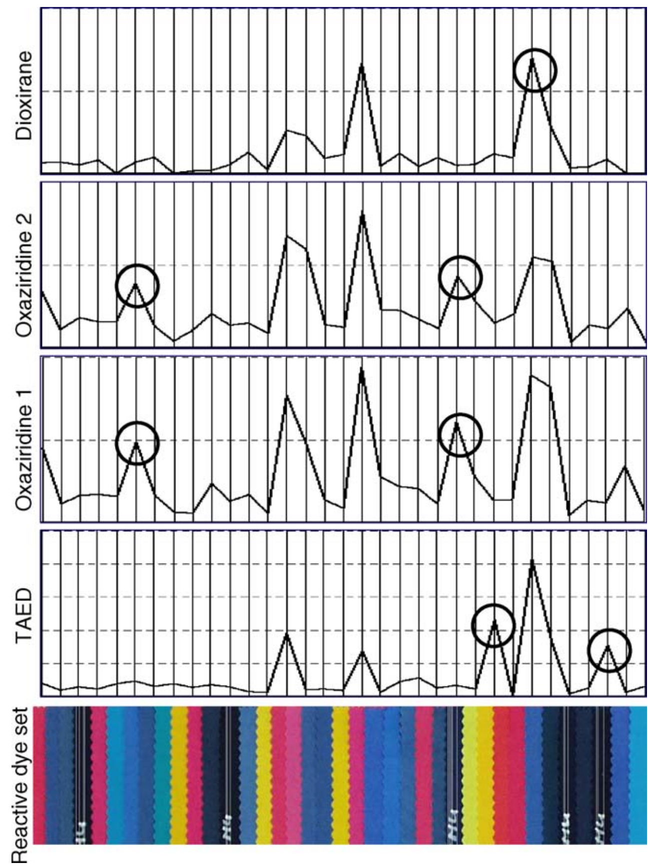

Fig. 10. Dye damage profiles of bleach systems on Reactive dye set.

This becomes also evident when using other dye sets and metal-free bleach catalysts (Fig. 10). On a newly developed Reactive dye set [14] TAED, oxaziridines and dioxiranes leave their individual fingerprints. Although used to activate the dihydroisoquinolinium quat to form the oxaziridine, TAED/perborate shows quite different fingerprints than the oxygen transfer agent. Oxaziridine 2 (in Fig. 10) differs from oxaziridine 1 (**4**) only by substituent R which does not influence the color damage profile. Surprisingly oxaziridine fingerprints differ from that of the dioxirane indicating different bleach mechanisms.

To summarize: about 25 % of all colored fabrics are damaged by state of the art bleach. This fact is known to consumers and generally accepted. New bleach systems have their own characteristic profiles. Even structurally related metal complexes have different damage profiles. Whereas the reactivity of a bleach system can be controlled via the usage concentration, the selectivity seems to be a product intrinsic property, which is currently out of control.

This makes the commercialization of new bleach systems more risky as new systems may attack other dyes than currently accepted bleach systems. However, new technology offers the opportunity to be more gentle to colors. Especially aerial bleaching systems are less aggressive and do not attack even sensitive sulphur dyes.

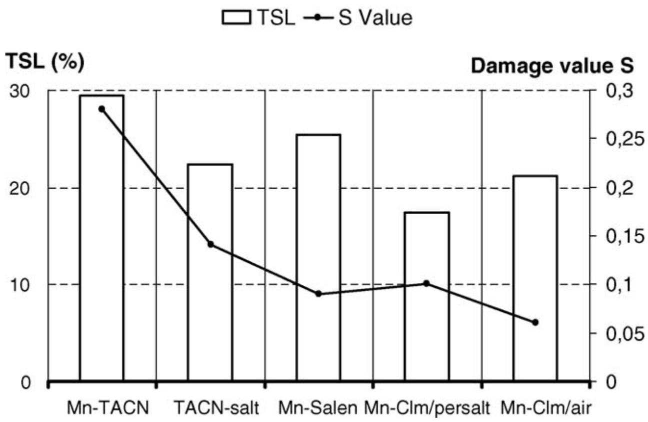

Fig. 11. Tensile strength loss and damage value *S* for bleach catalysts after 50 washing cycles at 40 °C.

3.3. Fabric damage

Since the failed market introduction of Mn-TACN in 1994, fabric care is the most critical hurdle for the market introduction of new bleach systems. Several methods for measurement of damage to cotton are published in the international standards. The total fibre damage or total wear, i.e. chemical and mechanical damage, is normally determined by means of tensile strength loss measurements on standard cotton. These measurements are quite laborious [12].

As an alternative the degree of polymerisation of the cotton can be determined, by measuring the viscosity of a dilute solution of the cotton. Copper ethylenediamine complex solution (Cuen) according to DIN 54270, part 2 is used as solvent. The resulting viscosity can be used to calculate the average degree of polymerisation (DP) of the cellulose and the damage value *S*. The difference between the DP before and after washing can be used to obtain information about the level of chemical damage. It should be noted that TSL measurements are more related to what consumers might experience in practice, as compared to the degree of polymerisation.

Repeated washing of garments damages its fibers to a certain extent. After 50 wash cycles at 40 °C, Mn-TACN shows the highest damage value *S* (Fig. 11). Even the TACN-salt seems to be more reactive in oxidizing the cellulose molecules of the cotton fibers than the other tested catalysts. Their *S* value is in the same range as TAED (S = approximately 0.1) under these conditions.

Tensile strength loss on white cotton caused by TAED is in the range of 18–20% after 50 cycles. Mn-Clm under peroxide as well as aerial bleaching conditions shows a quite similar behavior. All other catalysts are more reactive.

Comparing the results of both tests indicates that there is no direct correlation between *S* and TSL. As known from literature cotton can react with oxidizing agents in forming many different oxidation products (carbonyl groups). Research is currently ongoing to investigate if the tested catalysts cause characteristic oxidation profiles on molecular level.

According to ISO standard white cotton fabrics are used for damage tests.

But what does a *S* value of 0.3 or tensile strength loss of 30% after 50 wash cycles mean for the consumer? Is this relevant or not? No damage is visible by eye inspection. Unfortunately, neither the standard protocol nor the industry have defined limits for consumer relevant fabric care. In addition, in most cases dyed fabrics are even more sensitive to bleach systems than white cotton. Certain blue shade cotton fabrics can be severely damaged by aggressive catalysts such as Mn-TACN in less than 20 wash cycles.

Uncertainty and missing limits make the commercialization of new bleach systems unpredictable. Even more, if a new bleach system passes all the tests on cotton, additional fabrics such as polyesters, polyamides, etc., have to be tested to further minimize the risk of a product failure. On top, it has to be secured that all of the more than 20 different plastic materials of a modern washing machine are resistant against the bleach systems, as natural and synthetic rubbers are known to react with certain oxidizing agents.

3.4. Balancing benefits and risks

How can the risk of product failure be minimized? This question cannot be answered by the detergent industry alone. All parties involved in the value chain have to participate in such a risk assessment: chemical suppliers, dyestuff manufacturers, dye-houses, retailers, test institutes and consumer associations.

Intensive communication and consideration of all facts on a scientific, economic and ecological basis are necessary to assess the advantages and the risks of new bleach technologies and to find a consensus. The aim must be to achieve the greatest benefit for both, the consumers and the environment.

In addition, much more in-depth studies are needed to provide detailed insight into the bleach mechanism, the nature of the active species, their reactivity and selectivity to be able to design strategies to minimize the risk.

4. Conclusion

As bleach is a chemical reaction potential side reactions may occur, having a negative impact on the colors and fibers of a garment. Each bleach system has its characteristic stain removal, color and fabric damage profile (fingerprints), which differs from that of TAED. Whereas the reactivity can be managed via the usage concentration or a delayed release into the washing liquor, the potential negative impacts are not predictable and require extensive testing. A certain risk will always remain when a new bleach system is introduced into the market. Missing standards for consumer acceptable damage increase the risk.

Aerial bleaching systems seem to be the most promising candidates for the next generation of bleach systems, as they are more gentle to dyes and fibers than TAED. They are cost effective by using air, volume efficient and can be used in powder as well as in liquid applications. Such bleach systems might be affordable in most parts of the world, where the cost of activated systems put them out of reach for an average consumer.

Unfortunately, stain removal profiles of aerial bleaching systems do not match the standard consumer expectation. Whereas excellent performance can be achieved on colored oily stains, current catalysts still have deficits on hydrophilic tea and red wine stains. Improving the performance will be the challenge for further research.

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