

# USE OF DIFFERENT ACTIVATORS TO ENHANCE PAA BLEACHING OF COTTON - A COMPARISON STUDY

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## ABSTRACT

Peracetic acid (PAA) is an excellent alternative for hydrogen peroxide (HP) bleaching of cotton and has captured the interest of many researchers due to its environmental and economic benefits.

The main advantage of bleaching with PAA compared to HP is a satisfactory degree of whiteness without fibre damage which can be achieved in 40 minutes at 60°C and neutral pH, without the addition of auxiliary agents.

PAA is formed in an equilibrium reaction and commercial PAA solutions contain a certain amount of acetic acid and HP. Even at optimal bleaching conditions, a large part of PAA and HP remains unused. This weakness can be overcome by adding bleach activators which would convert HP to active peroxy acids and thus minimize residual HP.

The effect of three activators: N-[4- (triethylammoniomethyl) benzoyl] butyrolactam chloride (TBBC), tetraacetylenediamine (TAED) and nonanoylbenzene sulfonate (NOBS) on peroxy acids bleaching performance was studied. The rate of PAA and HP consumption and formation of peroxy acids during bleaching in the presence of cotton fabric was measured, assaying the influence of each oxidant on final whiteness.

Results have shown that TBBC, due to its cationic nature, had the greatest influence on bleaching performance, followed by NOBS and TAED.

## 1 INTRODUCTION

Due to the constant need of being environmentally friendly and cost effective, peracetic acid (PAA) is being popularised as an alternative to hydrogen peroxide (HP) bleaching. PAA and other peracids have been proven to be more potent oxidizing agents than HP, and therefore more effective at lower temperatures. However, for PAA to be considered an attractive alternative to HP, its bleaching efficiency must be made to be greater than the bleaching produced by HP in order to offset the relative higher cost of PAA.

Commercial PAA solutions contain some acetic acid and HP due to an equilibrium reaction. When used in cotton bleaching, PAA is consumed by two competitive pathways: oxidation of coloured impurities and wasteful reactions, such as spontaneous decomposition, hydrolysis or decomposition caused by the presence of heavy metal ions. Consequently, even at optimal bleaching conditions (60°C, pH 7.5) only a small fraction of PAA is consumed for bleaching and a large part of both oxidants, PAA and

HP, remains unused [1]. At these conditions HP remains inactive and does not affect the final bleaching [2]. This weakness can be overcome by incorporating bleach activators which convert HP to active peracids. Currently the most widely used bleach activators in the detergent industry are tetraacetylenediamine (TAED) and nonanoyloxybenzene sulfonate (NOBS). Both bleach activators can also be used in industrial textile bleaching [3-5]. Recently a cationic bleach activator, N-[4-(triethylammoniomethyl) benzoyl] caprolactam chloride (TBCC), was proposed for HP bleaching [6-10]. Under alkaline conditions, hydrogen peroxide reacts with TBCC to form a highly reactive peracid with cationic nature, which exhibits high substantivity towards negatively charged cotton surface [6-10]. Furthermore a butyrolactam based activator, N-[4-(triethylammoniomethyl) benzoyl] butyrolactam chloride (TBBC) was investigated in cotton bleaching with PAA. Our studies showed that by adding a small amount of TBBC a higher level of whiteness could be achieved with less fibre damage [11].

The purpose of this work was to compare the performance of TBBC, TAED and NOBS by following the consumption of PAA and HP and the formation of peracids during cotton bleaching. Also, a novel approach by using catalases was used to assay the influence of each oxidant on the final bleaching effect.

## 2 EXPERIMENTAL

### Materials

Scoured cotton fabric, 102 g/m<sup>2</sup>, was obtained from Tekstina, Slovenia. Persan S15, a 15% equilibrium solution of PAA, and HP (35% w/w) were supplied by Belinka Perkemija, Slovenia. Sodium carbonate, acetic acid and TAED were purchased from Fluka, Germany. CHT - Catalase BF was purchased from CHT, Switzerland. The bleach activators, TBBC and NOBS were supplied by Proctor & Gamble, USA.

### Bleaching

We assayed the influence of selected activators (TBBC, TAED, NOBS) on the final bleaching effect by performing three different bleaching experiments (Table 1):

- conventional bleaching with PAA (PAA<sub>eq</sub>)
- bleaching with pure PAA by degrading HP using catalase (PAA<sub>pure</sub>)
- bleaching with HP and acetic acid in an equivalent amount as in equilibrium PAA (HP)

Table 1: Bleaching experiments.

experiment	PAA <sub>eq</sub>	PAA <sub>pure</sub>	HP
agents			
Persan S15 (mL/L)	15	15	-
HP 30% (mL/L)	-	-	8,5
CH <sub>3</sub> COOH (mL/L)	-	-	2,15
Catalase (g/L)	-	0,5	-

All bleaching experiments were performed at 60°C, at pH 7.5 and at liquor to goods ratio of 20:1. The pH of the mixture was adjusted by adding 0.5M sodium carbonate. The temperature of all bleaching baths was raised from 40 to 60°C in 15 minutes. This step is of specific importance for the PAA<sub>pure</sub> bleaching experiment by giving catalase enough time to completely degrade HP. After that, both the activator (TBBC (1.5% owf), TAED (1% owf) or NOBS (1,5% owf)) and the scoured cotton fabric (15.0 g), were added and all bleaching experiments were performed:

- over 120 minutes in flasks in a shaking water bath (SWB25, Haake) at a frequency of 85 rpm for the determination of PAA and HP consumption and/or formation of peracids
- over 40 minutes in closed beakers on Atlas Launder-Ometer for the determination of whiteness index (WI) and degree of polymerization (DP).

Following bleaching all samples were washed in hot water, rinsed twice in cold water and dried under ambient conditions.

## Methods

### *Concentration of reactants*

The PAA and HP concentrations in the bleaching bath were determined via iodometric titration using a method developed in the Laboratory for Peroxide Chemistry in the Faculty of Chemistry and Chemical Technology, University of Ljubljana, to determine the concentration of both oxidants simultaneously [1].

This method is based on the reaction of both PAA and HP with potassium iodide. The concentration of released iodine was determined with standardized sodium thiosulphate. Since both oxidants react with potassium iodide at room temperature, the titration provided a value for total oxidant concentration. To determine the PAA concentration, titration with sodium thiosulphate was performed at 0°C, since HP reacts negligibly with potassium iodide at this temperature. The calculated difference between total oxidant and PAA concentration was equal to concentration of HP. All values reported were the average of at least two readings.

### *Whiteness*

Reflectance spectra were measured for each sample using a Datacolor Spectraflash SF 600 Plus-CT with the following settings: illuminant D65, large area view, specular excluded, UV included and CIE 1964 Supplemental Standard Observer (10 degree observer). Each sample was folded into four layers, the reflectance was measured five times, averaged, and CIE Whiteness Index (WI) values were then calculated for each sample using AATCC Test Method 110-1995 [12].

### *Damage to substrate*

Fibre damage was determined by measuring the degree of polymerization (DP-values) via a viscosimetric method [13]. For this purpose, fibres were dissolved in cuoxam.

### 3 RESULTS AND DISCUSSION

#### 3.1 Decomposition and formation of peracids

To assay the influence of each activator on bleaching performance of PAA, two different approaches were used. The concentrations of both oxidants (PAA and HP) during the bleaching process were measured as a function of time, from which second order rate constants were obtained under pseudo first order conditions (Table 2). The bleaching effect was assayed by measuring WI and DP.

**Table 2** Calculated second order rate constants of PAA and HP consumption in the presence of different activators (TBBC, TAED and NOBS) at 60°C and at pH 7.5.

experiment	PAA <sub>eq</sub>		PAA <sub>pure</sub>		HP	
	PAA	HP	PAA	HP <sup>b)</sup>	PAA	HP
reference <sup>a)</sup>	5,64 10 <sup>-2</sup>	1,69 10 <sup>-4</sup>	1,58 10 <sup>-2</sup>	3,51 10 <sup>-2</sup>	2,92 10 <sup>-2</sup>	3,55 10 <sup>-3</sup>
TBBC	4,27 10 <sup>-2</sup>	2,58 10 <sup>-4</sup>	1,52 10 <sup>-2</sup>	3,69 10 <sup>-2</sup>	2,76 10 <sup>-1</sup>	3,56 10 <sup>-3</sup>
TAED	3,60 10 <sup>-2</sup>	2,17 10 <sup>-4</sup>	1,44 10 <sup>-2</sup>	2,41 10 <sup>-2</sup>	2,95 10 <sup>-1</sup>	1,22 10 <sup>-3</sup>
NOBS	3,87 10 <sup>-2</sup>	2,13 10 <sup>-4</sup>	1,90 10 <sup>-2</sup>	1,92 10 <sup>-2</sup>	1,24 10 <sup>-1</sup>	1,91 10 <sup>-3</sup>

a) no activator added

b) formation instead of consumption

In the case of conventional bleaching the reaction rate for PAA consumption decreased after the addition of the activators. This was mainly due to the formation of more peracid, which is in accordance with previous findings. A slightly higher rate constant was observed in the case of TBBC. The peracid formed in the system with TBBC is probably more reactive and can readily react in oxidation reactions.

When HP is eliminated by the action of catalases, some HP is released during bleaching in order to keep up the equilibrium. With no hydrogen peroxide present to react with the activator no peracids are formed and therefore no changes in the rate constant were observed. Since catalases have no direct influence on PAA consumption, decreased PAA consumption can be ascribed to the shift in the equilibrium towards HP formation [14].

In the case of HP bleaching a large amount of peracids must be formed almost immediately after the addition of the activator since a fast consumption was observed in all cases.

However, rate orders are not enough to clarify the influence of the activators on PAA bleaching performance. Therefore, we measured WI and DP on all samples.

#### 3.2 Whiteness and damage of cotton substrate

The results of PAA bleaching in the presence of different activators (TBBC, TAED and NOBS) according to three different bleaching experiments (PAA<sub>eq</sub>, PAA<sub>pure</sub> and HP) are presented in Table 3.

**Table 3** Effect of different activators (TBBC, TAED and NOBS) on whiteness index (WI) and degree of polymerization (DP) of bleached samples.

activator	experiment	WI	DP
unbleached		15,9	2845
reference*	PAA <sub>eq</sub>	75,88	2334
	PAA <sub>pure</sub>	74,48	2337
	HP	31,69	2278
TBBC	PAA <sub>eq</sub>	78,93	2375
	PAA <sub>pure</sub>	74,38	2386
	HP	40,37	2351
TAED	PAA <sub>eq</sub>	76,11	2381
	PAA <sub>pure</sub>	74,96	2382
	HP	35,41	2338
NOBS	PAA <sub>eq</sub>	77,48	2359
	PAA <sub>pure</sub>	72,00	2348
	HP	38,33	2333

\* no activator added

The bleaching performance of PAA<sub>eq</sub> was improved regardless of the bleach activator used. However, the highest whiteness value was achieved in the presence of TBBC, followed in turn by NOBS and TAED. These results again confirm previous findings that cationic peracid formed from TBBC has a higher substantivity toward a negatively charged cotton surface [6-10].

When bleaching was done in the presence of PAA<sub>pure</sub>, a lower whiteness was achieved in all cases compared to PAA<sub>eq</sub> bleaching. Since no hydrogen peroxide was present, no additional peracids were formed, which resulted in a lower whiteness degree. Since a comparable whiteness value was achieved when no activator was added we confirmed previous findings that catalases have no influence on PAA bleaching performance [14].

After the addition of different bleach activators a comparable decrease in the DP values was noticed when compared to the unbleached sample. However, when HP bleaching was done without the addition of the activators a considerable decrease in the DP value was observed. By reacting with HP the activators suppressed its decomposition and therefore less damage was noticed.

#### 4 CONCLUSIONS

Different bleach activators have been studied to enhance the bleaching performance of PAA. Our results showed that less PAA is consumed when using TAED and NOBS, compared to the use of TBBC. If we postulate higher efficiency of activators by lower rate of PAA consumption, as a result of more peracids being formed, our findings would suggest that TAED and NOBS are more efficient activators than TBBC. However, a substantially higher WI obtained with TBBC implicates that the formed cationic peracid immediately and more readily reacts in bleaching reactions.

Regardless of the activator used a comparable DP value was observed. Fibre damage was minimal throughout the experiment with the exception of reference HP bleaching, where a lower DP value (higher damage) could be observed.

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