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Evaluation of Peracetic Acid as an Environmentally Safe Alternative for Hypochlorite

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Hypochlorite is one of the oldest industrially used bleaching chemicals. Due to its bleaching power even at low temperatures and its relatively low costs, hypochlorite is still used in the textile and laundry industries. However, the formation of highly toxic chlorinated organic by-products (AOX) during the bleaching process has limited its use over the last few years because these compounds are a potential hazard to the drinking water resources when discharged.[1,2] Table I shows typical data on the total AOX and $CHCl_3$ concentrations in spent hypochlorite bleaching liquids and rinse solutions.

In many countries in Europe very stringent discharge limits are already in place; e.g., Germany: 0.5 ppm or a maximum of 10 g/h, which make the use of hypochlorite almost impossible without costly wastewater treatment. For that reason, the textile industry is seeking environmentally safe alternatives for hypochlorite which are able to achieve attractive brightness under similar process conditions.

Peracetic acid has proven to be an effective bleaching agent in household detergents for more than 20 years and has also found wide application in the laundry industry. In household powder detergent, peracetic acid is generated *in situ* from sodium perborate and acetylated O or N-compounds (activators) such as tetraacetylethylenediamine (TAED).[3] In the textile industry, peracetic acid has been used successfully for the bleaching of colored indanthrene dyed goods and the bleaching of nylon blends.[4-7]

ABSTRACT

Bleaching tests were conducted to study the efficacy of peracetic acid (PAA) as a replacement for sodium hypochlorite in multistage bleaching processes of cotton and linen. The study showed that *peracetic acid is most effective as a bleaching agent in the pH range of 6 to 7.* The preferable bleaching temperature range is between 50-80C. The required dwell time for a peracetic acid bleaching stage is comparable to NaOCl bleaching. Typically, bleaching time is between 20-60 minutes depending on the temperature. As in all bleaching processes, the degree of brightness increases proportionally with bleaching agent concentration.

Bleaching of 100% cotton goods in rope form in a J-box with peracetic acid (1.5-2.5 g/L) at room temperature, followed by an alkaline H_2O_2 treatment at 90C yielded a brightness of over 90 (Berger). Linen yarns could be successfully bleached using a process consisting of scouring, alkaline H_2O_2 bleach and a PAA bleaching stage. Starting with a raw material with a brightness of 20, a final brightness number of 78 was obtained after the PAA bleaching stage. In all bleaching tests, the PAA process was found to be less fiber damaging than NaOCl.

KEY TERMS

Bleaching
Cotton
Hypochlorite
Linen
Peracetic Acid

Physical and Chemical Properties of Peracetic Acid

Peracetic acid is an equilibrium solution consisting of H_2O_2, acetic acid, water and peracetic acid.

$$H_2O_2 + CH_3COOH <\!\!-\!\!> H_2O + CH_3COOOH$$

Peracetic acid is commercially available for textile bleaching in 5% and 15% solutions. The physical and chemical properties of peracetic acid are listed in Table II.

Effect of Process Parameters

All the following results were obtained with 100% cotton single jersey goods at a liquor:goods ratio of 10:1 in an Ahiba laboratory device. This study was done to determine the most important process parameters for PAA bleaching knitted goods and yarns that are currently bleached with NaOCl. Brightness (or whiteness) is measured as a percentage of total reflection versus a white standard (Datacolor/Berger). Yellowness is measured on a scale of yellow to blue where a positive number denotes yellowness, a negative number denotes blueness and zero denotes neutrality. The degree of polymerization (DP) values were determined according to the modified cuoxam method described by Buechs and Mertens.[8] The standard bleaching conditions were 30 minutes dwell time at 60C, pH 6.5 and 2.5 g/L PAA. The DP value of the greige fabric was about 2600.

Effect of pH

The maximum bleaching effect is theoretically at pH 8.2 which corresponds to the pK value of the peracetic acid. Figs. 1 and 2 show the effect of pH on whiteness and DP values. Below a pH of 7 the brightness significantly decreases. At a pH of 9 only a slightly higher brightness is obtained but at the expense of the DP value due to decomposition of the PAA to O_2 and CH_3COOH. From this data, it can be concluded that *the optimum pH range* for a PAA bleaching stage is around 6-7.

Since PAA will replace NaOCl as a pretreatment to an alkaline H_2O_2 bleach, a process at slightly acid conditions has additional technological

Table I. AOX and $CHCl_3$ Concentrations in Bleaching Liquids (ppm)

	NaOCl Stage	H_2O_2 Stage	Rinse 1	Rinse 2
AOX	105	19	5	2
$CHCl_3$	11.5	1.1	0.3	0

Table II. Properties of PAA

	Physical Properties	
	5% PAA	**15% PAA**
Appearance		colorless liquid
Odor		pungent
pH 10% solution	2	2
Density (g/mL, 68F)	1.120	1.148
	Chemical Properties	
	5% PAA	**15% PAA**
H_2O_2	27.0	22
Acetic acid	6.3	16.6

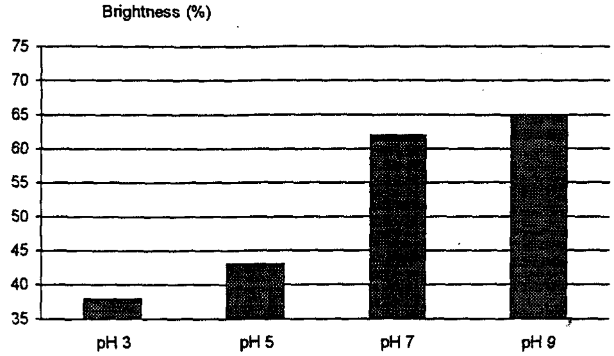

Fig. 1. Effect of pH on brightness.

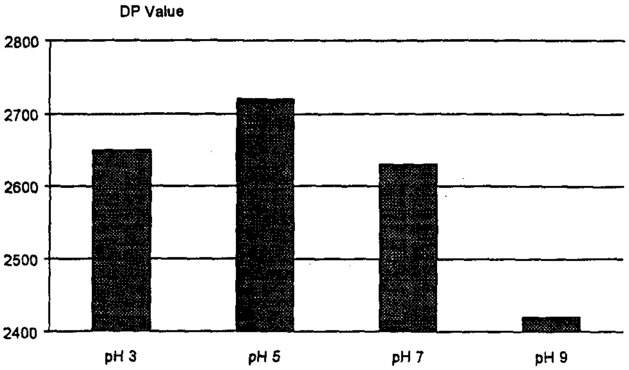

Fig. 2. Effect of pH on DP value.

advantages. At a pH of 6-7, the cellulose material tends to swell significantly less than under alkaline conditions, which means better liquor penetration and more effective removal of mineral impurities and metals. This advantage of PAA can be utilized when bleaching on jigs because a poor cleaning effect is obtained with this type of equipment due to its mode of operation. The improved cleaning of the fabric allows the use of sodium silicate as a stabilizer in the subsequent alkaline H_2O_2 bleaching stage. This results in a significant improvement of the quality of the goods (e.g., linen/rayon) and savings in chemical costs.

An additional advantage of the PAA bleaching stage is that most fabrics form fewer crease marks under neutral conditions. However, one disadvantage of the treatment at a lower pH is the incomplete removal of seeds and husks. This problem is well known in NaOCl bleaching and means, in practice, that NaOCl or PAA cannot be applied as a single-stage process on greige fabrics without an alkaline pretreatment (scour) or a subsequent alkaline H_2O_2 bleaching stage.

Effect of Temperature

As expected, the brightness increases with increasing temperature. The peracetic acid bleach can easily be adjusted to the bleach equipment parameters. Preferably, PAA should be applied at low temperatures as a pretreatment for an alkaline H_2O_2 bleach. At higher temperatures, the high vapor pressure of the PAA solution must be considered and bleaching should only be conducted in enclosed equipment due to the odor of the PAA. To avoid fiber damage, the preferred temperature range is from 50-80C. Figs. 3 and 4 show the effect of temperature on brightness and DP values.

Effect of Dwell Time

The dwell time is very important with respect to safety and economics. Typically, the bleach periods should be as short as possible. From Figs. 5 and 6, it can be seen that good bleaching results are obtained after 20 minutes. An extension of the bleaching time over 60 minutes does not yield significantly higher brightness. In contrast to the NaOCl process, only minimal fiber damage is obtained over long bleaching periods.

Effect of PAA Concentration

As in all bleaching processes, the degree of whiteness increases proportionally with higher bleaching agent concentration (Fig. 7). It is remarkable that even at relatively high PAA concentra-

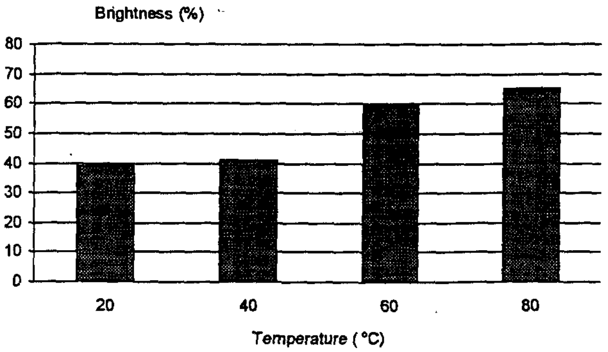

Fig. 3. Effect of temperature on brightness.

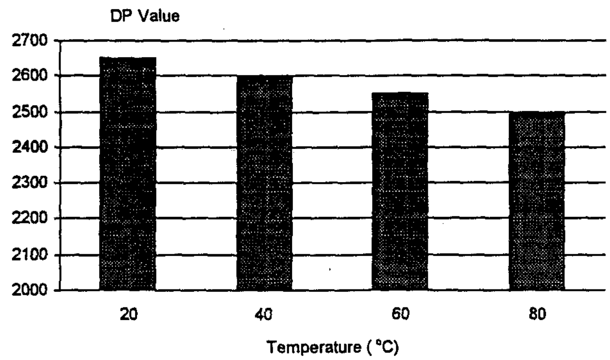

Fig. 4. Effect of temperature on DP value.

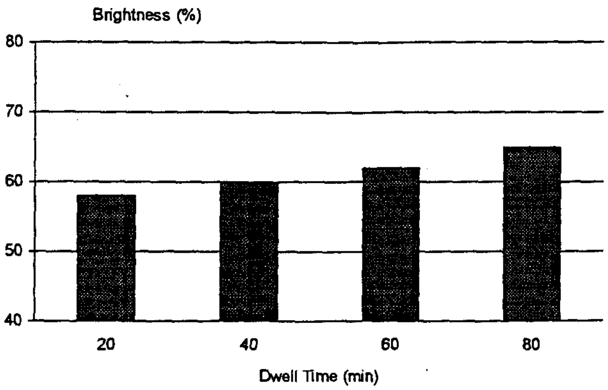

Fig. 5. Effect of bleaching time on brightness.

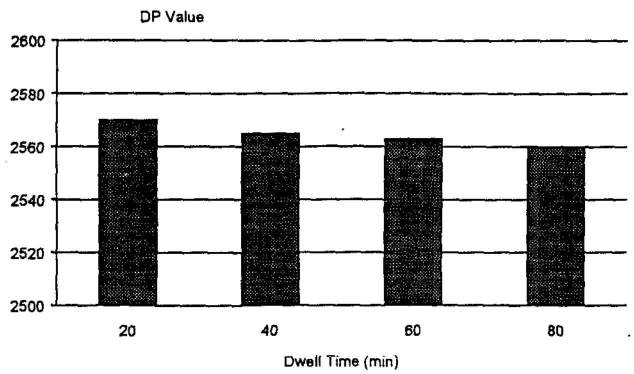

Fig. 6. Effect of bleaching on DP value.

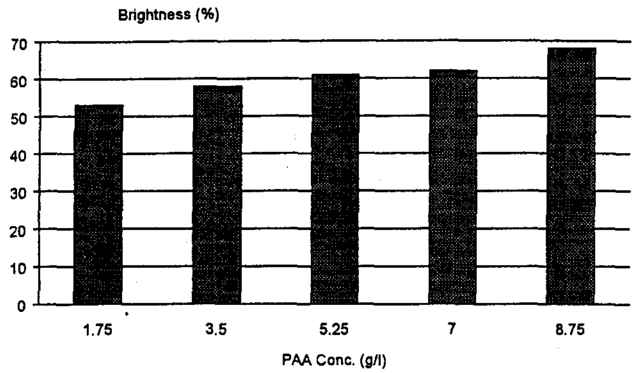

Fig. 7. Effect of PAA concentration on brightness.

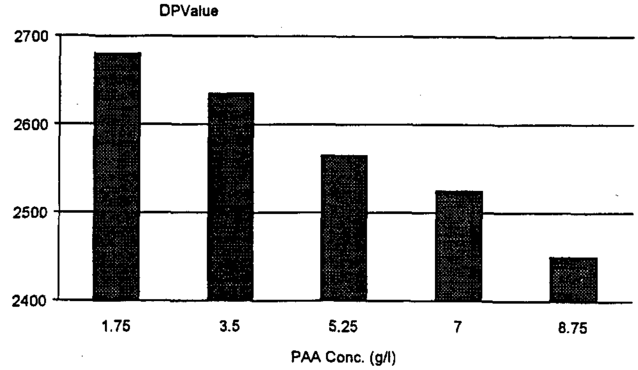

Fig. 8. Effect of PAA concentration on DP value.

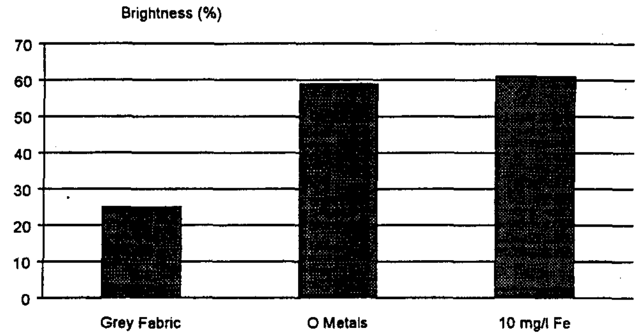

Fig. 9. Effect of iron on brightness.

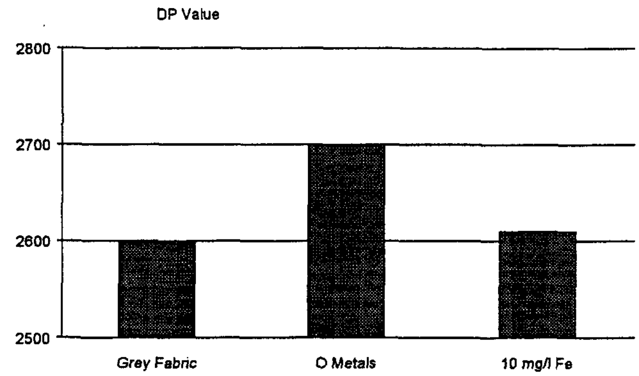

Fig. 10. Effect of iron on DP values.

tions only minor reductions in the DP values are obtained (Fig. 8). Overdosage of NaOCl always results in significant fiber damage and very often even lower brightness values are obtained.

Effect of Heavy Metals

Heavy metals are a common problem in the alkaline H_2O_2 bleach processes which often leads to catalytic damage of the fiber. To study the effect of iron ions, 10 ppm Fe (as ferric sulfate) were added to the bleaching liquor. The results of PAA bleaching tests with relatively high metal contamination indicated that the presence of Fe ions has no detrimental effect on the fibers due to the acidic bleaching conditions. Also, no loss in brightness was experienced in the presence of iron (Figs. 9 and 10). The slightly increased DP values can be attributed to the extraction of low molecular weight hemicelluloses.

Two-Stage Bleaching of Cotton

It is very difficult to replace hypochlorite when bleaching knitted goods using continuous bleaching ranges with relatively short dwell time (20-45 min). PAA is an excellent alternative to replace hypochlorite in the final bleaching stage without compromising brightness and process time. For example, knitted cotton goods can be bleached in a J-box by a process consisting of scouring, souring, PAA bleach and alkaline H_2O_2 bleach (Table III). As with the hypochlorite bleach, the PAA bleach can be conducted at room temperature. The final brightness values (90-92) obtained with PAA-H_2O_2 are at least equivalent to the NaOCl-H_2O_2 bleaching sequence (Fig. 11). The DP values clearly indicated that the PAA-H_2O_2 bleach combination results in significantly lower fiber damage (Fig. 12).

In Table IV the process conditions and bleaching results of another example are displayed where hypochlorite was substituted by PAA for bleaching knitted cotton goods. The subsequent H_2O_2 bleach was conducted in a continuous bleaching range (Galaxy, Brueckner). The results again confirm that PAA is a viable alternative for hypochlorite in the multistage bleaching of knitted goods and yields approximately the same brightness levels under similar process conditions.

Bleaching of Linen

Bast fibers are typically bleached either as roving or yarn in circulation apparatus with forced liquor circulation or as fabric in kiers, J-boxes or open-width bleaching ranges. For bleaching yarns,

Table III. Multi-Stage Impregnation Process

Process Stage	NaOCl-H_2O_2		PAA-H_2O_2	
A. Scouring				
B. Souring				
C. Bleaching Stage 1	NaOCl	20-35 mL/L	Buffer	0.4 g/L
	(3-5 g/L actual Cl)		Wetting Agent	1 mL/L
	NaOH	1-1.2 g/L	PAA (15%)	8 mL/L
	Temp.	18-20C	NaOH (50%)	1.7 mL/L
	Dwell Time	1 hour		
D. Bleaching Stage 2	Wetting Agent	1-2 g/L	Wetting Agent	1-2 g/L
	Stabilizer	2-4 mL/L	Stabilizer	2-4 mL/L
	Silicate	6-10 mL/L	Silicate	6-10 mL/L
	NaOH (50%)	2 mL/L	NaOH (50%)	2 mL/L
	H_2O_2 (35%)	20 mL/L	H_2O_2 (35%)	20 mL/L

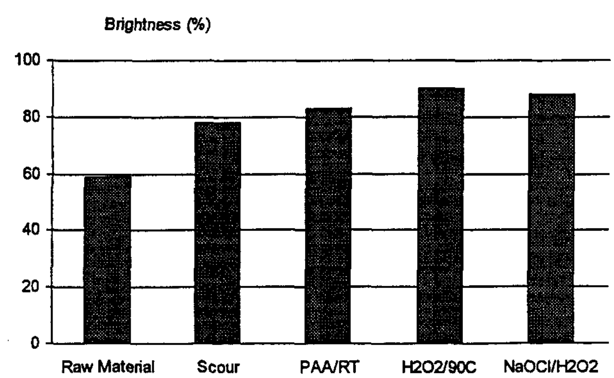

Fig. 11. Two-stage continuous bleaching of cotton in J-box.

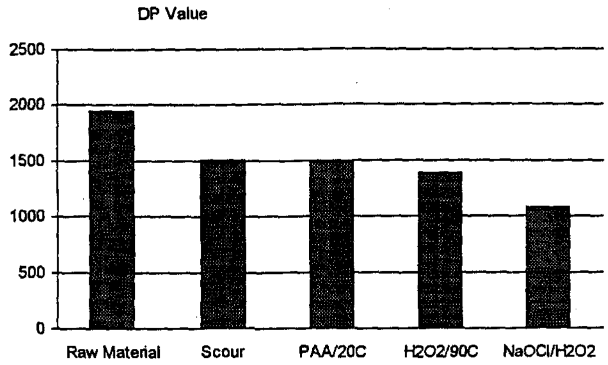

Fig. 12. Two-stage continuous bleaching of cotton in J-box.

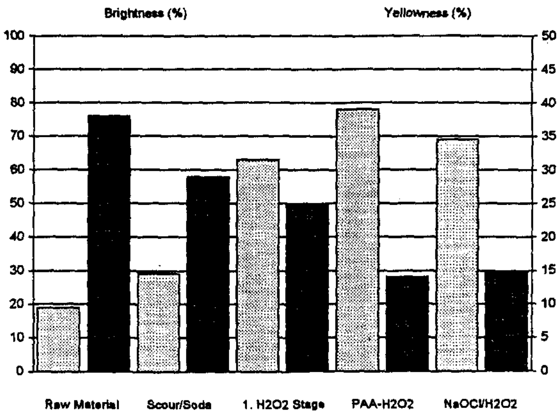

Fig. 13. Bleaching of linen on winchbeck.

a number of processes are available in which sodium hypochlorite or sodium chlorite are used in combination with H_2O_2. Linen yarns can be bleached without chlorine by the following process: scouring, alkaline H_2O_2, PAA, alkaline H_2O_2. After the first H_2O_2 stage, an acidic PAA bleach at a pH of 5-6 is applied at 80C. After complete consumption of the PAA, the pH of the spent bleaching solution is made alkaline with NaOH to utilize the residual H_2O_2 in a third bleach stage (Table V).

Starting with a raw material with a brightness value of 20, an increase in brightness to 65 was be obtained in the first H_2O_2 alkaline bleaching stage. A final brightness number of 78 was achieved after the PAA-H_2O_2 bleaching sequence compared to 68 obtained with a conventional NaOCl-H_2O_2 bleaching sequence. The combination of alkaline H_2O_2 and PAA is especially effective because natural pigments and woody matter (shives) in the bast fibers can best be removed by alternating the pH conditions from alkaline to acidic. A significant decrease of the yellowness from 38 to 12 was also achieved (Fig. 13).

Environmental Relevance of Peracetic Acid

PAA is environmentally safe since it decomposes to acetic acid and oxygen. Acetic acid is completely biodegradable. However, the acetic acid contributes slightly to higher BOD levels of the wastewater in the order of magnitude of 20-40 mg BOD/L. Comparing this number to the base load of COD/BOD typically present in a textile plant discharge (several hundreds of ppm), shows that this is not a major issue.

Conclusion

PAA has proven to be a viable and environmentally safe alternative to sodium hypochlorite. Advantages of the PAA process include comparable or higher brightness values with less fiber damage. Peracetic acid as an industrial chemical is easily available and can be safely introduced to an existing process design. PAA and its decomposition products are biodegradable and do not form any toxic by-products.

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Table IV. Bleaching of 100% Cotton Knitted Goods with PAA

Process Stage	NaOCl-H_2O_2		PAA	
Bleaching Stage 1	Impregnation Liquor Composition			
	NaOCl	20-35 mL/L	PAA (15%)	
	NaOH	1-1.2 g/L	$Na_4P_2O_7$	
	Wetting Agent	2 mL/L	NaOH	
	Liquor Pickup	100%	Wetting Agent	
	Dwell Time	30 min	Dwell Time	
	Temp.	20C	Temp.	
Bleaching Stage 2	Liquor Ratio 1:10		Liquor Ratio 1:10	
	Stabilizer	6 mL/L	Stabilizer	6 mL/L
	Silicate (38 Bè)	6 mL/L	Silicate (38 Bè)	6 mL/L
	NaOH	5 g/L	NaOH	5 g/L
	H_2O_2 (50%)	15 mL/L	H_2O_2 (50%)	15 mL/L
	Surfactant	2 mL/L	Surfactant	2 mL/L
	Brightener	optional	Brightener	optional
	Dwell Time	35 min	Dwell Time	35 min
	Temp.	20C	Temp.	20C
Brightness	88.6%	87.9%		
DP value (after bleaching)	1860	2155		
DP value (raw material)	2470	2470		

Table V. Linen Bleaching on Winchbeck

Scouring		H_2O_2 Bleach		PAA Bleach		Subsequent Charge	
Soda ash	5 g/L	H_2O_2 (35%)	5 mL/L	PAA (5%)	2.5 mL/L	NaOH (50%)	1.0 mL/L
NaOH (50%)	1 g/L	Wetting Agent	0.5 g/L	Wetting Agent	0.5 g/L	Stabilizer	0.3 mL/L
Wetting Agent	2 g/L	Stabilizer	0.5 g/L	Stabilizer	0.25 g/L	pH	11.6-11.2
Temp.	90C	NaOH (50%)	1.5 g/L	Temp.	80C	Temp.	80C
pH	11.8-10.5	pH	11.3-10.7	Dwell Time	50 min	Dwell Time	90 min
Dwell Time	90 min	Temp.	80C	pH	6.5		
	Dwell Time	2 hours					