Investigation of Bleach Active Compounds in Washing Bath

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*The washing effects of standard EMPA fabric with special soilings, laboratory soiled percale fabric and control RAL fabric have been investigated. Washing with addition of hydrogene peroxide or peracetic acid was performed in the laboratory machine, Lavamac, at 60 and 80°C. The washing performance of these bleach active compounds was evaluated in the bath composition with nonionic surfactants and sodium hydroxide for regulation of pH. Builders were not added in the laundry bath. Pre-washing was performed in the alkaline bath, pH 9-10 with different additions of enzymes and sodium hypochlorite. It was found that colored soiling such as red pepper chutney, red wine and fruit juices were removed at both temperatures, but more efficiently at the higher temperature. The washing effects with hydrogen peroxide were better than with peractic acid. The protein soiling as cocoa, milk/blood/ink and yolk were efficiently removed at lower washing temperature with enzymes in pre-wash. The effect of non-ionic surfactants was improved with enzymes. Pre-washing with sodium hypochlorite, followed by washing at 80 °C after 25 cycles, caused damage to textiles. The chemical wear **s** and the decrease of tensile strength and depolymerization were higher than the limited values according RAL. The damage of textiles washed at 60 °C was not evident. The whiteness degree of textiles after 25 cycles was below the limited value. The whiteness of the brightened fabric was not improved during 3 cycles indicating that the concentration of FBA should be increased or a different type of FBA should be applied.*

Key words: *bleach active compounds, washing with hidrogene peroxide, washing with peracetic acid, washing effects*

1. Introduction

Bleaching agents are important ingredients of a detergent composition. The main purpose is to remove bleachable stains because the surfactants and builders are not enough efficient to remove these stains during washing. The oxidative agents destroy chromophores of colored stains. The most dominant bleaches are sodium hypochlorite, able to bleach in the cold bath, and sodium perborate as the most frequently encountered source of hydrogen peroxide. Its oxidation is evident at a higher temperature, starting at 60 °C, and the optimum is reached at 90 °C. The use of sodium percarbonate has gained the importance in those countries where the boron compounds are restricted or banned from environmental reasons or regulations [1].

The washing habits in USA are specified by low temperature baths in the presence of sodium hypochlorite as the bleach active compound. The usage of hypochlorite in the finishing of textiles in the Europe is banned from environmental reasons due to reaction of active chlorine with amino acids producing toxic compounds in the wastewaters [2]. Sodium hypochlorite is still applied in the industrial laundries due to disinfection feature. During the last decade the satisfactory bleaching potential of hydrogen peroxide in the household and commercial laundries has been achieved by incorporation of bleach activators. The result is a peracid able to bleach and wash at lower temperature than convenient. These acylating agents, TAED (tetraacetylethylenediamine) and NOBS (sodium nonanoyl-oxybenzenesulfonate) react with hydrogen peroxide producing peracids; peracetic in the case of TAED and peroxynonanoic in the case of NOBS. The low temperature bleaching effectiveness is evident even at 40 °C. The antimicrobial, antivirus and antifungal performance of bleach activators is known from literature data. The effectiveness is lower than in the case of sodium hypochlorite [3, 4].

It was attempted to apply the original peracetic acid in the household washing machine, but it was very difficult due to its crumble during storage and trouble of incorporation in the powder detergent formulations. In spite of this, the application of peracetic acid in the textile industry and industrial laundry sector is still actual [5, 6]. The main advantage of peracetic acid as bleaching agent is no sense on the traces of heavy metals in the bleaching bath that are able to cause the damage of textiles in the case of bleaching with hydrogen peroxide. The environmental reference of peracetic acid when compared with perborate is safety. The effectiveness of peracetic acid is very similar to hydrogen peroxide utilized with bleach activators. This is the benefit due to minimization of energy as well as decreased amount of textiles washable at high temperatures [3]. The tendency to low temperature washing procedures has been actualized by increasing the portion of synthetic and regenerated fibres in textiles.

The most frequently used programme in the laundries includes the combination of two bleaching agents, sodium hypochlorite and hydrogen peroxide.

Peroxide is added into the washing bath, while hypochlorite, as disinfection agent, is added into the rinsing bath. It was proved that disinfection feature of hypochlorite can be deactivated by residual active oxygen from perborate bleaching when added in the start rinsing bath. It is recommended to add the hypochlorite at least 6 batches behind the washing unit [7]. It is impossible to follow in the laundries supplied with low capacity equipment. The most frequent recommendation is addition of hypochlorite in the prewashing bath to avoid its crumble caused by active oxygen. Hydrogen peroxide is dosed with other components in the washing bath. It is applicable for the component washing, where amounts of particular liquid component are dosed automatically in the machine.

It was interesting to investigate the influence of these components on the effectiveness of stain removal. For this purpose only a nonionic surfactant was used. Sodium hydroxide was added for pH regulation and no other builders due to exact evaluation of the bleaching agents. The primary and secondary effects were compared as a result of different combinations of bleaching agents with or without enzymes in the pre-washing bath.

2. Material, treatment and testing methods

The investigation of different bleach active compounds in the washing bath was performed on the EMPA test fabric No. 103 (EMPA-Eidgenössische Materialprüfungs und Forschungsanstalt). Combined EMPA washing test strips for Stain Monitor IEC, EN 60456 strips (art. 103) consists of 8 different standard stains (Tab.1).

Tab.1 EMPA test fabric

Label	Cotton
221	Bleached
101	Soiled with carbon black/olive oil
111	Soiled with blood
112	Soiled with cocoa
116	Soiled with milk/blood/ink
115	Soiled with immedial black
222	Raw
114	Soiled with red wine

Additional testing was performed on a laboratory soiled cotton percale fabric. Different soils were applied: yolk, cocoa, juice (peach/apple), factory and domestic red pepper chutney, coffee, lipstick Rose Crystal No. 200 (Loreal), pumpkin oil and grass were applied for the percale fabric.

The characteristics of the percale fabric were: 100% cotton; weight per m^2 190 g/m^2; warp thread density: 36 threads/cm and weft thread density: 27 threads/cm; warp yarn count: 16.6 tex and weft yarn count: 29.4 tex; sateen weave: 5/1.

Secondary effects were controlled after frequent washing of standard control cotton fabric, with no fluorescent whitening agents or additives according to DIN 53 919-1.

Washing was performed in the Lavamac 7 laboratory machine. The

Tab.2 Washing with addition of hydrogen peroxide

Component	1.1.	1.2.	1.3.	Component	1.4.	1.5.	1.6.
Pre-washing 40 °C				**Pre-washing 40 °C**			
Surfactants without enzyme	+	+	-	Surfactants without enzyme	+	+	-
Surfactants with enzyme	-	-	+	Surfactants with enzyme	-	-	+
Alkali	+	+	+	Alkali	+	+	+
NaOCl	+	-	-	NaOCl	+	-	-
Washing 60 °C				**Washing 80 °C**			
Surfactant	+	+	+	Surfactant	+	+	+
Alkali	+	+	+	Alkali	+	+	+
Hydrogen peroxide	+	+	+	Hydrogen peroxide	+	+	+
Rinsing				**Rinsing**			
Acetic acid	+	+	+	Acetic acid	+	+	+

Tab.3 Washing with addition of peracetic acid

Component	2.1.	2.2.	2.3.	Component	2.4.	2.5.	2.6.
Pre-washing 40 ºC				**Pre-washing 40 ºC**			
Surfactants without enzyme	+	+	-	Surfactants without enzyme	+	+	-
Surfactants with enzyme	-	-	+	Surfactants with enzyme	-	-	+
Alkali	+	+	+	Alkali	+	+	+
NaOCl	+	-	-	NaOCl	+	-	-
Washing 60 ºC				**Washing 80 ºC**			
Surfactant	+	+	+	Surfactant	+	+	+
Alkali	+	+	+	Alkali	+	+	+
Peracetic acid	+	+	+	Peracetic acid	+	+	+
Rinsing				**Rinsing**			
Acetic acid	+	+	+	Acetic acid	+	+	+

Tab.4 The composition of dosing components in the pre-washing and washing process

Component	Composition
Surfactant without enzyme	Nonionic surfactants with addition of FWA (stylbene product)
Surfactant with enzyme	Nonionic surfactants with addition of FWA (stylbene product) and enzyme (protease)
Alkali	Sodium hydroxide and polycarboxylate
Bleach active agents	NaCLO (120-150 g/l)
	H_2O_2 (35%)
	CH_3COOOH, (15%)
Neutralization	Acetic acid (80%)

tested fabrics were agitated with a cotton ballast fabric (5 kg) at 40 °C in the pre-washing and washing bath following the standard procedure during 25 minutes at 60 and 80 °C (Tab.2 and 3). After washing the fabrics were rinsed three times and neutralized with acetic acid. Centrifugal agitation followed pre-washing and rinsing procedures.

Dosing particular components from the tank devices was done automatically according to the following programmes (Tab.4).

Pre-washing bath was alkaline, from pH 9 to pH 10, while the pH of washing baths was approx. 10 with peroxide and between pH 7 and 8 with peracetic acid as bleach active compounds.

Standard control RAL and percale cotton fabrics were washed according to the following programmes (Tab.2 and 3) through 25 cycles. Secondary effects were tested after 25 cycles according to ISO 4312 [8].

3. Results and discussion

Primary and secondary washing effects were evaluated. The results obtained on the EMPA test strip fabric (EMPA) are presented in Tab.5 and 6. The washing performance of different bleach compounds in order to remove standard stain varied significantly.

The red wine and blood stains on the cotton fabrics were almost completely removed achieving a remission value similar to bleached cotton. A higher washing temperature (80 °C) is more favorable for the removal of red wine stains. A lower washing temperature (60 °C) is optimal only in pre-washing with sodium hypochlorite and washing with a peracetic acid component. This result was expected because it is possible to remove a colored stain with bleaching agents. The same effectiveness of both washing temperatures is evident in the case of blood where the main part of the

Tab.5 Remission values (R_{460}) of EMPA test fabric before and after washing with hydrogen peroxide

		R_{460} (%)						
Label	Cotton	0	1.1.	1.2.	1.3.	1.4.	1.5.	1.6.
221	Bleached	77.91	82.25	81.32	83.43	82.49	85.53	84.16
101	Soiled with carbon black/olive oil	15.00	33.35	27.75	29.18	31.68	34.7	35.66
111	Soiled with blood	16.59	73.29	72.54	77.68	73.84	78.02	72.69
112	Soiled with cocoa	15.97	34.05	36.80	49.38	38.48	37.86	46.49
116	Soiled with milk/blood/ink	13.37	25.12	23.04	44.04	30.36	28.91	42.37
115	Soiled with immedial black	29.51	34.51	32.17	32.14	56.28	35.13	35.32
222	Raw	56.86	65.93	65.61	65.71	69.40	69.00	69.98
114	Soiled with red wine	44.80	63.51	62.37	64.58	77.14	71.28	72.42

Tab.6 Remission values (R_{460}) of EMPA standard fabric before and after washing with peracetic acid

		R_{460} (%)						
Label	Cotton	0	2.1.	2.2.	2.3.	2.4.	2.5.	2.6.
221	Bleached	77.91	84.67	82.60	83.75	84.53	85.18	85.22
101	Soiled with carbon black/olive oil	15.00	26.85	25.65	27.00	33.3	24.85	29.01
111	Soiled with blood	16.59	74.57	69.70	74.87	74.45	60.86	73.4
112	Soiled with cocoa	15.97	38.18	37.61	49.54	34.00	35.18	42.43
116	Soiled with milk/blood/ink	13.37	27.77	22.57	37.58	23.25	19.15	34.30
115	Soiled with soot	29.51	49.22	32.52	33.73	46.81	33.79	35.97
222	Raw	56.86	68.38	64.11	63.75	67.54	68.01	67.42
114	Soiled with red wine	44.80	73.80	58.52	60.31	77.72	72.31	67.49

stain is removed during pre-washing. Enzyme presence is important for the removal of this stain.

The addition of enzyme in the peroxide and peracetic washing bath is positive due to a prominent protein nature of cocoa with milk stain. The removal of a mixed milk/blood/ink stain consisting of two protein based components is similar. The washing performance of the detergent with an enzyme component is prominent. The positive influence of a low washing temperature on the removal of this stain is evident. The washing performance of peroxide is more favorable than peracetic acid in this case, too.

Carbon black in olive oil is a very obstinate stain. High-temperature washing is more applicable when pre-washing was performed in a hypochlorite bath.

Similar results were obtained after washing of the soiled percale fabric. The washing effectiveness of all washing baths was the same in the removal of red wine and fruit juice stains. Bleach active compounds are key ingredients for these stains. The washing results with peroxide were slightly better than with peracetic acid. Pre-washing with hypochlorite is preferred to peroxide for the removal of lipstick stains in all wash baths.

Protein stains such are yolk and cocoa are better removed at 60 °C than at 80 °C in the peroxide bath. Peracetic acid as a bleach active compound was less effective than peroxide, but washing performance was satisfactory. These stains were removed almost completely in the peroxide bath at 60 °C. In most cases a red pepper chutney stain was also removed. Low-temperature washing is more efficient.

Pumpkin oil is removed in washing both at 60 and 80 °C, but peracetic acid was more efficient than peroxide.

The testing of EMPA standard stains, where intensity and density of soil are equal, is more convenient in order to asses the washing performance.

Tab.7 Secondary effects of standard control RAL fabric after 25 cycles in the washing bath with hydrogen peroxide and peracetic acid

	H_2O_2				CH_3COOOH		
Programme	ΔF (%)	s	P (%)	Programme	ΔF (%)	s	P (%)
1.1.	10.1	0.31	0.09	2.1.	12.0	0.31	0.16
1.2.	6.3	0.13	0.09	2.2.	7.9	0.10	0.14
1.3.	5.6	0.06	0.82	2.3.	7.3	0.28	0.13
1.4.	10.5	0.89	0.9	2.4.	16.6	0.83	0.21
1.5.	5.7	0.31	0.53	2.5.	11.6	0.43	0.13
1.6.	7.9	0.29	0.44	2.6.	10.8	0.31	1.53

The intensity, depth and density of laboratory deposited soils on the percale fabric are different and the washing results were expressed descriptively. In general, the tested stains were removed in low-temperature washing baths and a temperature rise in the case of protein stains produce a negative result due to the destabilization and destruction of enzymes. The second reason was the use of only one type of surfactant in the washing bath. The effectiveness of nonionic surfactants in high-temperature washing was weaker due to the cloud point. Literature data showed that the best washing performance of nonionic surfactants is around the cloud point [1]. A higher washing temperature combined with hypochlorite pre-washing was favorable only for the removal of obstinate oil stains (carbon black/olive oil). The testing results obtained are in good correlation with theoretical knowledge.

Secondary effects are also important for the washing performance, and they were evaluated after multiple cycles. The evaluation criteria after 3 and 25 wash cycles include testing breaking strength, polyme-

Tab.8 Whiteness degree with (W) and without UV (W*) stimulation of percale and standard control RAL fabrics before and after 1, 3 and 25 washing cycles

		PERCALE fabric			RAL fabric		
Before	W	138.1			77.2		
	W*	86.6			77.2		
Programme		1.	3.	25.	1.	3.	25.
1.1.	W	131.8	132.8	124.7	98.0	104.4	108.8
	W*	88.7	91.1	90.0	79.3	80.9	85.6
1.2.	W	127.9	125.9	115.5	93.8	92.9	95.4
	W*	88.0	89.3	89.1	79.1	79.9	82.7
1.3.	W	134.8	134.0	144.2	77.0	106.8	127.0
	W*	89.8	90.5	93.8	80.4	82.4	87.1
1.4.	W	124.7	126.8	124.7	78.1	104.9	113.5
	W*	88.7	90.4	91.3	79.5	82.3	86.8
1.5.	W	126.4	125.2	124.0	98.8	102.8	111.0
	W*	89.0	90.2	91.6	80.5	82.0	87.1
1.6	W	126.6	123.7	126.5	99.2	102.7	111.5
	W*	89.5	89.2	91.8	81.3	82.9	86.8
2.1.	W	136.0	135.5	132.1	101.3	102.0	117.8
	W*	90.4	91.3	92.6	77.6	80.2	87.2
2.2.	W	133.1	136.2	133.6	101.4	105.6	116.0
	W*	90.4	90.7	92.5	80.9	82.6	86.6
2.3.	W	137.4	135.8	134.4	98.8	105.2	119.9
	W*	90.3	92.0	94.0	80.0	83.1	87.4
2.4.	W	135.2	133.8	127.5	107.1	111.7	117.1
	W*	89.8	91.3	92.6	82.6	83.7	88.1
2.5.	W	139.6	138.6	129.7	116.3	122.2	120.8
	W*	90.4	92.3	92.6	83.1	85.4	88.6
2.6.	W	131.5	130.6	127.2	102.1	107.4	115.4
	W*	89.2	90.3	91.3	82.1	83.6	88.0

rization degree, *Eisenhut* chemical wear, whiteness degree with and without UV stimulation, ash content of standard control (RAL) fabric and whiteness degree of the percale fabric (Tab.7).

The limit value of breaking strength decrease (ΔF) after 25 cycles must not exceed 15% according the German regulations prescribed by RAL GZ-992/1 [9, 10]. The tested prewash and wash programmes fulfilled the RAL requirement, but the exception is only the sample washed with peracetic acid at 80 °C prewashed with sodium hypochlorite (2.4). In general, better effects were obtained in peroxide than in peracetic wash bath. A high washing temperature caused a higher damage of textiles than a low temperature. The decrease of the breaking strength is below 10% when the washing bath contains peroxide without hypochlorite in the pre-wash bath.

Eisenhut chemical wear, ***s,*** of standard RAL fabric pre-washed with hypochlorite, washed at 80 °C with peroxide and peracetic acid, exceed the limit value of 0.5 according RAL. The sodium hypochlorite, added in a small amount, damages textiles. A similar effect is the result of elevated temperature. The washing performance at 60 °C is very good in each case. The damage of textiles is below 0.3 indicating good washing performance according RAL.

The ash content of RAL fabric after 25 washing cycles exceeded the limit value of 0.7% only in one case. Meanwhile, these results are good due to washing conditions in hard water without addition of builders.

The required whiteness degree was not achieved in the tested wash programmes which can be explained by the fact that the standard control fabric was only pre-bleached (Tab.8), and the basic whiteness is only 77.2. The whiteness degree of the percale fabric, previously bleached with FWA, ranges from 10 to 15 units higher than in the case of RAL fabric. The RAL requirements are not fulfilled and a possible correction is the increased amount of FWA or application of another FWA type. Remission curves (Fig.1a) show that the removed amount of FWA during washing was compensated from the new bath. The cumulative effect of FWA is more pronounced on the RAL fabric because it was not previously saturated with FWA (Fig.1b).

4. Conclusion

The effectiveness of the tested wash programmes is confirmed only in the case of colored stains such as red wine, red pepper chutney and fruit juices. The performance of bleach active compounds able to destroy colored pigments is evident. Better results were obtained with peroxide in comparison with peracetic acid.

Removing protein stains such as coffee, yolk, milk and cocoa is more efficient at 60 °C than at 80 °C, where features of enzymes and nonionic surfactants are complete.

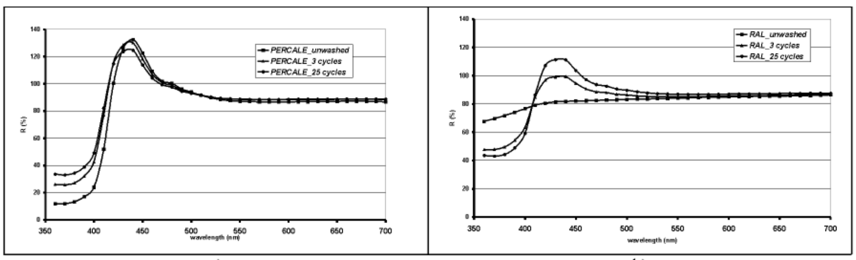
Removal of carbon black was efficient at higher wash temperatures when hypochlorite was a component of the pre-wash bath.

The choice of washing procedure would be based on the soil type to be removed.

Secondary washing effects tested by standard fabric according RAL are under tolerances.

Chemical wear of RAL fabric exceeded the limit value only after frequent pre-washing with hypochlorite, followed by washing at 80 °C, which should be taken in consideration.

It is possible to achieve the optimal whiteness through the additional testing of concentration range as well as different type of FWA.



a) b)

Fig.1 Remission curves of unwashed and washed a) PERCALE and b) standard control (RAL) fabrics

References:

[1] Smulders E.: Laundry Detergents, Wiley-VCH Verlag GmbH, Weinheim, 2002

[2] Katović D., K. Moskaliuk: Utjecaj upotrebe natrijevog hipoklorita za bijeljenje tekstilnog materijala na zagađivanje otpadnih voda, Tekstil **46** (1997.) 3, 139-144

[3] Soljačić I., T. Pušić: Njega tekstila, knjiga 1, Sveučilište u Zagrebu, Zagreb, 2005., 23-139

[4] Cai J.Y. et al: Bleaching of cotton and cotton/wool blends with TAED and NOBS activated peroxide systems, AATCC Book of Papers, N. C. USA 2000, 569-574

[5] Forte Tavčer P., P. Preša: Obrada pamuka pektinazama i peroctenom kiselinom, Tekstil **53** (2004.) 3, 110-118

[6] Hickman W.S.: Peracetic acid and its use in fibre bleaching, Rev. Progres Color **32** (2002) 13-27

[7] Gottlicher R.: Dezinfekcija u kupelji za ispiranje natrijevim hipokloritom u linijama za pranje, Tekstil **51** (2002.) 11, 537

[8] ISO 4312: Surface active agents - Evaluation of certain effects of laundering-Methods of analysis and test for unsoiled cotton control cloth

[9] Fijan S., S. Šostar-Turk: Quality parameters for washing in laundries in Slovenia, Book of Proceedings ITC&DC-Magic World of Textiles, 250-255, Dubrovnik 6-9 October 2002.

[10] Fijan S. et al: Primerjava primarnih učinkov pranja pri uporabi različnih postopkov pranja bolnišničnih tekstilij, Tekstilec **49** (2006) 4-6, 72-80