The primary effect of boosters in the washing process of cotton textiles stained with sunscreens

Vanja Šantak[1,2]*, Tanja Pušić[1], Ivona Vidić Štrac[3]
[1] University of Zagreb Faculty of Textile Technology, Zagreb, Croatia
[2] Ammonia d.o.o, Zaprešić, Croatia
[3] Croatian Institute of Public Health, Zagreb, Croatia
*Corresponding author: vanja.santak@gmail.com
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The complexity of stains from cosmetic products on textiles poses a challenge in washing processes. In this study, the primary effect of the washing process on cotton fabrics and cotton knitwear stained with two sun protection products (moisturising emulsion and balm) was analysed. The chemical activity in the process is driven by the booster Mulan Solar (agent- MS) and agent- MS supported by ozone at temperatures of 20 °C, 30 °C, 40 °C, 60 °C, 75 °C and 90 °C. The interaction between sunscreens and cotton materials was analysed using Fourier transform infrared spectroscopy (FTIR). The stain removal performance under the mentioned washing process conditions was analysed using remission spectrophotometry. The results showed that ozone enhanced the primary effect of agent-MS in removing sunscreen balm stains on cotton knitted fabric. It was confirmed that the primary effect in this complex system depends on the type of cotton substrate and the type of cosmetic agent.

Keywords: *cotton; woven fabric; knitwear; stains from sunscreen; washing process; booster MS; ozone.*

Izvorni znanstveni rad

Složenost mrlja od kozmetičkih proizvoda na tekstilijama predstavlja izazov u procesima pranja. U radu je analiziran primarni učinak procesa pranja pamučne tkanine i pamučnog pletiva s mrljama dva kozmetička proizvoda za sunčanje (hidratantna emulzija i balzam). Nosilac kemijske aktivnosti u procesu je pojačivač Mulan Solar (sredstvo-MS) i sredstvo-MS potpomognuto ozonom pri 20 °C, 30 °C, 40 °C, 60 °C, 75 °C i 90 °C. Analiza interakcije kozmetičkih proizvoda za sunčanje i pamučnih materijala provedena je metodom Fourierove transformacije infracrvenog spektra (FTIR). Metodom remisijske spektrofotometrije analizirana je moć uklanjanja mrlja u navedenim uvjetima procesa pranja. Rezultati istraživanja pokazali su da ozon pojačava primarni učinak sredstva-MS u uklanjanju balzama kozmetičkog proizvoda za sunčanje na pamučnom pletivu. Potvrđeno je da primarni učinak u ovom složenom sustavu ovisi o vrsti pamučnog supstrata i tipu kozmetičkog sredstva.

Ključne riječi: pamuk; tkanina; pletivo; mrlje od kozmetičkih proizvoda za sunčanje; proces pranja; pojačivač-MS; ozon

1. Introduction

When textiles are washed, dirt is removed, whereby four factors play a decisive role according to the theory put forward by Dr Herbert Sinner: temperature, time, mechanics and chemistry [1]. Theoretically, the proportions of all four process factors in Sinner's circle, which are linked by water, are approximately equal [2]. In the actual process, however, reducing the proportion of one factor proportionally increases the proportion of one or more factors.

The central part of the Sinner's circle belongs to water, which emphasises its importance in the washing process, especially for the transfer of thermal energy, which facilitates the removal of substances such as waxes and fats that turn into a liquid phase at 40 °C [3]. Water-soluble soil and most detergent ingredients dissolve in water, while insoluble detergent ingredients and insoluble soil are finely dispersed. Coloured pigments decompose by oxidation and become soluble or colourless compounds.

The primary effects of the washing process is judged by the strength of soil removal, which is achieved by the synergy of surfactants, chemical bleaching agents and their activators, enzymes and other detergent ingredients [4, 5].

The carriers of chemistry are detergents, which play a crucial role in maintaining the cleanliness and hygiene of textiles. Surfactants are important components of detergents that reduce the surface tension of water, enable better wetting of textiles and facilitate soil removal. Their tendency to self-associate leads to micelles that enclose and isolate dirt particles so that they can be removed during the washing process. Bleaching agents and their activators promote chemical reactions that break down coloured stains and preserve the whiteness of textiles [6]. Enzymes break down complex organic molecules such as proteins and fats, while polymers help to prevent the re-deposition of dirt on textiles [7].

Environmental guidelines, which stipulate lower water consumption, have prescribed an increase in the proportion of chemicals and a reduction in temperature and time. The chemical part of the washing process is increased by highly effective surfactants, enzymes and bleach activators.

In line with the principles of the circular economy, which focuses on sustainability and ecological awareness, the washing process technology aims to find efficient, economical and environmentally friendly methods. Ozone-assisted washing is one of the Key Enabling Technologies (KET). Ozone, a strong oxidising agent, has the potential to destroy and remove organic compounds and microorganisms at low temperatures [8-11]. This technology not only offers excellent cleaning and disinfection results, but also makes a significant contribution to maintaining the quality of textiles, extending their shelf life and preserving the freshness of colour tones [12, 13]. Given these benefits, ozone-assisted washing represents a step towards a more environmentally responsible and sustainable approach to the washing process.

Oxygen molecules absorb the radiation and decompose into two free oxygen atoms, which quickly react with another oxygen molecule to form ozone. Under the influence of UVB radiation, ozone rapidly decomposes into an oxygen molecule and a free oxygen atom [14]. Ozone molecules are unstable and tend to decompose into the usual diatomic form of oxygen and an oxygen atom or a hydroxyl radical, which quickly combines with substances in the environment. Dissolved in water (pH 7) at a temperature of 20 °C, ozone decomposes in 12 minutes, and when the temperature rises to 35 °C, the decomposition time is reduced to 8 minutes [11].

The synergistic effect of the individual washing factors contributes to the achievement of the primary effect, which is assessed on the basis of the degree of soil removal (S) after one to three washing cycles.

Soil is defined as particles or substances on surfaces that need to be removed, regardless of their useful composition or purpose [5]. The mechanisms of removal of natural stains from textiles during the washing process occur in three phases: (i) wetting and swelling of the textile and the stain, (ii) removal of the surface layer of the stain, and (iii) gradual removal of the remaining stain [15, 16].

Sunscreens protect the skin from harmful solar radiation and help to prevent premature skin ageing and other changes that can lead to serious diseases. According to Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products, UV filters are substances intended exclusively or mainly to protect the skin from certain UV rays by absorbing, reflecting or scattering UV radiation. UVB filters (octocrylene, homosalate, ethylhexyl methoxycinnamate, ethylhexyl salicylate), which absorb radiation in the wavelength range of 290-320 nm, and UVA filter (butyl methoxydibenzoylmethane), which absorb UV rays in the range of 320-400 nm, are predominantly used in these products. In addition, UVA/UVB filtres with a broader spectrum such as bis-ethylhexyloxyphenol methoxyphenyl triazine and titanium dioxide are used. According to the International Cooperation on Cosmetic Regulations (ICCR) [17], TiO_2 and ZnO nanoparticles are used as inorganic UV filters in numerous skin care products [18].

In this study, the efficacy of stain removal from sunscreens on cotton fabrics and knitted cotton fabrics was analysed by varying chemical action, booster (agent-MS) and agent-MS with the support of ozone in washing processes at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C and 90 °C.

2. Experimental Part

The experimental part describes the fabric and the knitted fabric, the sources of the stains - sunscreen, the composition of the booster agent MS and the washing procedure including the ozone-assisted washing process.

2.1. Materials

Sources of soiling - Sunscreens were applied to cotton fabric (PT) with a surface mass of 172.0 g/m^2 and knitted cotton fabric (PP) with a mass per unit area of 156.0 g/m^2.

Two types of sunscreens on the Croatian market were selected for the study:

- A moisturising emulsion (KP-M) for sun protection and skin care with a sun protection factor (SPF) of 20, containing UVA and UVB filters.
- An anhydrous product, a sun protection balm (KP-B) with SPF 30, also with UVA and UVB filters and a small amount of carrot root extract.

Table 1 lists the compositions of both products in descending concentration, focussing on the UV ingredients listed in the mandatory International Nomenclature of Cosmetic Ingredients (INCI) and underlined for clarity.

Tab.1 Ingredients of sunscreen cosmetic products

Sunscreen Cosmetic Product	
KP-M	Water, octocrylene, homosalate, stearic acid, ethylhexyl methoxycinnamate, ethylhexyl salicylate, C12-15 alkyl benzoate, butyl methoxydibenzoylmethane, denatured alcohol, titanium dioxide, potassium cetyl phosphate, glycerin, tocopheryl acetate, potassium hydroxide, phenoxyethanol, ethylhexylglycerin, shea butter, tetrasodium EDTA, carbomer (high molecular weight crosslinked polyacrylate polymers, hydrogenated dimer dilinoleyl / dimethylcarbonate copolymer), silica, fragrance, benzyl salicylate, citronellol, geraniol, hexyl cinnamal, butylphenyl methylpropional, limonene, BHT.
KP-B	Sunflower oil, white (beeswax), ethylhexyl-methoxycinnamate, bis-ethylhexyloxyphenol methoxyphenyl triazine, carrot root extract, vitamin E acetate.

The booster used was Mulan Solar, a liquid stain remover for textile sunscreens from Christeyns (agent-MS) [19]. This agent contains nonionic surfactants, ethoxylated fatty alcohols in a mass fraction of more than 60%. Despite the recommended dosage of booster agent-MS at a concentration of 80 ml/kg of laundry with a suitable detergent, agent-MS was used in this study at a concentration of 20 ml/kg due to the low mass of soiled cotton fabrics and knitted fabrics compared to the mass of clean cotton ballast (6 kg) without detergent. Clean white cotton fabric (PT) was used to analyse the whiteness under the conditions of the washing process.

2.2. Stain Application Method

Circular sunscreen patches with a diameter of 2 cm were applied with a spatula to 10 x 10 cm samples of cotton fabric and cotton knitwear, using a dimensioned graphite foil template for each patch to avoid contamination of the samples. The fabric and knit samples were dried at room temperature for 24 hours after staining.

2.3. Washing Process

The washing process at temperatures of 20 °C, 30 °C, 40 °C, 60 °C, 75 °C and 90 °C was carried out in a professional LG Giant-C MAX washing machine with a load capacity of 10 kg and a drum volume of 102.7 L, equipped with a BWO3 ozone generator, for the periods listed in Table 2.

Tab.2 Washing Process Times

T (°C)	20	30	40	60	75	90
t (h)	0:35	0:51	1:01	1:09	1:24	1:39

Table 3 contains the names and descriptions of the agents, materials and procedures used.

Tab.3 Designation of sampless and procedures

Label	**Description**
KP-M	Sunscreen product - hydrating emulsion
KP-B	Sunscreen product - balm
PT	Cotton fabric
PP	Cotton knitwear
PT-P	Cotton fabric - control
BO	Washing process without ozone
O	Washing process assisted with ozone

2.4. Methods

Sunscreen and cotton fabric and knit samples were analysed before and after being stained with sunscreen using ATR-FTIR spectroscopy on a

Spectrum 100S FT-IR UATR + TG/IR Interface TL8000 (RedShift) instrument from Perkin Elmer, USA, with Spectrum 100 software. The spectral analysis covered a range from 4000 cm^{-1} to 450 cm^{-1} with a resolution of 4 cm^{-1}.

A remission spectrophotometer, Spectraflash SF300 from DataColor, Rotkreutz, Switzerland, was used to evaluate the primary effect of washing process of stained cotton fabrics and knitwear with a standard D65 light source at d/8° geometry.

The remission value at a wavelength of 460 nm (R_{460}) was chosen to determine the differences (ΔR_{460}) between washed and unwashed samples, according to Eq.:

$$\Delta R_{460} = R_w - R_0 \qquad (1)$$

where

R_w is the remission value after the washing process,

R_0 is the remission from the stained position before the washing process, both at the wavelength of 460 nm.

The degree of whiteness, expressed as WGG was chosen as a parameter to characterize the impact of process conditions.

3. Results and Discussion

The composition of the sunscreens (KP-M and KP-B) in Tab.1 contains numerous ingredients, as the functional ingredients (UV filters) are enriched with additional substances that facilitate application, coverage and durability. Accordingly, the stains applied to the cotton fabric (PT) and the cotton knitted fabric (PP) are of heterogeneous composition. To establish the relationship between the sunscreen agents and the cotton fabric and knitted fabric, an FTIR analysis of the cosmetic agents and the cotton surfaces before and after the application of KP-M and KP-B was performed, as shown in Figs.1-4.

Figs.1-4 show that FTIR-ATR is a suitable method for determining the interactions between stains from sunscreens and cellulose substrates. Further research is planned to deepen the FTIR analysis of the effect of sunscreen removal as a function of cellulose substrate, temperature and washing process. The efficacy of stain removal from UV preparations on cellulose substrates will be monitored by remission spectrophotometry, with remission at 460 nm (R_{460}) selected as the characterisation parameter or effect (ΔR_{460}).

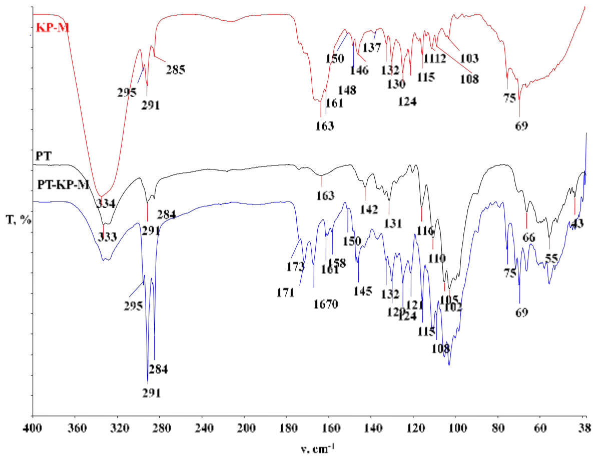


Fig.1 FTIR spectrum of cotton fabric, sunscreen KP-M and cotton fabric stained with KP-M

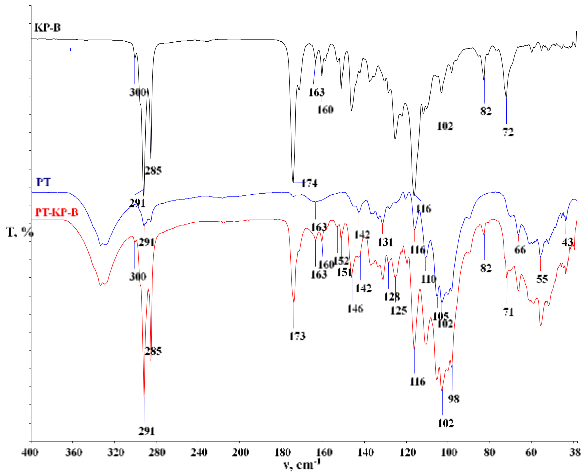


Fig.2 FTIR spectrum of cotton fabric, sunscreen KP-B and cotton fabric stained with KP-B

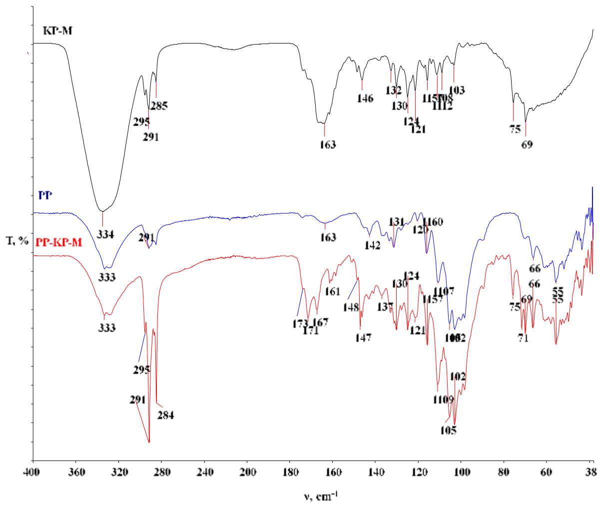


Fig.3 FTIR spectrum of cotton knitwear, sunscreen KP-M and cotton knitwear stained with KP-M

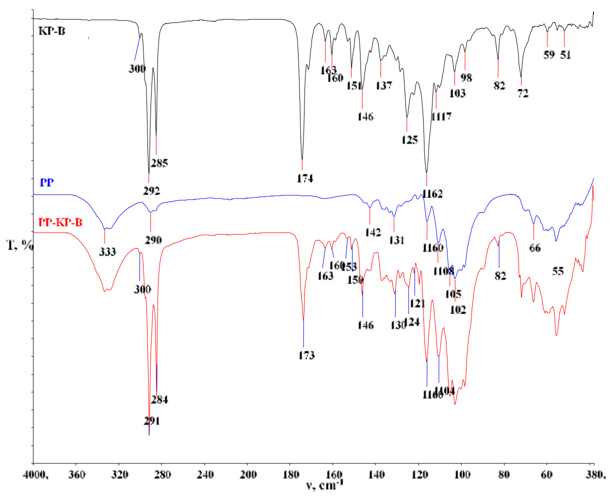


Fig.4 FTIR spectrum of cotton knitwear, sunscreen KP-B and cotton knitwear stained with KP-B

3.1. The primary effect in washing process of cotton fabrics

The results in Table 4 clearly show the low efficacy of agent-MS in removing stains from the sunscreen (KP-M) from cotton fabrics, with the washing temperatures having different effects on the stain removal performance.

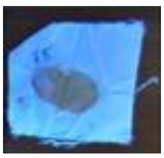
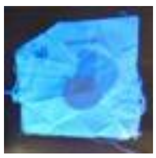
The chemical effect of agent-MS at 90 °C is unexpected considering its chemical composition, which contains a high proportion (60 %) of nonionic surfactants. Some chemical effect can be attributed to the alkalinity of agent-MS (pH 8.2). Washing at 90 °C shows better results than at lower temperatures, as the high temperature helps to remove the fatty bases of the sunscreen KP-M. The photographs of the surface of the cotton fabric taken in daylight in a room in Table 4, show that the washing process affects the creasing of the fabric at all temperatures, with the intensity increasing as the temperature rises. The photographs of the surface of the cotton fabric taken under exposure of UV lamp light, shown in Table 4, show an increase in the fluorescence intensity of the cotton fabric in the area of the stain. As the booster, agent-MS does not contain optical brighteners; this is attributed to the transfer of optical brighteners from the ballast to the cotton PT during the washing process. Stains from KP-M on cotton fabrics are clearly visible under UV light and their darkening is related to the temperature of the wash. Photos of fabrics after washing with the agent MS show the complexity of the interactions that occur during the washing of the textiles at the temperatures investigated.

Table 5 shows the primary effect of agent-MS and ozone when washing cotton fabrics stained with the cosmetic agent (KP-M) at the temperatures tested. The results show the limited efficacy of agent-MS with ozone in removing stains from the sunscreen KP-M compared to agent-MS alone. An enhanced chemical effect of agent-MS with ozone is visible at 30 °C. This synergy of the chemical effect of agent-MS and ozone shows better conditions for the removal of KP-M, which calls for further research on stain removal during washing with detergents. The appearance and intensity of KP-M stains on cotton fabrics in daylight under room conditions and under directed UV light in Table 5 confirm that the use of ozone in the washing process leads to specific changes and suggest that ozone has a potential to remove these stains.

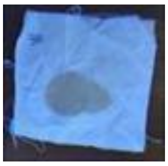
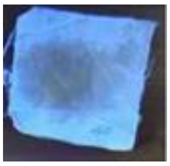
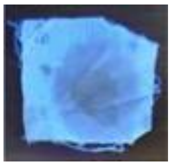
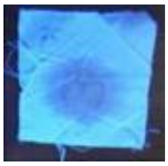
Fig.5 shows a comparison of the primary effect of agent-MS and agent-MS with ozone when washing cotton fabrics with KP-M stains at temperatures of 20 °C, 30 °C, 40 °C, 60 °C, 75 °C and 90 °C.

The favourable effect of ozone in the washing process with agent-MS shows their synergy at 30 °C. Table 6 shows the primary effect of agent-MS in the washing of cotton fabrics with cosmetic stains (KP-B) at the temperatures tested, together with photos of the cotton fabrics for each individual process.

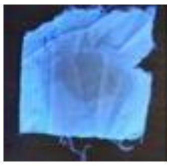
Tab.4 Remission from cotton fabric with KP-M stain (R_0), primary effect (ΔR_{460}) and photos of fabrics before and after the washing process at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C and 90 °C

T (°C)	20 °C	30 °C	40 °C	60 °C	75 °C	90 °C
R_0	ΔR_{460}					
75.98	2.82	1.96	2.83	3.34	2.20	6.13
						
						

Tab.5 Remission from cotton fabric with KP-M stain (R_0), primary effect (ΔR_{460}) and photos of fabrics before and after the ozone-assisted washing process at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C and 90 °C

T (°C)	20 °C	30 °C	40 °C	60 °C	75 °C	90 °C
R_0	ΔR_{460}					
75.88	1.06	6.05	-3.45	-3.48	3.23	1.19
						
						

Tab.6 Remission from cotton fabric with KP-B stain (R_0), primary effect (ΔR_{460}), and photos of fabrics before and after the washing process at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C, and 90 °C

T (°C)	20 °C	30 °C	40 °C	60 °C	75 °C	90 °C
R_0	ΔR_{460}					
76.80	-7.49	-6.48	-6.62	-0.89	-0.75	2.07
						
						

The values obtained for the primary effect (ΔR_{460}), which represent the difference in remission between the washed cotton fabric and the unwashed cotton fabric with the KP-B stain, show that the ability to remove stains from the KP-B sunscreen is weaker compared to the values in Table 4. This relationship is particularly pronounced at lower wash temperatures, where the ΔR_{460} values are mostly negative, meaning that the stains were not only poorly removed but also darkened during the wash. The effectiveness of KP-B removal improves with increasing washing temperature, which is due to the synergy of temperature and alkalinity. A high washing temperature has a positive effect on the primary effect by improving stain removal, but it is necessary to consider the effects of high temperatures on certain types of textiles, especially damage and colour changes.

Photographs of the surface of cotton fabrics taken in daylight in a room show that the washing process causes creases at all temperatures, the intensity of which increases as the temperature rises. Photographs of the surface of the cotton fabric taken under directed UV lamp light confirm the increasing intensity of fluorescence in the area of the stain. As no detergent was used, this phenomenon is attributed to the transfer of optical brighteners from the ballast to the cotton fabric during the washing process, as agent-MS does not contain optical brighteners.

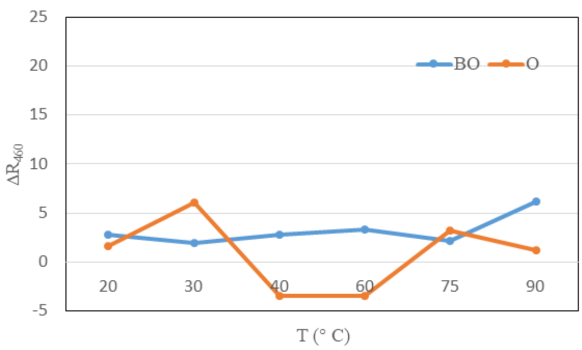


Fig.5 Comparison of the primary effect of agent-MS and agent-MS with ozone in the washing process of cotton fabric with KP-M stain at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C, and 90 °C

Tab.7 Remission from cotton fabric with KP-B stain (R_0), primary effect (ΔR_{460}), and photos of fabrics before and after the ozone-assisted washing process at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C, and 90 °C

T (°C)	20 °C	30 °C	40 °C	60 °C	75 °C	90 °C
R_0	ΔR_{460}					
66.3	3.77	5.12	10.37	15.17	15.30	14.62
						
						

Stains applied to the cotton fabric are clearly visible under UV light due to two migration phases, a middle, darker one and an outer, greasier one. The appearance of the KP-B stain after washing with agent-MS at 90 °C confirms the low remission values in Table 6.

Table 7 shows the primary effect of agent-MS and ozone when washing cotton fabrics with stains from the cosmetic product (KP-B) at the analysed temperatures, accompanied by photos of the cotton fabric for each procedure.

The results in Table 7 show a favourable synergistic effect of agent-MS and ozone in removing certain stains from the sunscreen (KP-B) at 60 °C, 75 °C and 90 °C. The effect of the nonionic surfactant of agent-MS is expected at 60 °C and 75 °C. The effect of ozone can be linked to its oxidative effect on stains from the sunscreen KP-B on cotton fabrics at lower temperatures (prewash and rinse cycles). Elevated washing temperatures, in particular 90 °C, can act on the saponification of fats and reduce their intensity. This described effect confirms the synergy of chemistry and temperature as factors of the Sinner's circle.

The appearance and intensity of KP-B stains on cotton fabrics under daylight in a room environment and under directed UV light in Table 7 confirm the favourable effect of agent MS and ozone in the washing process. The visibility of the KP-B stain on the cotton fabric is favoured by the increased fluorescence intensity at higher temperatures.

The migration zone of the components of the heterogeneous stain (KP-B), i.e. its spread from the centre to the edges after the washing process with the agent MS and ozone, is of lower intensity compared to the process with the agent- MS alone.

Fig.6 compares the primary effect of MS and MS with ozone when washing cotton fabrics with KP-B stains at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C and 90 °C.

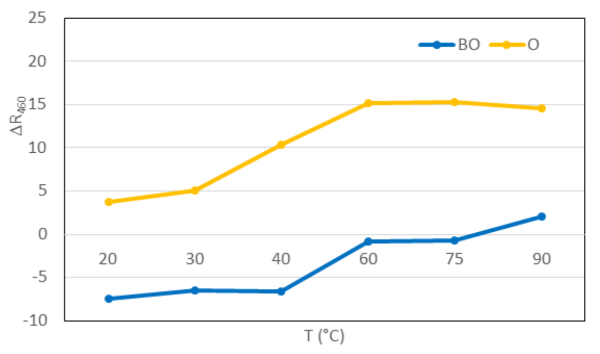


Fig.6 Comparison of the primary effect of agent-MS and agent-MS with ozone in the washing pro-cess of cotton fabric with KP-B stain at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C, and 90 °C

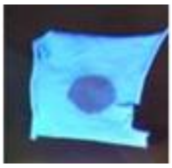
The primary effect shown in Fig.6 confirms the favourable effect of ozone and the synergistic effect with the agent-MS in removing stains from the sunscreen (KP-B) from cotton fabric at all temperatures.

3.2. Primary effect in the washing process of cotton knits

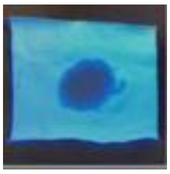
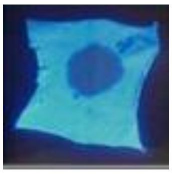
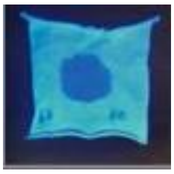
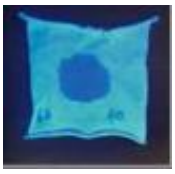
Table 8 shows the primary effect of the agent-MS when washing cotton knitted fabrics stained with the cosmetic agent (KP-M) at the analysed temperatures, accompanied by photographs of the cotton knitted fabrics for each individual process.

The results presented in Table 8 show that the most favourable primary effect of agent-MS occurs at a temperature of 90 °C, which is consistent with previous results for cotton fabrics. The effect is due to the saponification of the fats and the removal of the UV protection components soluble in them. The synergistic effect of high temperature, agent-MS and effective hydrodynamics is also confirmed for knit-wear with KP-M stains.

Tab.8 Remission from cotton knitwear with KP-M stain (R_0), primary effect (ΔR_{460}), and photos of the knitwear before and after the ozone-assisted washing process at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C, and 90 °C

T (°C)	20 °C	30 °C	40 °C	60 °C	75 °C	90 °C
R_0	ΔR_{460}					
85.91	-1.39	-2.26	4.78	9.37	1.63	15.99
						
						

Tab.9 Remission from cotton knitwear with KP-M stain (R_0), primary effect (ΔR_{460}), and photos of the knitwear before and after the ozone-assisted washing process at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C, and 90 °C

T (°C)	20 °C	30 °C	40 °C	60 °C	75 °C	90 °C
R_0	ΔR_{460}					
78.74	7.62	9.64	5.72	4.40	14.73	15.73
						
						

The appearance of washed cotton knitwear under daylight and UV-excited light differs from cotton fabric. Chemically and optically bleached cotton knitwear shows a stronger reflection in daylight and a more pronounced fluorescence intensity under UV light compared to cotton fabric which is only chemically bleached. Further studies on this topic are planned for chemically bleached fabrics and knitted fabrics.

Table 9 shows the primary effect of agent-MS and ozone when washing cotton knitted fabrics stained with the cosmetic product (KP-M) at the analysed temperatures. The results of the primary effect in Table 9 confirm the favourable influence of ozone on the activity of agent-MS in the removal of KP-M stains from cotton knitwear at all temperatures. The photographs of the cotton knit sample before washing under UV light shown in Tables 8 and 9 show that this stain also has two zones, a darker central area and a lighter peripheral area, which was not observed on cotton fabric.

The observed differences in the appearance of the KP-M stain on cotton knit and cotton fabric are due to the different structural characteristics and degree of processing.

Fig.7 shows a comparison of the primary effect of agent-MS and agent-MS with ozone when washing cotton knitted fabrics with KP-M stains at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C and 90 °C.

The described correlations between the primary effect of agent-MS and agent-MS with ozone when washing KP-M stains on cotton knitwear at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C and 90 °C are clearly shown in Fig.7. The most favourable temperatures for agent-MS with ozone are 30 °C and 75 °C, at which ozone provided a significant chemical boost in the removal of KP-M stains on cotton knitwear.

Table 10 shows the primary effect of agent-MS in washing cotton knitwear with cosmetic stains (KP-B) at the temperatures analysed, together with photos of the cotton knitwear for each procedure.

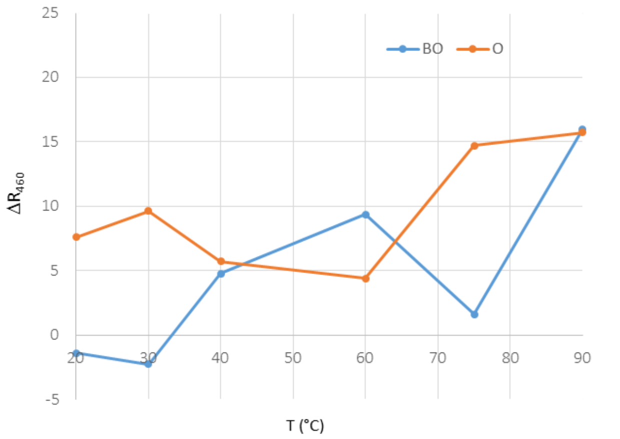


Fig.7 Comparison of the primary effect of agent-MS and agent-MS with ozone in the washing process of cotton knitwear with KP-M stain at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C, and 90 °C

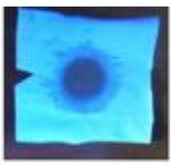
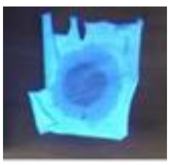
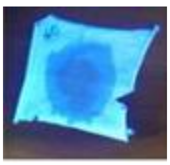
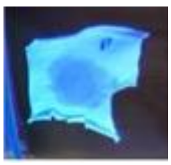
The results clearly show that elevated wash temperatures play a key role in the efficacy of agent-MS in removing KP-B from cotton knitwear, with the best results achieved at 75 °C and 90 °C.

These results confirm the importance of choosing the right washing temperature to achieve good results in the removal of certain types of stains.

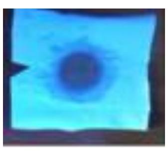
The appearance of KP-B stains on unwashed cotton knitwear under UV light is associated with migration zones and the spread of the oily phase of the balsam towards the edges, as was also observed on unwashed cotton fabrics. Increasing the washing temperature, especially at 75 °C and 90 °C, has a positive effect on reducing the intensity of this stain on the knitted fabric. The high temperature and the alkalinity of agent-MS contribute to the saponification of the oily phase of the stain.

Table 11 shows the primary effect of agent-MS and ozone when washing cotton knitwear with cosmetic stains (KP-B) at the temperatures tested, together with photos of the cotton knitwear for each individual process. The remission values listed in Table 11 show that the use of ozone in the washing process has a significant and favourable influence on the effectiveness of KP-B stain removal.

Tab.10 Remission from cotton knitwear with KP-B stain (R_0), primary effect (ΔR_{460}), and photos of the knitwear before and after the washing process at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C, and 90 °C

T (°C)	20 °C	30 °C	40 °C	60 °C	75 °C	90 °C
R_0	ΔR_{460}					
68.90	2.96	5.63	12.28	15.44	19.45	19.83
						
						

Tab.11 Remission from cotton knitwear with KP-B stain (R_0), primary effect (ΔR_{460}), and photos of the knitwear before and after the ozone-assisted washing process at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C, and 90 °C

T (°C)	20 °C	30 °C	40 °C	60 °C	75 °C	90 °C
R_0	ΔR_{460}					
67.84	4.68	8.41	11.13	16.65	20.85	22.38
						
						

These results suggest that ozone as an additional promoter in the washing process with agent-MS introduces additional chemical potential required for the reduction of intensity or complete removal of specific stains from sunscreens for cosmetic products which are challenging under modern washing conditions.

Fig.8 shows a comparison of the primary effect of agent-MS and agent-MS with ozone when washing cotton knitwear with KP-M stains at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C and 90 °C.

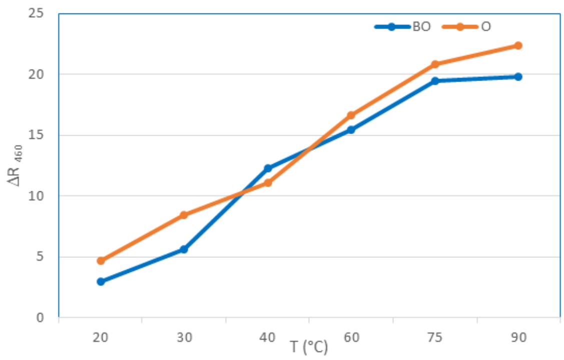


Fig.8 Comparison of the primary effect of agent-MS and agent-MS with ozone when washing cotton knitwear stained with KP-B at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C and 90 °C. Ozone enhances the effect of agent-MS at low washing temperatures, 20 °C and 30 °C, and at higher temperatures, 60 °C, 75 °C and 90 °C.

3.3. Comparison of the primary effects of agent-MS and agent-MS with ozone in the washing process of cotton fabrics and knitwear

Fig.9 shows the primary effect of agent-MS and agent-MS with ozone when washing sunscreen stains (KP-M and KP-B) on cotton fabrics and cotton knitwear at temperatures of 20 °C, 30 °C, 40 °C, 60 °C, 75 °C and 90 °C by four representations of the effect depending on the type of material.

It is obvious that:

- Agent-MS at 40 °C, 60 °C and 90 °C has a better effect in removing KP-M stains on cotton knitwear than on cotton fabric (Fig.9a)
- Agent-MS is more effective at removing KP-B stains from cotton knitwear than from cot-ton fabric at all temperatures (Fig.9b).
- Ozone enhances the chemical activity of agent-MS in removing KP-M stains from cotton knitwear at 20 °C, 30 °C, 40 °C, 75 °C and 90 °C (Fig.9c and 9d).
- Ozone enhances the chemical activity of agent-MS in the removal of KP-B stains on cotton knitwear at all temperatures (Fig.9d).

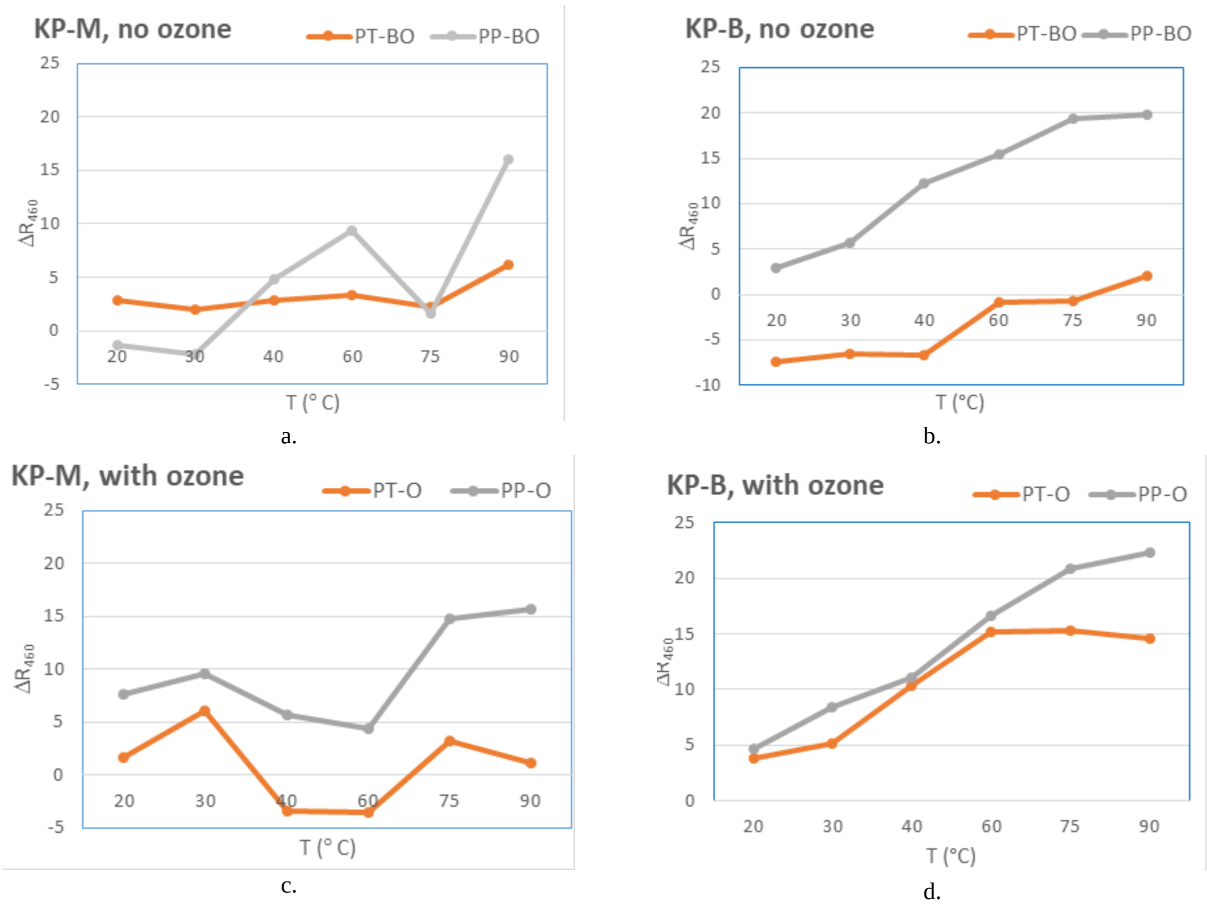


Fig.9 Comparison of the primary effects of agent-MS and agent-MS with ozone in the washing process of cotton fabrics and knitwear with sunscreen cosmetic product stains

- Ozone enhances the chemical activity of agent-MS in the removal of KP-B stains on cot-ton fabrics at all temperatures (Fig.9b and 9d).
- The influence of the cotton substrate is shown in Fig.9b and 9c.

3.4. Whiteness degree of standard fabric after the washing process

A standard chemically bleached cotton fabric PT-P was used as a reference indicator for the evaluation of whiteness during the washing process of cotton fabrics and knitwear stained with the cosmetic products KP-M and KP-B using agent-MS and agent-MS with ozone at 20 °C, 30 °C, 40 °C, 60 °C, 75 °C and 90 °C. Its mass (1.2 g) is negligible compared to the mass of the cotton ballast (6 kg).

Tab.12 shows the whiteness values (WGG) of the chemically bleached standard fabric – reference, before and after the washing process with agent-MS and agent-MS with ozone.

Tab.12 Whiteness degree (W_{GG}) of standard cotton fabric before and after the washing process with agent-MS and agent-MS with ozone

T (°C)	W_{GG}	
	BO	**O**
20	54.04	47.55
30	48.17	55.93
40	70.46	70.75
60	95.61	102.52
75	116.51	111.07
90	158.75	165.84
Before washing	43.0	

Higher washing temperatures improved the ability of the alkaline agent- MS based on non-ionic surfactants to degrade the stains of sunscreens (KP-M and KP-B). The degree of whiteness (W_{GG}) of the reference fabric before washing is 43.0, which corresponds to its condition (chemically bleached). The increase in whiteness of the reference fabric at all temperatures is due to the transfer of optical brighteners from the cotton ballast to the reference fabric during the washing process with agent MS and agent-MS with ozone, as can be seen from the appearance of the cotton fabric under UV light.

5. Conclusion

This study investigated the effects of boosters, agent-MS and agent-MS with ozone (without detergent) on the washing process of cotton fabrics and cotton knitwear stained with sunscreen cosmetic products at temperatures of 20 °C, 30 °C, 40 °C, 60 °C, 75 °C and 90 °C.

The partial removal of sunscreen stains during the washing process was attributed to the stubbornness of these stains on cotton textiles, the lower concentration of agent- MS and the absence of detergent in the process.

The results show that structural differences and the degree of finishing of cotton fabrics and knitwear influence the appearance of stains from sunscreen both before and after washing.

Ozone was found to enhance the chemical activity of agent-MS in removing sunscreen stains (KP-M, moisturising emulsion, and KP-B, balm) from cotton knitwear at 20 °C, 30 °C, 40 °C, 75 °C and 90 °C.

In addition, ozone also improved the chemical activity of agent-MS in removing KP-B balsam stains from cotton fabrics at all temperature ranges.

Future research will focus on evaluating the combined effect of boosters and detergents and the synergistic use of boosters, detergents and ozone in washing cotton textiles soiled with sunscreens at 20°C, 30°C, 40°C, 60°C, 75°C and 90°C.

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