Fibers and Polymers 2017, Vol.18, No.5, 1000-1010
DOI 10.1007/s12221-017-1056-2

ISSN 1229-9197 (print version)
ISSN 1875-0052 (electronic version)

Grouping of Various Stains to Develop Programs for a Front-loading Washer

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(Received October 28, 2016; Revised March 3, 2017; Accepted March 9, 2017)

Abstract: Stains from foodstuffs, cosmetics, and daily activities are frequently founded on our clothes. It is very annoying to remove stains, because extra treatment should be done before or after washing. A smart washing machine, which can operate adequately according to the types of stains on garments, will provide another convenience to users. In this study, the relative contributions of washing factors to the removal of stains depending on the type of stain and fiber, were investigated using domestic front-loading washers. The investigated washing factors were temperature, time, drum speed, and the ratio of motion time to pause time. Removal of 15 types of common stains on three types of cloths, such as cotton, polyester and cotton/polyester blend, was assessed. Stains were categorized by the origin: food, cosmetics, body, outdoor activities and factory work. Multiple regression equations containing interaction effects were obtained from the soiled cloths with these stains. Depending on the magnitudes of standardized regression coefficients for the effect of washing factors on the soil removal, the soiled cloths were divided into five groups: cloths soiled with oily materials, cotton cloths soiled with proteins, cloths soiled with insoluble particles, cloths soiled with highly unsaturated oils, and polyester cloths. Effective washing conditions for each group were suggested.

Keywords: Stains, Soil removal, Main washing factor, Regression coefficient, Clustering

Introduction

The great increase in concern about hygiene, as well as the ease of washing clothes using a washing machine, has led to clothes being washed more frequently despite mild soiling in many cases. Severe soiling is generally limited to underwear and white socks. Recently, the increasing tendency to wash clothes frequently is often to remove stains from foodstuffs and daily activities. Typical foodstuffs that cause stains are soup, soy sauce, red pepper, red wine, coffee, and cocoa. In particular, the deep color of red wine and cocoa readily results in stains, and the consumption of these products has been increasing. This is partly because red wine and cocoa contain polyphenols, which have anti-aging effects and promote blood circulation. Moreover, participation in sports and leisure activities is also on the increase to foster good health and wellbeing. Most people wear clothes specific to each sport or leisure activity, and then wash these clothes immediately afterwards regardless of the degree of soiling.

Today's simple-to-use and efficient washing machines are based on numerous studies of laundry conducted from the 1950s. These studies have been done on the analyses of soil components [1-3], the mechanisms of oily soil removal [4-8], the detergent ingredients to make washing more effective without adversely affecting the environment [9-12], the dynamics of laundry in washing machines to improve washing efficiency [13-15], the mechanical systems of washing machines [16-18], and the methods for evaluating soil removal [19-23]. Diverse types of domestic washing machines are currently on the market. Most of the wash programs are categorized by fiber type into cotton, synthetic, delicate, and wool fabrics; however, a breathable and waterproof fabric program has recently been included in some washers. There are also programs for dark and denim fabrics and for color care. Most household washing machines have not yet offered consumers the option to select a program based on the type of stains on clothing. Therefore, stained clothes have had to be pretreated before washing to remove stains so far. This is an annoying, time-consuming procedure. Nowadays, clothes are washed so frequently that washing under excessively strong conditions to remove particular stains is not only wasteful but also eco-destructive. Using stronger mechanical force, a longer time, and a larger amount of detergent than the proper washing conditions, clothes will become more damaged, and more electricity and water will be consumed. Washing machines need to provide enough programs to suit the lifestyles of current users.

The purpose of this study is to determine effective washing conditions according to the type of common stains as part of developing a smart washing machine. We have assessed the removal based on the type of stains caused by food stuffs, cosmetics, and outdoor activities. These stains were applied on cotton fabrics, cotton/polyester (PET) fabrics, and PET fabrics, all of which are common clothing materials and are principally washed using a washing machine. Usually staining occurs in small areas and causes color change. However, in order to be able to quantify the removal of the stains, cloths soiled with staining materials were used. To determine effective washing conditions for cleaning the stained cloths that are frequently encountered in our daily life, three kinds of cloths soiled with 15 different staining materials were purchased or manufactured in the laboratory. The number of soiled cloths was limited because evenly soiled cloths were needed to assess the removal.

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Experimental

Materials

Cotton, PET/cotton, and/or PET fabrics, which the majority of clothing is made from, were used for the soiled cloths in this study. The cloths and staining materials used in this study are presented in Table 1. The types of stains were food stuffs containing red pepper, soy sauce, ketchup, tomato/beef sauce, red wine, coffee, cocoa, and olive oil; cosmetics including lipstick and make-up; blood; grass and clay; and mineral oil and grease/quartz/iron oxide. The soiled cloths were purchased from EMPA (St. Gallen, Switzerland) or wfk Testgewebe GmbH (Krefeld, Germany), except for the cloths soiled with coffee, red pepper, and soy sauce, which were prepared in the laboratory. Commercial and frequently used fabrics were chosen for soiling because of simulating practical staining conditions. Additionally, EMPA or wfk soiled cloths also have various specifications for fabric structures.

Bleached cotton cloth (plain weave, 97 g/m^2), PET/cotton 65/35 cloth (plain weave, 107 g/m^2) and filament PET cloth (plain weave, 142 g/m^2) were purchased and then soiled in the laboratory. The amount of applied soils for most of the EMPA or wfk soiled cloths was not known. Consequently, it was impossible to soil the fabrics in the laboratory with the same degree as those from EMPA or wfk. To prepare more severe soiling than staining in our daily life, the degree of soiling was determined by the depth of color after soiling. After the fabrics were treated with various concentrations of staining materials, the optimal concentrations were determined in the laboratory.

To soil the cloths in the laboratory, instant coffee (30 g) was dissolved in water (1 *l*), brewed soy sauce (1 *l*) was added to water (1 *l*), and powdered red pepper (40 g) and

Table 1. Characteristics of soiled cloths

Soil class	Soil	Fiber	Sample code	Origin
Food	Red pepper	Cotton	RPC	Laboratory
		PET/cotton	RPPC	Laboratory
		PET	RPP	Laboratory
	Soy sauce	Cotton	SSC	Laboratory
		PET/cotton	SSPC	Laboratory
		PET	SSP	Laboratory
	Ketchup	Cotton	KCC	WFK 10065
		PET/cotton	KCPC	WFK 20065
	Tomato/beef sauce	Cotton	TBC	WFK 10090
		PET/cotton	TBPC	WFK 20090
	Aged red wine	Cotton	RWC	EMPA 122
	Coffee	Cotton	CFC	Laboratory
		PET/cotton	CFPC	Laboratory
		PET	CFP	Laboratory
	Cocoa	Cotton	CCC	EMPA 112
		PET/cotton	CCPC	WFK 30017
	Olive oil/carbon black	Cotton	OOC	EMPA 101
		PET/cotton	OOPC	EMPA 104
Cosmetics	Lipstick	Cotton	LSC	EMPA 141/1
		PET/cotton	LSPC	EMPA 142/1
	Make-up	Cotton	MUC	EMPA 143/1
		PET/cotton	MUPC	EMPA 144/1
Body	Blood	Cotton	BLC	EMPA 111
		PET	BLP	WFK 30063
Outdoor	Grass	Cotton	GRC	EMPA 164
	Clay	Cotton	CLC	WFK 10055
		PET/cotton	CLPC	WFK 20055
Factory work	Mineral oil/carbon black	Cotton	MOC	EMPA 106
	Grease/quartz/iron oxide	Cotton	GSC	EMPA 120

Table 2. Main washing conditions

Factor	Level		
Temperature (°C)	20	40	60
Time (min)	20	60	100
RPM	30	47	
Ratio of motion to pause time	0.5	1.7	10

finely ground raw pepper (17 g) were added to water (1 *l*) and then filtered through #22 mesh. The cloths were soiled evenly by turning them over in each solution with a liquor ratio of 1:10 at 40 °C for 1 h. To fix stains strongly into the cloths, the soiled cloths were dried in the air and then cured at 110 °C for 20 min. The soiled cloths were kept in a refrigerator until they were washed.

Washing and Soil Removal Assessment

Soiled cloths were laundered using a 13-kg front-loading washer (WR-HA139UW, Samsung Electronics, Korea) with 100 % cotton fabric ballast composed of two sheets, eight pillow cases, and some towels according to IEC 60456, making up a total load of 6.0 kg dry mass. Specimens (5×10 cm) were fixed to towels for washing. IEC 60456 reference detergent A* (0.2 g) was added, and tap water with 50 ppm hardness at 20 °C from a constant-temperature water tank was supplied to the washer. IEC 60456 reference detergent A* was composed of linear alkylbenzene sulfonate, soap, ethoxylated fatty alcohol, enzymes, and a foam inhibitor (77 %), sodium perborate tetrahydrate (20 %), and tetraacetylethylenediamine namely a bleach activator (3 %). Conditions of the main wash cycle are described in Table 2. After the main wash cycle, the cloths were rinsed three times and then dried at ambient temperature.

The surface reflectance of the original cloths and soiled cloths before and after washing was measured using a Color i5 spectrophotometer (X·rite, USA) with Color iQC software V 7.0 to assess soil removal. Soil removal was calculated according to equation (1) using the reflectance value [24,25] at the wavelength appropriate for each soiled cloth. In equation (1), R_S, R_w, and R_o are reflectance values for soiled cloth, washed cloth, and unsoiled original cloth, respectively. At least four experiments were performed for each set of conditions and the average values are reported.

$$\text{Soil removal (\%)} = \frac{R_w - R_S}{R_o - R_S} \times 100 \qquad (1)$$

Soil removal calculated from the reflectance values was compared with that determined from energy-dispersive X-ray (EDX) spectra (EX-250, Horiba, Japan) for PET/cotton cloth soiled with clay and cotton cloth soiled with grease/quartz/iron oxide. The contents of silica and aluminum on the cloths before and after washing were analyzed using EDX. The surface morphology of these soiled cloths was investigated using scanning electron microscopy (SEM; S-4200, Hitachi, Japan). Prior to SEM observation, samples were sputtered with platinum under vacuum.

Data Analysis

The data set consisting of 29 soiled cloths and 54 main washing conditions was analyzed using SAS 9.2 and PASW Statistics 17.02. A multiple regression analysis was performed using SAS 9.2 to estimate partial regression coefficients of the single factors and interaction terms of factor pairs in washing conditions. K-means clustering analysis was carried out using PASW Statistics 17.02 in clustering washing factors of the soiled cloths. Regression coefficients for the clusters were also estimated using SAS 9.2 to identify the factors affecting the soil removal.

Results and Discussion

Reflectance Spectra of Soiled Cloths

Reflectance spectra of the soiled cloths over the visible wavelength range of 360-750 nm are shown in Figure 1. To clarify each spectral line, spectra of 29 soiled cloths were nearly equally divided in the order in Table 1 into four parts. Most soiled cloths were brown and their reflectance increased with wavelength. However, the reflectance of the pink-lipstick soiled cloth increased markedly at 600 nm, and that of the grass soiled cloth exhibited a peak at approximately 550 nm and the lowest point at 670 nm. The cloth soiled with olive oil or mineral oil was gray because of carbon black, and showed identical reflectance over the entire visible wavelength region. The reflectance spectra of PET/cotton and PET fabric samples which were soiled with red pepper, soy sauce, and coffee in our laboratory had a peak at around 450 nm, probably due to fluorescent whitening agents. PET/cotton and PET fabrics were not extracted to remove fluorescent whitening agents. The reasons were the reflectance peak owing to fluorescent whitening agents did not only affected the reflectance at the specific wavelengths of those soiled cloths, but also we usually wear clothes made from. In this study, soil removal was calculated from the reflectance value at a suitable wavelength which was determined from the reflectance curve for each soiled cloth. The wavelength used to measure the reflectance value for each soiled cloth is listed in Table 3.

Soil Removal Depending on Washing Conditions

Soil removal at 20 °C, 40 °C and 60 °C is shown in Figure 2. The three graphs on the left are the soil removal obtained from the milder conditions of the main wash, including a washing time of 20 min, drum revolution speed of 30 rpm, and a ratio of motion time to pause time of 0.5. The three graphs on the right are the results using the harsher conditions with a washing time of 100 min, drum revolution rate of 47 rpm, and a ratio of motion time to pause time of 10.

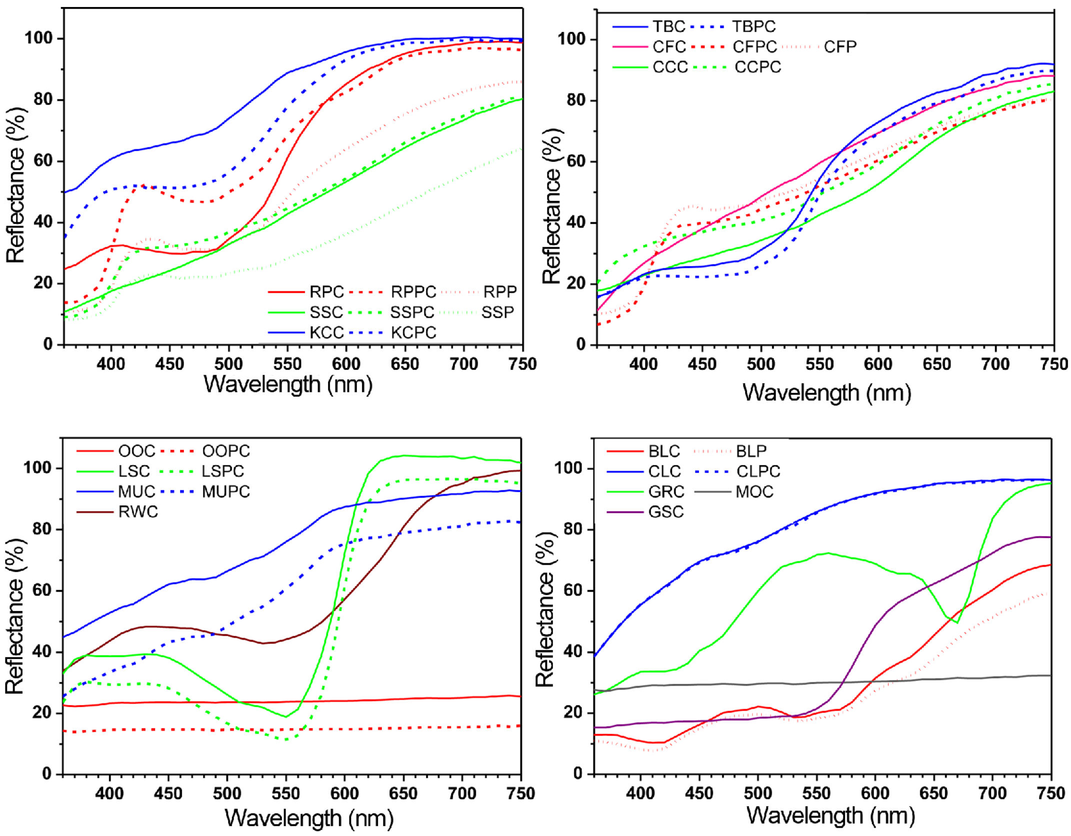

Figure 1. Reflectance spectra of soiled cloths.

Table 3. Wavelengths of soiled cloths used to determine *K/S* values

Wavelength (nm)	Soil	Soiled cloth samples
540	Olive oil/carbon black	OOC, OOPC
	Mineral oil/carbon black	MOC
580	Red pepper	RPC, RPPC, RPP
	Ketchup	KCC, KCPC
	Tomato/beef sauce	TBC, TBPC
	Grass	GRC
	Clay	CLC, CLPC
600	Soy sauce	SSC, SSPC, SSP
	Coffee	CCC, CCPC
	Cocoa	CFC, CFPC, CFP
	Make-up	MUC, MUPC
	Blood	BLC, BLP
620	Aged red wine	RWC
	Lipstick	LSC, LSPC
	Grease/quartz/iron oxide	GSC

Figure 2 shows that the PET fabrics had the greatest soil removal, followed by PET/cotton, and then cotton fabrics. At higher temperature, the differences in soil removal between the fiber types were smaller because the cotton fabrics showed the greatest improvement, followed by PET/cotton fabrics and then PET ones. Regarding the cloths soiled with lipstick and make-up, the PET/cotton fabrics showed less soil removal than from the cotton. Almost the same rate of olive oil was removed from the cotton and the PET/cotton cloths. It is widely known that oily soils can hardly be removed from hydrophobic PET fabrics. Morris and Prato [26] studied the removal of oily soils containing bandy black from fabrics by measuring the amount of silica present by using X-ray florescence analyses and color differences. They found that color difference was highly consistent with the difference between the amounts of silica present following washing. Also, less oily soil was removed from PET fabrics than from cotton or PET/cotton fabrics, and the removal of non-polar oily soils from PET fabric decreased as the wash temperature increased. The main ingredients of lipstick are non-polar wax, oil, organic dyes, and inorganic pigments. Make-up contains wax, mineral oil, and inorganic pigments like zinc oxide, titanium dioxide, and bismuth as well. It appears that a higher content of non-polar oil both in lipstick and make-up has been penetrated into PET fibers, resulting in lower soil removal during washing. Even at a washing temperature of 20 ^{o}C under harsher conditions of washing time, revolution speed and the

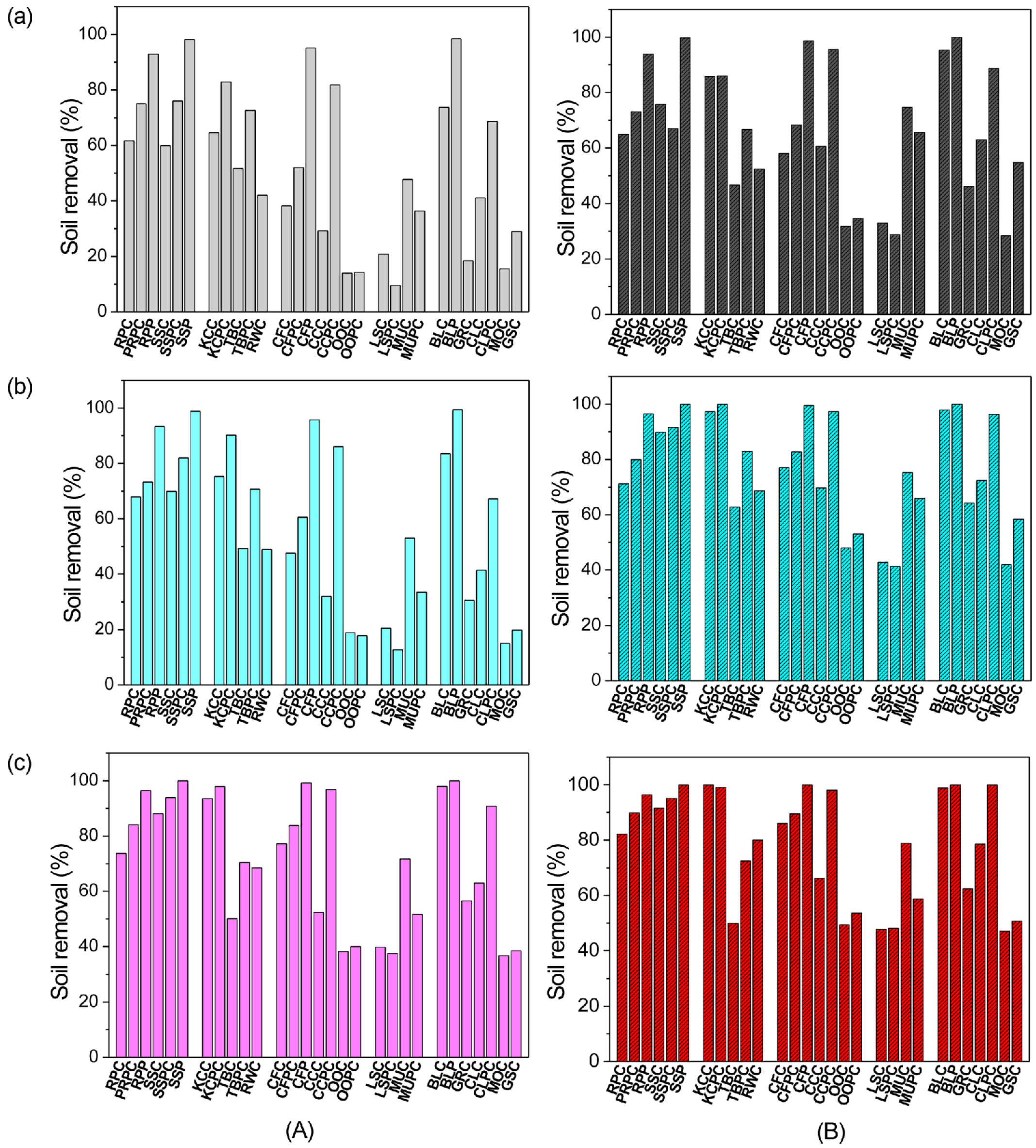

Figure 2. Soil removal under various washing conditions: (A) 20 min, 30 rpm, and ratio of motion time to pause time of 0.5, and (B) 100 min, 47 rpm, and ratio of motion time to pause time of 10. Wash temperatures of (a) 20 °C, (b) 40 °C, and (c) 60 °C.

ratio of motion time to pause time, 80 % or more of the stains were removed from all the cloths soiled with blood and ketchup; PET cloths soiled with coffee, soy sauce, and red pepper; and PET/cotton cloth soiled with cocoa. Therefore, some soils can be fully removed from even cotton fabrics at a low wash temperature.

Removal of make-up was moderate, 60-80 % was removed at 40 °C under stronger conditions. Cotton cloths soiled with tomato/beef sauce, red wine, coffee, cocoa, grass and clay showed the same. However, tomato/beef sauce, coffee and cocoa stains were considerably less removed from cotton cloths than from PET cloths. This is probably because melanoidin, a brown heterogeneous polymer generated from oligosaccharides, amino acids, and chlorogenic acid through the Maillard reaction during roasting coffee, penetrated into the hydrophilic cotton fabrics [27]. Insoluble cocoa powder is produced from cacao beans after removing the cacao butter, and its primary pigment is anthocyanin [28]. While cocoa could not penetrate into the PET fibers, it probably adhered inside the lumens and between the twists of cotton fibers, resulting in fairly low soil removal from cotton cloth.

Less than 60 % of the olive oil and the lipstick on the cotton and the PET/cotton cloth, and the mineral oil and the grease soil on the cotton cloth were removed at 40 °C even under the harsher washing conditions. From these results, we can conclude that it is difficult to remove oily soils. To

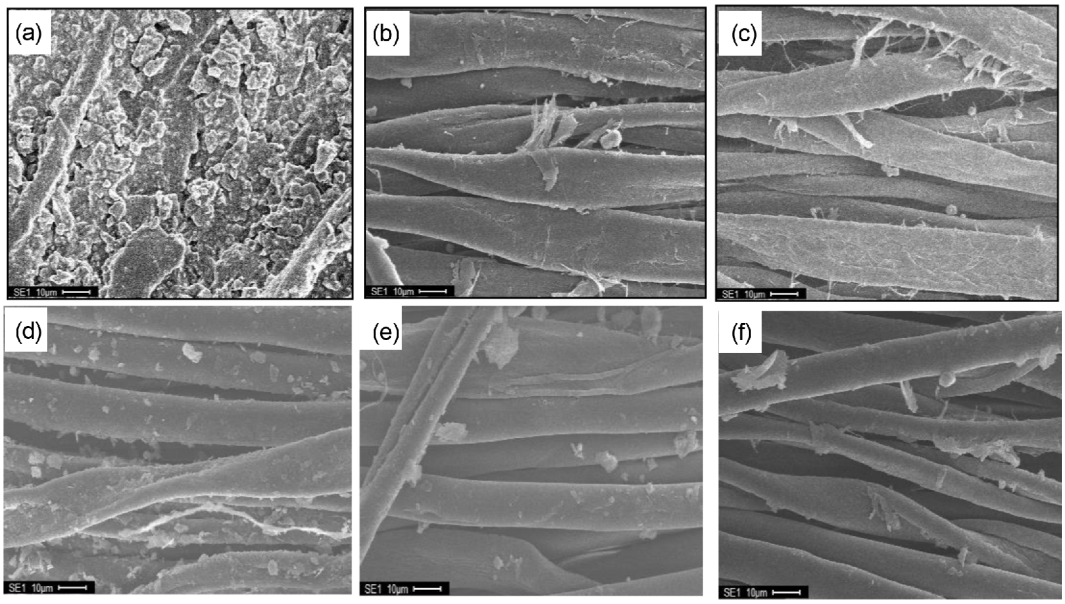

Figure 3. SEM images of cotton cloth soiled with grease/quartz/iron oxide (a) before washing, (b) after 44.6 % removal, (c) after 57.8 % removal. SEM images of PET/cotton cloth soiled with clay (d) before washing, (e) after 94.2 % removal, and (f) after 97.4 % removal.

increase the removal of these oily soils, using a higher concentration of the detergent would be recommended. Raising the washing temperature generally improved soil removal; a larger increase in soil removal was observed upon increasing the temperature from 20 to 40 ^{o}C, while a smaller increase was found upon further raising the temperature to 60 ^{o}C.

The amounts of silica and aluminum on the cloths soiled with grease/quartz/iron and clay were measured using EDX to compare the results with those obtained by colorimetry. As shown in Figure 3, the cloth surface is heavily soiled with the grease/quartz/iron oxide. The grease/quartz/iron oxide-soiled cloth is red because of the iron oxide, but the EDX intensity of the iron was too weak for it to be detected (Table 4). On the cloth soiled with grease/quartz/iron oxide, soil removal determined by EDX was much greater than that determined by colorimetry. Conversely, for the clay-soiled cloth, soil removal determined by EDX was lower than that determined by colorimetry. Even though these two methods both reveal soil removal by washing, the determined rates of removal were very different. Clothes are usually judged clean or dirty not by the actual amount of soil left, but by the appearance of the clothes. Therefore, it is more appropriate to determine the soil removal by colorimetry.

Table 4. Soil removal (%) of grease/quartz/iron and clay soiled cloths determined by different methods

Soil	*K/S*	EDX	
		Si	Al
Grease/quartz/iron oxide	44.6	94.5	
	57.8	97.6	
Clay	94.2	64.2	77.0
	99.9	89.2	88.8

Multiple Regression Coefficients of Main Wash Factors in Soil Removal

The effects of main washing factors on soil removal were investigated using multiple regression analysis. Interaction effects between the washing factors were also estimated (Table 5). Only the coefficients with statistical significance $p<.05$ are presented. Here, the unit of each wash factor was different and a larger intercept generally led to better soil removal. Cloths soiled with oily materials, such as PET/cotton fabric with olive oil or lipstick, and cotton fabric soiled with olive oil, mineral oil, grease, coffee, or grass showed poor soil removal with a negative intercept. The removal of most stains was affected by all four factors: temperature, drum speed, time, and the ratio of motion time to pause time. However, among the soiled cloths with very high soil removal, PET cloth soiled with red pepper, soy sauce, or coffee was affected by fewer than three washing factors. Additionally, PET/cotton cloth soiled with soy sauce was only affected by washing time. Among those samples with medium removal, cotton and PET/cotton cloths soiled with tomato/beef sauce were not affected by temperature and time, but only by drum speed and the ratio of motion time to pause time. PET/cotton cloth soiled with make-up or olive oil and cotton cloth soiled with lipstick or grease were not affected by drum speed or the ratio of motion time to pause time.

Table 5. Regression coefficients of main washing factors for soil removal

Soiled cloth	Intercept	Temp[1]	RPM	Time	Ratio[2]	Temp[1] × RPM	Temp[1] × Time	Temp[1] × Ratio[2]	RPM × Time	RPM × Ratio[2]	Time × Ratio[2]
RPC	33.15	0.27	0.48	0.15	2.53	.	.	.	.	-0.04	-0.01
RPPC	44.60	0.34	0.53	0.11	1.57	.	.	.	.	-0.03	-0.01
RPP	88.06	0.05	0.09	.	0.27		.	.	.	0.00	.
SSC	35.87	0.74	0.21	0.23	0.25	.	0.00	.	.	.	.
SSPC	72.82	.	.	0.19	.	0.00	.	0.01	0.00	-0.01	0.00
SSP	97.27	0.04	.	0.02	.	.	0.00	0.00	.	0.00	.
KCC	33.62	0.74	0.48	0.26	1.08	0.00	0.00	.	.	-0.01	0.00
KCPC	55.86	0.39	0.47	0.11	1.29	0.00	.	.	.	-0.02	0.00
TBC	21.39	.	0.49	.	2.65	.	0.00	-0.01	.	-0.04	-0.01
TBPC	44.67	.	0.33	.	2.50	.	0.00	.	0.00	-0.04	-0.01
RWC	28.37	0.20	0.24	0.07	-0.14	.	0.00	0.01	0.00	.	.
CFC	-6.13	0.95	0.57	0.31	0.55	0.00	.	.	0.00	-0.01	.
CFPC	19.55	0.61	0.39	0.31	0.58	.	.	.	0.00	-0.01	.
CFP	98.08	.	-0.16	.	.	0.00	.	-0.01	.	0.01	0.00
CCC	5.51	0.31	0.30	0.23	0.62	.	.	.		.	.
CCPC	66.49	0.25	0.35	0.21	0.58	0.00	0.00	.	0.00	-0.01	0.00
OOC	-17.58	0.60	0.35	0.30	0.37	.	0.00	.	.	.	.
OOPC	-6.10	0.45	0.16	0.18	.	.		.		0.01	
LSC	8.66	0.29	.	0.11	.	.	0.00	.	.	0.01	.
LSPC	-13.38	0.52	0.29	0.07	0.30	-0.01	0.00	.	.	.	.
MUC	17.06	0.72	0.50	0.24	0.43	-0.01	0.00	.	.	.	.
MUPC	16.06	0.32	.	0.31	1.05	0.00	0.00	-0.01	.	.	.
BLC	51.73	0.84	-0.15	0.38	0.79		-0.01	-0.01	.	.	0.00
BLP	97.13	0.05	0.03	0.01	0.07	0.00	0.00	0.00	.	.	.
GRC	-34.29	1.01	0.55	0.63	1.24	.	-0.01	.	0.00	-0.01	-0.01
CLC	16.17	0.43	0.27	0.20	0.69	.	.	.		.	0.00
CLPC	39.43	0.51	0.40	0.27	0.53	0.00	.	.	.	.	.
MOC	-3.65	0.41	0.13	0.13	0.39	.	.	.	.	.	.
GSC	-4.92	0.61	0.47	0.29	.	.	0.00	.	.	0.02	.

[1]Temp is temperature and [2]ratio is the ratio of motion time to pause time.

In all cases, the interaction effects were relatively low. Moreover, the interaction effect of drum speed and the ratio of motion time to pause time was negative in most cases; therefore, it is unnecessary to use a high drum speed and ratio of motion time to pause time together to get effective soil removal. This can be explained by a longer one-direction drum rotation imparting lower mechanical force on the fabrics as it decreased friction between the fabrics. The washing machine turns in the opposite direction when it restarts following a pause. For this reason; the lower the ratio of motion time to pause time, the more frequent change of the movement of the fabrics. Yun *et al.* [29] proved that as the fabric movement during laundering became more complex, mechanical force delivered to the fabric and the amount of soil removal increased.

The soil removal of each soiled cloth washed under different conditions can be estimated from a corresponding regression equation; however, it is difficult to compare the relative influence of each wash factor on the removal. The relative influence of main washing factors on the soil removal can be compared by standardized regression coefficients. They were determined and are presented in Table 6.

The standardized coefficients of each individual factor also affected soil removal like non-standardized ones for each sample, while the absolute values of the interaction coefficients of the former was greater than those of the latter. In general, temperature had the greatest effect on soil

Table 6. Regression standardized coefficients of washing conditions for soil removal

Soiled cloth	Temp[1)]	RPM	Time	Ratio[2)]	Temp[1)] × RPM	Temp[1)] × Time	Temp[1)] × Ratio[2)]	RPM × Time	RPM × Ratio[2)]	Time × Ratio[2)]
RPC	0.33	0.33	0.38	1.26	.	.	.	.	-0.87	-0.44
PRPC	0.67	0.57	0.42	1.23	.	.	.	.	-0.84	-0.39
RPP	0.40	0.36	0.08	0.79	.	.	.	.	-0.61	.
SSC	1.02	0.16	0.65	0.14	.	-0.23	.	.	.	.
SSPC	.	.	0.72	.	0.41	.	0.40	-0.34	-0.17	-0.23
SSP	0.46	.	0.59	.	.	-0.63	0.31	.	-0.18	.
KCC	1.15	0.41	0.81	0.68	-0.34	-0.46	.	.	-0.32	-0.22
KCPC	0.84	0.56	0.46	1.11	-0.40		.	.	-0.72	-0.35
TBC	.	0.37	.	1.46	.	0.55	-0.36	.	-0.83	-0.30
TBPC	.	0.21	.	1.19	.	0.19	.	0.29	-0.73	-0.38
RWC	0.25	0.16	0.17	-0.07	.	0.67	0.17	-0.22	.	.
CFC	0.91	0.30	0.59	0.21	-0.17	.	.	-0.17	-0.15	.
CFPC	0.76	0.27	0.77	0.29	.	.	.	-0.32	-0.15	.
CFP	.	-0.27	.	.	0.54	.	-0.81	.	0.44	0.25
CCC	0.40	0.22	0.61	0.32	.	.	.	.	.	.
CCPC	1.04	0.79	1.75	0.97	-0.34	-0.55	.	-0.67	-0.54	-0.39
OOC	0.79	0.25	0.79	0.20	.	-0.24	.	.	.	.
OOPC	0.56	0.11	0.45	.	.	.	.	.	0.17	.
LSC	0.44	.	0.32	.	.	0.31	.	.	0.13	.
LSPC	0.57	0.17	0.16	0.13	-0.27	0.54	.	.	.	.
MUC	1.16	0.44	0.77	0.28	-0.53	-0.43	.	.	.	.
MUPC	0.49	.	0.97	0.65	0.31	-0.49	-0.44	.	.	.
BLC	1.44	-0.14	1.30	0.54	.	-1.31	-0.24	.	.	-0.27
BLP	1.32	0.44	0.64	0.80	-0.48	-0.73	-0.31	.	.	.
GRC	1.01	0.30	1.25	0.49	.	-0.62	.	-0.26	-0.25	-0.19
CLC	0.57	0.20	0.54	0.37	.	.	.		.	-0.21
CLPC	0.85	0.35	0.88	0.35	-0.28	.	.	.		.
MOC	0.63	0.11	0.41	0.24	.	.	.	.	.	.
GSC	0.80	0.34	0.77	.	.	-0.55	.	.	0.36	.

[1)]Temp is temperature and [2)]ratio is the ratio of motion time to pause time.

removal, followed by time, the ratio of motion time to pause time, and then drum speed. Most individual standardized coefficients had positive values. However, in terms of drum speed, the PET cloth soiled with coffee and the cotton cloth with blood had negative standardized coefficients. In terms of the ratio of motion time to pause time, the cotton cloth soiled with red wine had negative coefficients; though their values were very small in all cases.

Most standardized interaction coefficients had negative values. Nevertheless, they were positive in some cases where the individual factors did not make a significant contribution to soil removal. This was the case with the PET/cotton and the PET cloths soiled with soy sauce, the tomato/beef sauce-soiled cloths, the PET cloth soiled with coffee, the cotton cloth soiled with lipstick or grease, and the PET/cotton cloth soiled with olive oil or make-up. Although the cotton cloths soiled with red wine and the lipstick-soiled cloths displayed positive coefficients for both washing temperature and time, they also had positive interaction coefficients. Therefore, a higher temperature and longer time can generate a synergic effect on soil removal from these cloths. Several factors displayed coefficient values of over 1, including temperature for the cotton cloth soiled with soy sauce, ketchup or make-up, and the PET cloth soiled with blood. The coefficient values of the ratio of motion to pause time are also over 1 for the cotton and PET/cotton cloths soiled with red pepper or tomato/beef sauce and the PET/cotton cloths soiled with ketchup. The two factors of temperature and time had coefficient values above 1 for the PET/cotton cloth soiled with cocoa and the cotton cloth soiled with blood or grass. In contrast, all the coefficient values of the drum speed were less than 1.

To apply our results directly to actual washing systems, the effect of washing factors on soil removal had to be simplified. Therefore, the stained cloths were divided into five groups depending on the washing factors which affected the washing efficiency of the soiled cloths to the same degree; these groups are shown in Table 7.

Group I included cloths soiled with oily materials such as olive oil, mineral oil, grease, lipstick and make-up; the only oil-soiled cloth excluded from this cluster was the PET/cotton cloth soiled with make-up. As mentioned before, lipstick and make-up contain non-polar wax and oils in which pigments are embedded. For Group I, the washing temperature had the greatest effect on soil removal, followed by time, interaction between drum speed and the ratio of motion to pause time, and drum speed. The soiled cloths included in Group I required washing under the harshest conditions because these materials were difficult to remove. Cotton cloths in Cluster I could be effectively washed at a temperature of 60 °C; however, the PET/cotton cloths were more likely to crease at such a high washing temperature. Therefore, the soiled cloths in Group I had to be washed at 40 °C for a longer time and at a faster drum speed. In addition to the mechanical factors of the washing machine, a higher concentration of detergent could make removal of

Table 7. Grouping of soiled cloths according to contributions of washing conditions to soil removal

Group	Soiled cloth	Temp[1)]	RPM	Time	Ratio[2)]	Temp[1)] × RPM	Temp[1)] × Time	RPM × Time	RPM × Ratio[2)]	Time × Ratio[2)]
I	OOC OOPC LSC LSPC MUC MOC GSC	0.53	0.10	0.32					0.17	
II	SSC CFC BLC GRC	0.56	0.04	0.54	0.07		-0.33			
III	RPPC KCC KCPC CFPC CCC CCPC CLC CLPC MUPC	0.39	0.15	0.29	0.18					
IV	RPC TBC TBPC		0.20		0.94		0.23	0.16	-0.63	-0.30
V	RPP SSPC SSP RWC CFP BLP	0.08					0.14			

[1)]Temp is temperature and [2)]ratio is the ratio of motion time to pause time.

oily stains more effective.

Group II included cotton cloths with relatively high soil removal. For this group, both wash temperature and time made larger contributions to soil removal, while the ratio of motion time to pause time and drum speed made fewer contributions. This group included cotton cloths soiled with soy sauce, coffee, blood, and grass, all of which contain proteins. The black color of the soy sauce and coffee comes from melanoidin formed through the reaction of sugar and amino acids [30], blood contains proteins including hemoglobin, and green grass contains chlorophyll, which is combined with grana, a protein in chloroplasts. Current commercial detergents and the detergent used in this study contain oxygen bleach as well as protease, both of which require a little higher wash temperature and longer washing time to perform effectively. However, it is necessary first to put cold water in the washing machine and then to increase the temperature because a high temperature from the start may denature proteins. It is desirable to keep the wash temperature around 50 ^{o}C and lengthen the washing time to obtain the optimal effects of protease and bleach. Soil removal from the grass-stained cloth is poorest in this group; adding oxygen bleach will effectively increase the removal from this cloth.

Group III included cotton and PET/cotton cloths soiled with ketchup, cocoa, or clay and PET/cotton cloth soiled with red pepper, coffee, or make-up. Cocoa and clay are composed of insoluble particles. The red color of ketchup comes from lycopene ($C_{40}H_{56}$) in tomatoes. Lycopene is a linear polyunsaturated hydrocarbon that is composed of eight isoprene units [31], insoluble in water. The color of lycopene is red because it contains unconjugated double bonds, as shown in Figure 4(a). Lycopene is an oily material but is more hydrophilic than saturated hydrocarbons because of its double bonds. It is therefore presumed that the removal of lycopene, like the removal of insoluble particles of cocoa and clay, is affected by not only mechanical force but also temperature and time, which increase fiber swelling. Once the soil removal had reached its maximum amount, no further increase in soil removal even with increase in temperature, time, and the ratio of motion time to pause time; due to the negative interaction coefficients of temperature and time, and time and the ratio of motion time to pause time. The removal of the stains from the cloths in Group III was affected to some extent not only by temperature and time but also by drum speed and the ratio of motion time to pause time. However, the effect of temperature on this group was lower than on Groups I and II. In this group, the cotton cloths also had poorer soil removal than the soiled PET/cotton cloths. Thus, it is desirable to use a higher concentration of detergent for the soiled cotton cloths than the soiled PET/cotton cloths included in this group.

Group IV included the cotton cloth soiled with red pepper and cotton and the PET/cotton cloths soiled with tomato/beef sauce. The soiled cloths in this group were positively affected by the individual factors of drum speed and the ratio of motion time to pause time. They were also influenced by various interactions between washing factors. They were negatively influenced by the interaction effects related to the ratio of motion time to pause time. Interaction effects between temperature and time and between drum speed and time had a positive effect on them, even though the amounts were very small. The red pigment in the red pepper is primarily capsanthin ($C_{40}H_{56}O_3$), a kind of carotenoid that is highly unsaturated oil and contains hydroxyl groups [32], as shown in Figure 4(b). Therefore, it could be removed better than the oils in Group I and was removed particularly well at a lower temperature.

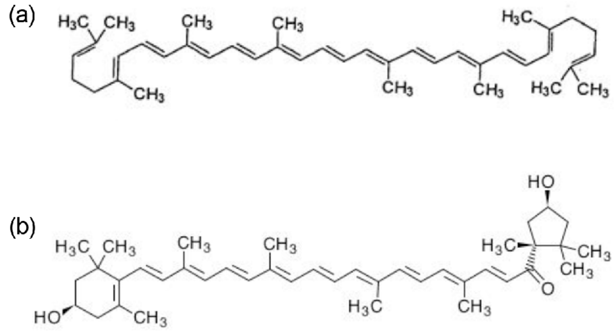

Figure 4. Chemical structures of (a) lycopene and (b) capsanthin.

Group V included the soiled cloths having the highest soil removal and all PET fabrics. The interaction factor of temperature and time, and the individual factor of temperature were the only significant factors contributing to the soil removal. Moreover, the coefficient values were very small. Washing at 20 ^{o}C was fully effective for soil removal from most cloths included in this group. The cotton cloth soiled with red wine have the lowest soil removal in this group. It was presumed this cotton cloth needed the interaction between temperature and time for effective stain removal, so this cloth was included in this group. Besides the washing factors for Group V, the red wine-soiled cotton cloth had to be washed in soft water using oxygen bleach with a multipurpose liquid detergent having a lower alkalinity to increase soil removal. This is because the color of anthocyanin in red wine strengthens as the alkalinity of the washing solution increases [33].

Conclusion

To propose washing machine programs that would effectively remove common stains from daily life, the effects of main washing factors on stain removal were determined using 15 different types of typical soiling materials on different cloths. Although some soiled cotton cloths showed effective soil removal even at a washing temperature of

20 °C, stains were removed less effectively from most cotton cloths than from PET/cotton and PET cloths. However, the removal of non-polar oily stains from PET cloth was poor. In the determined regression equations for the main washing factors affecting soil removal, a larger intercept indicated better soil removal and significantly smaller interaction effects. As for the standardized regression coefficients of main washing factors, washing temperature had the greatest effect on soil removal, followed by washing time, the ratio of motion time to pause time and drum speed had very small effects. Most of the interactional effects were negative. Clustering the results of stain removal based on main washing factors revealed that stain removal from cotton cloths soiled with oily materials was affected by temperature the most out of the investigated samples. Cotton cloths soiled with proteins were strongly affected by temperature and time and negatively affected by the interaction between these two factors. Soil removal of insoluble particles was affected by temperature and time, as well as by the ratio of motion time to pause time and drum speed. The removal of stains containing highly unsaturated oils was affected by the ratio of motion time to pause time, and cleaning of PET fabrics with relatively high soil removal was slightly affected by the interaction between wash temperature and time.

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