

# A New Laundering Method Using Aqueous Solution of High-polymer for Coating of Soiled Fabrics and Followed by Water Laundering

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## Abstract

A new laundering method was presented by the author, which may be named provisionally as "Polymer-coated Laundering Method", and by this method, a higher detergency than ordinal laundering methods, i. e. immersion of soiled fabrics in a solution of detergent, was attained. And this method have projected many interesting problems to the physical chemistry of detergency, and have broken the common and fixed idea about laundry and washing.

This laundering method was constructed from the following chief process; soiled fabrics were coated with a solution of high-polymer or the mixture of high-polymer and surfactant, then dried, and laundered in merely water. There were also many variations, for instance, laundering in a solution of detergent and the omission of the drying.

Fundamental conditions for this method, such as the amount of used high-polymer, laundering temperature, laundering time and the effect of surfactant were discussed with the soiled cotton fabrics. The effect of drying and its types was also discussed. Then the effect of this laundering method for hydrophobic fibers was compared with hydrophilic cellulosic fibers.

The obtained results of this method have driven off the fixed idea that soiled fabrics and garments must be laundered by the immersion of it in a solution of detergent or organic solvents, and it seems that there might be more variations of laundering method when high-polymers were effectively used.

## I. Introduction

Soiled fabrics and soiled garments are usually washed by the immersion in aqueous solution of detergent, or sometimes in organic solvents as the "dry-creaning". In the former case, however, there

is a great doubt why such abundant amount of detergents must be used in these washing bathes, for the most part of the detergents must be in the fur distance from the fabrics being washed, without any contribution to detergency, the first stage of which are generally thought as the adsorption of the detergent by the soiled fabrics.

From another point of view, water soluble high-polymers, especially sodium-carboxymethylcellulose (SCMC), are preferentially used as builders which are mixed with detergents for the purpose of increase the detergency of these detergents. This effect is usually thought owing to the electrolytic characteristics of SCMC, that is the repulsive force between the SCMC-adsorbed fabric and SCMC-adsorbed soil after the desorption of the soil from the fabric is attained.<sup>1)</sup>

There might be however a fundamental misunderstanding according to the authour's view, because such repulsive force is only the phenomenon at the stational state which comes after the soils have been separated from the fabrics, and there is no discussion about the first stage of the detergency, that is the cause of separation of soil from the fabrics.

Moreover there have been no literature about the detergency of these high-polymers alone, and this phenomenon is a so-called "blind site" of the discussion of detergency. When the detergency of the high-polymers was payed attention, not only electrolytic high-polymers, and also non-electrolytic high-polymers, such as methylcellylose (MC) and polyvinylalcohol-acetate (PVA-Ac), must be concerned in the field of washing.

From such many questions, the authour have discussed the behaviours of high-polymers in the deterging process, and presented a new laundering method, in which the aqueous solution of high-polymer was directly used onto the soiled fabric, followed by drying and then washing in water alone.

This idea of a new laundering method was already reported on the "Kogyo Kagaku Zasshi" in Japanese, and the name of this method was given provisionally as the "Polymer-coated Laundering Method"<sup>2)</sup>.

The chief processes of this method was as follows;

1) Soiled fabric was coated by or immersed in a solution of high-polymer. This solution could be the mixture of high-polymers and detergents, and this case was also called provisionally by the authour as the "Mixture-coated Laundering Method".

2) Soiled fabrics which were coated with high-polymer or the mixture were then dried in the open air. This drying could be omitted as shown later in III-4-2.

3) The dried fabrics were then washed in water alone. Of course this laundering bath could be aqueous solution of detergent, but there

was not so remarkable increase of detergency compared with water laundering.

With this new laundering method, the authour have been able to attain wonderful detergency, which was much higher than that of the ordinal method i. e. laundering of soiled fabrics directly in a solution of detergent. The chief results were reported in the following section of this article.

This study must project many leading and interesting problems to the field of detergency, detergent and high-polymer, and have driven the fixeds idea that soiled fabrics and garments must be washed by the immersion in a solution of detergent or in organic solvent.

But there were left some questions on the stand-point of physical chemistry of detergency, for instance, why this method showed so high detergency, how the polymer and soil were adsorbed or attached during the drying procedure, how these mixture were dried on the fabrics, and what role was performed by the mixed detergent.

## II. Materials and Methods

### 1. Soiled Fabrics

In a greater part of experimentals, soiled fabrics were prepared according to the "Temporary Test Method for Evaluating of Detergency" by the Japan Oil Chemists' Society, which was a thin cotton shirting soiled artificially by the immersion in the mixture of 0.4~0.6 g of carbonblack, 1.5 g of hardened beaf fat, 0.5 g of liquid paraffin and 400 g (250 cc) of carbon-tetrachloride, and the surface refractive indices were prepared in the range of 28~32% by the magneciumoxide scale<sup>3)</sup>.

To evaluate the detergency for other fibers than cotton, other fabrics made of several kinds of fibers were also used as the original fabrics, though the soiling method and the soiling mixture were mostly

Table 1. Construction of Used Fabrics.

Fiber	Fabric	Yarn		Density/cm		Thick-ness mm	Weight g/100 cm <sup>2</sup>	Surface Ref. Index
		W	F	W	F			
1. Cotton*	Shirting*	60	60	42	35	0.19	0.76	78.0
2. Cotton	Tussore	40	40/2	40	20	0.34	1.84	79.5
3. Rayon(F)	Taffeta	120d	120d	36	24	0.17	0.86	83.6
4. Teton(S)	Sheeting	40	40	27	26	0.39	1.74	78.4
5. Teton(F)	Taffeta	100d	100d	45	31	0.16	0.95	81.0
6. Vonnel(S)	Sheeting			21	18	0.45	1.74	71.2
7. Alon(S)	Tropical	52/2	52/2	24	19	0.36	1.78	78.1

\* base fabric of the test method of J. O. C. S.

4. 5. polyester fiber, 6. polyacrilic fiber, 7. acetylated viscose rayon

the same as the case of above mentioned test method.

But in some cases, the dispersing medium for carbonblack was replaced with water, and in other cases the amounts of the components of the artificial soils were widely changed from the test method<sup>3)</sup>.

### 2. *Applying Aqueous Solution of High-polymer*

The soiled fabrics were cut in  $5 \times 10$  cm pieces, and were pinned to a frame, then the known volume of the aqueous solution of high-polymer up was dropped on these test pieces of fabrics homogenously.

Mixed solutions of high-polymer and surfactant was also used for this purpose as described in I. Introduction. And in most experiments, same volume of water alone was dropped as a blank test.

These fabrics were then dried in the open air, except in the case of the experiment of III. 4-2, which was performed to find the effect of drying comparing with that without drying.

Table 2. High-polymers Used and Their Abbreviations.

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1.	MC—Methylcellulose, Degree of Sustitution (DS) was ca. 1.8
2.	PVA—Polyvinylalcohol, Degree of Polymerisation (DP) was 1100 and other
3.	PVA-Ac — Polyvinylalcohol-acetate, acetyl-group was 11.02 mole % left, D. P. 500 and other
4.	PVAc-MA—Sodium-salt of co-polymer of vinylacetate and maleic anhydride, D. P. ca. 600
5.	PVM—Polyvinylmethylether,
6.	PVM-MA—Co-polymer of vinylmethylether and maleic anhydride
7.	SA—Sodium-alginate, D. P. 153
8.	SCMC—Sodium-carboxymethylcellulose, D. S. 0.45, D. P. 245 and others
9.	Starch—Corn starch, starching temperature $93 \sim 95^\circ\text{C}$

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Table 3. Surfactant Used and Their Abbreviations.

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1.	Soap—Sodium soap, Commercial
2.	SDS—Sodium-laurylsulfate,
3.	SDBS—Sodium-dodecylbenzenesulfate
4.	POEOP—Polyoxyethylene-octylphenoether, D. P. of oxyethylene ca. 5~20
5.	POENP—Polyoxyethylene-nonylphenoether, D. P. of oxyethylene ca. 5 and 20
6.	POEL—Polyoxyethylene-laurylether, D. P. of oxyethylene ca. 15, and H. L. B. 15.6, cloud point $88 \sim 92^\circ\text{C}$

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### 3. *Evaluation of Detergency*

Laundering tests was carried out by the Launder-Ometer of Atlas Co., using 500 cc bottle. Each test piece was separately put into each bottle, then added 100 cc of water or a solution of detergent previously warmed at given temperature, and then the machine was driven for definite time.

After the washed pieces were dried, their surface refractive indices  $R_w$  were measured, and using the original refractive indices  $R_0$  and

those of the soiled fabrics  $R_s$ , deterative efficiencies (D%) were calculated with the following equation.

$$D\% = (R_w - R_s) / (R_0 - R_s) \times 100$$

Time for laundering was usually 20 minutes, and temperature for laundering was 40°C were adopted in most cases, but other conditions were also tried accordingly the purpose of experiments. However the size of fabric and the volume of laundering bath were maintained as the same throughout all experiments.

In all experiments, two and three test pieces were put into the same condition respectively, and all pieces of one experiment were randomized their order to be laundered and measured their reflectances. And then at last, the obtained deterative efficiencies (D%) were analyzed by statistics, and the significants of each element and mean errors of the experiments were calculated.

Two asterisks\*\* in foot notes of the tables of experiments mean the effects of elements and interactions of these elements at 95% reliance, and one asterisk\* shows that of at 90% reliance. And  $\hat{\sigma}$  indicates the mean errors of these experiments.

### III. Experiments and Results

#### 1. Survey of the Polymer-coated Laundering Method Comparing with the Laundering in the Solution of High-polymer

Specimens of the soiled cotton fabrics (No. 1 of Table 1) of the same lot were put into the same experiment, but half of them were coated with ten kinds of the solution of high-polymer (Table 2) and then after drying in the open air, laundered with water alone ( $M_1$  of Table 4), and the other half of them were immediately washed with the solution of these high-polymers, containing 0.01 and 0.1 g of high-polymer in 100 cc water ( $M_2$ ). The amount of the applied high-polymer in the case of  $M_1$  were 0.01 and 0.1 g respectively, namely same amounts of high-polymers were used in both cases, laundering temperature was 40°C, and washing time was 30 minutes (Table 4).

1) Generally speaking, the detergency of the polymer-coated laundering method  $M_1$  was higher than that of showed by the solution method  $M_2$ , especially when such electrolytic high-polymers as SCMC and PVAc-MA were used as the coating polymer. These detergencies were moreover much higher than that of the ordinal laundering used soap-solution, as showed at the footnote of the above Table 4.

2) Some kinds of high-polymers, such as Starch and MC, made lower the detergency when used for the polymer-coated laundering

Table 4. Detersive Efficiency (%) of the Polymer-coated Laundering Method with Water and That of Non-coated Fabrics Laundered with the Solutions of High-polymer.

Method Polymer	M <sub>1</sub> Polymer-coated			M <sub>2</sub> in Polymer Solution		
	Amount C <sub>1</sub> 0.01 g	C <sub>2</sub> 0.1 g	Mean	C <sub>1</sub>	C <sub>2</sub>	Mean
P <sub>1</sub> Starch	19.7	12.9	16.3	21.2	21.7	21.5
P <sub>2</sub> MC	18.0	0.6	9.3	12.2	14.9	13.6
P <sub>3</sub> PVA	21.0	11.6	16.3	19.1	27.5	23.3
P <sub>4</sub> PVA-Ac	31.1	33.3	32.2	22.4	38.2	30.3
P <sub>5</sub> PVM	32.5	37.8	35.2	17.5	42.8	30.2
Mean of non-electrolytic high-polymer	24.5	19.2	21.9	18.5	29.0	23.8
P <sub>6</sub> SCMC	63.2	68.2	65.7	17.8	39.9	28.9
P <sub>7</sub> SCM-Starch	21.0	27.1	24.1	25.5	30.1	27.8
P <sub>8</sub> SA	45.0	48.1	46.6	27.4	28.0	22.0
P <sub>9</sub> PVAc-MA	64.8	64.5	64.7	17.1	22.0	19.7
P <sub>10</sub> PVA-MA	27.7	23.9	25.8	11.2	24.0	17.6
Mean of electrolytic high-polymer	44.3	46.4	45.4	19.8	26.5	23.2

cf. Detersive efficiency % of non-coated fabric in water 19.8%,  
in 0.3% soap solution 36.2%  
Significants of elements; \*\*M, P, C, M×P, M×C, P×C, M×P×C,  $\hat{\sigma}=5.40$

method, and this result must be owed to the low solubilities of these polymers into water after the drying on the soiled fabrics. Then the more the amount of these polymers were used, the lower the detergency.

3) The values of detergencies of M<sub>2</sub> could be thought as deterging powers of these high-polymers when used similarly as detergent in ordinal washing, where solutions of detergent are used in which soiled fabrics are immersed. And by this method M<sub>2</sub>, electrolytic character of the high-polymer did not affect the final detergency, while the amount of the high-polymer was a big factor to increase the detergency.

## 2. Fundamental Conditions of the Polymer-coated Laundering Method

### 2-1. The Amount of High-polymer and the Washing Temperature

Cotton fabrics were soiled by II-1 and coated with 1 cc of solutions of high-polymer having different concentrations, for changing the coated amount of high-polymer, and after drying in the open air, laundered in merely water at 20, 40 and 60°C for 20 minutes (Table 5).

1) The increased amount of the used high-polymer increased the detergency, except in the case of using starch and MC, in which the effects of the amount showed reverse tendencies as already expected

Table 5. Deterstive Efficiency (%) of the Polymer-coated Laundering Method and Laundering Temperature.

Washing Temp. Amount	T <sub>1</sub> 20°C		T <sub>2</sub> 40°C		T <sub>3</sub> 60°C		mean	
	P <sub>1</sub> SCMC	P <sub>2</sub> SA	P <sub>1</sub>	P <sub>2</sub>	P <sub>1</sub>	P <sub>2</sub>	P <sub>1</sub>	P <sub>2</sub>
C <sub>1</sub> 0.0625 × 10 <sup>-2</sup> g	22.6	13.4	31.1	22.5	37.1	22.2	30.3	19.4
C <sub>2</sub> 0.125	27.6	26.1	34.5	27.6	30.9	27.5	31.0	27.4
C <sub>3</sub> 0.25	23.6	28.7	31.6	30.6	41.4	32.0	32.2	30.4
C <sub>4</sub> 0.50	32.7	36.0	48.9	40.8	50.9	57.3	44.2	44.7
C <sub>5</sub> 1.0	49.8	51.6	65.0	54.5	74.0	67.0	62.9	57.7
mean	31.3	31.2	42.2	35.4	46.8	41.2	40.1	35.9
mean of T	31.2		38.8		44.0		38.0	

\*\* P, C, T  $\hat{\sigma}$ =5.09

Table 6. Deterstive Efficiency (%) of the Polymer-coated Laundering Method and the Amount of High-polymer.

Washing Method Polymer Amount g	M <sub>1</sub> Polymer-coated in Water				M <sub>2</sub> in Polymer-solution			
	C <sub>1</sub> 0.005	C <sub>2</sub> 0.01	C <sub>3</sub> 0.05	mean	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	mean
P <sub>1</sub> Starch	17.5	16.6	15.9	16.7	14.8	21.8	21.6	19.7
P <sub>2</sub> MC	8.6	8.8	4.2	7.2	10.9	12.8	17.6	13.8
P <sub>3</sub> PVA-Ac	17.4	26.8	35.5	26.6	21.1	26.5	28.1	25.2
mean of non-electrolytic polymer	14.5	17.4	18.5	16.8	15.6	20.2	23.7	19.6
P <sub>4</sub> SCMC	32.4	65.4	72.4	56.7	21.0	24.3	29.5	23.6
P <sub>5</sub> SA	44.0	51.4	72.2	55.9	18.6	21.3	23.4	21.1
P <sub>6</sub> PVAc-MA	36.0	58.8	73.8	56.2	22.9	21.5	21.2	21.9
mean of electrolytic polymer	36.7	58.5	72.8	56.3	20.8	22.4	24.7	22.2

c. f. D% of ordinal laundering in water 20.4% in 0.3% soap solution 37.4%

\*\* M, P, C, M×P, M×C, P×C, M×P×C,  $\hat{\sigma}$ =1.58

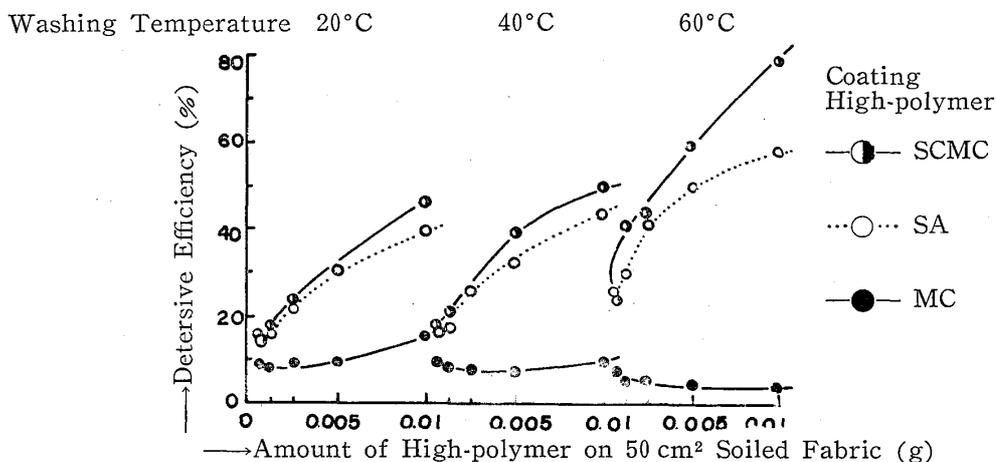


Fig. 1. Deterstive Efficiency of Polymer-coated Laundering Method and Washing Temperature and the Amount of High-polymer.

from the result of Table 4, and their detergencies were rather lower than that of merely water laundering of the non-coated soiled fabrics.

2) Higher temperature for laundering assisted the detergency usually as the result of increased solubility of high-polymer, but when MC was used, an increase of the temperature showed a negative effect, which was expected from the characteristics of its solubility.

## 2-2. Time for Laundering

The specimens (II-2) of soiled cotton fabrics were coated with 0.01 g of SCMC or MC, and after drying, laundered in water. And in the same experimental test equal numbers of non-coated specimens were also laundered in 0.01% of solutions of these high-polymers. Times of laundering were 5~30 minutes at 40°C.

1) Elongation of the laundering time for the polymer-coated laundering method ( $M_1$ ) did not so increase the detergency and some

Table 7. Effect of Laundering Time on the Detergency.

Washing Method		$M_1$ Polymer-coated and in Water			$M_2$ Non-coated in Polymer-solution		
		P <sub>1</sub> SCMC	P <sub>2</sub> MC	Diff. P <sub>1</sub> -P <sub>2</sub>	P <sub>1</sub>	P <sub>2</sub>	Diff.
T <sub>1</sub>	5 min	66.6	12.3	54.3	20.6	11.6	9.0
T <sub>2</sub>	10	66.0	16.6	49.4	19.9	18.7	1.2
T <sub>3</sub>	15	77.6	16.9	60.7	25.8	22.0	2.8
T <sub>4</sub>	20	73.1	20.1	53.0	33.1	26.5	6.6
T <sub>5</sub>	30	72.5	20.9	51.5	40.1	26.7	13.4
mean		71.2	17.3	53.9	27.9	21.1	6.8

\*\* M, P, T, M×P,  $\hat{\sigma}=2.77$

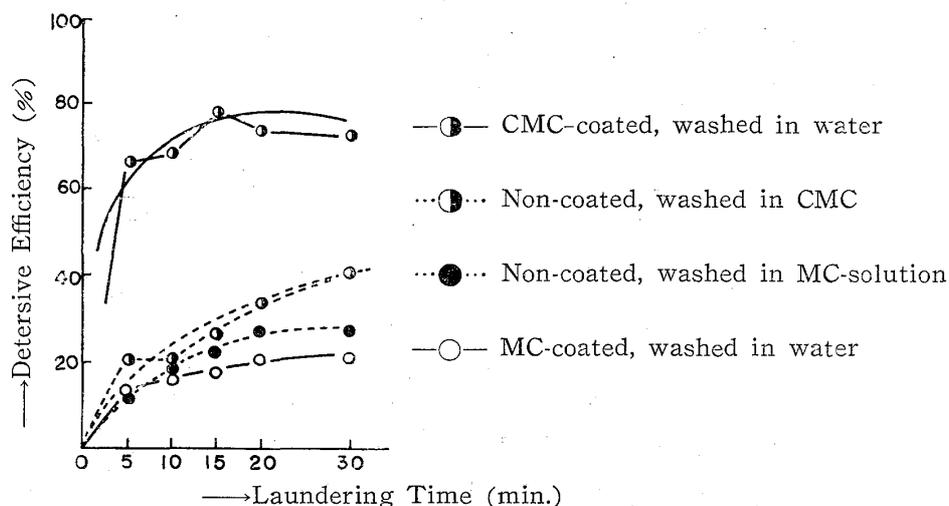


Fig. 2. Detergent Efficiency of the Polymer-coated Laundering Method and Washing Time.

equilibrium came soon after in about 15~20 minutes.

2) By the laundering in the solutions of high-polymer, however, the longer the washing time, the higher the detergencies. This phenomenon could be due to the slowness of the adsorption of high-polymer onto the fabrics from the solutions.

### 3. Effects of the Use of Surfactants for this Laundering Method

#### 3-1. Various Types of the Use of Detergent

The following 16 types of laundering tests, which were the combinations of four types of fabrics to be laundered and four types of washing bathes, were performed to find the effects of detergent by various using methods. SCMC as high-polymer and sodium-soap as detergent were used (Table 8).

Washed Fabric	Washing Solution
M <sub>1</sub> D <sub>1</sub> —Soiled fabric+Polymer	P <sub>1</sub> W <sub>1</sub> —Water alone
M <sub>1</sub> D <sub>2</sub> —Soiled fabric+Mixture of Polymer and Detergent	P <sub>1</sub> W <sub>2</sub> —Solution of Detergent
M <sub>2</sub> D <sub>1</sub> —Soiled fabric alone	P <sub>2</sub> W <sub>1</sub> —Solution of High-polymer
M <sub>2</sub> D <sub>2</sub> —Soiled fabric+Detergent	P <sub>2</sub> W <sub>2</sub> —Mixed solution of High-polymer and Detergent

Table 8. Detersive Efficiency (%) of Various Combinations of SCMC and Soap.

Solution for coating Washing Solution	M <sub>1</sub> Polymer-coated			M <sub>2</sub> Polymer was not coated		
	D <sub>1</sub> Polymer	D <sub>2</sub> Polymer + Soap	Diff. D <sub>2</sub> -D <sub>1</sub>	D <sub>1</sub> Water	D <sub>2</sub> Soap	Diff. D <sub>2</sub> -D <sub>1</sub>
P <sub>1</sub> SCMC absent W <sub>1</sub> Water	46.9	61.4	14.5	13.6	49.7	36.1
W <sub>2</sub> Soap	60.4	57.4	-3.0	29.0	37.7	8.7
P <sub>2</sub> SCMC present W <sub>1</sub> SCMC	48.3	59.4	11.1	20.2	55.0	34.8
W <sub>2</sub> SCMC + Soap	61.1	49.3	-11.8	30.8	50.8	20.0
mean	54.2	56.9	2.7	23.4	48.3	24.9

amount; M, D...high-polymer 0.01 g, detergent 0.1 g on fabric

P, W...high-polymer 0.03 g, detergent 0.3 g in each 100 cc of water.

\*\* M, D, W, M×D, M×P, D×W, M×D×P, \* P,  $\hat{\sigma}=3.45$  (repeated no. 3)

1) Laundering of the SCMC-coated fabrics in a soap solution showed higher detergency than that in water alone, but when washed in SCMC solution, detergency was almost equal as that in water.

2) Soiled fabrics coated with a solution of soap and dried could be also deterged more easily than the ordinal laundering method (M<sub>2</sub>D<sub>1</sub>-P<sub>1</sub>W<sub>2</sub>), but the detergency of the former was rather lower than those of fabrics coated with SCMC.

3) The application of the mixed solution containing SCMC and

soap for the soiled fabrics could increase the detergency, but when these fabrics were laundered in the mixed solution of SCMC and soap, their detergency decreased.

### 3-2. Laundering of the Soiled Fabrics Coated with Polymer Solution in Solutions of Detergent

The effect of the laundering in a solution of soap was compared with that in water alone.

The soiled cotton fabrics were coated with the solution of SCMC or PVA-Ac having three levels of degree of polymerization (DP) respectively, and after the drying, laundered in water or in 0.3% soap solution at 40°C for 30 minutes (Table 9).

Table 9. Effect of the Degree of Polymerization of High-polymer with which the Soiled Fabrics were Coated.

Washing Method		M <sub>1</sub> Polymer-coated			M <sub>2</sub> Polymer was not coated		
Washing Solution		W <sub>1</sub> Water	W <sub>2</sub> Soap	Diff. W <sub>2</sub> -W <sub>1</sub>	W <sub>1</sub>	W <sub>2</sub>	Diff.
Polymer	D. P.						
P <sub>1</sub> SCMC	452	38.8	56.6	17.8	21.7	34.6	12.9
P <sub>2</sub> „	580	51.1	64.2	13.1	23.0	31.8	8.8
P <sub>3</sub> „	687	56.5	64.2	7.7	25.3	33.9	8.6
mean		48.8	61.7	12.9	23.3	33.4	10.1
P <sub>4</sub> PVA-Ac	500	29.2	40.3	11.1	25.5	28.9	3.4
P <sub>5</sub> „	1100	27.1	43.6	16.5	18.1	27.6	9.5
P <sub>6</sub> „	2000	22.3	46.3	24.0	19.3	27.5	8.2
mean		26.2	43.4	17.2	21.0	28.0	7.0
P <sub>0</sub> none		13.6	29.0	15.4	13.6	29.0	15.4

amount of high-polymer; on the fabric; M<sub>1</sub> 0.01 g, M<sub>2</sub> 0 g  
 laundering bath; M<sub>1</sub>W<sub>1</sub> 100 cc of water alone, M<sub>1</sub>W<sub>2</sub> 0.3% soap solution  
 M<sub>2</sub>W<sub>1</sub> 0.03% polymer solution  
 M<sub>2</sub>W<sub>2</sub> mixed solution containing 0.3% soap and 0.03% polymer

1) The detergency in the solution of soap was higher than that in water in every cases, and this tendency was more clear when the SCMC of low DP and the PVA-Ac of high DP were used for the polymer-coated laundering method.

2) The differences of the detergencies between soap laundering (P<sub>0</sub>W<sub>2</sub>) and mixed solution laundering (P<sub>1~6</sub>, M<sub>1</sub>-W<sub>2</sub>) should be understood as the builder effects of these high-polymers, and these values were not so high. And the single effect of high-polymers in the laundering solution, that is the differences between P<sub>1~6</sub>, M<sub>2</sub>-W<sub>1</sub> and P<sub>0</sub>W<sub>1</sub>, was much higher, though the effect was much smaller than that when

the high-polymers were used as the polymer-coated laundering method M<sub>1</sub>.

### 3-3. Type and Concentration of the Detergents in Laundering Solution.

The soiled cotton fabrics were coated with the solutions of high-polymer and laundered in the solution of soap (Table 10) and in the solution of SDS or SDBS (Table 11), having various concentrations, at 40°C for 20 minutes. The amount of high-polymers on the fabric was 0.01 g respectively except the blank test P<sub>1</sub> of both experiments.

Table 10. Deterative Efficiency (%) of the Polymer-coated Fabrics and the Concentrations of Soap in Laundering Bath.

Conc. of Soap		Polymer	P <sub>1</sub> none	P <sub>2</sub> SCMC	P <sub>3</sub> PVA-Ac	mean
C <sub>1</sub>	0 %		17.2	48.6	29.0	31.6
C <sub>2</sub>	0.0125		30.0	48.9	30.8	36.6
C <sub>3</sub>	0.025		32.3	51.8	31.7	38.6
C <sub>4</sub>	0.05		35.0	50.1	31.1	38.7
C <sub>5</sub>	0.10		32.0	56.1	35.1	41.1
C <sub>6</sub>	0.25		33.9	65.6	41.6	47.0
mean			30.1	53.5	33.2	38.9

\*\* P, C, P×C,  $\hat{\sigma}=2.44$  (repeated numbers 3)

Table 11. Deterative Efficiency (%) of the Polymer-coated Fabrics and the Concentrations of Detergents in Laundering Bath.

Surfactant	Polymer		P <sub>1</sub> none	P <sub>2</sub> SCMC	P <sub>3</sub> PVA-Ac	mean
	Conc.					
W <sub>1</sub> SDS	C <sub>1</sub>	0 %	15.3	50.5	24.2	30.0
	C <sub>2</sub>	0.05	23.4	48.2	25.0	32.1
	C <sub>3</sub>	0.10	26.2	49.2	27.3	34.3
	C <sub>4</sub>	0.25	27.7	50.3	32.5	36.8
mean			23.1	48.8	27.3	33.3
W <sub>2</sub> SDBS	C <sub>1</sub>	0 %	15.3	50.5	24.2	30.0
	C <sub>2</sub>	0.05	15.6	50.1	25.6	30.4
	C <sub>3</sub>	0.10	19.5	50.7	30.0	33.4
	C <sub>4</sub>	0.25	28.2	52.6	32.7	37.8
mean			19.7	51.0	28.1	32.9
mean of all			21.4	50.3	27.7	33.1

\*\* P, C, P×W,  $\hat{\sigma}=3.31$  (repeated numbers 3)

1) Laundering in the solution of soap showed higher detergency than that in water alone for both high-polymers, and this effect was

not come from merely the effect of the concentration of soap as recognized by the values of  $P_1$ .

2) With the solutions of synthetic detergents, however, CMC-coated fabrics could not increase their detergency with the increase of the amount of the detergents. By the PVA-Ac-coated fabrics some increases of the detergency were appeared, but this effect was much smaller than that when they were laundered in the solution of soap.

#### 4. Applying the Mixed Solution of High-polymer and Surfactant on the Soiled Fabrics Followed by Water Laundering

##### 4-1. Amount of High-polymer and Surfactant for the Coating of the Soiled Cotton Fabrics

SCMC and PVA-Ac were selected as the applying high-polymer, and their final amount on the soiled fabrics was chosen as 0.01 g

Table 12. Detersive Efficiency (%) of the Soiled Cotton Fabrics Coated with the Mixture of High-polymer and Surfactant.

Polymer		$P_1$ none	$P_2$ SCMC	$P_3$ PVA-Ac	mean
Surfactant	Amount				
D <sub>1</sub> Soap	C <sub>1</sub> 0 g	19.7	59.6	28.1	35.8
	C <sub>2</sub> 0.0125	30.1	56.4	35.2	40.6
	C <sub>3</sub> 0.025	31.2	57.5	38.0	42.2
	C <sub>4</sub> 0.05	31.5	64.2	41.1	45.6
	C <sub>5</sub> 0.10	31.5	66.6	44.4	47.5
	C <sub>6</sub> 0.20	33.4	64.8	44.9	49.4
	mean		29.6	61.5	39.4
D <sub>2</sub> SDS	C <sub>1</sub> 0 g	16.9	53.6	25.5	32.0
	C <sub>2</sub> 0.0125	20.5	46.7	21.6	29.6
	C <sub>3</sub> 0.025	21.5	46.0	20.1	29.2
	C <sub>4</sub> 0.05	23.6	46.9	18.9	29.8
	C <sub>5</sub> 0.10	27.5	46.5	17.4	29.7
	C <sub>6</sub> 0.20	27.5	48.1	15.0	30.2
	mean		22.5	48.0	19.8
D <sub>3</sub> SDBS	C <sub>1</sub> 0 g	21.7	57.8	23.0	34.2
	C <sub>2</sub> 0.0125	26.4	49.0	25.3	33.6
	C <sub>3</sub> 0.025	29.7	49.7	29.2	36.2
	C <sub>4</sub> 0.05	31.5	55.6	31.0	39.4
	C <sub>5</sub> 0.10	31.5	56.3	41.5	43.1
	C <sub>6</sub> 0.20	30.4	59.2	44.0	44.5
	mean		28.5	54.6	32.3
mean of all		26.9	54.7	30.5	37.4

\*\* P, D, C, P×D, P×C, D×C,  $\hat{\sigma}=1.75$  (repeated numbers 3)

respectively. Surfactants were soap, SDS and SDBS, and combined solutions of the mixture of high-polymer and surfactant were prepared, and then dropped onto specimens of the soiled fabrics respectively, and after drying in the open air laundered in water alone at 40°C for 20 minutes (II-3). The final amounts of the surfactants on the specimens were prepared as 0~0.20 g per each specimen (Table 12).

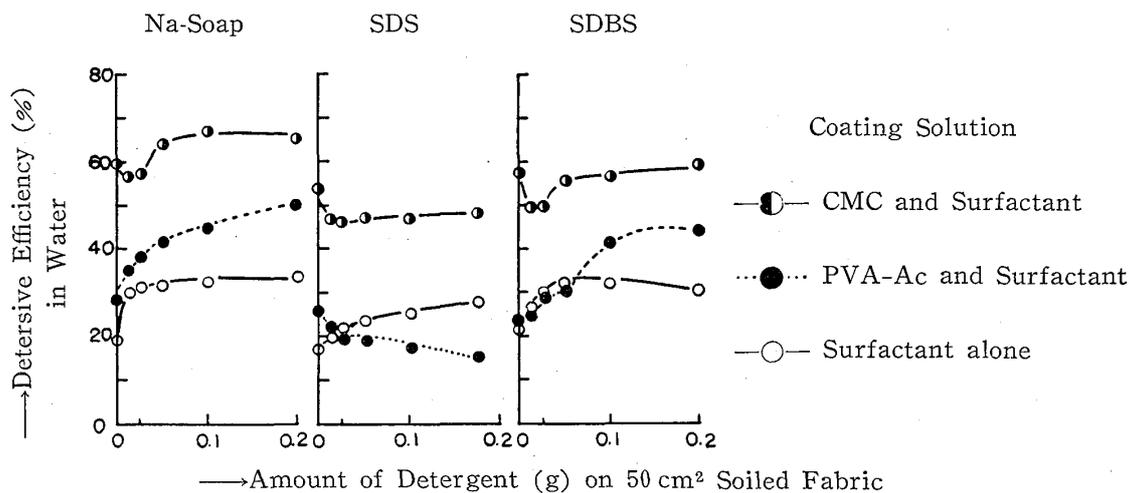


Fig. 3. Deteritive Efficiency of the Polymer-coated Laundering Method and the Amount of Mixed Detergent.

1) The application of the mixture of high-polymer and surfactant could not always increase the detergency of this polymer-coated laundering method, and by the mixed coating with SDS and high-polymer, the detergencies were rather decreased in comparison with that when these polymers were merely used. Moreover the detergency of the fabrics coated with SDS and PVA-Ac was much lower than that of the case in which only SDS were coated.

2) For PVA-Ac the increasing amount of soap and SDBD made higher the detergency, but for SCMC it had not so much effect, except when rather high amount of detergent, such as 5 times to SCMC, were used. While when the fabrics were coated with these surfactants solution alone, the amount of these surfactants was not so big factor.

Figure 3 shows the same data as the Table 12.

A similar experiment was carried out by changing the amount of high-polymers, i.e. from 0.005 to 0.02 g, and the amount of the surfactants was fixed as 0.05 g on each specimen of the soiled fabrics. After being coated with the mixed solution and dried, fabrics were laundered in water alone at 40°C for 20 minutes (Table 13).

3) The amount of high-polymer on the soiled fabrics did not greatly vary the detergency in the range taken in this experiment,

but in the case of with SDS, its effect was relatively higher than those of with soap and SDBS

4) With PVA-Ac the increase of its amount gave the lower detergency by the combination with soap and SDBS, while made higher when mixed with SDS, but this phenomenon was the same as the result of the last experiment (Table 12) concerning the ratio of the high-polymer and surfactant.

#### 4-2. The Effect of Drying of the Coated Fabrics on the Detergency

High detergency of this polymer-coated laundering method was seemed to due chiefly to the occlusion of the soil on the fabrics by the forming gel structure of high-polymer during the drying process. And if this assumption was proper, the detergency without drying must be much lower than that with drying as adopted in all experiments above.

The soiled cotton fabrics which were coated with polymer solution or mixed solution of polymer and soap were laundered, but half of them were washed after the drying in the open air overnight, and the other half of them were laundered after the overnight keeping in such wet air as 95% R.H. preventing the drying. The amount of polymer on the fabrics was 0.01 g, and that of soap was 0.05 g respectively.

Table 13. Detergent Efficiency (%) of the Soiled Cotton Fabrics Coated with the Mixture of High-polymer and Surfactant.

Surfactant	Polymer Name	Amount			mean
		C <sub>1</sub> 0.005 g	C <sub>2</sub> 0.01 g	C <sub>3</sub> 0.02 g	
D <sub>1</sub> Soap	P <sub>1</sub> SCMC	52.3	51.0	53.0	52.1
	P <sub>2</sub> SA	40.3	39.6	44.2	41.4
	P <sub>3</sub> PVA-Ac	38.7	36.1	29.2	34.7
	P <sub>4</sub> MC	36.7	45.5	43.1	41.8
	mean	42.0	43.1	42.4	42.5
D <sub>2</sub> SDS	P <sub>1</sub> SCMC	39.3	41.7	46.9	42.4
	P <sub>2</sub> SA	33.6	36.8	38.4	36.3
	P <sub>3</sub> PVA-Ac	11.7	17.2	18.1	15.7
	P <sub>4</sub> MC	16.9	19.7	25.9	20.8
	mean	25.4	28.9	32.3	28.5
D <sub>3</sub> SDBS	P <sub>1</sub> SCMC	48.5	46.5	47.2	46.1
	P <sub>2</sub> SA	31.9	31.1	34.9	31.0
	P <sub>3</sub> PVA-Ac	24.1	22.5	22.8	23.1
	P <sub>4</sub> MC	13.2	17.1	23.7	18.0
	mean	29.4	29.4	32.2	30.4
mean of all		32.2	33.8	35.6	33.9

tively. All of those specimens were laundered in water alone at 40°C for 20 minutes (Table 14).

A similar experiment was performed with the fabrics coated with the mixed solution of the high-polymer and soap, but in this case the keeping in wet air was omitted, and in place of them, two conditions

Table 14. Deterstive Efficiency (%) of Polymer-coated Cotton Fabrics in Water With and Without Drying After the Coating.

Drying Polymer	E <sub>1</sub> Dried in the open air		E <sub>2</sub> Kept in 95% RH without drying		Diff. E <sub>1</sub> —E <sub>2</sub>	
	D <sub>1</sub> Polymer alone	D <sub>2</sub> Polymer and Soap	D <sub>1</sub>	D <sub>2</sub>	D <sub>1</sub>	D <sub>2</sub>
P <sub>1</sub> none	15.7	45.4	19.6	52.0	-3.9	-6.6
P <sub>2</sub> SCMC	45.1	79.1	29.1	58.9	15.9	20.2
P <sub>3</sub> SA	40.1	55.9	19.1	54.2	21.0	1.7
P <sub>4</sub> PVA-Ac	24.6	60.7	28.2	43.9	-4.6	16.8
P <sub>5</sub> MC	26.7	48.3	15.5	30.7	11.2	17.6
mean	30.4	57.9	22.3	47.9	7.9	9.9

\*\* E, P, D, E×P, P×D, E×P×D, \* E×D,  $\hat{\sigma}=1.68$

Table 15. Deterstive Efficiency (%) of the Cotton Fabrics Having Various Carriers after the Coating with the Mixture of High-polymer and Soap.

Drying Polymer	E <sub>1</sub> Without Drying	E <sub>2</sub> Dried in the open air	E <sub>3</sub> Dried by Heat	mean
P <sub>1</sub> none	14.3	14.6	22.1	17.0
P <sub>2</sub> SCMC	47.7	50.8	57.0	51.8
P <sub>3</sub> SA	28.1	37.2	25.6	30.3
P <sub>4</sub> PVA-Ac	31.2	28.7	20.0	26.6
P <sub>5</sub> MC	33.5	38.0	34.5	35.3
mean	30.9	33.8	31.8	32.2

amount of high-polymer on the fabric was 0.01 g, that of soap was 0.1 g

were added. One of them was the laundering soon after the coating with the mixed solution, and the other was the laundering after the heat drying in hot 120°C air for 10 minutes (Table 15).

1) In most combinations, the drying process could increase the detergency when polymers were used, except in the case in which PVA-Ac was alone applied on the fabrics, and the latter tendency was much clearer when dried by heat even though soap was mixed.

2) The negative effect of heating was also appeared by the case of SA and MC, but it was not happened by SCMC.

3) The fabrics coated with soap alone showed the highest detergency when kept in the wet air, but the heat drying did not injured

their detergency comparing with the natural drying.

#### 4-3. Type of Soils and the Detergency of this Method

In the above experiments, soiled fabrics were the standard one which was described as the test of JOCS in II-1. As the composition and amount of the artificial soil were big factors for detergency of the ordinal laundering, these factors would be more effective for the polymer-coated laundering method, because of the longer contact time between the soil and detergent, and of the presence of drying process where the occlusion of soil by high-polymer might be occurred.

Five kinds of soiled cotton fabrics were prepared by changing the oily materials and their amount in soiling bath, but the sort of this material was as the same as used in the standard soiling. These soiled fabrics were coated likewise with the solutions of high-polymer or the mixture of high-polymer and soap respectively, the amount of high-polymer on the fabric was 0.01 g, and that of soap was 0.05 g through all of this experiment. And after the drying in the open air, then laundered in water alone at 40°C for 20 minutes (Table 16). For comparison, ordinal laundering of the non-coated fabrics was also done with 0.3% soap solution, which were noted in the column of reference.

Table 16. Effect of the Type and Amount of Soil on the Detergent Efficiency (%) of the Polymer-coated Laundering Method.

Oily Material in Soiling Bath (g)			S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>4</sub>	S <sub>5</sub>
Polymer	Soap	Liquid Paraffin Beaf Fat	0 0	2.5 0	10.0 0	0 2.5	0 10.0
P <sub>1</sub> SCMC	D <sub>1</sub> Absent (Polymer alone)		81.9	77.4	60.6	15.0	21.3
	D <sub>2</sub> Polymer and Soap		57.7	78.8	75.5	29.1	57.9
P <sub>2</sub> PVAc-MA	D <sub>1</sub>		80.8	90.1	69.5	21.7	38.8
	D <sub>2</sub>		68.4	90.2	84.2	48.3	65.8
P <sub>3</sub> PVA-Ac	D <sub>1</sub>		37.4	30.5	34.0	12.6	13.7
	D <sub>2</sub>		40.5	66.6	70.2	37.0	43.9
P <sub>4</sub> MC	D <sub>1</sub>		22.0	20.0	12.6	6.5	8.7
	D <sub>2</sub>		33.6	69.7	63.8	26.2	24.8
P <sub>5</sub> none	D <sub>1</sub> (Water alone)		21.0	23.7	20.4	8.5	9.4
	D <sub>2</sub> (Soap alone)		32.9	60.3	74.5	37.4	44.0
cf. Washed in 0.3% Soap (Polymer was not coated)			26.8	48.0	47.1	42.7	52.2

amount of soils was the value in 400 g (250 cc) of carbon-tetrachloride

\*\* S, P, D, S×P, S×D, D×S, S×D×P,  $\hat{\sigma}=1.92$

1) The order of the effect of the high-polymers was almost the same as in the previous experiments, i. e. SCMC and PVAc-MA were more effective than MC and PVA-Ac in the case in which the

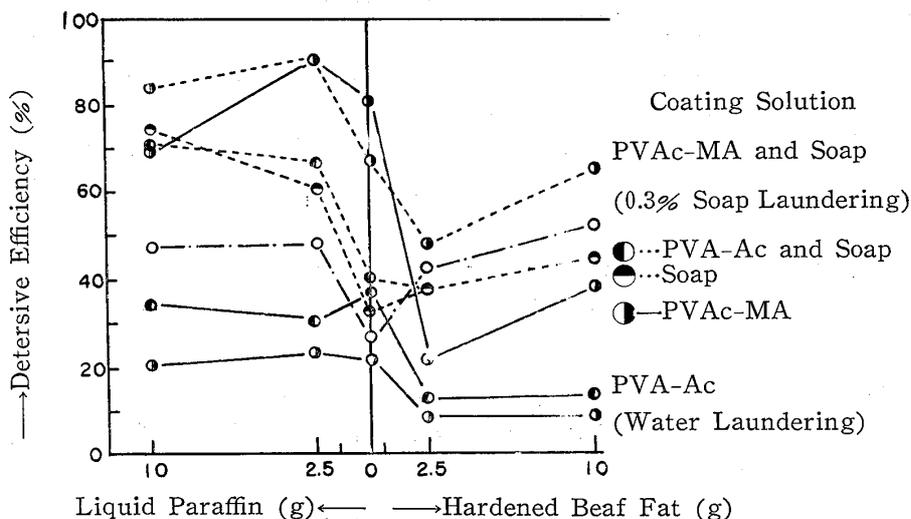


Fig. 4. Deteritive Efficiency and the Amount of Oily Materials in 250 cc of Soiling Medium.

polymers were alone used, but the increases of the detergency by the mixing of soap were performed relatively better when MC and PVA-Ac were used.

2) As the ordinal detergency, in which non-coated soiled fabrics were laundered in 0.3% soap solution, was low in the case of the fabrics on which merely the dry soil, i.e. carbonblack, was attached ( $S_1$ ), the detergency of the polymer-coated laundering method with SCMC or PVA-MA was much higher than that.

3) When liquid paraffin was used with carbonblack in the soiling mixture, ordinal detergency showed higher values than that when carbonblack alone was used, however the polymer-coated method could also perform much higher detergency than the former values.

4) While the presence of hardened beef fat in the soiling mixture, prevented the effect of the polymer-coated method, and there were not so remarkable detergency comparing with the ordinal laundering, even though soap was mixed.

5) The amounts of those oily materials scarcely changed the detergency of the polymer-coated laundering, and this result means that the oily materials were also occluded by the polymer which was coated on the fabrics.

#### 4-4. Applying Nonionic Surfactant with High-polymer

Nonionic surfactants must be also used for this laundering method, for they have laundering power according to their HLB values, and have adsorption characteristics to high-polymers<sup>4</sup>.

Six nonionic surfactants having various HLB values were chosen from the sample of No. 4 and 5 in the Table 3(II-2), and the soiled

fabrics of the standard cotton fabrics were coated with the solutions of them and the mixtures of surfactants and high-polymers. After the drying, the coated fabrics were laundered with water alone at 20 and 40°C for 20 minutes. The amount of high-polymer on each specimen was 0.01 g, and that of these surfactants was 0.05 g respectively (Table 17).

Table 17. Deterstive Efficiency (%) of the Polymer-coated Fabrics and the HLB of the Used Nonionic Surfactants.

Washing Temp.		T <sub>1</sub> 20°C			T <sub>2</sub> 40°C			
Surfactant	Polymer		P <sub>1</sub> none	P <sub>2</sub> SCMC	P <sub>3</sub> MC	P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>
	HLB							
S <sub>1</sub> POEOP	P=5	9.0	32.2	71.8	53.6	28.2	75.1	46.1
S <sub>2</sub> POENP	5	10.0	29.1	72.8	42.7	23.9	66.3	37.3
S <sub>3</sub> POEOP	10	12.6	45.3	59.0	53.1	50.6	62.6	44.5
S <sub>4</sub> POEOP	15	15.0	40.3	62.7	41.5	48.3	77.1	43.5
S <sub>5</sub> POENP	20	16.0	31.4	64.6	34.8	38.6	68.7	37.8
S <sub>6</sub> POEOP	20	16.8	26.6	62.6	40.9	32.1	73.4	33.6
mean			34.2	65.6	44.4	36.1	69.5	40.1
cf. D% of the ordinal water laundering					15.6	25.8		
D% in 0.2% S <sub>4</sub> solution					26.7	43.4		

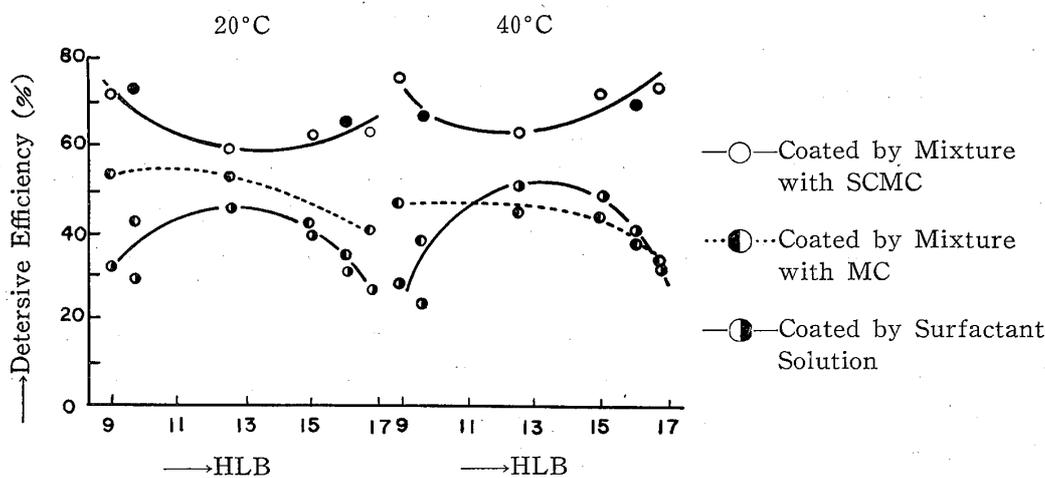


Fig. 5. HLB Values of Nonionic Surfactant and Deterstive Efficiency of the Polymer-coated Laundering Method.

1) When the surfactants were alone used for the coating (P<sub>1</sub>), the detergency of this method had its maximum value in the range of the HLB about 13~15 of the used surfactants, and this range was same as that when the surfactants were used for the ordinal laundering method.

2) However when SCMC was used with these surfactants, the detergency showed minimum value in that range, and with MC, the

detergency almost decreased according the HLB of surfactants.

Another experiment cited here was carried out using POEL (No. 6 in Table 3) to find the effect of the amount of nonionic surfactant when mixed with high-polymer for coating of the soiled fabrics. From 0 g to 0.1 g of it was coated with 0.05 g of high-polymer on each specimen, and after drying of fabrics, they were laundered in water at 20 and 40°C for 20 minutes (Table 18).

1) When the surfactant was alone coated, the detergency increased accordingly to the amount of the surfactant, this was very

Table 18. Detersive Efficiency (%) of the Polymer-coated Fabrics and the Amount of Used Nonionic Surfactant.

Washing Temp.	Polymer		P <sub>1</sub> none	P <sub>2</sub> SMC	P <sub>3</sub> PVA-Ac	P <sub>4</sub> MC	mean
	Amount of Surfactant	g					
T <sub>1</sub> 20°C	C <sub>1</sub>	0	11.5	62.6	15.0	16.7	26.5
	C <sub>2</sub>	0.0125	22.8	83.2	21.2	33.2	40.1
	C <sub>3</sub>	0.025	27.4	78.2	26.8	44.2	44.2
	C <sub>4</sub>	0.05	40.0	78.8	40.7	48.6	52.0
	C <sub>5</sub>	0.10	52.4	78.1	54.6	60.4	61.4
	mean			30.8	76.2	31.7	40.6
T <sub>2</sub> 40°C	C <sub>1</sub>		14.2	72.1	23.3	24.0	33.4
	C <sub>2</sub>		20.7	79.0	26.6	35.5	40.5
	C <sub>3</sub>		33.4	79.2	36.8	41.1	47.6
	C <sub>4</sub>		49.3	76.3	43.5	50.0	54.8
	C <sub>5</sub>		57.8	75.2	61.0	59.6	63.4
	mean			35.1	76.4	38.2	42.0

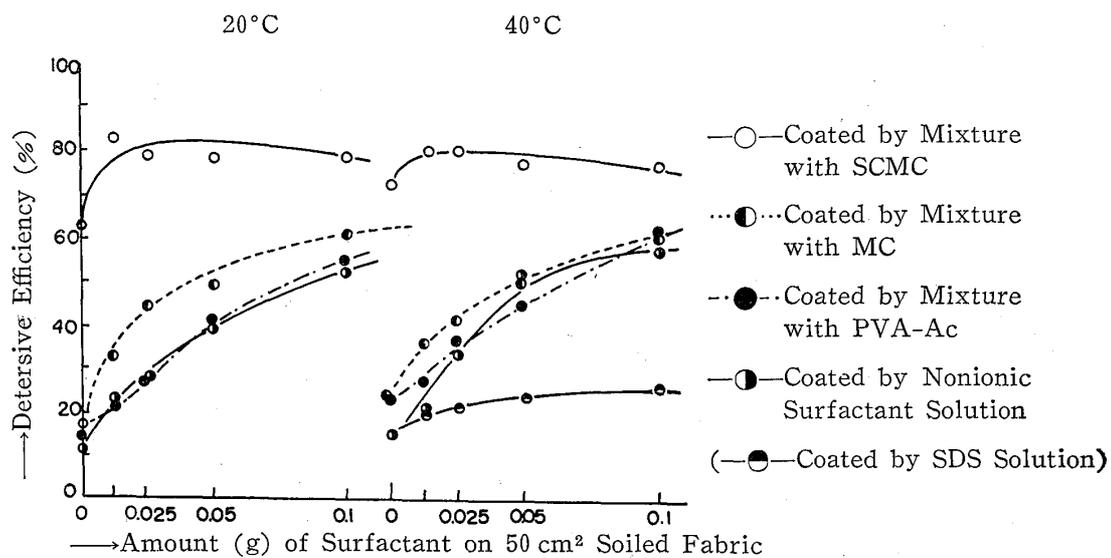


Fig. 6. Detersive Efficiency of the Polymer-coated Laundering Method and the Amount of Nonionic Surfactant on the Soiled Fabric.

different from the case of anionic surfactants (Table 12).

2) For the combination with SCMC, however, the effect of the amount of the surfactant did not appear, though the effect of the addition of the surfactant was recognized at 20°C laundering.

3) By the coating with the solution of the surfactant and MC, rather higher detergency was attained than that only the surfactant was coated. But with PVA-Ac there was no combination effect.

### 5. The Effect of this Laundering Method for Soiled Hydrophobic Fibers

All of the above mentioned experiments were carried out using cotton fabrics, so the swelling character and the adsorption of polymer solution by the fabrics were seemed to favourite this laundering method. While the soils on hydrophobic fibers, such as polyester fibers and polyacrylic one, would not be so easily separated, owing the lack of the adsorption of water which should help the adsorption of the soil by the fiber.

Then some experiments were tried using hydrophobic fibers, such as polyester fiber (Japanese trade name; Tetoron), polyacrylic fibers (Japanese trade name; Vonnell) and acetylated viscose rayon (Japanese trade name; Alon) comparing with cotton fabrics as the hydrophilic fiber.

#### 5-1. Fabrics Soiled by the Soiling Bath Using Carbon-tetrachloride as the Dispersing Medium for Carbonblack

Soiled fabrics were prepared with the fabrics made from Tetoron, cotton and viscose rayon, and they were coated with the solution of high-polymer or the mixture of high-polymer and soap. All of these specimens were laundered in water alone at 40°C for 20 minutes (Table 19).

Another experiment was similarly performed for three kinds of hydrophobic fabric, changing only the amount of soap for the coat-

Table 19. Detersive Efficiency (%) of the Soiled Various Fabrics.  
(Part 1) Spun Yarn Fabrics

Fabrics Coating Solution Polymer	F <sub>1</sub> Cotton Tussore			F <sub>2</sub> Tetoron Sheeting			mean
	D <sub>1</sub> Polymer alone	D <sub>2</sub> Polymer and Soap	Diff. D <sub>2</sub> -D <sub>1</sub>	D <sub>1</sub>	D	Diff.	
P <sub>1</sub> none	8.3	27.2	18.9	-1.6	20.2	21.8	13.5
P <sub>2</sub> SCMC	21.1	50.6	29.5	0.9	43.0	42.1	26.4
P <sub>3</sub> SA	9.0	33.2	24.2	3.5	48.0	44.5	23.4
P <sub>4</sub> PVA-Ac	8.0	32.4	24.4	1.8	55.3	53.5	24.4
P <sub>5</sub> MC	-0.3	39.0	39.3	-0.7	51.4	52.1	22.4
mean	9.0	36.4	27.4	2.4	43.6	41.2	22.4

## (Part 2) Filament Yarn Fabrics

Fabrics Coating Solution Polymer	F <sub>1</sub> Rayon Taffeta			F <sub>2</sub> Tetoron Taffeta			mean
	D <sub>1</sub> Polymer alone	D <sub>2</sub> Polymer and Soap	Diff. D <sub>2</sub> -D <sub>1</sub>	D <sub>1</sub>	D <sub>2</sub>	Diff.	
P <sub>1</sub> none	16.2	74.7	58.5	3.8	27.9	24.1	30.6
P <sub>2</sub> SCMC	52.6	82.0	29.4	13.1	21.3	8.2	42.3
P <sub>3</sub> SA	40.2	79.0	38.8	9.1	21.7	12.6	37.5
P <sub>4</sub> PVA-Ac	43.0	81.8	38.8	7.2	39.3	32.1	42.8
P <sub>5</sub> MC	27.7	75.5	47.8	12.5	40.5	28.0	39.1
mean	35.9	78.6	42.7	9.1	30.1	21.0	40.2

\*\* P, D, P×F, P×D, F×D,  $\hat{\sigma}=2.99$  —Part 1

\*\* P, F, D, P×F, P×D, F×D,  $\hat{\sigma}=3.06$  —Part 2

Table 20. Deterstive Efficiency (%) of the Soiled Hydrophobic Fabrics.

Fabrics Coating Solution Polymer	F <sub>1</sub> Alon Tropical		F <sub>2</sub> Tetoron Sheeting		F <sub>3</sub> Vonnel Sheeting		mean	
	D <sub>1</sub> Polymer alone	D <sub>2</sub> Polymer and Soap	D <sub>1</sub>	D <sub>2</sub>	D <sub>1</sub>	D <sub>2</sub>	D <sub>1</sub>	D <sub>2</sub>
P <sub>1</sub> none	-3.5	33.6	-0.1	11.8	-4.7	25.6	-2.4	23.7
P <sub>2</sub> SCMC	-1.9	37.2	1.7	16.8	-2.7	32.0	-1.0	28.6
P <sub>3</sub> SA	-7.9	32.2	0.7	19.8	-3.8	30.6	-2.0	27.5
P <sub>4</sub> PVA-Ac	-3.2	35.6	2.1	24.1	-1.9	25.3	-1.0	28.3
P <sub>5</sub> MC	-4.5	44.2	-0.7	29.2	-1.6	28.1	-2.3	33.8
mean	-4.2	36.6	0.7	20.3	-1.6	28.1	-2.3	28.4
	16.2		10.5		12.7		13.6	

\*\* F, D, F×D, P×D, \* P, F×P, F×P×D,  $\hat{\sigma}=3.47$

ing from 0.1 g (in Table 19) to 0.05 g on each specimen (Table 20).

1) When the high-polymers only were used for the coating of hydrophobic fabrics, water laundering of this method could not success to obtain high detergencies as compared with the merely water laundering (P<sub>1</sub>D<sub>1</sub>). This might be owed to the less affinity of adsorption of high-polymers by these fabrics.

2) The combination of soap in the coating solutions had more effect by the hydrophobic fabrics than by the cellulosic fabrics, and this phenomenon was much clear by the non-electrolytic high-polymer such as MC and PVA-Ac, especially by polyester fabric "Tetoron". In this sense, polyacrylic fabric "Vonnell" was some nearer to cellulosic fabrics.

#### 5-2. Fabrics Soiled by the Soiling Bath Using Water as the Dispersing Medium for Carbonblack

At the experiments of 5-1, fabrics were soiled by the standard

soiling method by JOCS<sup>3)</sup>, in which carbonblack was dispersed in carbon-tetrachloride as the medium. Then the soiling with it could somewhat stronger for the hydrophobic and oleophilic fabrics than that for hydrophilic cellulosic fabrics.

Spun Teton fabrics (No. 5 in Table 1) were soiled by the water-dispersed bath, where the oily materials such as liquid paraffin and beef fat were contained as the standard soiling method, and at the same time they were compared with that of having no oily materials. High-polymers were coated using their solutions, then the fabrics were dried and laundered in water alone or in 0.3% soap-solution at 40°C for 20 minutes (Table 21). The amount of the high-polymer on each specimen was 0.01 g. An equal experiment was carried out for cotton fabric with the same conditions (Table 22).

Table 21. Deterative Efficiency (%) of High-polymer-coated Teton Soiled by Water-dispersed Medium.

Oily materials Washing bath Polymer	O <sub>1</sub> Present			O <sub>2</sub> Absent			Diff. O <sub>1</sub> —O <sub>2</sub>		mean
	W <sub>1</sub> Water	W <sub>2</sub> 0.3% Soap	Diff. W <sub>2</sub> —W <sub>1</sub>	W <sub>1</sub>	W <sub>2</sub>	Diff.	W <sub>1</sub>	W <sub>2</sub>	
P <sub>1</sub> none	7.7	29.2	21.5	8.5	23.8	15.3	-0.8	5.4	17.3
P <sub>2</sub> SCMC	46.2	48.5	2.5	46.7	43.8	-2.9	-0.5	4.7	46.3
P <sub>3</sub> SA	35.8	42.8	7.8	41.6	40.8	-0.8	-5.8	1.9	40.3
P <sub>4</sub> PVA-Ac	31.3	42.1	10.8	42.9	40.4	-2.5	-11.6	1.7	39.2
P <sub>5</sub> MC	-2.5	19.2	21.7	1.9	16.4	14.5	-4.4	1.8	8.8
mean	23.7	36.4	12.7	28.3	33.0	4.7	-4.6	3.4	30.4

\*\* P, W, O×P, O×W, P×W,  $\hat{\sigma}=2.01$

Table 22. Deterative Efficiency (%) of High-polymer-coated Cotton Soiled by Water-dispersed Medium.

Oily materials Washing bath Polymer	O <sub>1</sub> Present			O <sub>2</sub> Absent			Diff. O <sub>1</sub> —O <sub>2</sub>		mean
	W <sub>1</sub> Water	W <sub>2</sub> 0.3% Soap	Diff. W <sub>2</sub> —W <sub>1</sub>	W <sub>1</sub>	W <sub>2</sub>	Diff.	W <sub>1</sub>	W <sub>2</sub>	
P <sub>1</sub> none	34.5	36.9	2.4	24.7	27.0	2.3	9.8	9.9	30.5
P <sub>2</sub> SCMC	61.1	61.2	0.1	56.2	54.9	-1.3	4.9	6.3	50.4
P <sub>3</sub> SA	54.2	49.1	-5.1	43.2	31.9	-11.3	11.0	17.2	44.6
P <sub>4</sub> PVA-Ac	57.5	50.9	-6.6	44.5	38.7	-5.8	13.0	12.2	47.9
P <sub>5</sub> MC	11.3	38.0	26.7	5.33	33.3	28.0	6.0	4.7	22.0
mean	43.7	47.2	3.5	4.8	37.2	3.4	8.9	10.1	40.7

\*\* P, O, W, P×O, P×W,  $\hat{\sigma}=2.14$

1) The coating with the high-polymer solution, except MC, had a great improvement in the detergency of the polyester fabrics, dif-

ferent from the case of the standard soiled one in which carbon-tetrachloride was used as the medium. And the presence of oily materials gave the rather lower detergency, though it was also much higher than that when soap was alone coated.

2) The laundering in the solution of soap could make still much higher the detergency, especially when the soils contained the oily materials. This phenomenon was not so clear by cotton fabrics, moreover reduced detergencies were appeared comparing with the mere water laundering.

Another experiment was performed for three kinds of hydrophobic fabrics, which were used in the experiment of Table 20. They were soiled by the water medium, and coated with the mixed solution of high-polymer and soap, then dried and laundered with water alone at 40°C for 20 minutes. The amount of high-polymer on each specimen was 0.01 g, and that of soap was 0.05 g respectively (Table 23).

Table 23. Deterative Efficiency (%) of the Soiled Hydrophobic Fabrics Coated With the Mixture of High-polymer and Soap.

Fabric Coated Solution Polymer	F <sub>1</sub> Alon Tropical		F <sub>2</sub> Tetron Sheeting		F <sub>3</sub> Vonnell Sheeting		mean	
	D <sub>1</sub> Polymer	D <sub>2</sub> Polymer and Soap	D <sub>1</sub>	D <sub>2</sub>	D <sub>1</sub>	D <sub>2</sub>	D <sub>1</sub>	D <sub>2</sub>
P <sub>1</sub> none	2.1	35.8	6.9	14.1	9.0	44.9	6.0	31.6
P <sub>2</sub> SCMC	11.9	44.2	46.0	29.1	52.3	52.8	36.7	42.0
P <sub>3</sub> SA	12.0	47.4	40.1	23.8	38.7	58.5	30.2	43.2
P <sub>4</sub> PVA-Ac	12.1	48.3	29.1	33.7	40.1	49.4	27.1	43.8
P <sub>5</sub> MC	2.9	46.5	10.8	39.9	19.6	51.1	11.0	45.8
mean	8.2	44.4	26.6	28.1	31.9	51.3	22.2	41.3
	26.3		27.3		41.6		31.8	

\*\* F, P, D, F×P, F×D, P×D, F×P×D,  $\hat{\sigma}=1.90$

3) The mixing of soap in the solution for coating had the most effect when MC (methylcellulose) was used as the high-polymer, as was already found at the experiment 5-1 using the standard soiling. But this phenomenon was less clear for polyacrylic fabric "Vonnell", because of an existence of some hydrophilic groups.

4) From these experiments, it seems that the polymer-coated laundering method could be also applied for hydrophobic fabrics, when the solution of high-polymer for coating was mixed with soap, or fabrics coated with polymer alone were laundered in the solution of detergent.

#### IV. Discussion

##### 1. *Possible Mechanisms of the Detergency of the Polymer-coated Laundering Method*

Why this method could show so high detergencies was an interesting problem. Though sufficient data on the physico-chemical background were not yet obtained to analyse the mechanism of this laundering method, the following processes must be considered.

1) Absorption of a solution of high-polymer by the soiled fabrics was occurred.

2) Adsorption of high-polymer by the fabrics and soils was performed during the drying of the coated fabrics. When the mixed solution was used, surfactant was also adsorbed.

3) Separation of the soils from the fabrics, and then the occlusion of the soils by the drying high-polymer was occurred during the drying.

4) Complete occlusion of the soil was performed into micro-gel structures of the dried layer of high-polymer.

5) Dissolution of the high-polymer occluding the soils was performed from the fabrics into water, in which the dried fabrics were immersed.

##### 2. *Effect of the Drying of the Coated Fabrics*

The third and fourth stages of the above considered mechanism were perhaps the most important processes of this laundering method, as were seen in the experiments III-4-2, especially for the case in which SCMC and other electrolytic high-polymers were used as the coating polymer.

When the drying was not fully achieved, the above mentioned occlusion of the soil did not attained, and the followed laundering in water was only a similar one, which laundering of the soiled fabrics immediately with a solution of high-polymer which was tried in the experiment of III-1.

Some of high-polymers such as PVA-Ac, however, have a tendency to be insolubilized by the tendency process, then a negative effect was appeared by the drying, and was more promoted by a heat drying.

##### 3. *Solubility of the High-polymer after Dried on the Fabrics*

Maintaining the solubility of the high-polymer after being dried on the fabrics was also one of great factors to perform this laundering method, because the lack of the solubility could not deterge the soil from the fabrics into the laundering solution, even though the occlusion of the soil was sufficiently achieved.

This was a main origin of the low detergency of this method,

when starch and MC alone were used for coating of the soiled fabrics. Starch itself had adsorbing power to the soiled fabrics, and when used in washing solution, rather higher detergency was attained comparing with SCMC solution and others.

As the second example, when MC was alone used for the coating negative detergency was appeared, but when used with the mixture with surfactant, much high detergency was presented by the followed water laundering. And as MC had lower solubility in water of higher temperature, the higher the temperature of laundering, the lower the detergency was obtained.

The solubility of the coated MC into the water in which the coated fabrics were immersed, was determined at various conditions by the anthron-sulfuric acid method<sup>5)</sup>. The detergency and the solubility were almost parallel, and the importance of the supposed mechanism 5) was seemed to be true.

However, when the fabrics were hydrophobic one, such as polyester fiber, coated high-polymers dissolved into water much more quickly and completely than from hydrophilic cellulosic fiber<sup>5)</sup>, but the detergency of this method were much lower than the case of hydrophilic one.

This reason seems to due to a quickness of drying of the solution of high-polymer on the hydrophobic fibers, and the polymer dried into a form of film without complete occlusion of the soil which must be separated from the fabrics. When the mixed solution of high-polymer and surfactant were used, the above tendency was rather reduced, and the migration of the soil from the surface of the fabrics to the net work of high-polymer could occur, and high detergency was obtained.

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