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Abstract

Based on the findings of interaction between dodecyl benzene sulfonate (DBS) and high molecular weight nitrogen compounds in natural soil in the first report of this series, artificially soiled clothes containing protein were prepared and a washing test was carried out with a use of DBS or nonyl phenol-polyoxyethylene adduct (NPEO). Cattle serum globulin, cod sperm protamine and feather keratin of wild duck were used as protein. The built DBS detergent showed better detergency on the artificially soiled clothes than the built NPEO detergent at a same surfactant concentration of 0.05%, although no difference was observed in the redeposition test between these detergents. A significant dissolving action of DBS was observed. Results indicate that when discussing the mechanism of dissolution of natural soil or in the course of modifying the artificially soiled clothes, a chemical reaction between DBS and protein had to be considered in addition to the well known physico-chemical surface activity of the surfactant for removal of soil.

Introduction

It has been recognized in washing tests that detergency on artificially soiled clothes gives different results from detergency on practical washing. This would mean that both quality and quantity of soils used in artificially soiled clothes are different from those of naturally soiled clothes. In a preceding report (1) the authors found that: natural soils contain high molecular weight nitrogen compounds or proteins in various forms and in fairly large amounts; dodecyl benzene sulfonate (DBS) has stronger ability to remove these nitrogen compounds from naturally soiled clothes; and correlation between detergency on artificially and naturally soiled clothes is not good as far as the DBS used.

In this study, artificially soiled clothes containing protein as a soil component were prepared and rinsed with water prior to washing tests. Washing tests were carried out with artificially soiled clothes by use of detergents formulated either DBS or nonyl phenolpolyoxyethylene (9.5 moles) adduct (NPEO) and sodium sulfate as a builder. A redeposition test and an estimation of dissolved nitrogen in washing solution were also carried out. The solubilizing action of the surfactants on proteins and physico-chemical surface activity of the test detergents were determined. By these experiments, the authors investigated soil removal from the artificially soiled clothes, intending to make an approach to more desirable composition for artificial soil.

Experiments and **R**esults

Preparation of Artificially Soiled Clothes Containing Protein

Artificially soiled clothes containing protein were prepared as follows: a swatch $(5 \times 10 \text{ cm})$ of cotton cloth was soaked in a suspension of 10 g of protein per liter of deionized water for 20 sec, air dried and kept in a desiccator. After 24 hr from the first soiling, the swatch was saturated in a suspension of 0.8 g of carbon black and 4 g of methyl ester of fatty acid per liter of carbon tetrachloride. The swatches of soiled cloth were aged for three weeks in a desiccator in the dark at 5 C.

The following proteins were used. Cattle serum globulin: cattle serum was salted out by using 50% saturated ammonium sulfate, then dialyzed; cod sperm protamine was prepared from codfish sperm by Kossel's method (2); feather keratin from wild duck was prepared by oxidation of wild duck's feather with hydrogen peroxide; and methyl ester of a mixed fatty acid (tallow-coconut 9:1) of AV 0.36, SV 200.7, IV 42.7 and mp 14.2–15.7 C was used.

The control of the artificially soiled clothes was prepared by treatment with carbon black and the ester only.

All artificially soiled clothes were placed in Launder-O-meter bottles and water was added at the ratio of 100 g of water per swatch and then rinsed for 5 min at 40 C. Rinsing was repeated six times to remove the soil which was water soluble or easily detached by mechanical agitation.

Washing Test

Test surfactants and the washing procedure were the same as those described in the preceding report (1). The test detergents had 7 parts of sodium sulfate and 3 parts of either DBS or NPEO. Surface tension and contact angle of the built detergent solutions are shown in Figure 1-a,b.

The detergency of the built NPEO on artificially

a. Surface tension of detergent used



soiled clothes containing no protein was generally higher than that of the built DBS detergent; but the detergency of the built DBS on soiled clothes containing protein was higher than that of NPEO when the surfactant concentration was above 0.05% (Fig. 2-a-d).









FIG. 2. Detergency concentration curves using artificially soiled cloth with or without protein.



FIG. 3. Redeposition test using artificially soiled cloth, with or without protein.

Redeposition Test

The redeposition test was carried out on artificially soiled clothes containing protein with the built detergent solutions of 0.05% as surfactant concentration. Namely, a swatch of artificially soiled clothes and a redeposition cloth (an unsoiled cotton cloth) were placed together in the Laund-O-meter bottle and were washed under the same conditions as in the washing test. Washing was repeated 10 times using the same redeposition cloth. Results are shown in Figure 3. Similar results were also obtained in the case of the soiled clothes containing other proteins and there was practically no difference in the power of anti-redeposition between detergents used.

Dissolving Test of Proteins by Surfactant

Twenty milliliters of phosphate buffer solution, ionic strength 0.01, pH 6.0 or 8.0, containing 40 mg of surfactant, was mixed with 20 ml of the same buffer solution suspending 10 mg of protein totalling 50 ml with the buffer solution. The turbidity measurement was made on the mixture after standing for 15 min by a photoelectric photometer (Nippon Seimitsu Kogaku, Type SEP-H) using a green filter and 30 mm cell. The results are indicated in Table 1-a,b.

TABLE I											
Effect of	Surfactants	on	Turbidity	of	$\operatorname{Protein}$	Suspension ^a					

		a) pH 6.	0	b) pH 8.0			
Surfactant	No sur- fac- tant	DBS	NPEO	No sur- fac- tant	DBS	DPEO	
No protein	1.1	1.3	1.5	1.1	1.3	1.3	
globulin	53.7	10,5	53.7	27.9	6.0	25.2	
protamine Wild duck	76.3	64.2	71.8	73.3	40.0	68.2	
feather keratin	15.3	10.4	13.6	8.9	6.8	9.4	

$$Turbidity = \frac{11 - (11 \cdot 11) \cdot 100}{100} \cdot 100$$

Td, diffused transmittance; Tt, total transmittance; Tf, factor (quantity of light scattered by instrument).

It was observed that addition of DBS lowered the initial turbidity of protein suspension, while addition of NPEO gave little or no change in turbidity.

Determination of Nitrogen Removed From Artificially Soiled Clothes Containing Protein

Artificially soiled clothes containing cattle serum globulin were washed for 5 min in each of the detergent solutions, 0.05% surfactant concentration. The liquid to cloth ratio was 100:1; the solution was stirred with a glass rod at the rate of 60 rpm. After 5 min the test swatch was transferred into a fresh washing solution; this procedure was repeated six times. The total time was 30 min. It was then rinsed twice with distilled water for 5 min each time. Each of the washing solutions and the twice rinsing was used for the determination of the amount of removed nitrogen by Kjeldahl's method. Distilled water was used as a blank test. The results indicated that DBS removed nitrogen compounds from the soiled cloth by degrees. About 95% of nitrogen compound adhered to the cloth was removed by washing with DBS, while only 59% was removed with NPEO (Fig. 4). There was practically no removal of nitrogen when distilled water was used.

Discussion

Using built DBS and NPEO detergents and artificially soiled clothes containing protein, detergency vs. concentration of surfactant, curves were plotted. The result showed that detergency of DBS on these artificially soiled clothes, contrary to its detergency evaluated with present artificially soiled cloth, was higher than that of NPEO when surfactant concentration was above 0.05%. This fact correlates with the result of the washing test on naturally soiled cloth shown in the preceding report (1).

In general the detergency is regarded as the comwas reported by other investigators (3); effective bination effects of direct soil-removing ability and anti-redepositing ability of a surfactant. The results of redeposition tests with artificially soiled clothes containing protein showed no difference between these two detergents. Therefore, the difference of detergency between these surfactants should be attributed to the difference in direct soil-removing abilities of the surfactants. Further consideration on direct soilremoving abilities of the surfactants led to the conclusion that the difference of detergency between these detergents could not be explained from the view point of physico-chemical surface activities of surfactants such as surface tension or contact angle.



FIG. 4. Nitrogen removal from artificially soiled cloth containing protein.

The chemical reaction between DBS and protein removal of nitrogen from artificially soiled clothes containing protein by washing with DBS detergent was observed in these experiments. It is suggested that chemical reaction between DBS and protein could be considered as a function in the mechanism of DBS detergency. The discrepancy in detergency between DBS and NPEO, when naturally soiled and artificially soiled clothes are used, might be caused from this reaction.

The experiment on the determination of removed nitrogen indicated that the reaction of DBS to protein took place by degrees. This phenomenon seems to be similar to bacteriolysis by DBS observed by some of the authors (4).

Thus, protein was incorporated as a prerequisite component in artificial soil, in order to give more coincident results with practical washing. This protein containing soil shows close properties to natural soil so far as detergency is concerned, especially in evaluating detergency of commercial synthetic detergents containing DBS.

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