

A Natural Soil and Mechanism of Removal

S. TOMIYAMA and M. HIMORI, Lion Fat & Oil Co., Tokyo, Japan

Abstract

Nitrogen compounds in natural soils are studied in relation to their effect on the soil removal mechanism in detergency.

Nitrogen compounds in various forms and in fairly large amounts are found in natural soils, and more than 24% of these nitrogen compounds are presumed to be high mol wt nitrogen compounds or proteins. These high mol wt nitrogen compounds which cannot be removed by water can be removed by the detergent action of sodium dodecyl benzene sulfonate (DBS). When the detergency of DBS was compared with nonyl phenol-polyoxyethylene adduct, the detergency for artificial soil cloths did not coincide with results obtained with naturally soiled cloths.

These data suggest that some interaction between DBS and nitrogen compounds might have contributed to the detergent action. If proteins were added to the present artificial soil formulation, better correlation might be expected between artificial and natural soil detergency results in DBS evaluation.

Introduction

ARTIFICIAL SOIL CLOTHS used in evaluating the performance of detergents often show discrepancies in rating detergents when compared with result obtained by practical wash tests. This is especially true when comparing dodecylbenzene sulfonate (DBS) and other surfactants. Because of this, many companies use troublesome and time-consuming practical wash tests in addition to artificial soil tests. This is especially necessary in Japan because of the very humid climate which might accelerate the degradation of natural soil.

The purpose of this study is eventually to formulate a soil cloth for evaluating detergency that will give better correlation with the results obtained with natural soil. This paper will discuss the nitrogen distribution found in a natural soil, the estimation of water insoluble nitrogen compounds removed by the detergent action of DBS, and the comparison of detergency and removal of water insoluble nitrogen compounds by DBS and NPEO [nonyl phenol-poly (9.5 mols) oxyethylene adduct] for naturally soiled cloths using the contents of the detergents at which

equivalent soil removal was obtained with an artificial soil cloth.

Experiment and Discussion

Soiled cloths were used as a source of natural soil. Cotton cloths, 11 × 25 cm, weight 4 g, were attached to working dress collars. The cloths were soiled by wearing for 3 days in August, and then aged for 20 days at room temp. The soiled sections of each cloth, about on third of the area, were cut into 2 mm strips for extraction. This procedure is shown in Figure 1.

Fifty-six grams of the soiled cloth strips were extracted with solvents. The first extraction was with petroleum ether in a soxhlet extractor. Then the strips were soaked sequentially in distilled water, 2% sodium chloride, 70% ethyl alcohol, and 0.2% sodium hydroxide. After the distilled water step, extraction procedures were repeated three times for each solvent at 25°C for 20 min.

The extracts from each step were separated from the cloth strips by filtering through paper and the three samples for each treatment were pooled. The five extracts were dialyzed and their nitrogen contents were determined before and after dialysis. The extracts were dried under vacuum. The nitrogen content extracted by the various solvent treatments are shown in Table I, before and after dialysis. Total nitrogen content of the soiled samples was 75.2 mg%. By the various extraction procedures 70.8 mg% or 94% of the nitrogen was recovered. After dialysis 16.9 mg% remained. Of the 16.9 mg%, 10.1 mg% was determined as water insoluble nitrogen compounds which could not be dialyzed through the cellophane tube.

Strips of the naturally soiled cloth were washed in 0.05% DBS solution and 10 ml of this wash solution was added to a column of Sephadex G-50 (Pharmacia Company). Column size is 2.5 cm diameter, 42.7 cm height and 26.8 g of dry Sephadex which regains 5.45 g water per 1 g gel, is packed. This was followed with 290 ml of distilled water. The effluent from the column was collected in 30–10 ml aliquots. The nitrogenous material content and DBS content of each fraction was determined by the Folin-Ciocalteu 1) and the Abbott method 2), respectively.

These data are presented in Figure 2. Two other curves are also given in this figure. An elution curve is given for nitrogenous materials removed by

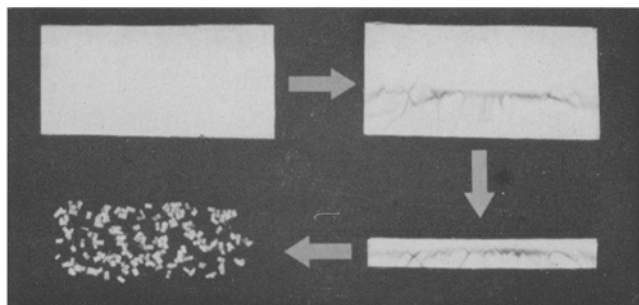


FIG. 1. Naturally soiled cloths.

TABLE I
Nitrogen in Natural Soils

Stage	Solvent	Nitrogen/mg% (wt. %)		(B)/(A) (%)
		Before dialysis (A)	After dialysis (B)	
1	pet. ether	0.0 (0.0)	— (—)	—
2	dist. water	58.8 (78.2)	6.8 (9.0)	12
3	2% NaCl	3.3 (4.4)	2.2 (2.9)	67
4	70% ethanol	3.0 (4.0)	2.6 (3.5)	87
5	0.2% NaOH	5.7 (7.6)	5.3 (7.0)	93
Total		70.8 (94.1)	16.9 (22.5)	24
Natural soils		75.2 (100)	— (—)	—

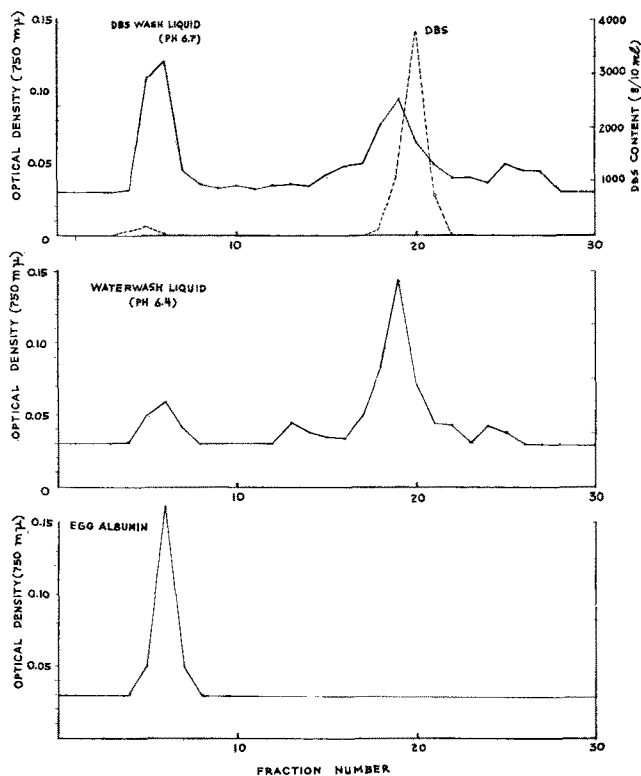


FIG. 2. Fractionation of nitrogen compounds in DBS solution dissolved from naturally soiled cloths.

distilled water and a curve for egg albumin which was used for a standard. There is a significant difference in the peak areas of fractions 4 to 9 between distilled water and DBS. The egg albumin curve shows that this peak indicates high mol wt compounds greater than 10,000. DBS might have a stronger or more selective reactivity with the higher mol wt nitrogen compounds, presumably proteins, in natural soils so as to solubilize them into the detergent solution. The strong affinity of DBS or alkylbenzene sulfonates for proteins has been discussed in the literature (3). We also found this phenomenon in a study of protein removal in a sweet potato starch purification process (4). These data showed when 0.1% concn of several surfactants were used to remove protein from sweet potato starch which originally contains 0.106% protein, DBS could remove 45.3% in contrast to 34.9% by NPEO. NPEO could remove only up to 40.5% even at a 0.5% concn. This purification process of starch had been applied commercially to improve starch quality in Japan. From these facts we presume, there might be no strict similarity in protein removal mechanism by DBS between starch and natural soils, but still we suspect that the DBS affinity for proteins is one of the distinctive functions that should be considered when the performance of DBS compounds is discussed.

The artificial soiling formulation used in this study is shown in Table II. Soiled cloths with a reflectance of $30 \pm 2\%$, using magnesium oxide as a standard

TABLE II
Artificial Soiling Formulation

Hydrogenated tallow (IV 3).....	1
Liquid paraffin.....	3
Carbon black.....	0.8
Carbon tetrachloride.....	500
Reflectant of soiled cloths.....	$30 \pm 2\%$
Aging of soiled cloths.....	10 days

TABLE III
Carbon Soil Removal of DBC and PONP
(Artificially Soiled Cloths)

Concn %	Carbon soil removal %	
	DBS	PONP
0.01	11.3	37.8
0.02	14.8	57.2
0.03	17.2	60.7
0.04	22.3	62.2
0.05	29.6	63.6
0.06	42.7	65.0
0.07	51.3	66.5
0.08	59.8	67.2
0.09	64.7	66.2
0.10	66.6	67.9

TABLE IV
Natural Soil Removal of DBS and PONP
(Naturally Soiled Cloths)

Surfactant	Concn.	Detergency	Amount of dissolved nitrogen
DBS.....	0.08%	$71.4 \pm 4.8\%$	21.4 mg%
PONP.....	0.03%	$38.5 \pm 19.5\%$	10.6 mg%

for 100% reflectance, were aged for 10 days in a cool dark container before use. Detergency concentration curves were obtained for DBS and NPEO with the soil cloths described above. The tests were run using a Launder-O-Meter. Conditions were one wash of 30 min and two rinses of 5 min each at 40C. Data are given in Table III. The detergency of NPEO is better than DBS for this artificial soil. The 0.03% NPEO is approximately equal to 0.08% DBS for removing carbon.

Soil removal from the naturally soiled cloths was determined for DBS and NPEO by the Launder-O-Meter method using the equivalent soil removing concns of 0.08% and 0.03%, respectively. Before washing, the soil cloths were rinsed three times in distilled water to remove water soluble soils. After drying, the reflectance of the cloths was measured at two points on the soiled part of the cloth to eliminate cloths that were unsuitable for testing. Twenty soiled cloths were cut in half to insure the same weight of cloth and soil load for both detergents. Washing conditions were the same as described for the artificial soil cloths. The results are given in Table IV along with the nitrogen content in the detergent solution after washing. Both detergents should have the same soil removal if the detergency results based upon the artificial soil were applicable to the naturally soiled cloths. However, DBS gave better detergency and removed more nitrogen than NPEO.

These results suggest that there might be some interaction, probably chemical or complex formation between DBS and proteins, in addition to such well-known effects as physical wetting, emulsification and suspending action during the wash process. In other words, we have to consider the effect of nitrogen compounds in an artificial detergency test, particularly when DBS is compared with other kinds of surfactants because the presence of nitrogen compounds in a soil might contribute to a difference in detergent performance.

REFERENCES

1. Folin, O., and V. Ciocalteu, *J. Biol. Chem.* 73, 627 (1927)
2. O. H. Lowry, et al., *Ibid.* 193, 265 (1951).
3. Abbott, D. C., *Analyst* 87, 286 (1962).
4. Lundgren, H. P., *J. Am. Chem. Soc.* 63, 2854 (1941); F. W. Putnam, and H. Heurath, *Ibid.* 66, 692 (1944); F. W. Putnam, and H. Neurath, *Ibid.* 66, 1992 (1944).
5. Fujii, T., et al., *Dempun Kogyo Gakkaishi (Technol. Soc. Starch)* 8, 1 (1960).

[Received October 21, 1964—Accepted February 16, 1965]