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Removability of Oils from Cotton Cloths

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It is well-known that oily substances attached to soiled cloths play an important role in the process of detergency. It seems, however, that the mechanism operating underneath the detergency process has not yet been firmly established.

According to a direct observation of the detergency process, the particulate constituent might give little trouble if the oily constituent could be removed first.[1] However, exactly the opposite may be true, that is, it may be held that it is rather particulate dirt that has become firmly attached to the textile itself, instead of adhering by means of a fatty film.[2] In fact, it seems most likely that the solid and liquid soils are under certain conditions, often removed independently.[3]

Yet it appears that no direct demonstration of the influence of oil on a quantitative basis has ever been made. The present authors, using the gas-chromatographic technique, tried to determine the removability of oily substances from cotton cloths, paying particular attention to the type of oil used. The present report will be concerned with the desorption of three different types of oils with the same carbon chain and with the correlation of the desorption with the detergency.

1) T. Fort, Jr., H. R. Billica and C. K. Sloan, *Text. Res. J.*, **36**, 7 (1966).

2) E. Howarth and L. P. S. Piper, *ibid.*, **36**, 856 (1966).

3) K. Durham, "Surface Activity and Degergency," Macmillan Co., London (1961), p. 72.

Experimental

Oils. The three types of oils used were dodecane $C_{12}H_{26}$, dodecyl alcohol $C_{12}H_{25}OH$, and lauric acid $C_{12}H_{24}O_2$, each with a twelve carbon chain. We attempted to use oils with a shorter carbon chain, but we found that alkanes of less than 12 carbons evaporated rather quickly upon gas-chromatographic analysis and upon weight-loss measurement as well. The dodecane and lauric acid were both extremely pure, showing the presence of only one peak on a gaschromatogram. The dodecyl alcohol was purified from commercial lauryl alcohol by repeated distillation under reduced pressure, but it still showed about 7% content of homologous alcohols.

Cloths, Carbon Black, and Carbon Tetrachloride. These were used as assigned by a standard detergency test method.*1

Detergents. The sodium dodecyl sulfate (SDS), which had been purchased from Wako Junyaku Co., Ltd., was purified once by recrystallization from ethanol. The polyoxyethylene condensate of nonyl phenol ($\bar{p}$=7.5 NPE) was used as obtained from the Toho Chemical Co., Ltd. The household detergent mixture

*1 JIS-C9606 (1968).

was a recently-purchased one. The gaschromatograph used was a Hitachi K-53 type apparatus, equipped with a rising temperature programer. The sensitivity was $10-2\times10^2$. Its column was packed with chromosorb W with phosphoric acid plus polyethyleneglycol.

Procedure. An oil-impregnated cotton cloth was prepared by applying 0.5 cc of an equimolar mixture (2.4×10^{-4} mol of each/cc) of dodecane, dodecyl alcohol, and lauric acid in CCl_4 to a piece of cloth (10×5 cm) by means of a micropipet. After the evaporation of the solvent, the oiled cloths were aged for 3 days before use. The oiled cloth was washed with a scrub-*o*-meter in the usual manner at 30°C for 10 min, and then rinsed for 3 min. Ion-free water was used throughout. Washed cloths from 12 runs were collected and air-dried, and the residual oils were extracted in ether with soxlet for 12 hr. After the removal of the ether, 1 cc of CCl_4 was added to this remaining oil in order to analyze it by gas chromatography. The relative contents of the three oils were calculated by the ordinary triangle method.

By a separate detergency test, we made three types of artificially soiled cotton cloth, in each test using the same amount of a different oil instead of using hardened tallow and paraffin. The cloth was impregnated with carbon black and oil in CCl_4.

The washing time was made 20 min, while keeping the other conditions the same as above.

The detergency may be expressed as; $D = \dfrac{R_W - R_S}{R_O - R_S}$

where R_W: reflectance of the washed cloth
R_S: reflectance of the soiled cloth
R_O: reflectance of the original cloth before soiling.

All the detergency data are averages of four runs made under the same conditions and examined by means of statistical calculations.

Results and Discussion

Table 1 shows the residual oil contents of washed cotton cloths. These are calculated from the gaschromatograms, a sample of which is shown in Fig. 1. As is clearly indicated here, overwhelmingly more dodecyl alcohol remained than the corresponding alkane and acid. In other words, the alcohol was most difficult to remove by any detergent solution including SDS and NPE. Table 2 shows the detergency of water alone, SDS, NPE, and a commercial detergent mixture on cloths artificially soiled with carbon blacks and with one of the three oils. For any of the detergent systems listed in Table 2 except for the commercial detergent, which alone contains alkaline builders, it was found that detergency is strongly dependent on the soiling oil. The influence of oil on the removal of carbon particles from cloths is very clear. In almost all cases, except for the commercial detergent formulation, the detergency for soiled cloths increases in the order of: without oil>alkane>alcohol>acid.

These two results may be summarized by saying that the removability of oil out of cotton cloth by these detergents is definitely: alkane>acid>alcohol in the order of ease, while the removability of carbon soil with regard to the presence of oil is in the order of: without oil>alkane>alcohol>acid. This, in turn, should be interpreted as meaning that the removability of oil is not parallel with that of soiled soil, *i.e.*, carbon black.

The soiled cloth without oil exhibits the highest detergency, and the presence of lauric acid, which should behave like solid, (mp 44°C) interferes with the removal of carbon soil most strongly. The exception of the commercial detergent regarding

TABLE 1. UNREMOVABLE OILS IN COTTON CLOTHS AFTER WASHING

Detergent system	Residual oil (ratio against alkane)		
	Alkane	Alcohol	Acid
Water	1	715	10
NPE 0.25%	1	71	44
SDS 0.25%	1	240	34

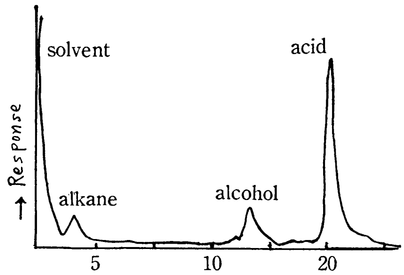

Fig. 1. A GL Chromatogram of residual oil (SDS 0.25%; sensitivity $10-2\times10^2$).

TABLE 2. DETERGENCY ON ARTIFICIALLY-SOILED CLOTHS

Soiling Composition	Detergency %			
	Water	SDS	NPE	Commercial detergent
Carbon black	27.6	51.0	59.2	52.3
Carbon black plus alkane	25.3	54.1	54.2	57.7
Carbon black plus alcohol	19.4	45.8	41.5	48.7
Carbon black plus acid	14.8	30.2	30.0	59.3

(Concentration of detergents: 0.25%)

the order of detergency with respect to acid appears to be very reasonable, because the acid soil may be removed more easily by alkaline builders like sodium tripolyphosphate in detergent formulation. As for the removal of oily dirt, emulsification may be considered to be of importance.[3]

However, it may also be interesting to add that alkane is much more difficult to emulsify than alcohol by these detergent solutions at concentrations of 2.5% or less when emulsification test are carried out by an ordinary method.[4] We have found that alcohol was most easily emulsified, even to a thixotropic gel, while acid, being a solid, never went into emulsion at 30°C.

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4) S. Hayashi and N. Sasaki, *Yukagaku*, **16**, 467 (1967).