Development of Screening Tests for Hard Surface Cleaners: I. Artificial Soil Removal From Linoleum Surfaces

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Abstract

A quantitative method for evaluating performance of hard surface cleaners has been developed based on a series of modifications of previously proposed tests. The principle involves the mechanical cleaning of artificially soiled linoleum with a Gardner Straight Line Washability Machine. A quantitative estimation of the relative cleaning efficiency is determined photometrically and results are expressed as per cent return to original whiteness. Statistical evaluations have shown the method to be reproducible and applicable for discerning differences in formulations, concentration and surfactant structure. The test method details are described and experimental results showing ethylene oxide content optimization of commercial linear primary alcohol-based nonionics, as well as builder effects, are presented.

Introduction

Hard surface cleaning products today are, for the most part, rather complex multi-component systems. As such, they afford a myriad of formulating variations. To optimize such products, a realistic assessment of their relative cleaning efficiency is quite desirable, with the need for reliable test methods generally agreed upon. A literature search (1) of past methods has revealed that most method development has occurred either in areas of metal degreasing, glass or ceramic cleaning, or both. A few, of special interest here, simulate a "janitorial" type of operation where artificially soiled surfaces are mechanically scrubbed with a brush or sponge. No method of this type has received wide acceptance, primarily because of poor reproducibility.

The basic cleaning approach of most of the scrub-type methods tested proved quite similar and, we believed, realistic. Therefore, no attempts were made to change the gross mechanical procedure. Our efforts, for the most part, were directed towards defining the source of variance within these methods, then making the changes necessary to increase overall reproducibility.

The method that has evolved has proven quite reproducible and should be a useful tool to those concerned with hard surface cleaner evaluation.

Method Development

A tested method developed by R. L. Liss and T. B. Hilton (2) and later proposed by an ASTM subcommittee on hard surface cleaning, typifies those of interest. The procedure involves mechanical scrubbing of vinyl floor tiles which have been soiled with an iron oxide pigment dispersed in an oil-solvent system. A quantitative estimation of the relative cleaning efficiency is then determined photometrically. The method has not received wide acceptance, primarily because most investigators found the soil either too easy or too difficult to remove. We attribute this, in part, to the relatively soil resistant quality of the vinyl tile and, to some extent, to the degree of soil polymerization. Test specimens prepared under mild dry-cure conditions cleaned totally whereas others, using more severe conditions, were unaffected by scrubbing. Under conditions affording a more realistic cleaning range panels cleaned nonuniformly, making it difficult to assess detergency photometrically.

In an attempt to overcome this effect, various substrates were examined and one was found which proved usable. This material, also recommended by Rohm and Haas for similar testing (3), is readily soiled under mild conditions and does not require excessive polymerization for soil retention.

Reproducibility using the new substrate, though much improved, indicated deficiency in other areas. As a result all steps of the procedure were reexamined and changes made where appropriate.

Test Method and Procedure

Substrate Pretreatment

Test panels were cut from 6 ft wide linoleum (Armstrong, plain white standard gauge, pattern No. 23) roll stock to 4 × 17½ in. rectangular strips. These in turn, to assure a more hydrophilic surface, were mechanically scrubbed (Gardner Straight Line Washability and Abrasion Machine, Model W-G-2000) 100 strokes with a sponge (DuPont Fine Grain Cellulose Photographic Sponge Size 6A-F, cut to 2¾ × 3¾ in. dry) containing 75 ml of distilled water at 25 ± 2 C, and one teaspoon of household cleanser (Easterday Cleanser: sodium perborate, 1.00%; sodium dodecylbenzene sulfonate, 1.20%; inert, 97.80%). The sponge during this operation was under a 475 g load (sponge housing box, See Fig. 1). After scrubbing the panels were rinsed with tap water (ambient temperature), then hung vertically to dry for 30 min at room temperature. They were then stored under constant temperature and humidity (70 ± 2 F; 50% RH) for 24 hr or more before soiling.

Artificial Soil Composition and Preparation

The soil used for this method, consisting of an iron oxide pigment dispersed in a solvent-oil mixture,

[1] Presented at the AOCS Meeting, New York, October, 1968.

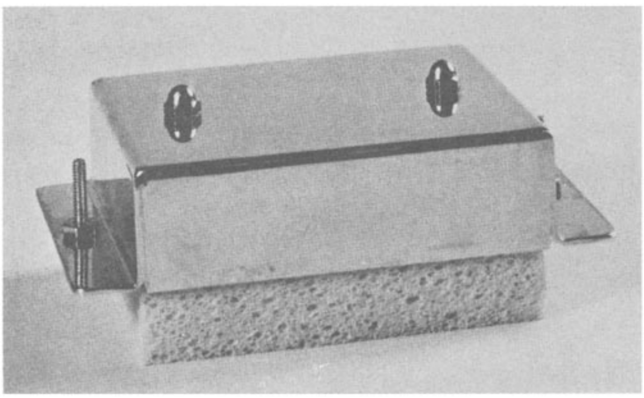

FIG. 1. Sponge in sponge housing box.

had the following composition: metallic brown oxide (Pfizer metallic brown no. B-3881), 40 g; Shell kerosene (hydrotreated ASTF 640, Aromatics, 15.3% v), 24 g; Shell Sol 360 (Min bp 300 F max. 330) (6% aromatics, 49% naphthenes, 45% paraffins), 24 g; liquid petrolatum, heavy USP (Nujol Plough), 2 g; lubricating oil (Shell Tellus No. 27, nondetergent), 2 g; hydrogenated vegetable oil (Flake White, Procter and Gamble Co.), 2 g; Total, 94 g.

The soil was prepared as follows. First, the vegetable shortening was added to a mixture of the hydrocarbon solvents to assure dissolution. Next, the oily components were added, and finally the pigment. The mixture was then stirred, using a Labline magnetic stirrer, for 2 hr at room temperature before use.

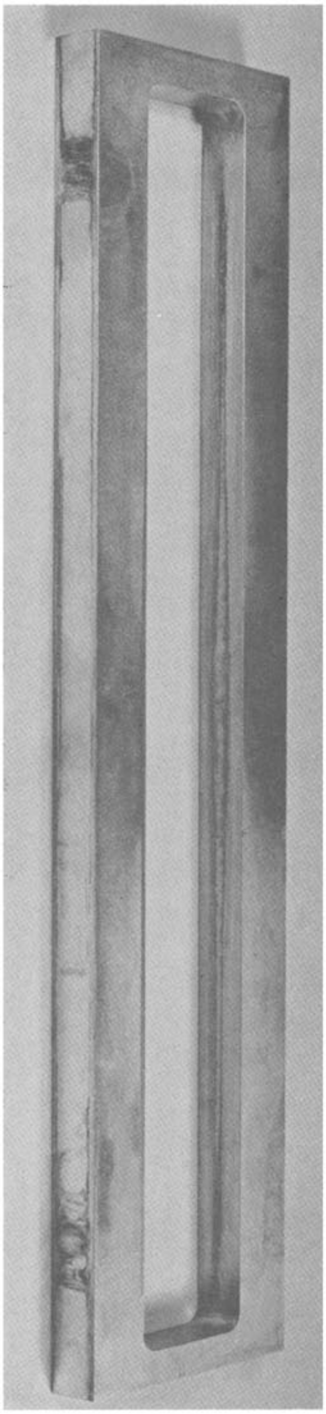

FIG. 2. Metal template.

TABLE I
Effect of Post Cure Aging on Soil Removal[a]

Post cure acclimatization time, hr	Reflectance, (%)
1	49
48	45
72	31.2
144	28.9

[a] Prominent commercial hard surface cleaner used at twice recommended use concentration.

Soiling of Test Panels

Test panels were soiled by drawing 4 g of soil mixture the length of the panel. A 3 in. doctor blade, set to a clearance of 0.004 in., was used and a final soil layer of approximately 0.002 in. in thickness was obtained. Panels were subsequently dried for 1 hr at ambient temperature, cured for 20 min at 105 C in a forced draft oven, then conditioned for 2 hr at ambient temperature before use. All panels were used between 2–5 hr after final conditioning.

Cleaning Operation

Past methods (2,4,5) specified that the cleaning solution be dispensed dropwise, by burette, during the actual scrubbing operation. We found that a good deal of the cleaner fell upon the brush housing and, therefore, never came in contact with the soil. To standardize the amount of cleaner per run, the entire specimen was covered with cleaner to a known depth. This proved cumbersome, and was later changed in favor of a procedure (3) requiring a lesser volume of cleaning solution.

Soiled panels were placed in a Gardner apparatus wash tray and clamped flat using an aluminum template (4 × 17½ × ¾ in. with a center cut-out of 2 × 16 in.) and four C-clamps. The template was so constructed as to act as a cleaning solution (alkaline cleaner: surfactant, 10; tetrapotassium pyrophosphate ($3\,H_2O$), 4; H_2O, 86) reservoir through which the scrub brush (Gardner Lab., No. WG-2000-A) traveled during cleaning. Seventy-five milliliters of wash liquor, at the selected product concentration and room temperature, were added and the panel presoaked 1 min before scrubbing 200 strokes (equal 100 back and forth cycles). On completion, the panels were removed, rinsed with cold tap water, and then air dried at room temperature. They were next trimmed to the area of the brush path, 1½ × 12½ in., then evaluated.

Discussion of Test Detail

Substrate Variability

The linoleum used in this method is light sensitive and any showing variance in color was discarded. All stock should be stored so as to minimize this effect.

Uniformity of Soil and Substrate Preparation

It is most important to mix the soil thoroughly before preparing samples. Two hours at room temperature has proven satisfactory but, due to rapid separation on standing, the soil mixture must remain

TABLE II
Effect of Alkalinity of Builder

Inorganic salt[a]	pH[b]	Reflectance, %
NaOH	11.9	53.9
TSP	10.6	49.5
STPP	9.6	41.5
Na_2SO_4	6.8	26.4

[a] Anhydrous weight basis.
[b] Light duty formulation containing surfactant (Neodol 23–6.5)–inorganic salt–H_2O (10:4:86). Used at a 0.16% surfactant concentration.

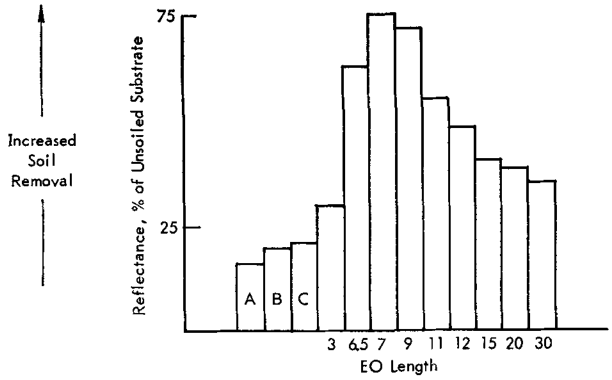

FIG. 3. Relative cleaning efficiency of linear primary alcohol ethoxylates. Cleaning formulation: 0.3% surfactant, 0.12% tetrapotassium pyrophosphate. A, uncleaned substrate; B, distilled water washed; C, tetrapotassium pyrophosphate only.

stirring while removing aliquots during the panel-soiling operation.

Panels soiled in this manner were uniform in appearance both before and after cleaning. Soil mixed only 5 min gave panels with many streaks. Reflectance values ranging over 30 units within a given specimen were not uncommon for the 5 min group, whereas up to 20 units' difference in mean reflectance was observed between groups. We attribute the variance associated with the 5 min specimens to the gritty nature of the soil, which tends to scratch the substrate surface. By increasing the soil mixing time, the soil becomes more finely dispersed, thus decreasing this effect. It is important to point out that even after 2 hr of mixing scratching can occur, though to a lesser degree. To further minimize this effect, the doctor blade should be drawn but once across the surface of the substrate.

Brush Pretreatment

Soil removal depends, in part, upon the degree of stiffness of bristle. A definite decrease in cleaning occurs with repeated use, leveling out after four to five panels. To minimize this effect, brushes were soaked 30 min in distilled water at room temperature before use, and washed with hand soap and hot water between uses. This was followed by a cold distilled water rinse once again, to assure to some degree the uniformity of bristle stiffness before each use.

Cleaning Operation

All wash liquor must be retained within the metal template reservoir during the cleaning cycle. Loss will vary results.

To nullify any effect attributed by a possible skewed scrub brush, the brush was reversed end for end during the last half of each cleaning cycle. Liss and Hilton (2) recommended a similar procedure for use with their sponge.

Dry-Cure Conditions

Dry and cure times and temperatures must be carefully controlled. Longer residence times or elevated temperatures, or both, increase soil polymerization, causing mottling. This results in poor reproducibility, and panels become increasingly more difficult to clean (see Table I).

Quantitative Evaluation

A photometric device (Gardner High-Sensitivity Reflectance Head, LJX-HS-1d) equipped with a blue filter was used to measure detergency in terms of reflectance. The instrument was standardized to indicate 100% reflectance with unsoiled, cleanser-scrubbed linoleum. Reflectance values obtained with test panels, therefore, read directly as per cent return to original whiteness. Readings were taken at five points along the length of the specimen, beginning 2 in. from one end and every 2 in. thereafter.

A computer was used to calculate the mean, variance and standard deviation of the reflectance measurements. The program was written to discard observations greater than three times the standard deviation, and then to recalculate on the basis of the revised population.

Preliminary work at a 95% confidence limit established the number of replicates at four panels, with a difference of three reflectance units significant in the 70% to 100% reflectance range. For values less than 70%, 10 units were considered significant.

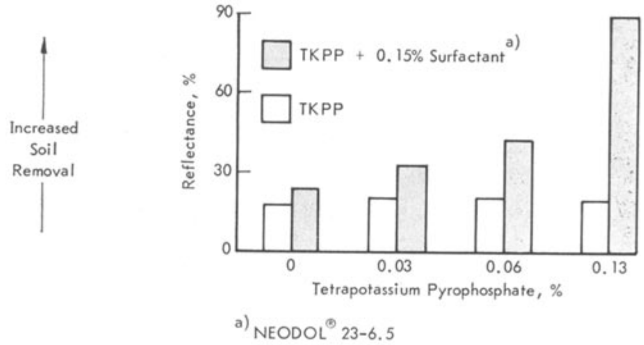

FIG. 4. Effect of tetrapotassium pyrophosphate on cleaning efficiency.

Results

As an example of the method, various linear primary alcohol ethoxylates (based on Neodol alcohols by Shell Chemical Company), containing from 3 to 30 EO (ethylene oxide) units, were examined for relative cleaning efficiency. The comparison was made using a light duty cleaner diluted to a surfactant content of 0.3%. The results (see Fig. 3) indicate that optimum cleaning occurs in the 6.5 to 9 EO range which, in turn, represents approximately 60% to 65% EO on a total product basis.

In addition, various alkaline inorganic builders were compared (by weight) for effect on detergency. A light duty formulation was used at a builder concentration of 0.064%. Results (see Table II) indicate that more efficient cleaning occurs in the more alkaline salts.

Finally, a study was made to determine the effect of tetrapotassium pyrophosphate concentration on detergency. Three levels of inorganic salt were compared both in the presence and absence of surfactant. It is of interest to note (see Fig. 4) that regardless of inorganic concentration, cleaning potential lies dormant until the addition of surfactant.

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