ties (Curran & Evans—*J. Dairy Sci. 33,* 1). The use of detergent sanitizers in dairy utensil cleaning considerably lowered the bacterial count of milk produced (Puhle—*Soap Sanit. Chemicals 26,* No. 12, 133; Lindquist—*Proc. 12th Intern. Dairy Congr. 3,* 294). In a test of 142 surface active agents for bacterial action against tubercle bacilli the materials were not considered good as a group (Smith *et al.*—*Pub. Health Repts. 65,* 1588).

Certain chlorinated diaromatic methanes when added to soaps induced powerful bacteriostatic activity (Price-Bonnett—*Surgery 24,* 542; Bean & Berry—*J. Pharm. Pharmacol. 2,* 484). Alexander *et al.* (*Research, Surface Chemistry Suppl. 1949,* 299, 309, 317, 325) studied bacterial action of soap and detergents and mixtures of these with electrolytes and phenols, and discussed the data from such colloid aspects as particle surface, absorption on particles, effect of micelle, etc. Bactericidal activity of surface-active agents was comparable to their hemolytic action (Haldenwanger—*Zentr. Bakt. Parasitenk. Abt. 1,* 153, 263) and protein precipitation (Haurowitz—*Bull. faculte med. Istanbul 12,* No. 3, 183). It was suggested that some sort of combination takes place with micelles.

In one investigation the relation between structure of invert soaps and their antimycotia power were recorded (Jerchel & Kimmig—*Chem. Ber. 83,* 277). Mold growth on eggs in storage was inhibited or completely prevented by dipping the eggs in solutions of certain cationic detergents.

The effect of general use of synthetic detergents on bacterial sewage processing was investigated (Waddams—*Surveyor 109,* 39; Elton—*Inst. Sewage Purification J. and Proc. 1949,* 351). Primary sedimentation, bacterial activity, sludge digestion, or methane production were not affected when tested in concentrations likely to be encountered in sewage treatment.

Floor Cleaner Evaluation

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CONSIDERABLE research has been devoted in the past 15 years to the evaluation of soaps and surfactants[1] as detergents for textiles, particularly cotton and wool. Relatively little has been reported however in the scientific evaluation of such detergents as floor and all-purpose cleaners, despite their volume usage. A notable exception is Harris and his coworkers, who recently reported (6) the evaluation of synthetics, built and unbuilt, for this purpose. Another contribution has been that of DuBois, who extended (3) the detergency test method of Gilcreas and O'Brien (5) to include linoleum cleansing, but this method does not simulate actual practice and was rejected for this reason.

In their paper, Harris *et al.* stressed a satisfactory test method and the necessity for following prescribed precautions to obtain duplicable results and presented a statistical treatment of the data. No attempt was made however to compare the detergent properties of a soap against those of another or of a soap against those of a surfactant.

Our object in presenting this paper is three-fold: a) to describe a test method which yields replicable results; b) to record the benefit of our experience with liquid soaps vs. synthetics as floor cleaners; and c) to present a statistical treatment of the data obtained with the hope that in the future most, if not all, such experimental data will be weighed statistically to substantiate further any conclusions derived.

It is an accepted fact that a satisfactory test method should simulate practical conditions as closely as possible and should yield results which can be duplicated under practical or "use" conditions. Accordingly a detergency test method for floor cleaners should utilize the surfaces and the soils as well as the cleaning equipment and methods of cleaning encountered in actual practice. Where necessary or advisable, modifications in technique may be made so long as they do not affect the results appreciably.

[1] Coined by General Aniline and Film Corporation to connote surface active agents, including penetrants, emulsifiers, wetting agents, foaming agents, and detergents.

In our work we employed light-colored linoleum as the surface but had to resort to a synthetic soil (4) as the test soil, due to the complexity and variability of natural soils depending on their environments. Preliminary results on natural soil collected from our office, laboratory, and plant floors over a period of months revealed the advisability of adopting a synthetic soil for our detergency studies so as to permit duplication of results and provide a more difficult measure of detergency.

The preparation of test panels and their soiling were accomplished as described below.

Test Panels. The whitest plain linoleum available was used in this investigation. It was Armstrong's Heavy Grade Battleship Linoleum with Safety Back Standard Gauge. Actually its color was yellowish-white. Panels measuring 5¾ in. by 5¾ in. were cut from a large section of the linoleum, and these were scrubbed individually by means of a good grade of scouring powder and a bristle brush to remove the factory finish. The panels were rinsed thoroughly with plain water and were allowed to dry overnight before soiling.

Standard Soil and Soiling. The standard soil used was essentially that described in Federal Specification for Cleaner; for Painted Surfaces, Containing Synthetic Detergent, P-C-431 (4).

The freshly prepared soil suspension was well mixed and was then applied by means of a three-quarter-inch camel's hair brush to an area 2½ in.

Substance	Grams
Metallic Brown (C. K. Williams and Co., B-3881)[2]	20
Hydrogenated Vegetable Oil (Crisco)	1
Petrolatum, light yellow, U.S.P.	1
Lubricating Oil (SAE-80)	1
Kerosene	20
Carbon Tetrachloride	20

[2] Consists of 80-85% Fe_2O_3 and 2% maximum calcium as $CaCO_3$; remainder is silica and silicate minerals.

by 4 in. centered on the linoleum panel so that as uniform a coating as possible was obtained. (Slight variations in film thickness have no effect. Any excess soil is removed by friction within the first two or three passages of the sponge.) The panels were air-dried for one hour and were then heated for 10 minutes in a horizontal position in an oven set at 80 ± 3°C. All panels of a given series were heated simultaneously to avoid any possible slight differences in baking time or temperature and were used within three hours after removal from the oven. (It was found initially that aged panels clean more difficultly and variably.)

Detergency Apparatus. The apparatus consists essentially of a ½-hp., geared electric motor and a mechanism through which the motor imparts oscillating motion to a sponge box assembly across the test panel. The power is transmitted from the motor to a driving arm by means of two pulleys (a 2-in. pulley on the motor shaft and a 6-in. pulley on the cam shaft) connected with a V-belt and a 5½-in. cam, Figure 1. A string is attached from the driving arm to each end of the sponge box assembly, guided by a pulley on each side. The tension of the string is just sufficient to take up any slack. The path of travel of the sponge (duPont, fine-pore cellulose, film sponge) is 12 in., and its speed is 52 oscillations (complete cycles) per minute. The test panel is clamped into place by means of two flat bars, fastened by wing nuts, so that it will remain flat throughout the test. This is not shown in the diagram. The flat bars also serve to keep the sponge in its intended path. The total weight of the stainless steel box, cellulose sponge, lead washers, iron weight, and 50 ml. of test solution (known collectively as the sponge box assembly) is 16 oz.

Equipment similar to that used in this investigation is available from H. A. Gardner Laboratories Inc. Bethesda, Maryland.

Detergent Test Solutions. From our preliminary work it soon became apparent that a standard or reference detergent was required for comparison

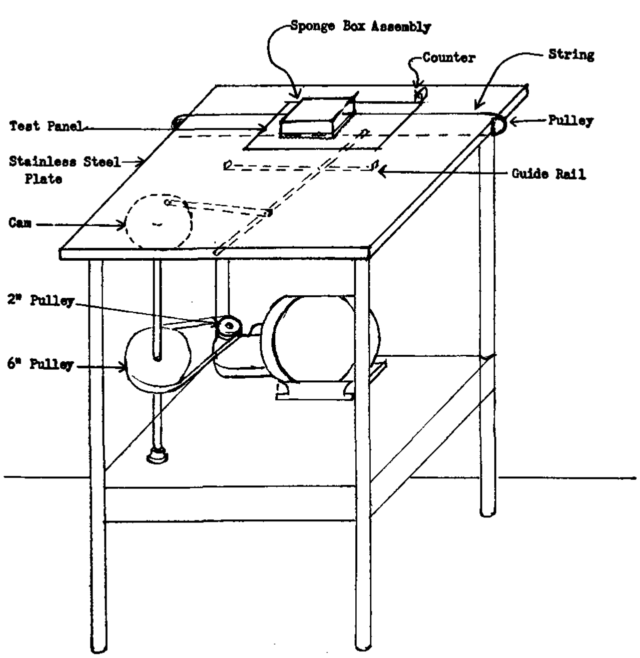

FIG. 1. Detergency apparatus.

purposes. A modified vegetable oil soap cleaner,[3] prepared by saponification of blended cocoanut and corn oils by potassium hydroxide, was selected as the standard. Its preparation was under our direct control, and its composition could be assured. The detergents evaluated are described in Table I.

TABLE I
Detergents Evaluated

Detergent	% Non-volatile	Remarks
Standard Cleaner	31	A modified vegetable oil soap cleaner
Cleaner A	8	Mixture of equal parts of a non-ionic detergent and a polyphosphate
Cleaner D	18.7	Liquid potash soap containing 1.8% inorganic phosphate
Cleaner E	16	Aqueous solution of an anionic synthetic detergent

The cleaners were evaluated according to the manufacturers' instructions and, in some cases, increased concentrations were also studied to determine if detergency could thus be increased to a point where it became comparable to the standard. St. Louis tap water of about 90 p.p.m. hardness was used to prepare the required dilutions. All solutions were tested at room temperature (25°C.).

Procedure. One hundred fifty ml. of the test detergent solution were poured into an enamel vegetable freshener pan, 14 in. long by 8 in. wide by 4½ in. deep. The test panel was introduced into this solution, face down, and allowed to soak for 60 seconds. It was then removed and placed in position in the detergency apparatus. Meanwhile 50 ml. of the detergent solution were poured over the cellulose sponge in the stainless steel box. The assembly box was set in place and the motor started. The sponge was allowed to pass over the test panel 100 times for 50 complete cycles, completed in just under 60 seconds. Approximately six ml. of detergent solution were allowed to drip onto the test panel for the 50-cycle period. The test panel was then removed from the apparatus, rinsed thoroughly under running tap water, and allowed to air dry. The light reflectance of the washed, soiled panel was determined as described below.

Light Reflectance. Photovolt's photoelectric glossmeter, model 660, equipped with a green tri-stimulus filter, was used for reflectance measurements of the unsoiled, washed panels, of the soiled, unwashed panels, and of the soiled, washed panels. The instrument was calibrated against a standard plaque, giving 76.5% reflectance relative to it.

Soil Removal Factor. The soil removal factor for each detergent was calculated from the following formula:

$$\text{S.R.F.} = \frac{R_3 - R_2}{R_1 - R_2} \times 100$$

where S.R.F. is the soil removal factor,

R_1 is the light reflectance of the original panel (unsoiled but washed),

R_2 is the light reflectance of the soiled, unwashed panel and

R_3 is the light reflectance of the soiled panels after washing.

[3] Manufactured by Vestal Laboratories Inc., St. Louis 10, Mo., under the trade name "Briten-All."

After numerous duplicable determinations R_1 was assigned a value of 51 and R_2 a value of 7.

To stress the relationship among the S.R.F. values of a given series, we introduced a new factor, relative detergency (R.D.) calculated as follows:

$$\% \text{ R.D.} = \frac{\text{S.R.F.}_x}{\text{S.R.F.}_{\text{Standard}}} \times 100$$

The values for the 10 test panels for each concentration were averaged. These results were then reported as a percentage of the soil removal obtained with the standard cleaner.

The S.R.F. and R.D. values found for a number of floor cleaners at various dilutions are given in Table II.

TABLE II
Relative Detergencies of Competitive Floor Cleaners

Detergent	Oz. used per gallon	% active ingredient	R_3	S.R.F.	% R.D.
Standard Cleaner	2	0.5	43.4	82.7	100
Cleaner A	2	0.13	18.1	25.2	31
Cleaner D	2	0.3	27.7	47.0	57
Cleaner E	2	0.26	34.2	61.8	75
Standard Cleaner	2	0.5	48.2	94.8	100
Cleaner A	4	0.26	34.2	61.8	65
Cleaner D	3	0.45	39.8	74.6	78
Cleaner E	2.5	0.325	37.5	69.4	73
Standard Cleaner	2	0.5	46.6	90.0	100
Cleaner A	6	0.39	44.9	86.1	96
Cleaner D	4	0.6	43.7	83.5	94
Cleaner E	3	0.39	36.0	65.9	73

Statistical Analysis. Certain of our data was analyzed statistically to determine if the differences observed were really different or due possibly to chance. Our first attempt was to analyze the data by means of the method of "t's" (2) as shown in Table III.

TABLE III
Statistical Analysis: Observations on Standard Cleaner, Cleaners A, D, and E; Concentrations of Two Ounces per Gallon; 10 Test Panels for Each Solution

Panel	R_3			
	Standard Cleaner	Cleaner A	Cleaner D	Cleaner E
1	42.2	20.2	33.0	32.8
2	46.8	16.0	31.8	37.6
3	43.0	17.0	31.4	33.0
4	44.6	17.6	26.4	24.0
5	46.2	19.2	22.2	32.0
6	43.8	17.2	26.6	32.0
7	44.2	18.4	27.4	42.8
8	37.6	19.2	22.8	39.0
9	44.0	17.8	24.6	37.6
10	42.0	18.2	31.0	31.2
	$\bar{x}=43.4$	$\bar{y}=18.1$	$\bar{z}=27.7$	$\bar{a}=34.2$
	$Ex^2=18{,}929.5$	$Ey^2=3{,}290.28$	$Ez^2=7{,}820.3$	$Ea^2=11{,}942.6$
	$\frac{Ex^2}{N}=1{,}892.95$	$\frac{Ey^2}{N}=329.03$	$\frac{Ez^2}{N}=782.03$	$\frac{Ea^2}{N}=1{,}194.26$
	$\bar{x}^2=1{,}883.56$	$\bar{y}^2=327.61$	$\bar{z}^2=767.29$	$\bar{a}^2=1{,}169.6$
	$s^2x=9.39$	$s^2y=1.42$	$s^2z=14.74$	$s^2a=24.7$
	$\frac{s^2x}{N}=0.939$	$\frac{s^2y}{N}=0.142$	$\frac{s^2z}{N}=1.474$	$\frac{s^2a}{N}=2.47$

The symbols used may be defined as follows:

a) $\bar{x}$ = Arithmetic mean of light reflectance readings of washed panels
b) N = Number of panels washed
c) E = Sum of
d) s = Standard deviation
e) s^2x = Standard deviation squared $= \frac{Ex^2}{N} - \bar{x}^2$
f) Let $w^2 = \frac{s^2x}{N} + \frac{s^2y}{N}$
g) $$t = \frac{(\bar{x} - \bar{y}) - 0}{w} \times \sqrt{\frac{2N-2}{2N}} \quad (7),$$
where $v = 2N - 2$ or the degrees of freedom. This *t* is the Student *t*.

t for 10 panels = 2.878 for a statistical probability of 0.99 (99 chances in 100 of being correct), using both tails of the curve for rejection purposes.

To determine if the difference found between the Standard Cleaner and Cleaner A is statistically significant we proceeded as follows:

$$w^2 = \frac{s^2x}{N} + \frac{s^2y}{N} = 0.939 + 0.142 = 1.081$$

$$w = \sqrt{1.081} = 1.04$$

$$t = \frac{(43.4 - 18.1) - 0}{1.04} \times \sqrt{\frac{18}{20}} = 23.1$$

Hence the chances were 99 in 100 that the difference found was significant and that the Standard Cleaner is the superior detergent. The "t" values found for the above reflectance readings are given in Table IV.

TABLE IV
t Values Calculated for Detergency Results Found Using Two Ounces of Cleaner per Gallon of Water

	Standard Cleaner	Cleaner A	Cleaner D	Cleaner E
Standard Cleaner	......	23.1	9.58	4.72
Cleaner A	23.1	......	7.16	9.45
Cleaner D	9.58	7.16	......	3.10
Cleaner E	4.72	9.45	3.10	......

The "t" values all exceeded 2.878 and therefore the values were all significant, that is, the chances were 99 out of 100 that all the values obtained were significant, considering both tails for rejection purposes.

The "t" values for the second series—results for which are given in Table II—are presented in Table V.

TABLE V
t Values Calculated for Detergency Results Found Using Increased Concentrations of Cleaner (cf. Table II, Second Section)

	Standard Cleaner	Cleaner A	Cleaner D	Cleaner E
Standard Cleaner	......	14.1	9.77	18.4
Cleaner A	14.1	......	4.70	1.71
Cleaner D	9.77	4.70	......	4.02
Cleaner E	18.4	1.71	4.02	......

All values were statistically significant except the differences between Cleaners A and E, where the detergent differences observed were probably due to chance.

For the third series, the results for which are given in Table II, third section, there was no significant difference among the results for the Standard Cleaner,

Cleaner A, and Cleaner D; however significant differences existed between the results for these cleaners as opposed to that for Cleaner E. These results showed that 6 oz. of Cleaner A and 4 oz. of Cleaner D were equivalent in detergency to 2 oz. of the Standard Cleaner. It was also shown that increased concentrations of Cleaner E did not effect an increase in detergency but rather that the detergency levels off at or about a concentration of 2 oz. per gallon.

This method has been successfully applied by us to the critical evaluation of floor cleaners on a price/performance basis and may likewise prove useful to large consumers with laboratories at their disposal. For example, if the detergency results showed that twice as much of product A as of product B must be used to attain the same degree of detergency, then product A would have to sell at one-half the price of product B in order to be able to compete favorably with the latter.

The method of t's was used to evaluate our data preliminarily with the full realization that a better or more appropriate method exists for the comparison of more than two sets of data. This method is known as the Analysis of Variance and by it "a set of more than two means can be legitimately compared by means of the F distribution in the following manner" (8).

The above example of relative detergencies obtained by the use of four detergents showed that if there were no differences between the detergents, the means of the light reflectances should be about the same; that is, the differences should be small and due solely to fluctuations arising in random sampling. From the values shown in Table VI, where the readings in Table III have been changed to express the differences between the observed light reflectances (R_3) and an arbitrary value of 43, it was apparent that the differences were quite large.

TABLE VI

Deviations of Observed Light Reflectances from Assumed Standard of 43 (cf. Table III)

	Detergents				Totals
	Standard Cleaner	Cleaner A	Cleaner D	Cleaner E	
1	−0.8	−22.8	−10.0	−10.2	−43.8
2	3.8	−27.0	−11.2	−5.4	−39.8
3	0.0	−26.0	−11.6	−10.0	−47.6
4	1.6	−25.4	−16.6	−19.0	−59.4
5	3.2	−23.8	−20.8	−11.0	−52.4
6	0.8	−25.8	−16.4	−11.0	−52.4
7	1.2	−24.6	−15.6	−0.2	−39.2
8	−6.4	−23.8	−20.2	−3.0	−53.4
9	1.0	−25.2	−18.4	−5.4	−48.0
10	−1.0	−24.8	−12.0	−11.8	−49.6
Totals	3.4	−249.2	−152.8	−87.0	−485.6
Means of the deviations	0.34	−24.9	−15.3	−8.7	......

To be able to test whether or not there are any significant differences between means, it was necessary to find standard errors and standard errors for differences of means, as will be shown.

Testing Procedure

The total sum of squares (A)[4] of the deviations of the light reflectances from the general mean can be divided into three sums of squares, i.e., the sum of squares of the deviations of the means of the various detergents from the general mean (B), the sum of squares of the deviations of the means of sets of panels from the general mean (C), and the sum of squares due to error (D).

[4] Letters in parentheses refer to corresponding sections of Table VII.

a) *Total Sum of Squares* $= \Sigma(x - \bar{x})^2$

$$= (-0.8)^2 + (3.8)^2 + (1.6)^2 + \ldots + (-11.8)^2 - \frac{(-485.6)^2}{40} = 3886$$

b) *Sum of Squares Between Means of Detergents* $= 10\,\Sigma(\bar{x}_D - \bar{x})^2$

$$= (3.4)^2 + (-152.8)^2 + (-249.2)^2 + (-87)^2 - \frac{(-485.6)^2}{40} = 3408$$

c) *Sum of Squares Between Means of Panels* $= 4\,\Sigma(\bar{x}_p - \bar{x})$

$$= \frac{(-43.8)^2 + (-39.8)^2 + \ldots + (-49.6)^2}{4} - \frac{(-485.6)^2}{40} = 90$$

d) *Sum of Squares Due to Error* $= A - (B + C)$.

Table VII, where the above considerations were applied to our data, gives the analysis of variances for the relative detergencies obtained.

TABLE VII

Analysis of Variance for Data in Table VI

Source of variation	Sum of squares	Degrees of freedom	Variance
Total (A)	3886	39	99.6
Between means of detergents (B)	3408	3	1136
Between means of sets of panels (C)	90	9	10
Error (D)	388	27	14.4

The error variance is an estimate of the variance of the parent population of the light reflectances of the test panels. Comparing the error variance with the variance between means of detergents, it follows that the value of F (Snedecor's F, a ratio of any two unbiased estimates of variances which are to be compared) is:

$$F = \frac{1136}{14.4} \text{ or } 78.9$$

From Table V in Hoel (7), for 27 and 3 degrees of freedom and a probability of a 1% error, the F value is 26.55. If the calculated F value is larger than 26.55, it is said to be significant with a statistical probability of 0.99 (99 chances in 100 of being correct). (Note: If the calculated F value is less than 26.55, then there is no significant difference between any two means of detergents.) Here, since F has a value of 78.9, there is a significant difference between at least two of the detergent means.

Let us now proceed to test the difference between the means for all of the detergents, taken two at a time. The standard error of any of the means of the detergents is

$$s_{mean} = \sqrt{\frac{\text{Error variance}}{N}} = \sqrt{\frac{14.4}{10}} = 1.2$$

and the standard error of the difference of the means is

$$s_{difference\ of\ means} = \sqrt{(1.2)^2 + (1.2)^2} = 1.69$$

$$t = \frac{(\text{Mean of Stand. Cleaner} - \text{Mean of Cleaner A})^5 - O}{1.69}$$

$$t = \frac{43.4 - 18.1}{1.69} = 15$$

The t value corresponding to 27 degrees of freedom (cf. Table VII, 27 represents the degrees of freedom for the error variance) from Student t tables is 2.771 for a statistical probability of 0.99 (99 chances in 100 of being correct), again using both tails for rejection purposes. Other means can be tested in this way. A difference between two means as great as 4.68 (1.69×2.771) is significant. Table VIII, presenting the other t values calculated by this method, shows that all detergent values observed are statistically significant, substantiating our preliminary statistical analysis.

TABLE VIII

t Values, Calculated from Error Variance Obtained from Analysis of Variance, for Detergency Results, Using Two Ounces of Cleaner per Gallon of Water

	Standard Cleaner	Cleaner A	Cleaner D	Cleaner E
Standard Cleaner	......	15.0	9.3	5.4
Cleaner A	15.0	......	−5.7	−9.5
Cleaner D	9.3	−5.7	......	−3.85
Cleaner E	5.4	−9.5	−3.85	......

The data for the increased concentrations of the competitive detergents may be similarly analyzed.

For the analysis of our data, we selected the percentage light reflectance values.

Conclusion

Our data show that the detergency test described is satisfactory for the evaluation of detergents, revealing any real differences among detergents. In the application of the method certain precautions must be followed to insure reasonably good duplicability. A synthetic standard soil, such as that described herein, is required. Secondly, the factory finish on the linoleum should be removed before soiling. Furthermore care must be exercised in the soiling of the panels so as to provide an even coating of soil. For purposes of comparison, a standard detergent should be employed in each series. Another precaution is to bake at one time all panels to be used in a series and to use these panels the same day they are baked.

If the data are not analyzed statistically, it is more reliable to consider the relative detergency values only. Thus different sets of data obtained at different times may be compared satisfactorily. However it is our recommendation that all such detergency data be analyzed statistically to avoid undue influence of occasional, widespread variations.

Some of the results obtained in the laboratory by means of this method have been substantiated in the field, where the Standard Cleaner was also shown to be the superior detergent.

The method described may well be used by purchasing departments as a guide to purchasing detergents on a price/performance basis. For example, if 4 oz. of Detergent X are equivalent in detergency to only 2 oz. of Detergent Y, then Detergent X would have to sell at half (or less) the selling price of Detergent Y.

Two methods for the statistical analysis of data have been described. The method of t's is recommended for a comparison between two sets of data, whereas the Analysis of Variance should be used for a comparative study of more than two sets.

[5] It can be shown that this quantity is derived from the difference between "Mean of Standard Cleaner" and "Mean of Cleaner A-43" or the difference between the means of the deviations shown in Table VI. For example, $(43.4 - 18.1) = 25.3$ as does $[0.34 - (-24.9)]$.

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