A Miniature Dishwashing Evaluation Method[1]

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Abstract

A new procedure for evaluating dishwashing products has been developed. Good precision and favorable correlation with older methods are obtained with minimum requirements of manpower, time and materials.

Hydrogenated vegetable oil shortening proves to be an ideal soil for dishwashing evaluation if the physical state of the soil is carefully controlled. With such control, it is seen that dishwashing performance is a linear function of detergent concentration. Fatty soil and its effect on foam is discussed and compared with other soils. Variations of evaluation results with water hardness are described.

Introduction

THE CONNECTION BETWEEN foaming and successful performance in a dishwashing product has been the subject of much discussion. It is generally agreed that whether justified or not, the housewife equates foaming with cleaning dishes. This attitude produces a major criterion in the consumer acceptance of a product for this purpose. It is not enough to evaluate a dishwashing product on its foaming alone, but without acceptable foam performance all other evaluations become less meaningful.

The detergent industry has constantly strived for an ultimate evaluation procedure for foaming performance. For years, Colgate-Palmolive has utilized a practical dishwashing test as described by Spangler (1). Hydrogenated vegetable oil is used as the soil in this test. None of the other soils or other procedures offered in the literature (2–12) appear to offer any over-all advantage compared to this method.

The industry's decision to convert to biodegradable surfactants resulted in a pressing formulation problem because of the need for completely new and biodegradable light-duty dishwashing liquids. A large number of surfactants had to be screened for use in the new products. The evaluation problems were magnified by other considerations which demanded a multicomponent system, thereby allowing complex interactions of substituents. Therefore, time-consuming evaluation methods requiring considerable manpower could not be used. Furthermore, a screening method was necessary which would give reproducible data over a long period of time. Only with such a tool could a reliable store of knowledge be set forth permitting the development of the desired compositions. This paper describes a test method designed to serve as a prime evaluation method for dishwashing products.

Method Development

General Considerations

The practical dishwashing test described by Spangler (1) has consistently related to consumer acceptance of dishwashing products. No strong arguments have been presented against the use of a foam end-point as a measure of surfactant performance in dishwashing. Therefore, a rapid bench scale test based on the practical test would seem desirable. A scaling-down of the amounts of detergent, water, and hydrogenated vegetable oil by a factor of 1:15 allows results to be expressed as "plates washed" in direct relation to the practical test. For these evaluations it is necessary to have a nonporous soiled surface since light-duty liquids do not completely remove soil from a porous material under mild agitation normal to hand dishwashing. Scott (13) reports conditions resulting in similar findings with built detergents. Therefore, in testing dishwashing liquids using soiled porous substrates, the soil introduced will not constantly relate to soil consumed.

For the nonporous surface required, small watchglasses have proven to be ideal. The use of two sizes of watchglasses holding different quantities of soil allows much testing time to be saved with no reduction in precision. "Three-plate" units can be washed at definite intervals until the quantity of foam remaining warns the operator of the approaching end-point. At this point "one-plate" units are introduced, with the time elapsing between the introduction of each new "plate" being reduced to one third of the interval allowed for the larger units. This factor results in test data directly proportional to time elapsed as is the case in the practical method mentioned above.

A camel hair brush is substituted for a dishcloth not only for convenience of handling but also to prevent exertion of excess force on the soil surface. As discussed later, reproducibility depends in part upon a constant removal of fine layers of the soil as contrasted to breaking off large globoids which resist emulsification.

The largest source of error in a dishwashing evaluation using hydrogenated vegetable oil is directly attributable to conditions under which the soil is handled. The ambient temperature at which the melted hydrogenated vegetable oil solidifies affects the test results. Furthermore, unless the melted soil is sampled at a constant temperature, the quantity applied to the plates can vary considerably. For these reasons it is necessary to carefully control the temperature of the soil before applying it to the plates and to then allow the soil to solidify at a standard temperature.

Test Method

Equipment and Materials. 1) Water bath which maintains 160F ± 2°. 2) Hydrogenated vegetable oil (Crisco vegetable shortening, manufactured by Procter & Gamble). 3) Deep dish watchglasses (1½ in. and 1 in. diameters). 4) Two automatic pipets, 2.0 ml, adjusted to deliver 0.36 g and 0.12 g of soil respectively. 5) Crystallizing dishes or any cylindrical vessel of approximately 6 in. diameter and 3 in. depth. 6) Electric timer. 7) Graduated cylinder, 500 ml. 8) Camel hair brush, ½ in. width, 1 in. long, flat. 9) Stock solution, 25,000 ppm as $CaCO_3$, 3Ca to 2 Mg.

Procedure. 1) Melt Crisco in beaker in constant temperature bath at 160F, add small amount of Sudan red dye. 2) Distribute large and small watchglasses (clean) in approximately a 5:1 ratio. 3) Insure that the air in the vicinity of the glasses is 76F ± 1F. Immerse the 0.36 g adjusted pipet in the melted soil a few minutes to allow thermal equilibrium. Volumetrically deliver 0.36 g to each large

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watchglass. Repeat the process with the other pipet and the small watchglasses. 4) Allow Crisco to solidify by cooling at room temperature (76F ± 1) for at least 30 min. A temperature within a few degrees of this should then be maintained until tests are completed. 5) Introduce the desired amount of dishwashing product into the crystallizing dish. This is done by adding an exact volume of a standard dilute solution of the test product to the vessel. The standard concentration for the test is considered to be 0.15 g of dishwashing product per 100 ml of solution in the test vessel. However, any reasonable concentration can be run. 6) Add to the crystallizing dish 400 ml of water of the desired hardness at 120F ± 1F. The water is prepared beforehand by use of the proper ratios of 25,000 ppm stock solution and demineralized water. 7) Timer is started, solution is splashed around vigorously with the brush to generate some foam (amount is unimportant) and a three-plate unit is introduced. Holding the watchglass partially below the surface, the soil is gently worked into the test solution with the camel hair brush. The solution is vigorously splashed with the brush to generate foam and especially to emulsify visible particles of soil. This should be done with the brush pressing on and the handle perpendicular to the bottom of the vessel. The motion should be random, not circular. At 45 sec, another three-plate unit is introduced and brushed clean and the solution splashed; this is repeated at each succeeding 45-sec interval. 8) When the foam begins to look weak, the one-plate units are then used at 15-sec intervals. The experienced operator can easily tell when to stop using three-plate units and will therefore need no more than two or three one-plate units. The end-point is taken at that point when almost no *stable* foam can be generated by splashing. Isolated groups of bubbles or a lacy ring of light foam, or both, will be produced at this point by splashing. A completely "dead" solution is not sought, since in certain cases this is impossible to attain, and false end-points would result. The judgment of the end-point is difficult for the new operator but is soon grasped by practicing. To check any end-point, the operator can add one more one-plate unit. If splashing produces either a surface condition generally unchanged in character or a dead solution, the extra unit is discarded. If, however, the quantity of foam decreases markedly, then this last unit is counted with the others. 9) The three-plate and one-plate units are counted and total number of plates are recorded. 10) The entire procedure is repeated and the mean of the results is calculated for the particular sample.

Results and Discussion

Comparison with Earlier Method

The miniature procedure was designed to obtain data comparable to the results from a practical dishwashing test so that a relationship to previous data could be retained. Various formulations were evaluated by the two methods using 0.15% of product. Different operators were utilized for the separate methods. From the results shown in Table I it can be seen that the two methods give quite similar results regardless of the water hardness.

Precision

A bottle of a commercial light-duty dishwashing liquid was tested 43 times using individually weighed samples. On 27 other occasions the test results were obtained from volumetric sampling of a dilute solution of the product. A comparison of the test results from the two procedures is shown in Table II.

TABLE I

Practical Dishwashing vs. Miniature Method
Plates washed (average)

Practical		Miniature
	50 ppm	
31.0	A	31.0
20.5	B	20.0
26.0	C	27.0
33.8	D	33.5
	100 ppm	
37.5	E	37.5
32.5	F	30.5
35.5	G	35.5
38.5	H	37.5
33.5	I	35.0
	250 ppm	
29.5	E	31.5
27.5	F	28.5
31.0	G	29.0
33.0	H	34.0
30.5	I	29.0

It is seen that the volumetric sampling yields test results with a narrow range which are more closely grouped about the mean. The range of the deviation from the mean with gravimetric sampling is only slightly greater than that which could be predicted from the precision of the balance used. Good reproducibility is obtained by the volumetric sampling procedure; the size of the samples required for the present test method precludes the gravimetric sampling either on the basis of reduced precision or increased sampling time.

A statistical analysis of the volumetric sampling data shows a standard deviation of 0.771. The 95% *confidence* limits for the mean are 34.2 ± 1.5. Assuming a normal distribution as supported by the results, *tolerance* limits such that the probability is 0.95 that at least 95% of the distribution will be included within the tolerance limits are 34.2 ± 2.0 based on the 27 replications made. This means that any additional test on the same sample should be within ±2.0 plates of the true mean with a probability of 0.95. In addition, the standard deviation of the mean of duplicate tests is $0.771/\sqrt{2}$ or 0.546. Therefore, the mean of duplicate tests will be within ±1.1 plates of the true mean for the formula based upon the estimate of 0.771 as the universe standard deviation.

Fatty Soil and Foam End-Point

The use of a vegetable shortening in dishwashing evaluations has been a long-standing practice. However, the possibility of test variations due to differences in the physical state of the fatty soil has largely been ignored. The present study has uncovered some interesting points concerning the physical state of the fatty soil. For example, good reproducibility is obtained when the laboratory temperature is kept con-

TABLE II

Comparison of Sampling Methods

Miniature test result (plates)	Frequency of result	
	Gravimetric sampling	Volumetric sampling
31	0	0
32	8	1
33	9	3
34	18	14
35	6	9
36	2	0
37	0	0

stant for successive tests. When the temperature is allowed to vary, the resulting data also vary. It is found that a carefully controlled cooling rate is very important for good reproducibility when using melted hydrogenated vegetable oil as the soil.

A microscopic examination of the solidified material obtained by rapidly cooling the melted fat reveals a much finer crystalline structure than when the fat is slowly cooled. If it is very rapidly cooled by dry ice-acetone, a gelatinous material results. A comparison of dishwashing evaluations by the miniature method shows the variation of results obtained when the plates are made by solidifying the melted soil at different cooling rates. The data in Table III are from a standard light-duty formulation used at 0.15% concentration.

All the plates used in the experiments of Table III were allowed to reach room temperature before testing except the uncooled liquid. This was added to the test solution in volumetric increments. The data show that test results are related to the particle size of the solid hydrogenated vegetable oil; as a liquid, there appears to be an effect only after some crystallization occurs.

The soil of interest is composed of a variety of fats, some liquid and some solid at room temperature. A comparison of solid and liquid fats on the basis of foam-depressing properties bears out the conclusion above. Powered tristearin or tripalmitin have definite but weak foam-depressing activity. On the other hand, large amounts of liquid corn oil, olive oil, and soybean oil have no noticeable effect on the foaming of a test solution when poured in and dispersed with a brush. However, tristearin melted in hot corn oil and cooled to room temperature is a very effective foam-depressant. It appears that the melted tristearin recrystallizes in a smaller particle size which is more effective as a foam-breaker than the original powder particles.

The hydrogenated vegetable oil which has been solidified from the melted state by cooling at room temperature (75F) is a semisolid mass of crystals and liquid oil. It was seen above that at normal test conditions, typical vegetable oils do not affect the foam. However, when corn oil is dispersed in a test solution and agitated in a Waring Blendor, the shearing action collapses the voluminous foam. From this, it appears that the fatty oils only affect foam when the oil is divided into discrete particles of a size not obtained in normal dishwashing. The minimal amount of agitation produced by a brush or dishcloth allows liquid oils to remain as relatively huge globules since they resist subdivision in water.

Therefore, it would seem that fatty material depresses and "kills" foam when the fat particles interact with the surfactant, which then is no longer available to foam. It appears that the increased effectiveness of finely divided fatty material in depressing foam is due to the greater number of fat particles present when the particle size is decreased.

TABLE III

Dishwashing Results—Soil Solidified at Different Rates

Cooling rate	Physical state	Plates washed
None (used uncooled)	Liquid	60 + (no end-point!)
Slow	Large "mushy" 'crystals	38
Normal (cooled at room temp.)	Fine crystals	34
Rapid	Very fine crystals	27
Very rapid	Gelatinous	22
None (used unmelted)	Amorphous	19

Fatty Soil-Detergent Relationship in Dishwashing

From the above discussion it is evident that there should be a fundamental relationship between the quantity of surfactant in a dishwashing test solution and the number of dishes washed (and correspondingly the amount of test soil involved). However, Smith and Taylor (9) report that the number of plates washed is almost independent of the quantity of soil (a commercial cooking fat) on the plates. They propose instead an effect on foam end-point by the solid surfaces of the plates. An experiment was designed to demonstrate the soil-detergent interaction. The miniature procedure is used as described except that sets of 1½ in. watchglasses were soiled with 0.24 g, 0.36 g, 0.48 g and 0.60 g of melted hydrogenated vegetable oil and then allowed to cool as described earlier. These are respectively two-plate, three-plate, four-plate, and five-plate units. The 1½ in. watchglasses were washed at 45-sec intervals regardless of the weight of the soil except in the last test. Two four-inch watchglasses each containing 2.16 g of the soil (equivalent to a total of 36 plates) were also prepared. The formulation tested at 0.15% concentration in this series of experiments is that one described in the discussion of precision, and had a mean test result of 34.2 ± 1.5 plates with 95% confidence. If the total weight of soil introduced is the controlling factor, then these *two* 4-in. watchglasses should, and do, produce a foam end-point since they contain more than 34.2 ± 1.5 plates of soil. Table IV shows the results of these experiments. The approximate time elapsed from beginning of test until the end-point is noted, as is the temperature of the test solution at the end-point.

One-plate units were used at 15-sec intervals near the end-point in B and C. A comparison of C with D, which used only four-plate units, shows the value of this procedure, since the test result from D could only be in multiples of four and therefore, could come no closer to the true mean than 36 plates. The same argument applies to the results of E and F, which are also high. Test G, contrary to the procedure for the other tests, had 34 plates of soil introduced with no time between the addition of the various watchglasses containing differing quantities of soil. The foam did not collapse as soon as the necessary quantity of soil was present, but only when the temperature reached approximately 105F. The same phenomenon is noted in test F, where the soil was also introduced with no time increment. Table IV shows that varying the number of "solid surfaces washed" and the weight of soil on each surface results in variations of the time interval to the end-point, with concomitant temperature drops. The *only* constant result is the total weight of soil used. Therefore, the number of plates washed must be constant since a plate is defined as some definite weight of soil.

Solution Temperature and Foam End-Point

The data of Table IV leave the question of the effects of temperature gradient unanswered. To investigate this, a series of tests was performed on the formulation used above. Table V shows results obtained by following the standard procedure with the exception that the temperature was kept constant throughout each test.

It is evident that the foam end-point depends only on the quantity of soil introduced, as long as the test solution is not above some maximum temperature when the necessary amount of soil is present. This

TABLE IV

Miniature Dishwashing with Different Weights of Soil on Plates

Test	Number of watchglasses	Wt. of soil on watchglass, g	Total wt. of soil, g	Test result in "Plates"[a]	Time elapsed, sec	Temperature at end-point, F
A	17 (1½ in.)	0.24	4.08	34	765	94
B	11 (1½ in.)	0.36	3.96			
	1 (1 in.)	0.12	0.12			
			4.08	34	510	96
C	8 (1½ in.)	0.48	3.84			
	2 (1 in.)	0.12	0.24			
			4.08	34	375	97.5
D	9 (1½ in.)	0.48	4.32	36	375	——
E	7 (1½ in.)	0.60	4.20	35	330	99.5
F	2 (4 in.)	2.16	4.32	36	130	105
G	5 (1½ in.)	0.60	3.00			
	2 (1½ in.)	0.48	0.96			
	1 (1 in.)	0.12	0.12			
			4.08	34	195	104.5

[a] Total wt. of soil divided by 0.12 g.

maximum is obviously below 120F since the test performed at 120F did not reach an end-point but was discontinued with no end in sight. Removing a test solution from the 120F bath after 34 plates of soil have been introduced and allowing it to cool at room temperature results in a total collapse of the foam at 85F. When a test following the normal procedure reaches an end-point at 34 plates and is then heated to over 120F, the foam is rejuvenated from the "dead" solution, and the end-point is reached again only by cooling to 85F. From these facts it is apparent that a solution temperature of 120F or higher melts the crystalline forms of the hydrogenated vegetable oil whether it is in the form of fresh plates or of particles already emulsified by detergent. In the case of the standard miniature procedure performed at 75F room temperature, the water is poured at 120F into the test vessel but the temperature drop immediately brings the solution temperature down to about 114F. Thus, the crystalline forms of the introduced hydrogenated vegetable oil are not changed and the end-point remains independent of the solution temperature.

Other Soils

The effects of some common food soils on foam have been studied. A standard concentration of detergent solution (initial temperature 120F) was mildly agitated and a water dispersion or solution of the soil added in timed increments. Reduction or collapse of the surface foam could then be observed and a semiquantitative determination of the amount of soil used could be obtained.

Neither soluble nor insoluble proteins show any depressant action on foam. Generally, water soluble proteins like albumin and hydrolyzed gelatin tend to stabilize foam while insoluble proteins like keratin and casein seem to have no effect. Water dispersions of whole food including milk, mayonnaise, and powdered egg produce varying degrees of foam depression but not total collapse. Addition of trace amounts of crystallized hydrogenated vegetable oil, however, brings on the total collapse. It would seem that these food soils may be collapsing the detergent foam but are themselves still foaming. The addition of some solidified fat in such cases is similar to the common household procedure of adding a little butter to prevent foaming in powdered milk.

TABLE V

Miniature Dishwashing with Constant Solution Temperature

Temperature, F	Plates washed	Time elapsed, sec
120	60 + (no end-point!)	2700 +
110	33	495
100	34	510
90	32	480

The phospholipid, lecithin, is a major component of egg yolk and is the principal emulsifying agent in mayonnaise. This material used alone is effective in collapsing detergent foam but produces enough foam itself to mask an end-point. Traces of crystallized fat, as before, allow total foam collapse. It has been found that the weights of powdered egg or lecithin producing an end-point in the presence of a trace of crystallized fat can be related to a standard miniature test using only the crystallized fat. Table VI lists the relative amounts of each soil used on three light-duty liquid formulations of widely different compositions. The tests with lecithin and powdered egg were performed using the method described above, with a very small amount of crystallized hydrogenated vegetable oil added before agitation was started. The series using hydrogenated vegetable oil by itself was done by the miniature dishwashing procedure. The data in Table VI were obtained for each soil separately by letting the weight of each soil used for formulation X equal unity and expressing the results for the other formulations with the same soil as ratios to X.

The performances based on quantity of soil consumed to reach an end-point are shown to have approximately the same relation to each other regardless of which soil is used. The results indicate that the use of a fat such as hydrogenated vegetable oil is quite satisfactory for dishwashing evaluations. Thus the use of another soil mixed with such a fat as proposed in earlier methods seems unnecessary.

Detergent Concentration and Performance

The discussion of soil-detergent relationships showed that a definite weight of soil is required to reach an end-point for a particular concentration of detergent. The literature abounds, however, with examples of differing "standard" concentrations. Furthermore, a basic question exists as to how the performances of different formulations relate to one another when tested at different concentrations. It would

TABLE VI

Amounts of Soil to Reach End-Point

	Relative amounts of each soil		
	Lecithin	Powdered egg	Hydrogenated veg. oil
Formulation X	1.0	1.0	1.0
Formulation Y	1.5	1.5	1.6
Formulation Z	1.7	1.8	1.8

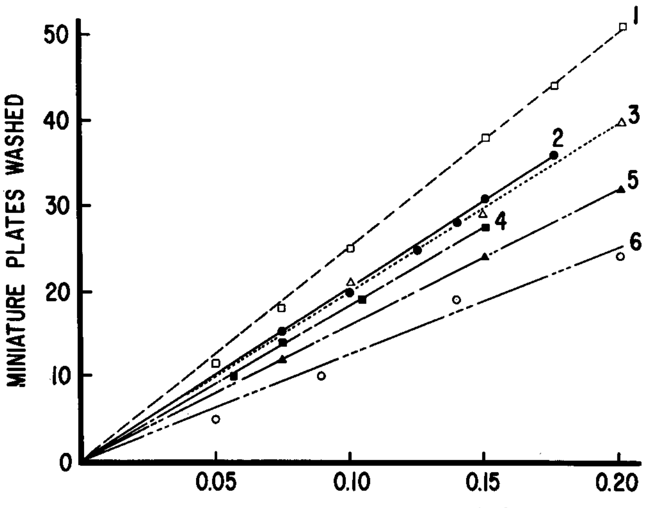

FIG. 1. Performance variation with detergent concentration; 100 ppm water.

appear that the confusion over the basic relationships in dishwashing evaluation might be due to data variations inherent to the various methods used in the past. The demonstrated reproducibility of the miniature dishwashing test should be ideal to uncover fundamental relationships.

Figure 1 shows the miniature dishwashing performances at various concentrations for six light-duty dishwashing formulations. The formulations differ widely both in total surfactant content and in the identity of the components. The data show that the plates washed are a linear function of the quantity of detergent used in the test over a realistically wide concentration range.

A point of interest is to be noted in Figure 1. The results at 0.075% concentration for formulations 1, 2, and 4 fall within a range of four plates. The same comparison at 0.15% shows a total spread of ten plates. It would appear, therefore, that evaluations carried out below 0.1% by older methods having less precision than the miniature procedure would not have been able to differentiate among these three formulations.

Water Hardness Effects

Totally different performance-hardness interactions over a wide hardness range were demonstrated by Anstett, Munger, and Rubinfeld (14) for two light-duty liquid detergents by using the miniature procedure. These two formulations differed only in the carbon-chain length and phenyl position of a straight-chain alkylbenzene sulfonate component. It would appear that the complex formula differences possible in light-duty liquids due to amounts, identities and ratios of the various components should produce diverse performance-hardness interactions. Figure 2 shows miniature dishwashing performance variations obtained from testing different types of liquid formulations at 0.15% concentration at various water hardnesses. It is obvious that different compositions can perform in various ways over a hardness range. Other authors (6) have shown data of the same type for liquids; Anstett et al. reported a similar conclusion for light-duty powder systems.

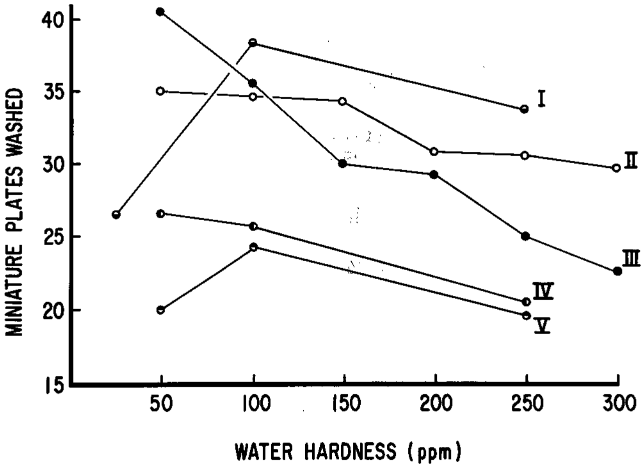

FIG. 2. Performance variation with water hardness; 0.15% product concentration.

Adding to this a consideration of the concentration effects for various formulas at constant hardness as seen in the preceding Figure, one realizes the complexity of data obtainable under varied conditions. It has been evident in the past that large numbers of tests must be performed on a given composition for comparative dishwashing evaluation unless concentration, hardness, and method are standardized. When these conditions are standardized by utilizing "cafeteria" testing as reported by Edwards and Stupel (12), the further complication of different soils on each plate is introduced. It is quite understandable why these authors found it necessary to report the average of 20 individual washes for each composition tested. Even then, their results for certain compositions going from one hardness to another show some conflicting performances at two different cafeterias. The miniature test, on the other hand, gives essentially the same result at a given hardness when employed in different locations.

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