Automatic Determination of the Foam End Point in a Simulated Dishwashing Test

G. M. HARTWIG, Shell Development Company, Emeryville, California 94608

Abstract

The disappearance of foam when increments of soil are added is frequently used to assess the foam performance of surfactants in dishwashing. A small scale screening test has been published using a Terg-o-tometer to generate foam and disperse the soil. However, the end point is difficult to determine visually because of the violent agitation of the surface. A method has been developed, whereby the surface foam reflectance is automatically and continuously recorded from four beakers of surfactant solution simultaneously. Near the end point, the rate of foam disappearance is determined and the complete foam disappearance can be interpolated from the instrumental recorded curves. Comparisons are given for experienced operator and instrumentally determined end points which are shown to be in agreement.

Introduction

THE PERFORMANCE OF LIGHT DUTY dishwashing liquid detergents is evaluated by means of foam stability. The ability of a detergent to foam in the presence of soil is considered the most important property and is directly related to cleaning in actual use. Although many methods have been developed to measure foam stability, a simulated dishwashing method published several years ago by W. G. Spangler (1) is considered very useful. This method uses a Terg-o-tometer modified to accommodate beakers of detergent solution visibly positioned on an elevated platform. The simulated dishes are in the form of small pieces of terry cloth that have absorbed a small amount of hydrogenated vegetable oil (Crisco). The detergent solution is agitated by the Terg-o-tometer and the simulated dishes are added at regular intervals until the foam disappears. The number of simulated dishes used by this method approximates the number of dishes washed in an actual dishwashing test.

One of the difficulties of this test is the determination of the end point, which requires that the operator note when the surface of the detergent is one half covered with foam. As the surface is being violently agitated and the foam is gradually dis-appearing it is difficult to determine the end point visually. An operator requires considerable amount of experience to be able to determine a reproducible end point. Another end point frequently used is when the foam has completely disappeared from the surface. In many instances, the foam has a tendency to linger and only gradually disappear, with a small fringe of foam on the edge remaining for some time. Both of these end points can be determined by means of a photoelectric method of foam detection. This method continuously measures, by means of photocells, the amount of light reflected from the surface of beakers of detergent solution. The reflectances are recorded on two-strip charts.

The Colgate simulated dishwashing method has been in use at our laboratories for several years, however, without the use of photocell detection, which is a recent innovation. During this time, it has been desirable to modify the method and equipment in several ways to improve the reproducibility of results. Variation in end points have been traced to the positioning of the agitator paddles relative to the liquid surface. An improved paddle support and rigid control of the beaker size has minimized this problem. A more accurate timer has been added to the Terg-o-tometer and a counter to determine the agitator speed. Other changes to increase the number of determinations per day have been made in the method of cutting terry cloth swatches and in the dispensing of fat on the cloth.

Description of the Modified Terg-o-tometer

A drawing of the modifications made to the Tergo-tometer is shown in Fig. 1. The light sources used are four 100-w incandescent bulbs in aluminum reflectors. Positioned in front of each bulb is a disc of pyrex infrared heat absorbing glass to minimize heating of the detergent solution. The light is reflected from the surface of the foam or liquid in the beaker through a blue filter and a lens to four pairs of cadmium sulfide photo receptors located on each side of the stirring shafts, positioned to view only the surface of the liquids below. A red dye is used in the detergent solution and the blue filter increases the contrast between the liquid and foam. The signal from the photocells goes to a control box shown on the right side of Fig. 1, and the circuit diagram is shown in Fig. 2. This control box is used to damp the rapid fluctuations from the photocells caused by the oscillating liquid surface. The control box also supplies voltage by means of mercury batteries to the photocells which are light sensitive resistors. A variable bucking voltage is located on the control box to provide an adjustment for maximum The modified signal from the control box light. then enters two dual channel recorders which continuously and simultaneously record the signal from the four pairs of photocells on two 5-in. strip charts. A chart speed of 1 in./min is used, employing Varian chart paper no. 5A marked 4 divisions/in., 1 division corresponding to 15 sec, or 1 simulated dish.

The aluminum panel where the beakers are located is coated with a dull black finish to minimize unwanted reflections. Thin black plastic discs are mounted on the agitator shafts just over the paddles to reduce reflections from the paddles. A list of parts for modifying the Terg-o-tometer is given in Table I.

Description of Operation

Adjustment of Equipment for Recording Reflectance

The Varian recorder used is very sensitive and light responses can give a signal that is too large to be recorded. To regulate this, two standards of reflectance are required to adjust all four recorder pens to be the same and within the chart range. The white standard used is 65% reflectance as measured



FIG. 1. Modified Terg-o-tometer.

- 1. Terg-O-Tometer
- Terg-O-Tometer
 Switch-On/Off Lights
 Lamp with Pyrex Filter
- Glass
- 4. Control Box

6. Stirring Rod Spacer 7. Stirring Rod 8. Reflector 9. Stirring Rod Disconnect

5. Beaker

by a Gardner reflectometer using a green filter, and the dark standard, 15% reflectance. Gardner $4^{1}/_{4}$ -in. sq porcelain standards were used. The adjustment for the white standard is made by using both the maximum light resistor on the control box or on the recorder. The dark standard is adjusted to the high end of the scale by using the range adjustment on the recorder. As each control influences the other, both have to be changed to acquire the desired range.

10.	Light Holder
11	Dhotos 11 Assault

- 11. Photocell Assembly 12. Wiring
- 13. Output Connectors

Equipment and Materials

The operation is similar to that previously described (1) with a few exceptions. Terry cloth swatches $\frac{1}{2} \times \frac{11}{2}$ in. are die cut using a Hytronic cutting machine (United Shoe Machinery Corp., Boston, Mass.). The terry cloth used is style 6063, 36 in. wide (Wellington Sears Co.) which requires a special order of 1,000 yards or more in which a

Surface Coated Black
 1% Diameter Discs-Black

17. Maximum Light Adjustment

16. Heat Absorbing Glass

TABLE I List of Parts

Item	Quant.	Model No.	Description	Manufacturer
			Control panel	
1	1	CU 2109A	Housing	Bud Radio, Inc., Willoughby, Ohio
2	8	4RM-4-R	Cell, mercury 1.34 V	Mallory, Indianapolis, Indiana
3	4	510	Potentiometer, five turn $10,000 \Leftrightarrow$	Spectrol, San Gabriel, Calif.
4	4	RN20X1002F	Resistor, deposited carbon $10,000 \Leftrightarrow$	Texas Instrument, Dallas, Texas
5	8	TE1162	Capacitor, tantalum 100 µf 15 VDC	Sprague Electric, North Adams, Mass.
6	4	31-221	Connector, BNC	Star-Tronics, Inc. Georgetown, Mass.
7	4	11	Multidial for potentiometer	
			Light source	
8	2		Lite Bar	Smith Victor, Griffith, Indiana
9	4	100AX/W	Lamp, 100 w	General Electric, Cleveland, Ohio
10	4	M4	Reflector	Colortran Industries, Burbank, Calif.
	4		Pyrex infrared heat absorbing glass, 4 in. diameter by ¼ in. thick	Corning Glass, Corning, N.Y.
			Photocell assembly	
	8		Holder	Shell Development, Emervville, Calif.
12	16		Lens, Dbl. Cvx 11 mm diameter by 29 mm focal length	Edmund Scientific, Barrington, N.J.
13	8	5M2L	Photocell, Cadmium sulfide	Clairex, Inc., N.Y.
14	8	4-72	Filter, Glass blue-green	Corning Glass Works, Corning, N.Y.
15	2		Switch DPST 6A-125V	Any
16	1	7243	Terg-o-tometer	U.S. Testing, Hoboken, N.J.
17	2	G-22-A	Recorder, Strip chart 2 channel	Varian Assoc., Palo Alto, Calif.





Note: Unit Consists of Four (4) of Above

B1 B2 Mercury Battery CL1 CL2 Cd5 Photocell

FIG. 2. Wiring diagram for control box.

fabric with no finish is requested. Any finish on the fabric affects the foam destroying capacity of the Crisco-absorbed swatches. For cutting, the terry cloth is placed on $\frac{1}{8}$ in. aluminum flat platters $(12 \times 18 \text{ in.})$, which are covered with one thickness of masking tape. During the cutting of about 200 swatches per platter, some of the cotton fibers along the lines of the cut are imbedded in the masking tape to the extent that the swatches remain in place during soiling but can be readily removed when needed.

A modified oil can is used for soiling the cotton terry cloth swatches. This dispenser can be adjusted so that the amount of melted Crisco ejected with each stroke can be controlled. A screen diffuser is attached to the tip of the spout to spread the melted Crisco over the swatch; $0.3 \pm .05$ g is applied to each swatch. The swatches are cooled for 1 hr before using.

Preparations for Operation

Four 1500-ml beakers with an inside diameter variation of not more than 1 mm are mounted on the Terg-o-tometer with the agitator and modified guides. Each combination is numbered and used together. The guide of each is adjusted so that when 400 ml of detergent solution is used, the agitator is immersed to the same depth in each liquid. The detergent solution is heated to 115F and 1 ml of .08% solution of Rhodamine B dye is added to

TABLE	II
Surfactants	Used

Anionics	
LAS	Linear alkyl benzene sulfonate (average carbon $= 11.4$)
Coco 3EOS	Coconut alcohol (3EO) ethoxysulfate. Sodium salt
N25-3A	Carbon 12-15 Neodola (3EO) ethoxysulfate. Ammonium salt
N23-1A	Carbon 12-13 Neodol (1EO) ethoxysulfate. Ammonium salt
N23-2A	Same with 2EO
N28-3A	Same with 3EO
N23-5A	Same with 5EO
Nonionics	
N23-5	Carbon 12-13 Neodol (5EO) ethoxylate
N23-7	Same with 7EO
N23-9	Same with 9EO
N23-11	Same with 11EO
Foam Promoters	
LDMAO	Lauryldimethylamine oxide
LMEA	Lauricmonoethanolamide
LDEA	Lauricdiethanolamide
LMEA-1	Lauricmonoethanolamide-1EO
Commercial Prod	lucts
A	Light duty liquid
в	Same
C	Same
D	Same

^a Shell Trademark.



FIG. 3. Conditions after 2 minutes of agitation.

increase contrast between foam and liquid. The Terg-o-tometer is adjusted to 75 rpm with the speed control as a rough guide. A more accurate determination is made using the Gralab Universal Timer and the rachet counter mounted on the front.

Operation

With the detergent solutions in place, generally three samples and a reference detergent, the solutions are agitated for 1³/₄ min to build up a foam layer (Fig. 3), while the recording pens have moved to the left indicating a higher reflectance. The lights are turned off briefly to indicate on the chart the start of the run, and one swatch is added to each beaker at 15-sec intervals until the foam has disappeared. Figure 4 shows the test near the end of the run where beakers 2 and 4 have very little foam and the corresponding pens have moved to the right. Figure 5 shows an example of two curves made by the recorder. The left side shows the foam build-up and start of the run and the right side shows the foam disappearance.

End Point

In many instances, the complete disappearance of foam occurs only gradually. For that reason, a more reproducible end point is when the surface of the beaker is about 50% foam. This point corresponds to the inflection point of the reflectivity curve, and is the point where the foam is disappearing at the most rapid rate. The intersection of two lines, one with the same slope as the inflection point, and the



FIG. 4. Near end of run,

Bited Order, 8/A Hardness, 100 Disket Disket Ternary Blends and Coco 3EOS LASYN23-5.4/LDEA 97 5/22 5/10 42.5(6/15.2) 24 41.60 150 34.2 24.3 LASYN23-5.4/LDEA 97 5/22 5/10 42.5(6/15.2) 24 41.60 150 34.2 24.5 LASYN23-5.4/LDEA 55/33/12 14 150 25.6 26.5 LASYN23-5.4/LDEA 55/32/12 24 150 25.6 26.5 LASYN23-5.4/LDEA 55/32/12 24 150 27.5 28.6 LASYN23-5.4/LDEA 55/32/12 24 150 27.5 28.0 LASYN33-10 34 150 24.5 24.0 24.6 LASYN33-10 34 150 27.6 28.2 28.2 N25-3A/LDEA <th colspan="8">Comparison of Instrument and Operator End Points</th>	Comparison of Instrument and Operator End Points							
Land Active matter ppm Inst. Oper. Ternary Back Straw-Gov 2010 67.4/20.25/10 21.5/07.3/10 3.4 150 23.4 23.6 23.8 LAS/R25-3A/LDEA 55/33/12 1.4 150 24.4 150 24.5 24.6 LAS/R25-3A/LDEA 55/33/12 1.4 150 26.4 26.3 26.4 26.3 26.4			Conc, g/1,	Hardness, ppm	Dishes ^a			
Termary Banda and Core 31008 1.8 / 122 - 3/, 10 EA 57, 5/22, 5/10 32, 5 / 47 9, 10 34 150 25, 4 25, 4 LAS/N25-3/LDEA 55, 733/12 14 150 25, 6 25, 5 LAS/N25-3/LDEA 55, 733/12 14 150 25, 6 25, 5 LAS/N25-3/LDEA 55, 733/12 34 150 25, 4 25, 5 LAS/N25-3/LDEA 55, 733/12 34 150 25, 4 25, 5 LAS/N25-3/LDEA 55, 733/12 34 150 25, 4 25, 3 LAS/N25-3/LDEA 55, 733/12 34 150 25, 3 25, 3 LAS/N25-3/LDEA 55, 733/12 34 150 25, 3 25, 3 LAS/N25-3/LDEA 55, 733/12 34 150 25, 3 25, 3 LAS/N25-3/LDEA 55, 733/12 34 150 25, 3 25, 3 LAS/N25-3/LDEA 55, 733/12 34 150 25, 3 25, 3 N25-3/LDEA 85/15 34 150 25, 3 25, 3		Біеца	Active matter		Inst.	Oper.		
LAS/N25-3A/LDEA 55/35/12 34 150 94.2 94.3 LAS/N25-3A/LDEA 55/35/12 1.6 160 19.4 19.8 LAS/N25-3A/LDEA 55/35/12 1.6 160 24.5 25.4 25.4 LAS/N25-3A/LDEA 55/35/12 34 150 25.4 25.4 25.4 LAS/N25-3A/LDEA 55/35/12 34 150 25.7 26.0 LAS/N23-3A/LDEA 55/35/12 34 150 25.7 26.0 LAS/N23-3A/LDEA 55/35/12 34 150 25.4 25.3 Coce 3EO/LDEA ^N 55/33/12 34 150 25.3 25.3 Binary Blends With Feam Prometers N25-3A/LDEA 85/15 34 150 24.6 25.4 N25-3A/LDEA 85/15 34 150 24.7 24.6 N25-3A/LDEA 85/15 34 150 24.7 24.6 N25-3A/LDEA 85/15 34 150 24.7 24.6 <	Ternary Blends and Coco 3EOS	67.5/22.5/10	.24	150	23.8	23.8		
LAS/N25-3A/LDEA 55/33/12 16 34 34 36 36 36 36 36 36 36 36 36 36 36 36 36		45/45/10 21.5/67.5/10	.24 .24	$150 \\ 150$	$\substack{\textbf{24.2}\\\textbf{26.0}}$	$\substack{\textbf{24.0}\\\textbf{26.3}}$		
14 150 20.9 20.9 14 150 20.4 20.9 14 150 20.4 20.9 14 150 20.4 20.9 14 150 20.4 20.9 14 150 20.4 20.9 14 150 20.4 20.9 14 150 20.4 20.9 14 150 20.4 20.9 14 150 20.3 20.9 14 150 20.3 20.9 14 150 20.3 20.9 15 150 10.0 24.4 150 20.3 15 150 21.4 21.5 21.4 21.5 15 150 21.4 21.5 21.4 21.5 15 150 21.4 21.5 21.4 21.5 15 150 21.4 21.5 21.5 21.5 16 150 21.4 21.5 21.5 21.5 16 150 22.5 22.5 22.5 22.5 16 150 22.5 22.5 22.5 22.5 16 150 150 150	LAS/N25-3A/LDEA	55/33/12	.16	50	19.4	19.3		
124 150 25.6 25.6 133 160 26.4 26.5 145 55.78 26.4 26.5 145 55.78 26.4 26.5 145 55.78 26.4 26.5 145 55.78 26.4 26.5 145 55.78 26.4 26.5 145 55.78 26.4 26.5 145 55.78 26.7 26.0 145 55.78 26.7 26.0 145 55.78 26.7 26.0 145 55.78 26.7 26.0 145 56.78 26.7 26.0 145 150 26.3 26.2 145 160 21.4 21.5 150 21.4 21.5 21.5 150 22.4 150 29.0 150 22.4 20.0 20.0 150 22.5 23.0 23.0 150 22.6 28.0 28.0 150 150 15.0			.16 .24	150	20.9 6.3	20.8		
LAS/N23-1A/LDEA 55/38/12 33 360 26.4 36.8 LAS/N23-1A/LDEA 55/38/12 34 150 27.6 28.0 LAS/N23-3A/LDEA 55/38/12 34 150 27.6 28.0 LAS/N23-3A/LDEA 55/38/12 34 150 27.6 28.0 LAS/N23-3A/LDEA 55/38/12 24 150 26.3 26.2 Does 505 10 24 150 26.3 26.2 Biary Bloads With Foar Promoters 55/33/12 24 150 21.8 22.8 N35-SA/LDEA 55/15 16 150 21.8 22.8 N35-SA/LDEA 85/15 24 150 29.0 30.4 N25-SA/LDEA 85/15 16 160 24.3 24.8 N25-SA/LDEA 85/15 24 150 29.0 30.4 N25-SA/LDEA 85/15 24 150 25.2 33.0 N25-SA/LDEA 85/15 24 150 25.4 33.0 N25-SA/LDEA 85/15 24 150 15.0 15.0 N25-SA/LDEA 85/15 24 150 15.0 15.0 N25-SA/LDEA 85/15 24.5			.24	50	25.6	25.3		
130 150 28.9 28.9 145/N23-14/LDEA 55/33/12 24 150 25.7 28.0 145/N23-4/LDEA 55/33/12 24 150 27.6 28.0 145/N23-4/LDEA 55/33/12 24 150 27.6 28.0 145/N23-4/LDEA 55/33/12 24 150 27.6 28.0 145/N23-4/LDEA 55/33/12 24 150 24.8 26.0 145/N23-4/LDEA 55/33/12 24 150 24.8 26.0 150 25.7 27.6 27.6 27.6 27.6 150 27.4 150 27.4 27.6 27.6 150 27.4 150 27.4 27.6 27.6 150 29.0 85/15 24 150 29.0 80.4 N25-3A/LDEA 85/15 24 150 23.7 24.0 160 23.7 24.0 24.0 26.0 26.0 161 160 23.7 24.0 26.0 26.0 163 160 23.7 24.0 26.0 26.0 164 160 23.7 24.0 26.0 26.0 165 25.7 <td></td> <td></td> <td>.24 .24</td> <td>300</td> <td>24.4</td> <td>23.8</td> <td></td>			.24 .24	300	24.4	23.8		
LAS/N22-1A/LDEA LAS/N23-5A/LDEA LAS/N23-5A/LDEA 55/38/12 55/38/12 24 24 24 150 150 25.7 24.8 26.0 24.5 Oceo 2EOS 100 .24 150 26.3 26.3 LAS/N23-5A/LDEA 55/38/12 .24 150 26.3 26.3 LAS/Oceo 3EO/LDEA ^b 55/38/12 .24 150 26.3 26.3 Binary Elevel With Foam Promoters 85/15 .16 50 21.8 22.8 N25-3A/LDEA 86/15 .24 150 22.8 26.3 N25-3A/LDEA 85/15 .24 150 22.7 24.0 .24 150 22.7 24.0 26.0 26.0 N25-3A/LDEA 85/15 .24 150 22.7 24.0 .25 150 22.6 26.0 26.0 26.0 26.0 N25-3A/LDEA 85/15 .24 150 27.5 27.8 27.8 N25-3A/LDEA 160 16.0 16.0 16.0 16.0 16.0 16.0<			.82 .32	50 150	$28.9 \\ 26.4$	29.8 26.8		
LAS / N23-2A / LDFA 56 / 33 / 12 24 150 24.6 28.0 LAS / N23-2A / LDFA 56 / 33 / 12 .24 150 24.8 26.0 LAS / N23-2A / LDFA 55 / 33 / 12 .24 150 26.3 26.2 LAS / Oceo 3EO / LDFA 55 / 33 / 12 .24 150 26.3 26.3 Binary Blends With Foum Promoters	LAS/N23-1A/LDEA	55/33/12	.24	150	25.7	26.0		
LAS/N23-34/LDEA 05/33/12 24 150 24.8 25.0 Oceo 3EOS 100 .24 150 26.3 26.2 LAS/Oceo 3FO/LDEA* 56/33/12 .26 26.3 26.2 Binary Blends With Feam Promoters	LAS/N23-2A/LDEA	55/33/12	.24	150 150	27.6 24.5	28.0 24.3		
Occo 3EO S 100 24 150 26.3 26.2 LAS/Occo 3EO/LDEA 5/33/12 3.4 160 25.3 25.3 Binary Blends With Foam Promoters N25-3A/LDMAO 85/15 16 160 21.4 22.5 N25-3A/LDMAO 85/15 16 500 23.4 25.5 23.2 N25-3A/LDEA 85/15 24 150 23.7 24.0 23.0	LAS/N23-5A/LDEA LAS/N23-5A/LDEA	55/33/12	.24	150	24.8	25.0		
LAS/Oseo 3EO/LDEA ^V 55/33/12 24 150 25.3 25.3 Binary Blends With Poam Promoters N25-3A/LDEA 85/15 16 50 21.4 22.8 N25-3A/LDEA 85/15 24 150 27.8 27.8 N25-3A/LDEA 85/15 24 150 22.4 24.8 N25-3A/LDEA.1 85/15 24 150 23.0 23.0 Binary Blends With Nonionics 16 150 18.4 18.3 12.3 LAS/N23-7 70/30 24 150 18.4 18.3 12.3 N26-3A/LMEA.1 85/15 24 150 18.9 12.3 12.3 LAS/N23-7 70/30 24 150 18.4 18.3 12.3 12.3 12.3 <td< td=""><td>Coco 3EOS</td><td>100</td><td>.24</td><td>150</td><td>26.3</td><td>26.2</td><td></td></td<>	Coco 3EOS	100	.24	150	26.3	26.2		
Binary Blends With Foam Promoters 55/15 16 50 21.8 22.4 22.4 22.4 22.5 N25-3A/LDMAA 85/15 160 21.4 22.4 22.5 150 22.4 22.5 22.5 24.5 22.5 22.5 24.5 24.5 24.5 25.6 33.6 33.0 27.5 27.8 Binary Blends With Nonionics 24.5 150 18.4 16.3 24.5 150 18.4 18.3 18.3	LAS/Coco 3EO/LDEAb	55/33/12	.24	150	25.3	25.2		
N25-3A/LDMAO 85/15 13 160 21.4 24.5 32 50 30.4 32.5 32.3 30.4 32.5 N25-3A/LMEA 85/15 .24 150 29.0 30.4 N25-3A/LDEA 85/15 .16 50 24.3 24.6 N25-3A/LDEA 85/15 .16 50 24.3 24.0 .24 150 22.6 23.0 24.0 24.0 .24 150 22.6 23.0 24.0 24.0 .24 150 22.6 23.0 24.6 23.0 N25-3A/LMEA.1 85/15 .24 150 27.5 27.8 Binary Blends With Nonionics 1 1.6 15.0 15.0 15.0 LAS/N23-7 70/30 .16 15.0 15.0 15.0 .100/0 .24 150 15.3 10.3 13.3 .24 150 10.3 13.3 13.3 15.0	Binary Blends With Foam Promoters	/	10	50	01.0	00.8		
N25-2A/LMEA 85/15 150 27.8 27.8 27.8 32.5 N25-3A/LMEA 85/15 160 50 24.3 29.0 30.4 N25-3A/LMEA 85/15 166 50 24.3 24.8 24.8 1.6 150 22.7 24.0 24.0 24.0 24.0 24.0 .16 150 22.6 33.0 30.0 30.0 30.0 30.0 N25-3A/LMEA.1 85/15 .24 150 27.5 27.8 33.0 N25-3A/LMEA.1 85/15 .24 150 27.5 27.8 30.0 N25-3A/LMEA.1 85/15 .24 150 18.1 18.2 30.0 N25-3A/LMEA.1 85/15 .24 150 18.3 12.3 12.0 15.0 16.3 16.3 15.0 <t< td=""><td>N25-3A/LDMAO</td><td>85/15</td><td>.16</td><td>150</td><td>21.8 21.4</td><td>22.8 21.5</td><td></td></t<>	N25-3A/LDMAO	85/15	.16	150	21.8 21.4	22.8 21.5		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $.24	150	27.8	27.8		
N25-3A/LMEA 85/15 .24 150 29.0 30.4 N25-3A/LDEA 85/15 .16 50 24.3 24.6 .24 150 22.0 24.0 24.0 24.0 .24 150 22.0 23.0 23.0 23.0 N25-3A/LMEA-1 85/15 .24 150 22.6 23.0 Binary Blends With Nonionics			.32	150	29.5	32.3		
N25-3A/LDEA 85/15 16 50 24.3 24.8 .24 150 23.6 29.0 .32 150 32.6 33.0 N25-3A/LMEA-1 85/15 24.8 32.6 33.0 Binary Blends With Nonionics	N25-3A/LMEA	85/15	.24	150	29.0	30.4		
N25-3A/LMEA-1 85/15	N25-3A/LDEA	85/15	.16	50	24.3	24.8		
32 50 32.6 33.0 N25-3A/LMEA-1 85/15 .24 150 27.5 27.8 Binary Blends With Nonionics			.10 .24	150	28.0	29.0		
N25-3A/LMEA-1 85/15 2.4 150 27.5 27.8 Binary Blends With Nonionics 1.45/N23-5 70/30 3.6 150 18.4 18.3 LAS/N23-7 70/30 3.6 150 15.9 16.3 N00/00 2.44 150 15.9 16.3 80/20 2.44 150 19.9 19.8 80/20 2.44 150 19.9 19.8 80/20 2.44 150 19.9 19.8 80/20 2.44 150 19.9 19.8 80/20 2.44 150 19.9 19.8 80/20 2.44 150 19.3 19.3 10.0 3.22 150 20.6 20.8 11.4S/N23-9 70/90 2.44 150 16.7 16.8 1.AS/N23-9 70/90 2.44 150 22.7 22.5 1.AS/N23-9 70/90 2.44 150 22.7 22.5 1.1			.32 .32	50 150	32.6 32.6	33.0 33.0		
Binary Blends With Nonionics 148 18.4 18.3 LAS/N23-5 70/30 .16 150 18.4 18.3 LAS/N23-7 70/30 .16 150 15.9 16.3 100/0 .24 150 15.9 16.3 15.9 80/20 .24 150 18.3 12.3 16.3 .24 150 19.9 19.8 19.3 19.3 .221 50 24.2 22.0 22.0 22.4 150 19.3 19.5 LAS/N23-9 70/30 .24 150 19.3 19.5 1.45 1.45 18.4 16.3 16.7 16.8 16.7 16.8 16.7 16.8 16.7 16.8 16.7 16.8 16.7 16.8 16.7 16.8 16.7 16.8 16.8 16.8 16.8 16.8 16.8 16.8 16.8 16.8 16.8 16.8 16.8 16.8 16.8 16.8 16.8 16.8	N25-3A/LMEA-1	85/15	.24	150	27.5	27.8		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Binary Blends With Nonionics							
LAS/N23-7 70/30 70/30 16 150 150 16.0 16.3 22.3 100/0 24 150 18.3 22.3 70/30 24 150 19.9 19.8 24 50 20.1 20.0 24 50 20.1 20.0 24 150 19.3 19.3 32 50 24.2 22.0 32 50 24.2 22.0 32 50 24.2 22.0 32 50 24.2 22.0 32 150 20.6 20.8 32 150 19.3 19.5 1.AS/N23-9 70/30 2.24 150 19.3 19.5 LAS/N23-9 70/30 2.24 150 19.3 19.5 LAS/N23-9 10/30 2.24 150 19.3 19.5 LAS/N23-9 20.1 19.8 Commercial Detergents Light duty liquid A 0.4 50 22.7 22.5 0.8 150 33.9 34.5 0.8 150 22.4 33.0 Light duty liquid B 0.4 50 21.8 21.8 0.8 150 22.4 22.5 0.8 50 32.7 32.8 0.8 150 22.4 22.5 0.8 150 28.6 28.8 Light duty liquid C 0.4 50 18.3 16.8 0.8 150 28.6 28.8 Light duty liquid D 0.4 50 18.3 16.8 0.8 150 28.6 28.8 Light duty liquid D 0.4 50 18.3 16.8 0.8 150 25.2 25.5 Light duty liquid D 0.4 50 18.3 16.8 0.8 150 25.2 25.5 Light duty liquid D 0.4 50 18.3 16.8 0.8 150 25.2 25.5	LAS/N23-5	70/30	.24	150	18.4	18.3		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	LAS/N23-7	70/30	.16	150	15.0	15.0		
80/20 70/80 .24 .24 150 .94 20.1 .93 20.0 .93 20.1 .93 19.3 .93 .32 150 20.6 20.8 20.6 20.8 .32 150 20.6 20.8 20.6 20.8 .32 150 20.6 20.8 20.6 20.8 LAS/N23-9 70/80 .24 150 16.7 16.8 LAS/N23-91 70/30 .24 150 20.1 19.8 Commercial Detergents .24 150 22.7 22.3 Light duty liquid A 0.4 50 22.7 22.5 .0.8 50 33.9 34.5 33.0 Light duty liquid B 0.4 50 21.8 21.8 .0.8 50 32.7 32.8 33.0 Light duty liquid C 0.4 50 18.3 16.5 .0.8 150 22.6 22.8 25.5 Light duty liquid D 0.4 50 18.2 13.0 .0.8 150 25.2 25.5 25.5 L		100/0	.24	$150 \\ 150$	18.3 19 9	22.3 19.8		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		70/30	.24	50	20.1	20.0		
60/40 .32 150 20.6 20.8 LAS/N23-9 70/30 .24 150 19.3 19.5 LAS/N28-11 70/30 .24 150 20.1 19.8 Commercial Detergents .24 150 22.7 23.3 Light duty liquid A 0.4 50 22.7 22.5 0.8 50 33.9 34.5 0.8 150 32.4 38.0 Light duty liquid B 0.4 50 21.8 21.8 0.8 150 32.7 32.8 38.0 Light duty liquid C 0.4 150 22.4 22.5 0.8 150 32.4 38.0 38.0 Light duty liquid C 0.4 150 22.4 22.5 0.8 150 28.6 28.8 28.8 Light duty liquid C 0.4 150 16.4 16.5 0.8 150 28.9 29.0 0.8 150 28.5 Light duty liquid D 0.4 150 13.6 13.8 0.8 <td></td> <td></td> <td>.24</td> <td>150</td> <td>$19.3 \\ 24.2$</td> <td>19.3 22.0</td> <td></td>			.24	150	$19.3 \\ 24.2$	19.3 22.0		
LAS/N23-9 70/30 .24 150 16.7 16.8 LAS/N23-11 70/30 .24 150 20.1 19.8 Commercial Detergents .24 150 22.7 23.3 Light duty liquid A 0.4 50 22.7 22.5 0.8 50 33.9 34.5 0.8 150 32.4 38.0 Light duty liquid B 0.4 50 21.8 21.8 0.8 150 32.4 38.0 32.4 38.0 Light duty liquid B 0.4 50 21.8 21.8 38.0 Light duty liquid C 0.4 150 22.4 22.5 38.8 Light duty liquid C 0.4 50 18.3 16.5 0.8 150 28.6 28.8 38.5 Light duty liquid D 0.4 50 18.3 16.5 0.8 150 28.9 29.0 25.5 Light duty liquid D 0.4 50 18.2 13.0 0.8 150 22.3 22.5			.32	150	20.6	20.8		
LAB/N23-11 70/30 .24 150 20.1 19.8 Commercial Detergents	LAS/N23-9	60/40 70/30	.24 .24	150	19.3	19.5		
Commercial Detergents 0.4 50 22.7 23.3 Light duty liquid A 0.4 150 22.7 22.5 0.8 50 33.9 34.5 0.8 50 32.4 38.0 Light duty liquid B 0.4 50 21.8 21.8 0.8 50 32.7 32.8 38.0 0.8 50 32.7 32.8 38.0 0.8 50 32.7 32.8 38.0 0.8 150 28.6 28.8 38.0 Light duty liquid C 0.4 50 18.3 16.8 0.8 150 28.9 29.0 38.0 0.8 150 25.2 25.5 38.0 Light duty liquid D 0.4 50 18.2 18.0 0.4 150 13.6 13.8 38.0 0.8 150 22.3 22.8 38.0 0.8 50 13.2 13.0 38.0	LAS/N23-11	70/30	.24	150	20.1	19.8		
Light duty liquid R 0.4 150 22.7 22.5 0.8 50 33.9 34.5 0.8 150 32.4 38.0 Light duty liquid B 0.4 50 21.8 21.8 0.8 50 32.7 32.8 32.8 0.8 50 32.7 32.8 32.8 0.8 150 28.6 28.8 38.0 Light duty liquid C 0.4 150 16.4 16.5 0.8 50 28.9 29.0 32.8 Light duty liquid D 0.4 50 18.3 16.8 0.8 150 26.5 25.5 25.5 Light duty liquid D 0.4 50 18.2 13.0 0.4 150 13.6 13.8 38.0 0.8 50 22.3 22.8 32.0 0.8 150 13.6 13.8 38.0 0.8 50 22.3 22.8 32.0 0.8 150 20.8 20.5 32.0	Commercial Detergents		0.4	50	22.7	23.3		
0.8 50 33.9 34.0 0.8 150 32.4 33.0 Light duty liquid B 0.4 50 21.8 21.8 0.8 50 32.7 32.8 32.7 32.8 0.8 50 32.7 32.8 32.7 32.8 0.8 150 28.6 28.8 36.6 28.8 Light duty liquid C 0.4 150 16.4 16.5 0.8 50 28.9 29.0 32.7 Light duty liquid D 0.4 50 18.2 13.0 0.4 150 13.6 13.8 36.9 0.8 150 25.2 25.5 25.5 Light duty liquid D 0.4 50 18.2 13.0 0.4 150 13.6 13.8 38.0 0.8 50 22.3 22.8 32.8 0.8 150 20.8 20.5 32.4	Light duty iquid 1		0.4	150	22.7	22.5		
Light duty liquid B Light duty liquid B Light duty liquid C Light duty liquid C Light duty liquid D Light duty liquid D 0.4 0.4 0.4 0.4 0.4 0.4 0.4 0.4			0.8	150	32.4	33.0		
Light duty liquid C Light duty liquid C Light duty liquid D Light duty liquid D 0.4 50 18.3 16.8 0.4 150 16.4 16.5 0.8 50 25.2 25.5 Light duty liquid D 0.4 50 18.2 13.0 0.4 150 13.6 13.8 0.8 50 22.3 22.8 0.8 150 20.8 20.5	Light duty liquid B		0.4	50 150	21.8	21.8		
0.8 150 28.6 28.8 Light duty liquid C 0.4 50 18.3 16.8 0.4 150 16.4 16.5 0.8 50 28.9 29.0 0.8 150 25.2 25.5 Light duty liquid D 0.4 50 18.2 13.0 0.4 150 13.6 13.8 0.8 50 22.3 22.8 0.8 150 20.8 20.5			0.4	50	32.7	32.8		
Light duty liquid C 0.4 50 18.3 16.8 0.4 150 16.4 16.5 0.8 50 28.9 29.0 0.8 150 25.2 25.5 Light duty liquid D 0.4 50 13.2 13.0 0.4 150 13.6 13.8 0.8 50 22.3 22.8 0.8 150 20.8 20.5			0.8	150	28.6	28.8		
Diamond Diamond <t< td=""><td>Light duty liquid C</td><td></td><td>0.4</td><td>50 150</td><td>$18.3 \\ 16.4$</td><td>16.8 16.5</td><td></td></t<>	Light duty liquid C		0.4	50 150	$18.3 \\ 16.4$	16.8 16.5		
0.8 150 25.2 25.5 Light duty liquid D 0.4 50 13.2 13.0 0.4 150 13.6 13.8 0.8 50 22.3 22.8 0.8 150 20.8 20.5			0.8	50	28.9	29.0		
Light duty liquid D 0.4 50 13.2 13.0 0.4 150 13.6 13.8 0.8 50 22.3 22.8 0.8 150 20.8 20.5			0.8	150	25.2	25.5		
$egin{array}{ccccccccc} 0.8 & 50 & 22.3 & 22.8 \ 0.8 & 150 & 20.8 & 20.5 \end{array}$	Light duty liquid D		0.4 0.4	50 150	$\begin{array}{c} 13.2\\ 13.6\end{array}$	13.0 13.8		
			0.8 0.8	50 150	$22.3 \\ 20.8$	$22.8 \\ 20.5$		

* Average of four replicate runs. ^b Average of 24 replicate runs.

second representing no foam, will determine a point that can be called a complete foam disappearance end point. These two figures, the 50% point and no foam end point, should be more meaningful than one end point alone for this indicates how rapidly the foam disappears.

In the examples shown in Fig. 5, product 1 has a 50% end point of 27.5 dishes and a no-foam end point of 28.4 dishes. The corresponding values for product 2 are 29.0 and 30.0 dishes.

Comparison of Instrument and Operator End Points

A combination of binary and ternary blends of light duty liquid formulations, including four commercial blends at various concentrations and water hardnesses were tested. These experiments were designed to show a comparison of operator vs. instrument determined end points with a wide variety of practical formulations. The materials and abbreviations used are given in Table II. The formulations were made according to Table III and the solutions were numbered. The amount of each solution and the water hardness and solution number were printed on IBM cards using 58 conditions overall. In addition, a ternary blend of linear alkyl benzene sulfonate-coconut ethoxy sulfate (with 3EO)-lauric diethanolamide was printed on six cards. The 64 cards were shuffled and printed. This was repeated three more times and the samples were run in this order.

An experienced operator determined the end point in the usual way (by noting the 50% foam end point) and the end point was also determined from the reflectance curve using the inflection point. A comparison of these two values is given in Fig. 6. The difference between instrument and operator for values between -1.0 and +1.0 dish is given as a



Time 🗕

FIG. 5. Reflectivity curve.



FIG. 6. Difference between instrument and operator (dishes).

function of the number of times this occurred. A total of 237 end points were compared and about 90% of these were within one dish.

The four results from the instrument reflectance curves and from the operator were each averaged and are given in Table III. The averages are also shown generally to agree within one dish.

ACKNOWLEDGMENT

R. C. Quinn constructed and assembled the equipment and Lois V. Black performed the analysis.

REFERENCE

1. Spangler, W. G., JAOCS 41, 300 (1964). [Received May 1, 1968]