for all animal esterases examined so far and at 8.3 for all plant esterases.

4. A procedure is described for preparing the substrate, phenolphthalein dibutyrate, in pure form in the shape of long, thin colorless flakes of m.p. 91.5°C. (uncorrected).

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A Method for the Quantitative Determination of Relative Wear of Soap Bars

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AS a result of current interest on the part of manufacturers of fine toilet soaps in those properties of their product which are of importance, consumer-wise, in a highly competitive business, the perfection of techniques by means of which soap lathering characteristics may be evaluated has been the object of extensive research. But although a variety of methods for the estimation of foam producing power of soaps, measurement of foam stability, and study of foaming properties of soap solutions have been reported, the question of lathering power of soap bars has received little attention. Accordingly, since the lathering behavior of soap bars is influenced not only by the chemical characteristics of constituent materials but also by physical fixations proceeding from various manufacturing circumstances, tests involving measurement of foam production of soap solutions are insufficient in bar lathering studies, and need of a test applicable to whole bars is indicated. The significance of a means of determining relative wear of soap bars as an analytical device in bar lathering studies becomes apparent when one observes that to obtain lather from a bar of soap, a yield of soap solution must, by some wearing action, be effected.

Examination of the scientific literature pertaining to soaps, detergents, and allied subjects, failed to reveal the existence of a method for the quantitative determination of relative wear of soap bars. Yet, the effects of variations in soap processing on lathering properties of the bars must be disclosed by information derived from whole bars. This paper therefore is presented for the purpose of describing what is believed to be an accurate, quantitative method for the determination of relative wear of soap bars of all sizes and shapes.

Selection of Samples

While the several bars comprising each of the nine groups of samples (A to I, inclusive) were prepared with the intention that they be alike in all respects. sample members of particular groups were intentionally caused to exhibit properties different from those of samples of other groups by a variety of alterations in the manner of treatment of the soap during the course of its being made into finished bars. Small variations in the dimensions of the sample bars belonging to a given group could not be avoided but were duly taken into account in the final calculations. Data compiled during the testing of the samples are given in Table I.

TABLE I
Wearing Characteristics of Soap Bars

Group	Sample	Original thickness, inches	Final thickness, inches	Strokes	Wear Number
A	1	1.053	0.903	40	3.8
	2	1.061	0.912	40	3.8
	3	1.056	0.903	40	3.9
B	1	1.114	0.939	40	4.3
	2	1.110	0.936	40	4.3
C	1	1.088	0.894	40	4.9
	2	1.095	0.900	40	4.9
D	1	1.078	0.942	30	4.5
	2	1.048	0.876	40	4.5
	3	1.078	0.901	40	4.5
E	1	1.101	0.928	39	4.4
	2	1.107	0.929	40	4.4
F	1	0.964	0.803	40	4.6
	2	0.967	0.806	40	4.5
G	1	1.101	0.923	40	4.4
	2	1.109	0.932	40	4.4
	3	1.109	0.928	40	4.5
	4	1.103	0.922	40	4.5
	5	1.110	0.932	40	4.4
H	1	1.112	0.915	40	4.9
	2	1.097	0.995	20	4.9
I	1	1.107	0.921	40	4.6
	2	1.112	0.925	40	4.6

Apparatus

In Figure 1 the main parts of the wear-testing apparatus are shown. The frame, in which the sample is secured, and the sponge paddle were constructed of ⅛″ pressed wood. The paddle handle, frame side blocks, and sample holding pieces were cut from white pine stock. The parts were assembled, and the finished apparatus was painted. Heavy wall neoprene tubing was then slipped over the sample holding pieces, finishing them as shown in the drawing. The paddle was slightly thinned along the edges with sand paper so that it moved easily in the frame grooves. In operation, a little silicone lubricant applied to the upper surface of the paddle proved to be additionally helpful in this connection.

Care in the selection of a sponge material for the wearing surface was found to be necessary, and those sponges which exhibited a tendency to produce uneven wearing of sample bars were discarded. A section, uniformly 1 1/16″ thick, cut from a soft, fine textured cellulose sponge of rectangular cross section, was finally chosen and was fastened to the paddle by means of rubber cement.

The entire assembly, ready to use, is shown in Figure 2. A 7½-gallon container for the wash water was

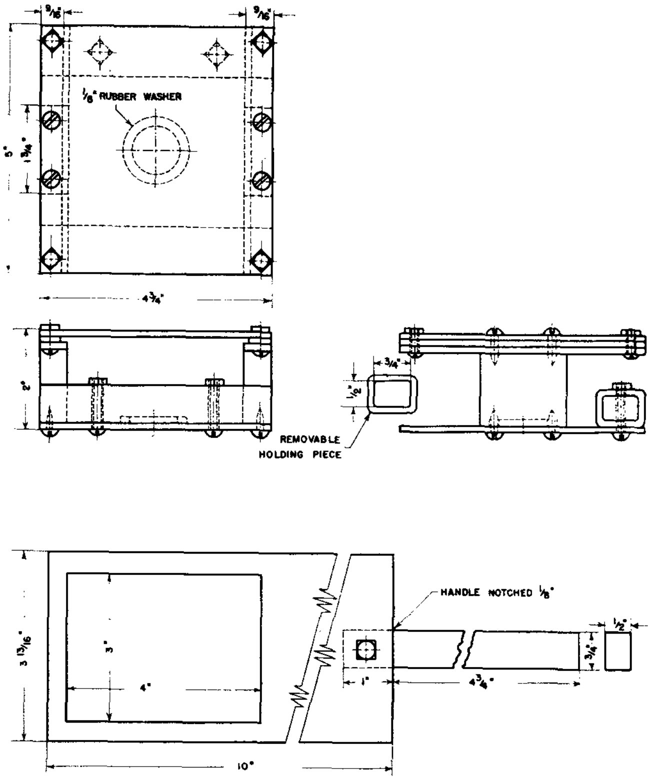

FIG. 1. A method for the quantitative determination of relative wear of soap bars.

provided, together with a mixer and a suitable assortment of stands and clamps. The rubber washer upon which the sample rested in the frame served to protect a small area on the bottom of the bar from the effects of excessive wetting. The movable sample holding piece was secured with Hoffman type clamps (not shown in illustration), placed at either end after the sample was in position.

Washing of the Samples

The thickness at the center, of the sample to be tested, was determined to the nearest thousandth of an inch by means of a pair of vernier calipers. The sample was then placed upon the rubber washer inside the frame. After centering the washer beneath the sample, the front sample holding piece was fastened in place with the Hoffman clamps. Warm tap water was placed in the 7½-gallon container, and the temperature of the water adjusted to 100°F. by the addition of hot or cold water from the tap, agitation being supplied during the process by the electric mixer. Excess water was then removed from the container until the volume of the remaining liquid was about 18 liters. This arbitrarily assigned volume of water was the same for all samples tested and was indicated by a mark on the inside of the container. The sample was then washed by passing the sponge to and fro over the bar 40 times at intervals of 30 seconds between strokes. At the end of each stroke (over and back motion of the sponge), the sponge was immersed in the warm water, which was under constant agitation by the mixer, until it was time for the next stroke. Twenty minutes were required for the washing operation. At the end of that time the sample was removed from the frame and allowed to dry over-night. The soapy water was emptied from the container, the entire apparatus washed, and fresh water added in preparation for the next sample.

The last operation performed on the sample prior to the calculation of the Wear Number was the measurement of the thickness of the dry, worn bar. Before this could be done however it was necessary to scrape away the circular strip of deformed soap, on the bottom of the bar, that resulted from the action of water which seeped between the surfaces of the washer and the sample. The final thickness of the sample was then determined. From the two-thickness measurements, taken at approximately the same point before and after wearing, the Wear Number of the sample was calculated.

Calculation

In order to develop a formula by means of which the Wear Numbers of tested samples could be calculated, it was resolved that the thickness of a bar is defined as the distance in inches between points at the approximate geometric centers of opposite faces of the sample and that suitable modification in the shape of the bar would be made to provide that this distance be not exceeded by that separating any other opposite points on opposite faces. If, then, the thickness of a sample after s wearing strokes have been applied is t,

$$\frac{dt}{ds} = -kt, \qquad (1)$$

where —k is a constant, since the pressure of the wearing surface on the sample, which pressure determines the rate of change of thickness, is a function of t in compliance with Hooke's Law. Integration of (1), allowing s to vary between 0 and S and t correspondingly between t_o and t_f gives

$$\log_e \frac{t_f}{t_o} = -kS. \qquad (2)$$

where t_o and t_f are the sample thicknesses before and after wearing, respectively. From (2) then,

$$-k = (1/S)\log_e (t_f/t_o). \qquad (3)$$

Equation (3) states that the ratio t_f/t_o is, for a given

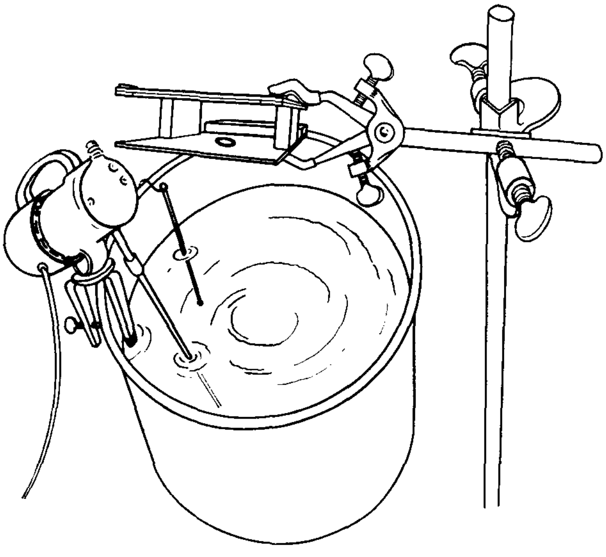

FIG. 2. A method for the quantitative determination of relative wear of soap bars.

sample, worn by S strokes, a constant. The number 1,000k where k was determined from (3) was called W, the Wear Number of the tested sample.

General Comments

In the event that a sample to be tested is too large to be readily accommodated by the wear testing apparatus, appropriate modifications in the size and shape of the sample may be effected by means of a sharp knife or a fine vegetable grater. It is important however that the opposite faces of the sample, between which the sample thickness is measured, are nearly parallel. If a bar must be thinned in order to fit the apparatus, soap should be removed only from the face opposite that to be worn. Samples which initially are too thin may be raised to the desired height in the frame by means of suitable shims. The total thickness of the shims (accurately measured) is added to the original thickness of the bar and also to its final thickness in order to obtain t_0 and t_f respectively. Since the thickness of the washer does not figure in the calculations, the same washer, or at least washers of like thicknesses, should be used in the testing of all bars that are to be compared.

Summary

A method for the quantitative determination of the relative wear of soap bars has been developed. The method is fairly simple and rapid, requiring about an hour of labor and from 8 to 12 hours of aging of samples during the test. The method is based upon the measurement of thickness of samples before and after subjecting them to wear by a sponge and warm water. Application of the method to samples of different thicknesses and surface areas shows good reproducibility, and the method is believed to be applicable in studies which require high sensitivity.

Acknowledgment

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The Iodine Number of Lanolin

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DURING the course of some work for a client, our attention was called to the empirical nature of the iodine number of lanolin. The U. S. Pharmacopeia, XIV Revision, states that the iodine number of anhydrous lanolin "is not less than 18 and not more than 36, using 800 to 850 mg. of the Wool Fat, page 705." The page cited refers to the section on the analytical determinations to be made on fats and fatty oils, and on page 708 the determination of the iodine value by the Hanus method is described. This section prescribes the use of 25 cc. of "iodobromide T. S.," 10 cc. of chloroform, a holding time of 30 minutes "protected from light," and subsequent titration with 0.1 N thiosulfate (after adding potassium iodide). The final paragraph reads: "Note: If more than half of the iodobromide T. S. is absorbed by the portion of substance taken, the determination must be repeated, a smaller portion of the substance under examination being used."

The description of "Iodo-bromide Test Solution," page 939, merely states that it shall be made by dissolving "13.2 grams of iodine in 1,000 cc. of glacial acetic acid with the aid of gentle heat if necessary. Cool the solution to 25° and determine the iodine content in 20 cc. by titration with 0.1 N sodium thiosulfate. Add to the remainder of the solution a quantity of bromine equivalent to that of the iodine present." Outside of the fact that the directions for preparing the Hanus solution are rather sketchy, the definition of the strength of the solution is somewhat vague. Also no warning is given that the exact strength is important.

If we assume, as is commonly done, that the finished solution shall contain 13.2 g. of iodine plus an equivalent amount of bromine per 1,000 cc. then 25 cc. of this solution should require 52 cc. of 0.1 N thiosulfate in titrating the free halogens present. But, as most chemists know, such a Hanus solution gradually deteriorates on standing in the laboratory. Furthermore it has come to our attention that at least one chemical supply house selling Hanus solution makes it up so that the thiosulfate equivalent is 60 cc. or more.

In other words, different laboratories may happen to use Hanus reagent that is above or below the prescribed strength for the determination of the iodine value of U.S.P. lanolin and not appreciate that such departures from the standard can affect the value obtained. Furthermore it may not be appreciated that variations in the weight of the sample of lanolin used can also affect the result even if less than half the reagent is consumed in the iodination. In order to illustrate these possibilities, and others, we have carried out the following tests:

Reagents and Apparatus Used

Hanus Solutions. The method of preparation suggested in paragraph 26.16 of the 7th Edition of Methods of Analysis of the A.O.A.C. was followed as being more detailed and convenient. Four different solutions were made up, i.e., the standard solution (thiosulfate equivalent approximately 52 cc. 0.1 N); a stronger solution with an equivalent of approximately 57 cc.; and 2 weaker solutions (made by diluting a stronger solution with glacial acetic acid) having equivalents of about 47 cc. and 42 cc., respectively. In each determination 25 cc. was used.

Potassium Iodide Solution. The N solution prescribed by the Pharmacopeia was used, 30 cc. for each determination.

Chloroform and Carbon Tetrachloride. The U.S.P. grade was used, 10 cc. for each determination.

Sodium Thiosulfate. 0.1 N made as per the U.S.P. and standardized against exactly 0.1 N potassium dichromate solution.