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_o 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.

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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.

Pipettes. One 25 cc. pipette was used throughout for measurement of the Hanus solution. Likewise a single 10 cc. pipette for the chloroform (or carbon tetrachloride). Neither of these were recalibrated.

Burette. One 50 cc. burette was used throughout for all measurements of the thiosulfate solution. It was not re-calibrated.

Flasks. The usual glass stoppered iodine flasks were used.

Lanolin Used. Four different samples of U.S.P. anhydrous lanolin were melted together at a minimum temperature and thoroughly mixed. Each time samples were to be weighed out the lanolin was just melted. The mouth of the bottle holding the sample was closed by a cork carrying a dropping tube. Samples were weighed directly into the iodine flasks and are believed to be accurate to within ± 0.1 mg.

Procedure. The directions given in the Pharmacopeia were followed rigidly, with the exception of the variations noted below. In addition, the temperature was noted in each case.

The Effect of Reagent Strength

Lanolin samples weighing between 0.800 and 0.850 g. were used in each case. Determinations were run in duplicate with each of the Hanus solutions. Time of standing was 30 minutes ± 5 seconds. Blanks were run each time a set of determinations were run.

The results are given in Table I.

TABLE I

The Effect of Reagent Strength on the Iodine Value

Reagent Used	Average Reagent Blank[a]	Average Sample Weight[a]	Average Iodine Value[a]
	cc.	*g.*	
Standard	51.83	0.8256	28.21
Stronger	58.69	0.8320	31.09
Weaker	47.31	0.8222	27.05
Weakest	42.60	0.8097	25.69

[a]Average of two determinations each.

The Effect of Sample Weight

In weighing out a sample, it is very easy to get less than 0.800 g. or more than 0.850 g. into the flask and more or less of a temptation not to add or subtract from the sample taken in order to come between the limits. In the following tests smaller samples lying between 0.700 and 0.750 g. and larger samples between 0.900 and 0.950 g. were compared with the above 0.800-0.850 g. samples, using each Hanus solution. The results are shown in Table II.

TABLE II

The Effect of Sample Weight on the Iodine Value

Reagent Used	Average Sample Weight[a]	Average Iodine Value[a]	Average Excess Reagent[a]
	g.		*%*
Standard	0.7267	31.33	65.3
	0.8256	28.21	65.2
	0.9176	26.90	62.3
Stronger	0.7361	33.80	66.5
	0.8320	31.09	65.4
	0.9325	29.34	63.2
Weaker	0.7200	29.42	64.7
	0.8222	27.05	63.0
	0.9111	25.17	61.7
Weakest	0.7129	28.38	62.7
	0.8097	25.69	61.6
	0.9192	23.64	59.8

[a]Average of at least two determinations each.

The Effect of Time

It is obvious from the foregoing data that the iodination of lanolin is not a "dead-stop" reaction. Hence it is to be expected that time is also a very important factor. The following Table III gives the results obtained by varying the time. The standard Hanus solution was used throughout.

TABLE III

The Effect of Variations in Time on the Iodine Value

Sample Weight	Time	Iodine Value
g.	*min.*	
0.8482	10	27.28
0.8453	20	27.84
0.800-0.850	30	28.21
0.8428	40	29.02
0.8470	60	29.66

Chloroform Compared to Carbon Tetrachloride as Solvent

Normann (4), in 1939, intimated that the use of carbon tetrachloride instead of chloroform when the Kaufmann (3) bromine method was used on samples of "wool fat" gave much lower iodine values. When the Wijs method was used, the differences were similar but smaller. Ganssle (1) stated that the solvent used for the lanolin had no effect in the case of the Hanus method. It seemed worth while to check Ganssle's statement, and hence two pairs of determinations were run, using similar weights of samples and carbon tetrachloride in one pair versus chloroform in the other. Of course, the same times and amounts of Hanus solution were used. The results are shown in Table IV.

TABLE IV

Carbon Tetrachloride vs. Chloroform

Sample Weight	Solvent	Iodine Value
g.		
0.8160	Chloroform	29.39
0.8219	Chloroform	29.41
0.8136	Carbon tetrachloride	28.62
0.8010	Carbon tetrachloride	28.91

The Use of an Accelerator

Norris and Buswell (5) describe their experience in using a catalyst to speed up the iodination of fats, using both the Wijs and Hanus reagents, particularly tung oil, and state that the addition of mercuric acetate in the Hanus method "gives values identical with those obtained in the standard Hanus method on non-conjugated fats, wtih the exception of castor oil, where the ricinoleic acid content is responsible for higher values obtained by the rapid method. On conjugated fats the method is unsatisfactory."

Likewise, Hiscox (2) describes her experience with the catalyst in determining the iodine value by the Wijs method of a considerable number of oil and fat samples. She used 5 cc. of 2.5% mercuric acetate in glacial acetic acid per determination instead of the 10 cc. used by Norris and Buswell and found that a much smaller amount of the reagent could be used, though a large excess did no harm.

Since the composition of lanolin is so different from most fats and oils, it seemed of interest to try out the use of the mercuric acetate catalyst. The results are shown in Table V.

TABLE V

The Use of a Catalyst in the Determination of the Iodine Value of Lanolin

Sample Weight	2.5% Mercuric Acetate Used	Time of Standing	Iodine Value
g.	*cc.*	*min.*	
0.8469	10	2	19.83
0.8404	10	3	31.51
0.8477	10	4	31.58
0.8415	10	5	33.49
0.8479	10	10	34.61
0.8482	5	2	27.97
0.8404	5	3	28.99
0.8448	5	4	29.37
0.8479	5	5	29.11

The Effect of Temperature

The above determinations were made at room temperatures varying from 18°C. to 28°C. To check the effect of temperature a pair of determinations were run at 15°C. and another at 30°C., using the standard method. The results are given in Table VI.

TABLE VI

The Effect of Temperature on the Iodine Value

Sample Weight	Temperature	Iodine Value
g.	°*C.*	
0.8408	15	27.84
0.8444	15	27.80
0.8479	30	30.01
0.8400	30	30.22

Discussion

It will be noted from the last column of Table II that in every case the unreacted reagent amounted to considerably over the 50% excess required by the U.S.P. method. Even in the experiments with mercuric acid catalyst where the iodine value was as high as 34.6, the excess reagent amounted to over 53%. Generally it was 60-66.5%. Hence if one were to use a reagent that was as weak as 20% below standard and samples approaching 1 g., he would have an adequate excess. Of course, as is shown, the values obtained would be very low.

The results obtained speak for themselves. The iodine value of U.S.P. anhydrous lanolin depends markedly on such factors as the strength of the reagent, the size of the sample, time of standing and temperature. Hence if different laboratories are to obtain concordant results on the same sample of this material, they must adhere fairly rigidly to the U.S.P. directions, both explicit and implied. The sample weight must be 0.800-0.850 g.; 25 cc. of the reagent must have a thiosulfate equivalent of close to 52 cc. 0.1 N; the time of standing must be very close to 30 minutes; and extremes of temperature must be avoided. This last requirement is not mentioned by the Pharmacopeia but should be agreed upon.

While the use of mercuric acetate as a catalyst can shorten up the time of standing markedly and hence might be a convenience in a busy laboratory, the time factor is critical, the details of the determination would have to be agreed upon in order to avoid dispute.

Either chloroform or carbon tetrachloride can be used as the sample solvent. This checks with Ganssle's (1) observation.

Conclusion

The determination of the iodine value of U.S.P. anhydrous lanolin is an empirical one. Very close attention is necessary to the various factors concerned in the determination, sample weight, Hanus reagent strength, time, and temperature.

The addition of mercuric acetate will speed up the iodination markedly, but again details of the determination will have to be determined.

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The Aliphatic Alcohols of Wool Wax. V. Studies in Waxes[1]

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EARLY investigators have isolated, from the unsaponifiable part of wool wax, monohydric long chain alcohols which they described as cetyl (1), lano-octadecyl (2), carnaubyl (3), ceryl (3, 4, 5), and a diol $C_{21}H_{40}(OH)_2$ (2). According to present standards however the evidence that pure compounds were isolated and identified appears to be inadequate. Recently the presence has been reported in the wax of two series of even carbon number: the normal alcohols from C_{18} to C_{26} (6) and a series of 1,2-alkanediols, C_{16} to C_{24} (7). The chain in the latter series is probably branched.

Initial attempts to isolate aliphatic alcohols from wool wax in this laboratory were made by chromatographic methods on alumina. Although there was some separation of the types of alcohols present, it was evident that the resolution of a homologous series into its pure components by such methods would be difficult if not impossible.

In view of the outstanding success of the low pressure distillation techniques employed by Weitkamp (8) in the isolation of the wool wax acids, it was decided to distill by similar techniques the acetates of the residual alcohols after the removal of most of the accompanying cholesterol and triterpene alcohols by other means.

Ten branched chain alcohols have been separated by this means. They belong to two homologous series: six dextro-rotatory ante-iso alcohols (terminal group, sec-butyl) of odd carbon number, C_{17} to C_{27}, and four iso alcohols (terminal group, isopropyl) of even carbon number, C_{20} to C_{26}.

[1] Part IV of this series: Reference (9).

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