A Test for Neutral Oil in Soap or Fatty Acids

By JOHN E. RUTZLER, JR.
Pilot Laboratory, Inc.

THE present methods[1] for the determination of neutral oil in soap or fatty acids are time consuming and tedious, although the results are quantitative. This fact provides a utility for a rapid quantitative method for the estimation of unsaponified oil in soap or fatty acids.

Lewkowitsch states[2], "In order to test for unsaponified fat (in fatty acids) 3 cc. are dissolved in 15 cc. of 95% by volume alcohol, and 15 cc. aqueous ammonium hydroxide is added." Geitel says[3] that under these conditions turbidity will appear if there is unsaponified oil present, and that if the amount of unsaponifiable matter present is large, the results of the test are not reliable.

This test has been examined critically by the author. A sample of coconut oil acids was prepared by saponification of the oil, and subsequent acidification of the soap. The acids were then neutralized in the presence of excess alkali, boiled, and the acids re-liberated, using hydrochloric acid. These acids contained about 0.35% unsaponifiable matter. Several experiments were made using double the proportions suggested by Lewkowitsch. The net result was that upon making mixtures of acids containing known amounts of neutral coconut oil and proceeding to test as above, the test was found to be positive down to 0.078% neutral oil present. It was also found that if only half of the amount of alcohol specified is used, the oil particles do not become peptized, and the test is negative. The emulsions formed were not at all stable, because the ammonium hydroxide saponified the suspended oil particles within an hour or so.

Due to the fact that the blank experiment (no oil present) on the above acids showed a very slight haze, another sample of acids was prepared in a slightly different manner. The oil was saponified in the presence of approximately 15% excess alkali, a mixture of NaOH, and KOH being used. After standing in a warm place for five days, the soap was decomposed and the acids liberated by prolonged agitation with dilute sulfuric acid. The acid liquor was then changed, and the fatty acids agitated for four hours with a concentrated solution of sodium bisulfite in order to lower the amount of unsaponifiable matter present. They were then washed three times with fresh water, the wash water being completely removed each time. The acids were dried by heating to 80° C. under vacuum of approximately 700 mm. The unsaponifiable matter in these acids was about 0.10% after this treatment.

When the above-described acids were tested by the Lewkowitsch method, using double the quantities prescribed, not even a slight haze was noticed.

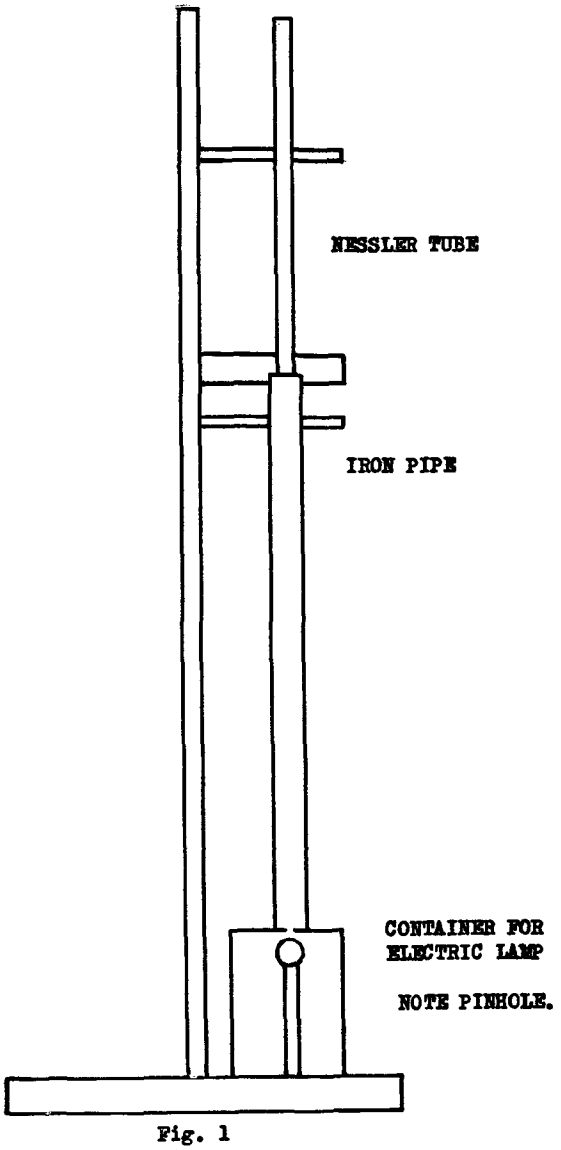

Fig. 1.
Emulsometer

It was found that with these acids no amount of oil less than 1% could be detected using the Lewkowitsch test. It therefore became necessary to sensitize the test. This was done by

mixing known amounts of technical white mineral oil with the fatty acids. Four preliminary experiments were made with the following results: one drop to technical white oil mixed with the fatty acids gave no turbidity; when two drops were used a slight haze was evident; when two drops of the mineral oil and one drop of neutral coconut oil were mixed with the acids a slight turbidity was noticed; finally, when four drops of the mineral oil were mixed with the acids great turbidity was evident.

The weight of 6cc. of the acids was accurately determined to be 5.376 grams. The weight of one drop of the oil from which the acids were made was found to be 0.0124 gram. The oil was dropped from a pipette, the opening of which was very small. Next, the weight of one drop of technical white oil as dropped from another pipette was found to be 0.0175 gram. These weights were determined at 26 degrees centigrade, plus or minus two degrees. All subsequent work was performed at this temperature.

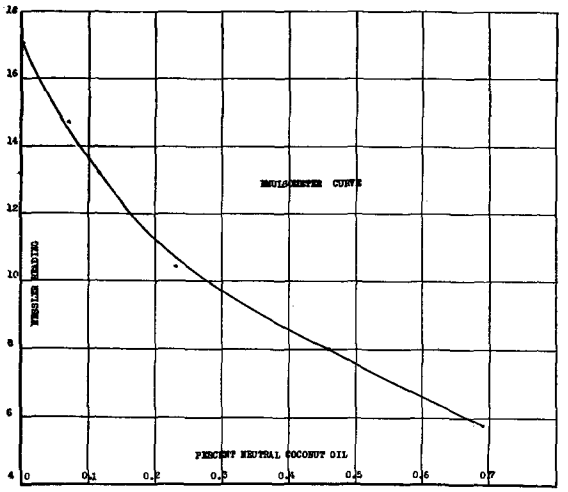

Fig. 2
Emulsometer Curve

The next step was to make use of the emulsometer shown in figure 1. The emulsometer consists simply of an electric light (100 watts), shielded by a round container with a pinhole in the top,. From the top of the container a pipe of small diameter extends upward. On the top of the pipe a Nessler tube is supported. Therefore the distance from the light to the Nessler tube is fixed. This distance was 93.2 centimeters in the case of the instrument used for the work here described. The purpose of the pipe is to obviate light reflection and disturbances so that the instrument may be used in daylight. Three preliminary experiments were made, using the emulsometer. Three drops of technical white oil were mixed with 6cc. of the fatty acids, and one drop of neutral coconut oil added. This solution was neutralized with concentrated ammonium hydroxide, as prescribed by Lewkowitsch. The resulting emulsion was slowly poured into the Nessler tube until the light from the electric lamp was no longer visible. So much emulsion was necessary that the graduated capacity of the Nessler tube was exceeded. The test was further sensitized by using four drops of mineral oil, following the above procedure. The height of the emulsion in the Nessler tube at the point of light extinction was found to be 25.5 units. The procedure was repeated using one half of the amount of neutral coconut oil. It being impracticable to try to measure out a half of a drop of the oil, one drop was mixed with 12 cc., of the acids and to 6 cc. of the solution four drops of technical white oil were added. The solution was then neutralized as before. This time the emulsometer reading was 25.0 units. This data is just the reverse of what it should be. The difficulty was apparent, however, for on the same emulsion the height in the Nessler tube necessary to cause extinction of the beam of light became progressively less as its age increased. Whether this phenomenon is the result of partial coalescence due to saponification of the oil, or is due to a fairly large time factor in the peptization of the oil particles, is not immediately apparent. The phenomenon, however, does necessitate making the emulsometer readings at a given time after the formation of the emulsion.

The difficulties having been ironed out, the test was reduced to a quantitative basis by the following procedure. Six cc. of the fatty acids above described were measured very carefully in a 10cc. graduate. Four drops of technical white oil were added to the acids, using a standard pipette. Again, using a standard pipette, the desired number of drops of neutral coconut oil were added. The graduate was then shaken as thoroughly as possible without covering the top. This solution was carefully poured into a 100 cc. graduate. After draining for a short time the 10 cc. graduate was thoroughly washed with 95% ethyl alcohol, the washings being put into the 100 cc. graduate, until the total volume in the larger graduate was 36 cc. The 100 cc. graduate was then rotated rapidly to secure a uniform solution. To this solution 30 cc. of concentrated ammonium hydroxide was added, the time at which the addition was started being carefully noted. The emulsion was then stirred with a clean glass stirring rod until the system began to foam. The system was allowed to stay in the graduate for three

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