Summary

A crystallization method has been developed for the determination of saturated fatty acids in soybean oil. The method is simple and rapid. The results obtained by this method agree quite well with those obtained by the use of the Bertram oxidation method and are about 2 percent higher than those obtained by the use of the modified Twitchell method. The procedure recommended seems to give satisfactory results on soybean and cottonseed oils, but it will probably have to be modified for use with highly unsaturated oils such as perilla, or with oils such as olive which contain large amounts of oleic acid.

LITERATURE CITED

(1) Bertram, S. H., Z. Untersuch, Lebensm, **55,** 180-182 (1928).
(2) Brown, J. B., and Stoner, G. G., J. Am. Chem. Soc., **59,** 3-6 (1937).
(3) Fat Analysis Committee, Oil and Soap, **12,** 285-290 (1935).
(4) Hilditch, T. P., and Priestman, J., Analyst, **56,** 354-367 (1931).
(5) Martin, W. S., and Stillman, R. C., Oil and Soap, **10,** 29-30 (1933).
(6) Official and Tentative Methods of the American Oil Chemists' Society, pp. 44b-44f.
(7) Pelikan, K. A., and Von Mikusch, J. D., Oil and Soap, **15,** 149-150 (1938).

pH Meter Control of Spent Soap-Lye Purification

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Introduction:

In the usual method of clarification of spent soap-lyes for glycerine recovery, alkaline salts are neutralized with a strong acid, insoluble fatty acids are precipitated by a strong acid from the soap dissolved in the spent lye, and fibrous semi-colloidal impurities are adsorbed to the flocculent precipitate of aluminum or iron salts. After the addition of a diatomaceous filter-aid, the treated lye is filtered. The clear liquor is then neutralized with caustic soda to a value of pH 8-9 which is least corrosive to the evaporator. The flocculent precipitate which is a product of the caustic soda and the portion of the aluminum or iron salt soluble at the acid pH value of the treatment is allowed to settle out or is filtered off. The weak liquor after the second treatment is evaporated to 80% crude glycerine and the dropped salt is recovered.

It has been the experience of this plant that the use of colorimetric pH control in the recovery of glycerine from spent soap-lye did not give consistently good results. A review of the literature offered nothing except colorimetric pH control. Consequently, closer control was attempted with the electric pH meter. This led to the problem of ascertaining the optimum pH range for the treatment prior to filtration.

Theoretical:

Four factors had to be considered in the ideal method of treatment:

1. The pH value at which soap is completely broken down into insoluble fatty acid.
2. The proportion of strong acid necessary to accomplish this.
3. The optimum pH range of coagulation of the aluminum or iron salt allowable under the conditions of treatment.
4. The amount of aluminum or iron salt to completely adsorb the unfilterable fibrous impurities.

Soap as the salt of a weak acid exerts a buffer action against the addition of strong acid and consequently tends to hold up the pH value of its solution until it is completely broken down into insoluble fatty acids. Since these insoluble fatty acid constituents of the soaps found in spent lye are of practically the same nature in every spent lye, then the hydrogen ion concentration of the completely precipitated fatty acids is a constant value fixed by their ionic dissociation. This hydrogen ion value can be determined by plotting the electrometric titration of spent lye with strong acid and noting the characteristic point of inflection which marks the end of the buffer action of the soap in the lye.

The proportion of acid for each treatment of spent lye can be determined by the proportion of acid needed to lower the pH value of a sample to the point of inflection.

The optimum pH range of coagulation of the iron or aluminum salt can be obtained by observing the appearance of the floc at and below the pH value of the point of inflection.

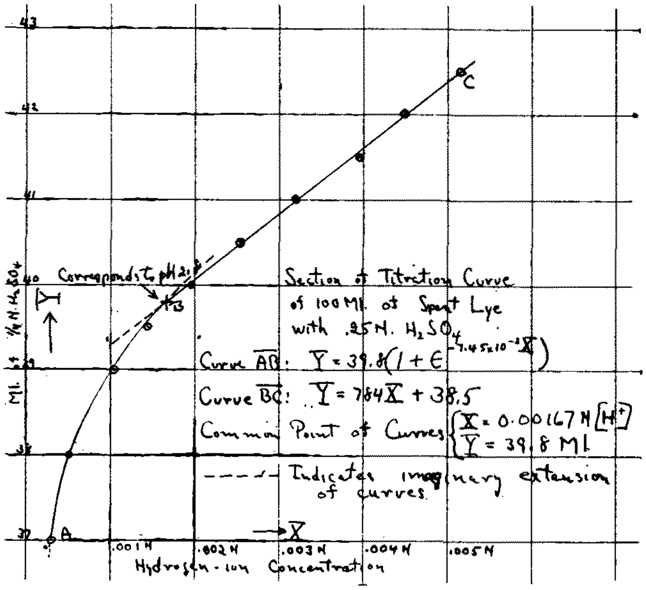
The amount of coagulating salt necessary for complete adsorption should differ for lyes from varying sources. This can be found by direct tests on each individual batch of spent lye.

Experimental:

This paper will deal with sulfuric acid and aluminum sulfate as the chemicals used in treating spent lye. However, the methods used in this paper are also applicable to the hydrochloric acid-ferric chloride method of treatment.

A number of 100 ml. samples were titrated, using a glass-electrode pH meter, and .25 normal sulfuric acid. The curves represting pH values vs. ml. of acid all had a marked break in continuity near the value pH 3.0. Filtered samples of lyes which were titrated to a value higher than pH 3.0 showed a further precipitation of fatty acid on adding more strong acid. Conversely, filtered lyes of a value lower than pH 3.0 showed no precipitate with the addition of strong acid. Hence, it was concluded that this break represented the pH value at which precipitation of insoluble fatty acid was completed.

For a more accurate determination of the "break," the section of the titration curve between the pH values 3.5 and 2.3 was then plotted on graph paper substituting hydrogen-ion concentrations for pH values. This gave a broken line which consisted of two curves, one of which was evaluated to the formula $Y = 784X + 38.5$ and the other to the formula $Y = 39.8\ (1 + \Sigma^{-7.45 \times 10\text{-}3X})$ where X is the hydrogen-ion concentration, and Y is the volume of quarter-normal sulfuric acid used. The common point of these curves is $X = 0.00167$, and $Y = 39.8$, which corresponds to a pH of 2.8. (See illustration) At this value the buffering action of the soap is entirely spent, and the remainder of the titration conforms to the nearly-straight line of an unbuffered solution titration.



The optimum coagulation of the alumina precipitate of aluminum sulfate occurs near neutrality. However, the conditions of the treatment of spent lye set the maximum pH value at 2.8. On observing the appearance of an alumina floc in filtered weak glycerine liquor at different pH values, the amount of precipitate decreased steadily from its maximum near neutrality with a decrease in pH value. At pH 2.8 the floc was noticeably smaller. Below this value, it decreased sharply until at pH 1 it had practically gone into solution. Therefore, it was concluded from these two findings that pH 2.8 was the optimum value for treatment of all spent lyes.

To find the correct proportion of aluminum sulfate for a particular sample of spent lye, the following method was tried:

> To five portions of the sample, various amounts of a standard 1% aluminum sulfate solution were added to represent certain proportions of aluminum sulfate to volume of sample. These portions were titrated with sulfuric acid to a pH of 2.8 and were filtered through an ordinary filter paper.

The following tabulations give the results:

Portion	Lbs. Aluminum Sulfate 1000 Lbs. Lye	Observations
A	½	Turbid, yellow filtrate, with slow rate of filtration. Finally, filter plugged.
B	1	Same as sample "A"
C	1½	Opalescent filtrate, faintly yellow. Slow rate of filtration.
D	2	Clear, nearly water-white filtrate. Rapid flow.
E	2½	Brilliant, nearly water-white filtrate. Rapid flow.

As can be readily seen, portion "E" which contains 2½ lbs. aluminum sulfate per thousand pounds of lye, gives the best results for this sample. Samples of spent lye from other sources were tested in this manner. The proportion of aluminum sulfate to spent-lye for complete clarification ranged from 1 lb. to 3 lbs. per thousand.

Method of Procedure:

This method of procedure is based upon the experimental findings and is applicable to any grade of spent-lye.

Portions of an average sample from an untreated batch are tested to find the correct proportion of aluminum sulfate according to the procedure as outlined in the experimental section of this paper. Usually, only two or three tests are sufficient to find the correct proportion. To a 100 ml. portion of the sample, the correct proportion of standard aluminum sulfate solution is then added. This portion is then titrated with quarter-normal sulfuric acid to a pH of 2.8, and the volume of acid is noted.

From the volume of titrating acid used, the amount of technical acid for each batch may be calculated.

When the predetermined amounts of aluminum sulfate and sulfuric acid are added to the batch of spent lye, the mixture is well agitated, and an average sample is obtained. This is checked for a pH reasonably close to 2.8, and if necessary, any readjustment with acid or caustic is made at this point. A filtered portion is tested for clarity and with acid for further precipitate. If this method is followed accurately, then an adjustment is rarely necessary.

When the batch is filtered, an amount of caustic which is determined by electrometric titration on a sample of clear liquor is added to the filtered batch to bring the pH to 8-8.5. This value of pH 8-8.5 is said to be least corrosive to evaporators.

On neutralizing the filtered liquor, the dissolved aluminum sulfate is converted to an alumina floc. This may be allowed to settle out, and the settling returned to an untreated batch; or, it may be filtered off, but not in the same filter press used for the acid filtration. The batch is then ready for evaporation.

This procedure may be modified by having the operator add enough sulfuric acid to prevent foaming over in the treatment tank, while agitating a batch for sampling. The method of procedure, as outlined above, may start at this point without impairing the efficiency of the method.

Discussion:

The experimental findings cleared up much of the vagueness and error in current literature. It established a definite point at which complete precipitation of fatty acid occurs as contrasted to the vagueness of "Acid to litmus and neutral to methyl orange," as found in the literature. The ammonium hydroxide test for excess aluminum sulfate is of no significance since there will always be a precipitate of alumina from dissolved aluminum sulfate. The amounts of aluminum sulfate suggested in the trade publications of from five to fourteen pounds per thousand pounds of lye are greatly in excess of actual requirements.

Summary:

The electric pH meter has served to fix the limits for the optimum pH range of the acid-alum treatment of spent-lyes, to predetermine the proportions of acid and aluminum sulfate to be used for each treament, and to check the actual treatment prior to filtration. As a result of this close control, time and materials have been saved, a consistently good clear yield of crude glycerine has been obtained, and production has been uninterrupted.

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*NOTE: To avoid ambiquity in terms pH value and hydrogen-ion concentration, the author wishes to point out that as pH values increase, hydrogen-ion concentration decreases.