Spent Soap Lye Purification

WM. J. GOVAN, JR.
Wurster & Sanger, Inc., Chicago, Illinois

Introductory

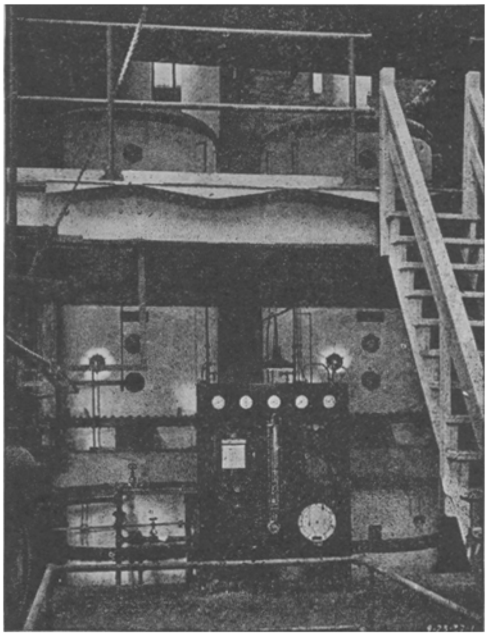
LITTLE detailed information on the subject of spent soap lye purification has been published in recent years, although it is apparent that the problem has been worked out satisfactorily in many individual cases. Since the ultimate purity of refined glycerine is largely dependent upon the quality of treatment given to spent lyes, there is a need for a well-delineated, feasible method of control over this operation. It is the purpose of this paper to describe such a method.

Spent soap lyes (2, 3, 4) are the wash liquors discharged from the soap kettle room to the glycerine department to be treated and evaporated for recovery of their glycerol content. These liquors contain a large amount of sodium chloride in solution and are practically free of caustic soda. They contain also in solution or suspension, as impurities, alkaline salts, soaps, nitrogenous and other organic matter. These impurities must be removed if a satisfactory, marketable grade of soap lye crude glycerine is to be produced. Alkaline salts are neutralized with acid. Soaps are decomposed by acid to their fatty acids and as such, are removed along with nitrogenous and other organic matter, by a flocculating agent. After purification, the solution is evaporated to soap lye crude glycerine of 80% or greater glycerol content. Salt is recovered during the evaporation, dried, and stored for re-use in the soap kettles.

The basic systems of spent soap lye purification which are in general use today have been described by Sanger (4) and Wurster (5, 6). They are the "single treatment" and the "double treatment." In the former, acid and a flocculating agent are added. The impurities are filtered off, leaving a slightly acid feed liquor for the glycerine evaporator. In the latter system, an additional treatment is given in which caustic soda is added to the filtered liquor from the acid treatment. The resulting floc is either filtered out or allowed to settle. If the floc is allowed to settle out, clear liquor may be drawn directly into the evaporator. The double treatment produces a more thoroughly purified liquor which, being slightly alkaline, is less corrosive to equipment.

THE methods of control of lye purification operations have kept pace with technical developments of the chemical industry over the past twenty odd years. Early empirical "cut-and-try" methods of treatment gave fay to titrimetric (4) tests for estimating chemicals for treatment. Acid required for neutralization of the lye was determined by direct titration using phenolphthalein indicator. This method presupposed the absence of excessive quantities of dissolved soap and buffer salts in the lye for its success and on that account was limited in its usefulness.

Spent soap lyes, containing excessive amounts of dissolved soaps from improperly "grained" kettles or containing alkaline salts such as phosphates, borates, and silicates derived from soap scrap added directly to the kettles, cannot be tested accurately by the phenolphthalein end point method. Nevertheless, the scientific approach of this method was a good beginning.



Double Effect Soap Lye Glycerine Evaporator.

Later it was established that there was a definite optimum pH range (1) for the acid treatment of lye, at which value maximum precipitation of impurities occurred. This fact led to control of the treatment by pH measurement. At the same time, in conjunction with pH control, a simple test was devised by which the minimum amount of flocculating agent necessary to adsorb and remove these organic impurities could be determined. By this means, the limitations of earlier methods of control were overcome, since the effectiveness of the newer method was not limited by variations in quality of spent soap lye.

The method of controlling pH in the acid treatment may be either direct or indirect. In the indirect method, comparative colorimetric pH standards are used. During the course of the treatment, the plant operator withdraws and filters samples from the treatment tank after each addition of acid, adds an indicator of the desired pH range to the filtrate, and compares its color with that of established pH standards. In this way, he can approach and arrive at the optimum pH for the treatment.

The direct method consists of titrating a sample of each batch of lye to the desired pH value and calculating from the titration the stoichiometrically equivalent quantities of chemicals needed in the treatment. In this way, the exact quantities of acid and flocculating agents are determined in advance of the treatment by a simple five minute test in the plant laboratory.

The method of conducting this short test and the operation of the lye treating plant under direct pH control is given in detail here.

Testing Procedure

Reagents and Apparatus:

Standard $0.5N$ Hydrochloric Acid.

Standard $0.5N$ Sodium Hydroxide.

Standard Solution of Alum (Aluminum sulfate $Al_2(SO_4)_3 \cdot 18H_2O$) in water, 1 ml. of solution contains 0.030 gram of alum.

Standard Solution of Ferric Chloride ($Fe\,Cl_3 \cdot 6H_2O$) in water, 1 ml. of solution contains 0.015 gram of $Fe\,Cl_3 \cdot 6H_2O$.

Solution of methyl orange indicator, one gram of indicator to 100 ml. of water.

Solution of phenolphthalein indicator, one gram of indicator to 100 ml. of 95% alcohol.

Glass electrode pH meter.

Acid Treatment Tests: For the purpose of the following description, the treatment chemicals are hydrochloric acid and lump ferric chloride. The glass electrode pH meter is the testing instrument.

One hundred ml. of sample from the spent soap lye batch is measured into a 250 ml. beaker. Five ml. of Ferric Chloride Solution corresponding to ¾ pound of ferric chloride per thousand pounds of spent lye is added. The contents of the beaker are titrated with $0.5N$ HCl with the aid of the pH meter to a value of 4.3 ± 0.3.

The resulting mixture is filtered. If the filtrate is cloudy, it is an indication that more ferric chloride is needed. In that event, additional 100 ml. portions of sample are tested as before, but using larger amounts of Ferric Chloride Solution until the mixture filters clearly. A second test is rarely necessary, since with a little experience the analyst can gauge the necessary amount of ferric chloride from the appearance of the lye sample.

The volumes of standard acid and Ferric Chloride Solution are recorded for calculating the amounts of muriatic acid and ferric chloride for the actual treatment.

Alternate Procedure: If a pH meter is not available, an alternate procedure may be carried out with methyl orange to indicate the end point of the titration. As before, a 100 ml. portion of the sample is measured into a beaker. Two or three drops of methyl orange indicator are added. Ferric Chloride Solution is added. The mixture is titrated with $0.5N$ HCl past the end point of methyl orange to a distinct shade of pink. To save time, only one-half of the combined volume of the mixture is filtered into a 100 ml. graduate. The combined volume may be taken as being the sum of the volumes of the original sample, the acid used in titration, and the standard Ferric Chloride Solution. The change in volume due to precipitation is a negligible factor. The portion of clear filtrate is back-titrated with $0.5N$ NaOH to the methyl orange end point. The volume of $0.5N$ NaOH is recorded. A little observation and experience will enable the analyst to detect the point where the definite pink color is just discharged. This point is not critical and 0.2 or 0.3 ml. of $0.5N$ NaOH beyond the end point does no harm.

Since the back titration is done on a portion of the filtrate equivalent to half the original 100 ml. sample, the resultant effective volume of $0.5N$ HCl may be calculated as being equal to twice the volume of $0.5N$ NaOH deducted from the volume of $0.5N$ HCl used in titrating the sample beyond the orange end point.

As before, the volume of Ferric Chloride Solution and the effective volume of $0.5N$ HCl are recorded for calculating the exact amounts of muriatic acid and ferric chloride for the actual treatment.

It should be noted that if alum is substituted in the treatment in any proportion for ferric chloride, then a corresponding amount of Alum Solution is substituted for the Ferric Chloride Solution in the test without changing the procedure. The use of sulfuric acid in the treatment likewise does not change the testing procedure in any way.

Calculations: The flocculating agent, ferric chloride or alum, is determined from formula (1).

$$F = \frac{cfM}{m} \tag{1}$$

"F" is weight in pounds of ferric chloride or alum to be added to treatment.

"c" is volume in ml. of Ferric Chloride or Alum Solution.

"f" is grams of ferric chloride or alum per ml. of Ferric Chloride or Alum Solution.

"M" is weight in pounds of batch of spent lye (calculated as having specific gravity of water).

"m" is volume in ml. of sample tested.

The acid, hydrochloric or sulfuric, is determined from formula (2).

$$A = \frac{saM}{m} \tag{2}$$

"A" is weight in pounds of acid to be added to treatment.

"s" is the acid conversion factor.

"a" is volume in ml. of standard $0.5N$ HCl titrated.

"M" is weight in pounds of batch of spent lye (calculated as having specific gravity of water).

"m" is volume in ml. of sample tested.

The acid conversion factor "s" represents the stoichiometric relationship between the normality of the titrating acid and the kind and strength of treatment acid.

For 20° Be muriatic acid and standard $0.5N$ HCl, the factor is 0.0579. It is derived as follows:

1 ml. of $0.5N$ HCl is equivalent to 0.0182 gram of anhydrous HCl.

0.0182 gram of anhydrous HCl is equivalent to 0.0579 gram of 31.5% HCl (20° Be muriatic acid).

Therefore, 1 ml. of $0.5N$ HCl is equivalent to 0.0579 gram of 20° Be muriatic acid and the number 0.0579 is the conversion factor between $0.5N$ HCl and 20° Be muriatic acid.

Factors for other acids are given in Table 1.

TABLE I

One milliliter of $0.5N$ HCl is equivalent to:

Factor	Acid
0.0652 grams	18° Be Muriatic
0.0579 grams	20° Be Muriatic
0.0518 grams	22° Be Muriatic
0.0316 grams	60° Be Sulfuric
0.0263 grams	66° Be Sulfuric

An example of a typical treatment will illustrate the application of the two formulas for determining the amounts of chemicals. A batch of spent lye undergoing treatment weighs 20,000 lbs. (calculated as having specific gravity of water). The treatment chemicals are lump ferric chloride, alum, and 20° Be muriatic acid. 5 ml. of 1.5% Ferric Chloride Solution, 2 ml. of 3% Alum Solution, and 8.6 ml. of $0.5N$ HCl are required to titrate a 100 ml. sample of lye to a pH of 4.3 and to produce a light, clear filtrate.

Substituting in formula (1),

$$\frac{5\times0.015\times20{,}000}{100}=15 \text{ pounds of lump ferric chloride.}$$

$$\frac{2\times0.030\times20{,}000}{100}=12 \text{ pounds of alum.}$$

Substituting in formula (2),

$$\frac{0.0579\times8.6\times20{,}000}{100}=100 \text{ pounds of } 20^\circ \text{ Be muriatic acid.}$$

When the amounts, 15 pounds of ferric chloride, 12 pounds of alum, and 100 pounds of 20° Be muriatic acid, are added to the batch of spent lye, the pH of the lye will go to 4.3 and the lye will then be ready for filtration.

The use of methyl orange indicator for pH regulation is adequate and satisfactory. The glass electrode pH meter, however, is more accurate and should be used if available.

Alkaline Treatment Test: A 100 ml. sample of the filtered liquor is taken. Five or six drops of phenolphthalein indicator are added. The solution is titrated with $0.5N$ NaOH to the phenolphthalein end point and the amount of standard base is recorded.

Calculation: Caustic soda (NaOH) required in the second treatment is determined from formula (3).

$$B=\frac{tbM}{m} \tag{3}$$

"B" is the weight in pounds of caustic soda to be added to treatment.

"t" is caustic soda conversion factor.

"b" is volume in ml. of standard $0.5N$ NaOH titrated.

"M" is weight in pounds of batch of spent lye (calculated as having specific gravity of water).

"m" is volume in ml. of sample tested.

The caustic soda conversion factor "t" is derived in the same manner as the acid conversion factor "s." For 95% NaOH flake caustic, the factor "t" is 0.021.

An example of a typical second treatment will show how the formula is applied. 3.5 ml. of $0.5N$ NaOH are used to titrate a 100 ml. sample of filtered lye to the phenolphthalein end point. The sample is taken from a 20,000 pound batch. 95% NaOH flake caustic soda is the treatment chemical.

Substituting in formula (3),

$$\frac{0.021\times3.5\times20{,}000}{100}=15 \text{ pounds of flake caustic, which is the amount needed}$$

to bring the batch to a pH of 8.5 to 9.0.

Plant Operation

Equipment: The capacity of the individual units of equipment will vary according to the requirements of each spent soap lye purification plant. The units consist of the following (see Fig. 1):

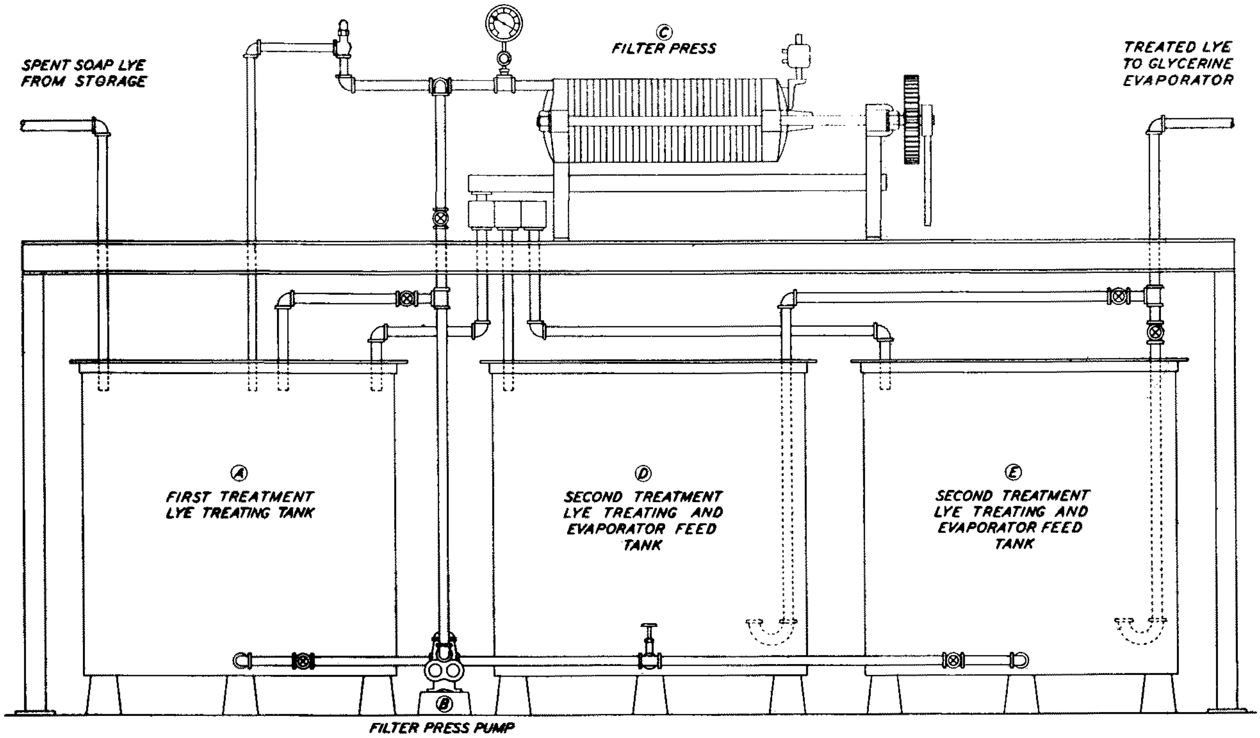


FIG. 1. Double Treatment Spent Glycerine Lye Treating Plant. This illustration shows arrangement of tanks for first and second treatment, using filter press for first treatment, and settling and decantation for second treatment. The method requires only one filtration and permits the use of the double treatment with a minimum of equipment as only one filter press is required.

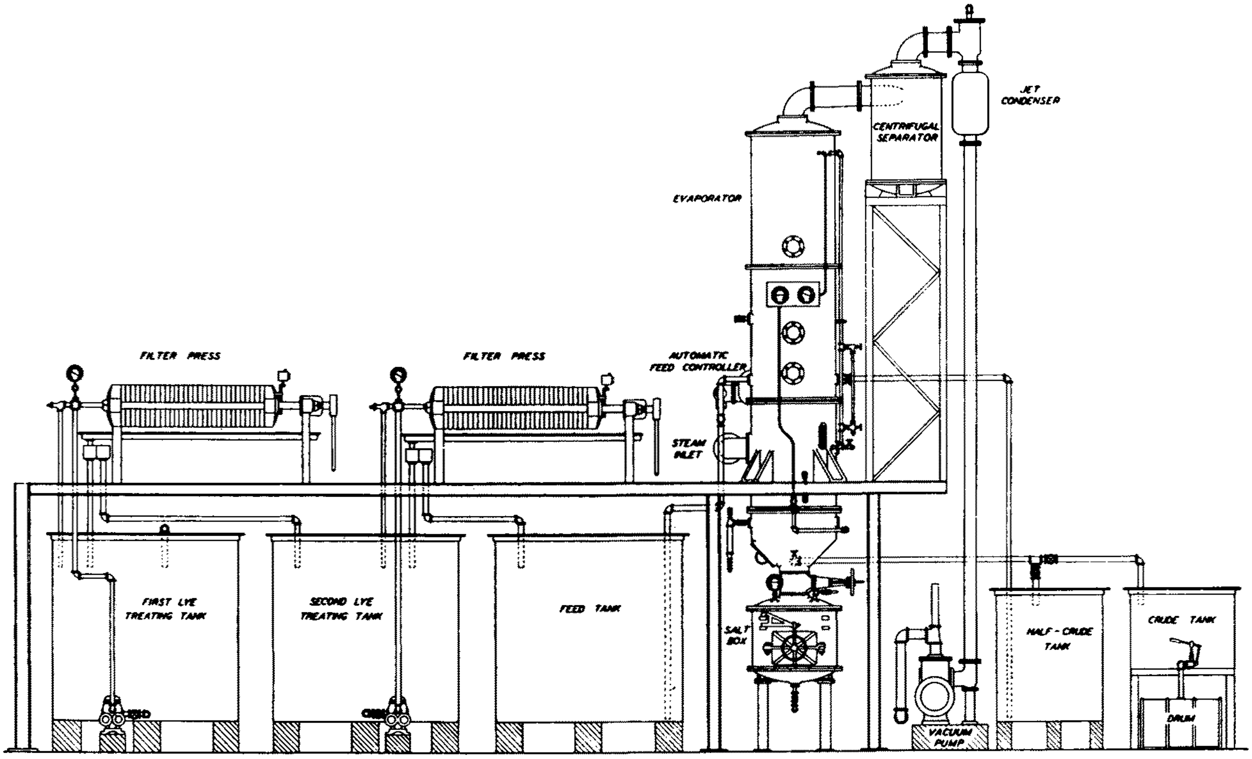


FIG. 2. Complete Double Treatment Spent Glycerine Lye Treating and Evaporating Plant. This illustration shows tanks for first and second treatment, separate filter press for each treatment, evaporator feed tank, evaporator, and tanks for semi-crude and crude glycerine.

A. One first-treatment lye-treating tank furnished with heating coils and means for air and steam agitation.

B. One filter press pump.

C. One filter press of plate and frame design.

D. and E. Two second-treatment lye-treating tanks. One serves as an evaporator feed-tank, while the other, after being filled with filtered liquor, is undergoing treatment. By using the two tanks alternately, a continuous supply of feed liquor is assured for the glycerine evaporator and the amount of lye fed to the evaporator can be measured. The second-treatment tanks are furnished with means for air and steam agitation.

Means of weighing treatment chemicals should be provided. Generally, it is sufficient to furnish a portable platform scale, suitable buckets for weighing muriatic acid, sulfuric acid, caustic, alum, and filter aid. A glass carboy with calibrated graduations on the vertical side may be used for measuring acid in place of weighing bucket and scale. An acid carboy pump of the pneumatic type is then used to dispense the correct amount of acid.

Acid Treatment: A measured amount of spent soap lye, previously cooled and skimmed of hard soap, is pumped into the first-treatment tank A. The contents of the tank are agitated for a few minutes and a liter sample of the lye is withdrawn for testing. The lye tank is heated to 115° F. to 120° F. and the necessary amount of acid and flocculating agent, as determined from the test of the lye sample, are added with steam or air agitation. When the batch is thoroughly mixed, a sample is drawn and filtered. If the filtrate is clear, sufficient flocculating agent has been added. If the filtrate remains clear after the addition of two or three drops of acid, enough acid has been added.

When the batch is ready to filter, the required amount of diatomaceous filter aid is added just prior to filtration. Gentle steam or air agitation is continued while the treated lye is pumped through the filter press in order to keep the filter aid in suspension. The filtrate is returned to the first-treatment tank A until it comes through clear. The clear filtrate is then discharged to one of the second-treatment tanks, D or E, whichever one is empty.

Alkaline Treatment: The filtered liquor in the second-treatment tank is agitated with air or steam for a few minutes before a sample is withdrawn for testing. The required amount of caustic (NaOH) as determined from testing the sample, is added. The contents of the tank are agitated for five or ten minutes to mix the caustic thoroughly with the liquor. The floc produced by the reaction between the alum or ferric chloride dissolved in the filtered liquor and the added sodium hydroxide is allowed to settle undisturbed to the bottom. Within four or five hours, the alkaline treatment will settle into two layers. The upper layer consists of clear liquor free of floc; the bottom layer is a slurry of the floc and represents about 5% of the contents of the tank. The clear liquor which has a pH of 8.5 to 9.0 is drawn into the evaporator from a point just above the layer of floc. The distance between this point and the bottom of the tank is about one-tenth the height of the tank.

When the clear liquor has been withdrawn from the tank down to the level of the opening of the feed pipeline, the residual slurry of floc at the bottom of the tank is then pumped back into the first-treatment tank A to be added to a fresh batch of untreated spent lye.

The second-treatment, as described herein, is satisfactory if reasonable care is used in the settling operation. The initial investment in equipment is reduced and the labor of handling a second filter press is eliminated. However, it is preferable, where these considerations are not sufficiently important, to pass the second-treatment through a second filter press (see Fig. 2). This will prevent a possibility of contamination in the feed liquor to the evaporator.

Muriatic acid, although its initial cost is higher, is preferred to sulfuric acid. The use of sulfuric acid in the treatment is objectionable in that it produces sulfates which interfere with subsequent plant operations. Feed liquor containing excess sulfates may form a hard scale inside the glycerine evaporator tubes, reducing the rate of evaporation and causing shutdowns for its removal. Sulfates also contaminate the salt recovered on evaporation of the lyes, making the salt less effective in the "graining out" operation of the soap kettles.

A combination of ferric chloride and alum in which alum is used in the proportion of ½ to ¾ pounds per thousand pounds of lye produces an efficient floc for removing impurities in the lye. The purpose of the alum is to produce a voluminous floc which will aid in the settling and filtration of the finer floc of ferric chloride. The use of alum alone as the flocculating agent will give satisfactory results in most cases. However, it must be kept in mind that its use will introduce a slight amount of sulfate which will contaminate the salt recovered on evaporation. Allowance for the proportionate amounts of alum and ferric chloride in the treatment should be made by adding the corresponding amounts of Standard Alum and Standard Ferric Chloride Solutions to the spent lye sample being tested.

As a rough guide, the following table indicates normal ranges for materials used in treatments:

TABLE II

Material	Pounds of Material Per 1,000 Pounds of Lye
Alum, $Al_2(SO_4)_3 \cdot 18H_2O$	1½ to 3 pounds
Ferric Chloride, lump, $FeCl_3 \cdot 6H_2O$	¾ to 1½ pounds
Anhydrous Ferric Chloride, $FeCl_3$	½ to 1 pound
Muriatic Acid, 22° Be, HCl	3½ to 8 pounds
Muriatic Acid, 20° Be, HCl	3½ to 9 pounds
Muriatic Acid, 18° Be, HCl	4 to 10 pounds
Sulfuric Acid, 66° Be, H_2SO_4	2 to 5 pounds
Sulfuric Acid, 60° Be, H_2SO_4	2½ to 6 pounds
Filter Aid, diatomaceous	1 to 5 pounds
Caustic Soda, Flake, 95% NaOH	½ to ¾ pound

However, the amounts of materials may vary over a larger range depending on the source of the spent lyes and on individual plant kettle operations. Lyes from poor kettle stock will require greater amounts of treatment materials.

Summary

Herein is described a method of spent soap lye purification which has the following advantages:

(1) Places the control of the product under the laboratory.

(2) Consistently yields a glycerine feed liquor of the highest possible quality.

(3) Conserves equipment, labor, and treatment materials.

(4) Uses facilities which are either present in or can be readily obtained by the soap plant.

REFERENCES

(1) Govan, W. J., Jr., Oil & Soap, P. 108, Vol. *XVII*, No. Five, May, 1940.

(2) Guillaudeu, A., Ind. & Eng. Chem., Vol. *29*, P. 729, July, 1937.

(3) Lawrie, James W., "Glycerol and the Glycols," A.C.S. Monograph 44, 1st ed., PP. 37, 46, New York, The Chemical Catalog Co., 1928.

(4) Sanger, W. E., Chemical and Metallurgical Engineering, Vol. *XXVI*, No. Twenty-Six, June 28, 1922.

(5) Wurster, O. H., Soap, Vol. *V.*, No. 1, September, No. 2, October, 1929.

(6) Wurster, O. H., Oil & Soap, Vol. *XIII*, Nos. 10 and 11, PP. 246-253, 283-286, October and November, 1936.

Routine Turbidimetric Determination of Tin in Soap

GERALD M. COMPEAU and EUGENE W. BLANK

Research and Development Department, Colgate-Palmolive-Peet Co.
Jersey City, N. J.

THE addition of tin salts to soap to inhibit the development of rancidity has been patented (1). No analytical methods have been reported for the determination of tin in soap and this investigation was undertaken to provide for its estimation in the concentrations of tin to be expected in this connection, i.e., 0.01% to 0.25% tin.

A simple procedure which first suggests itself, of ashing the soap and analyzing the ash for tin, leads to immediate analytical difficulties as the tin salts are either partly reduced to the volatile metal or converted to the refractory tin oxide. In either case the tin is lost for quantitative purposes. Allen, in giving ash methods for various products, notes that the negative results of some workers when tin is known to be present is probably due to poor tin recovery from the ash (2). Results of the present investigation lead to the conclusion that the use of magnesium nitrate (3, 4) as an ash-aid provides for ready and quantitative tin recovery from the ash.

The analytical literature provides many methods for the determination of tin. Of these, the usual iodimetric and gravimetric methods require higher tin concentrations than are met with in soap analysis and almost all the colorimetric methods depend on the reducing action of the stannous ion and hence suffer from their being subject to many interferences. The present work has indicated that while known stannous chloride solutions give excellent color reactions in very low concentration, stannic chloride solutions are difficult to reduce in low concentration and give discordant, and often negative, results. It has been found that the estimation of the tin as a suspension of stannic sulfide (5) best lends itself to the immediate problem.

Procedure

Preparation of Sample: Weigh a 10 ±0.1 gram sample into an 85 mm. porcelain dish containing a short, stout glass rod. Add 10 ml. of a saturated