

(b) That the Allen-Marquardt can be applied to any type of distilled liquor.

(c) That the Allen-Marquardt certainly must tend to give results that are somewhat too low, but that this is a fault applying equally to the other extraction processes—such as the Roese.

(d) That no process yet devised—or likely, in the very nature of the problem, to be devised—can give perfect results. That as between the various processes it is a choice of evils, but that the evil attendant on the use of the Allen-Marquardt process is less than in the case of the other processes.

Experience derived from experiments on a very extensive scale [*in the laboratory of the Bureau of Chemistry, Dept. of Agriculture*, (loc. cit.) *in the laboratory of the West Australian Government* (loc. cit.); in my own laboratory (loc. cit.) &c.] has shown that concordant results may be obtained by the Allen-Marquardt process and that, as far as the amyl alcohol is concerned, the results are practically quantitative. Experience has again shown that the Roese process is most unreliable and sometimes quite impossible.

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## A REAGENT IN THE CHEMISTRY OF FATS.

(SECOND PAPER)<sup>1</sup>

BY E. TWITCHELL.

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In my first paper I gave what seems to me a sufficient explanation of the special catalytic action of a series of *stearosulphonic acids* in causing the hydrolysis of glycerides of the higher fatty acids. In the presence of an excess of water a stearosulphonic acid will cause an acceleration of the hydrolysis of esters in general by virtue of its acid character, but it is a special reagent where the esters of the insoluble fatty acids are concerned as the hydrolysis of these is not accelerated by other strong acids.

A catalytic agent which would accelerate the hydrolysis of a particular class of esters in presence of an excess of water would also accelerate the esterification of their acid and alcoholic constituents in the presence of an excess of either of these two and a deficiency of water. I have found that the process of esterification of the higher fatty acids does in fact rapidly take place in the presence of a small amount of a stearosulphonic acid under conditions where, without this catalyser, the process would be so slow as not to be noticeable. The completeness of the reaction depends on the removal of the water formed and therefore the catalytic action of the stearosulphonic acids applies especially to the esterification of the higher fatty acids and alcohols which are not readily volatile at 100°, be-

<sup>1</sup> Read before the Cincinnati Section, Feb. 13.

cause at this temperature the reaction takes place rapidly and the water formed can be separated from the less volatile alcohols and acids by evaporation.

The process of esterification is carried out in the laboratory in the following simple way:—An alcohol, for instance glycerol, and a fatty acid, with a small percentage of *naphthalenestearosulphonic acid* are heated in an open vessel on the water-bath. The water produced by the reaction is evaporated as soon as formed and, after a certain time, the combination of the glycerol will be found to be complete if the fatty acid is in excess, while in the reverse case, if the glycerol is in excess, the combination of the fatty acid will be complete. The esterification is, of course, not absolute, but so nearly so that quantitative results may be obtained as will be shown in the following examples.

In the first place a solution of pure naphthalenestearosulphonic acid was prepared as follows: the crude compound was dissolved in about five times its volume of ether. This ethereal solution was washed several times in a separatory funnel with dilute hydrochloric acid and was then shaken with about one-half its volume of water. The aqueous layer which had extracted most of the naphthalenestearosulphonic acid from the ether, was then washed several times with small quantities of ether and finally heated to expel dissolved ether. The aqueous solution was made to contain about 10 per cent. of naphthalenestearosulphonic acid and was used as the catalytic agent in the following experiments.

*Quantitative Esterification of Glycerol.*—Some "C. P. glycerine" of commerce was dissolved in water and diluted so that the solution contained 1 per cent. of the original substance. This was analyzed by the bichromate method which showed the original sample to contain 95.36 per cent. of glycerol.

For the fatty acid I used commercial "stearic acid," which is chiefly a mixture of palmitic and stearic acids. This was purified by boiling with dilute hydrochloric acid and then drying. In the following I shall call this simply *stearic acid*.

5 cc. of the glycerol solution (representing 0.05 gram of the original sample) were measured into a round bottomed flask. To this was added 1 gram of the stearic acid and 2 cc. of the naphthalenestearosulphonic acid solution. The open flask was heated on a water-bath. In a half hour all visible moisture had evaporated. The heating was continued 4 hours longer. Then about 50 cc. of neutralized alcohol were poured into the flask and the solution titrated with standard caustic soda solution (using phenolphthalein as indicator), 8.08 cc. were required to neutralize the uncombined fatty acid. 1 gram of *stearic acid* and 2 cc. of the reagent solution without the *glycerol* were treated in exactly the same way and after the heating required 12.43 cc. of the standard alkali. The difference be-

tween 12.43 and 8.08 = 4.35 represents the amount of glycerol combined with the stearic acid. The standard alkali solution was of such a strength that 1 cc. was equivalent to 0.02 gram of KOH, and this would correspond to 0.01093 gram of glycerol. These figures would therefore show the percentage of glycerol in the sample to be— $\frac{4.35 \times 0.01093 \times 100}{0.05}$   
= 95.09.

When the mixture was heated in a dish instead of a flask the results were generally one or two per cent. lower, due no doubt to an evaporation of glycerol which is prevented, when a flask is used, by the cooling on the sides and neck. Thinking that loss of glycerol as well as of fatty acids might be prevented and at the same time the water quickly removed by attaching a vacuum pump to the flask, I tried this experiment, but found little difference in the results.

On adding the alcohol preparatory to titration, the reagent being still active, there is danger of some ethyl esters being formed, especially if the solution is heated as it must be to dissolve all the remaining fatty acid. To avoid this danger I added enough of the standard alkali at once to neutralize the acidity of the reagent, after which the solution was heated and the titration completed.

A sample of "dynamite glycerine" tested 97.30 per cent. glycerol by the bichromate method, and by the above described method, 96.62 per cent.

I have given these examples to show the completeness of the esterification of glycerol by this method. As a general analytical process it would have to be applied to crude glycerines containing impurities which, according to their nature, would have to be considered.

*Quantitative Esterification of Other Alcohols.*—This method would be especially suited to the alcohols found in waxes. Of these I had available the alcohols separated from Chinese wax which are supposed to consist chiefly of ceryl alcohol.

One-half gram of this substance, 1 gram of *stearic acid* and 2 cc. of the naphthalenestearosulphonic acid solution were heated in an open flask on the water-bath for 4 hours as in the case of glycerol. Neutralized alcohol was then added and the solution titrated with standard alkali (of which 1 cc. corresponded to 20 milligrams of KOH). 8.73 cc. were required. The blank (without the crude ceryl alcohol) required 12.45 cc. The difference, 12.45 — 8.73 = 3.72 represents the hydroxyl replaced by the fatty acid. Expressing this in milligrams of potassium hydroxide for 1 gram of the substance under examination, would give  $\frac{3.72 \times 20}{0.5} = 148.8$ ,

which may be called the *hydroxyl value* of the substance and is the number of milligrams of potassium hydroxide, having the same amount of hydroxyl as has 1 gram of the alcohol.

The *hydroxyl value* is analogous to the *acetyl value*, but is not the same, since it is calculated on the weight of the original substance and not on the weight of the substance plus the acetyl radical added. In the case of the crude ceryl alcohol I had no test to determine whether the combination had been complete, except that a longer time of heating did not cause further combination, and, moreover, when under the same conditions the ceryl alcohol was in excess the fatty acid was completely esterified, as I will show later.

*Quantitative Esterification of Hydroxy Fatty Acids or Their Glycerides.*—This refers to the alcoholic hydroxyl of the acid. A typical glyceride of this class of acids is castor oil.

0.2350 grams of castor oil, 1 gram of *stearic acid* and 2 cc. of the reagent solution were heated for 4 hours in an open flask on the water-bath. After this neutralized alcohol was added and the titration required 10.67 cc. of the standard alkali. The blank required 12.44, and, from the acid value of the castor oil, it was calculated that 0.2350 grams would require 0.03 cc. of standard alkali to neutralize its acidity. Therefore,  $12.44 + .03 - 10.67 = 1.80$  represents the alcoholic hydroxyl replaced by the fatty acid. The *hydroxyl value* is therefore  $\frac{1.80 \times 20}{0.2350} = 153.2$ .

A rather large excess of stearic acid was used in this case, perhaps more than necessary, but the total alcoholic hydroxyl in the reaction includes the glycerol already combined with the fatty acid in the castor oil, and in deciding on the excess of acid needed, this total hydroxyl must be considered and not simply the free hydroxyl.

The fatty acids were prepared from some of the same castor oil and treated as follows: 1.0365 grams of the fatty acids, 1 gram of stearic acid and 2 cc. of the reagent solution were heated for 4 hours as before, dissolved in alcohol and titrated. 13.93 cc. of standard alkali were required. The blank tested 12.44 cc. and, from the acid value, the 1.0365 grams of fatty acid required 9.72 cc. of standard alkali to neutralize them. The *hydroxyl value* is therefore  $\frac{(12.44 + 9.72 - 13.93) 20}{1.0365} = 158.8$ .

In this case the stearic acid is hardly necessary as there is almost a sufficient excess of acidity in the castor oil fatty acids themselves. Omitting the stearic acid, the hydroxyl value obtained was 154.6.

The values, both of the neutral fat and of the acids, are somewhat lower than would be calculated from the acetyl values usually given for castor oil.

The same process was applied to various fats and fatty acids supposed to contain no alcoholic hydroxyl. Plainly with these fats the excess of stearic acid need not be so large and with the fatty acids no stearic acid at all need be used.

The following *hydroxyl values* were found for a number of different fats and fatty acids:—

Lard .....	1.8
" fatty acids .....	8.3
Tallow " .....	2.3
Olive oil .....	6.4
" " .....	5.0
Cotton Seed Oil .....	7.8
" " " .....	8.2
" " " fatty acids .....	12.8
Castor Oil .....	149.0
" " fatty acids .....	161.4

It was thought possible that, especially in the case of the highly oxidizable fatty acids, hydroxyl compounds might be formed, due to the action of the air during the heating process. The air was therefore expelled and the water vapor was carried off by conducting a current of dry hydrogen into the flask during the time of heating, but practically the same results were obtained as before. The current of hydrogen has, however, an advantage in that it prevents darkening of the mixture. In the case of oxidizable oils this darkening is considerable and may interfere with obtaining a sharp end reaction in the titration.

Mono- and diglycerides in the presence of an excess of fatty acid will combine with the latter, forming triglycerides when treated by this method. The experiments with glycerol show that the reaction will be complete.

*Quantitative Esterification of Fatty Acids.*—The ordinary mixture of higher fatty acids, such as is found in tallow, was used for this investigation.

1 gram of fatty acid, 1 gram of "C. P. glycerine" and 2 cc. of the naphthalenestearosulphonic acid solution were heated on the water-bath in the manner previously described.

In the presence of this excess of glycerol the fatty acids should esterify as should also the naphthalenestearosulphonic acid as to its carboxyl radical, while the acidity of the  $\text{SO}_3\text{H}$  radical should remain free. This acidity I have shown<sup>1</sup> can be determined by titrating in aqueous solution with standard alkali and using methyl orange as indicator. 2 cc. of the naphthalenestearosulphonic acid used in this experiment required 1.02 cc. of my standard alkali to neutralize it to methyl orange. After heating the mixture of glycerol, stearic acid, and naphthalenestearosulphonic acid for 4 hours on the water-bath, it was dissolved in neutral alcohol and titrated, using phenolphthalein as indicator. The amount of standard alkali required was 1.12 cc. Then  $1.12 - 1.02 = 0.10$  cc. represents the fatty acid uncombined, about 1 per cent. of the whole.

<sup>1</sup> This Journal, January, 1900.

One and a half grams of the alcohols obtained from Chinese wax, 0.3 gram of fatty acid and 2 cc. of the reagent solution were heated as in the foregoing experiments and required 1.00 cc. of standard alkali to neutralize, showing that the fatty acid had been completely esterified to within the limits of accuracy of the test. I took pains to prove that the free acidity was really due to the  $\text{SO}_3\text{H}$ , radical.

Amyl alcohol is slowly evaporated from an open flask on a water-bath, but if a sufficient excess is used, fatty acids can be completely combined with this alcohol.

About 1.2 grams of fatty acid and exactly 2 cc. of the naphthalene-stearosulphonic acid solution were heated in an open flask on the water-bath. As soon as the bottom of the flask appeared dry about 2 cc. of amyl alcohol were added and the heating continued 4 hours. On adding neutralized alcohol and titrating it was found that 1.04 cc. of standard alkali were required, which corresponds closely to the acidity to methyl orange of 2 cc. of the reagent.

As might be expected the acids of rosin are not esterified by this method.  
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## A CONTRIBUTION TO THE CHEMISTRY OF THE BLEACHING OF FLOUR.

By S. AVERY.

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### Introduction.

For some time the writer has given more or less attention to the bleaching of flour. On withdrawing from the work of the Nebraska Experiment Station it seems desirable to publish the results at hand. The work is being continued by my colleague in the University and successor as Chemist of the Station, Dr. F. J. Alway. I am under obligations to him for valuable suggestions and for a part of the data here presented.

For many years proposals have been made and patents issued for bleaching cereal products with sulphur dioxide. British patent to Beans No. 2,502, issued in 1879, appears to be the first to mention chlorine as a bleaching agent. Modern bleaching of flour may be regarded as dating from 1898. French patent No. 277,751, issued to Frichot, discloses the use of nascent oxygen in a gaseous condition to be brought in contact with the flour in a finely divided state. Ozone is the chemical substance especially mentioned. It is recommended that ozone be prepared by electricity. British patent No. 1,661 to Andrews, discloses also the use of nascent oxygen and recommends the use of nitrogen peroxide as a bleaching agent. U. S. patent to Alsop No. 759,651, of 1904, discloses the use of air treated by electricity. The general introduction of bleaching into American mills dates from about the time of the last-named patent.