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ANALYSIS OF SYNTHETIC
TANNING MATERIALS

BY

EDWARD WOLESENSKY, Chemist

Bureau of Standards

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ANALYSIS OF SYNTHETIC TANNING MATERIALS

By Edward Wolessky

ABSTRACT

Methods are described for the determination of acidity, total sulphur, total inorganic matter, free sulphuric acid and sulphates, nonvolatile matter, total organic matter, and the tanning material in synthetic tanning materials which are sulphonated condensation products. These methods are mostly adaptations of principles or modifications of methods already known, and are based on experience gained in the analysis of such synthetic tanning materials in the course of an investigation of these products.

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I. INTRODUCTION

The analysis of synthetic tanning materials, which are usually sulphonated condensation products of aromatic compounds and commonly known as "syntans," naturally presents some problems which are not encountered in the analysis of the ordinary vegetable tanning materials. Consequently, in the course of an investigation of synthetic tanning materials at the Bureau of Standards it was frequently necessary to devise methods of analysis of these products to meet new situations. While no special investigation was conducted to develop or perfect methods of analysis per se, nevertheless a considerable amount of this kind of work was done at one time or another during the above-mentioned investigation of synthetic tanning materials; and in order that the results of this experience might be available to others engaged in the study or analysis of such materials, it has been considered worth while to publish such of the methods used in this laboratory as were shown by experience to give the most reliable results and to be generally the most satisfactory. No claim is made that the methods hereinafter described are the best that can

be devised for the purpose, or that they embody any new principles or reactions, neither is any originality claimed for them. They merely represent the application of well-known methods and principles modified and adapted to the problems in hand as occasion required. It should also be explained that the primary object of these methods was reliability of results, and that speed and simplicity were only secondary considerations.

II. ACIDITY

The accurate determination of the acidity of a syntan is one of the most important determinations in the analysis of these products not only because of the action of acids on hide or leather during tanning, but also because, as will be seen later, certain other determinations depend upon the determination of the acidity. Because of the strong color of most syntans, this problem usually resolves itself into one of the accurate determination of the end point in the titration of the sample. In a few cases the syntan itself acts as its own indicator, but the color change is rarely sharp enough to indicate the end point accurately. Undoubtedly the best method of determining the point of neutrality is by means of the potentiometer, where this is available, but good results have also been obtained in this laboratory by using an indicator paper as an outside indicator. The titration may be made with a normal solution of sodium hydroxide, using congo red paper to determine the approximate end point and making the final adjustment with the aid of red and blue litmus papers. It should not be necessary to describe the details of this titration here, since these may be obtained in any good text on acidimetry. While considerable practice and skill in manipulation are required to determine the exact point of neutrality by the method indicated, an experienced analyst should have no difficulty in obtaining good results.

It will be found most useful to express the acidity in terms of sulphuric acid.

III. TOTAL SULPHUR

The method which, on examination, would appear to be the best suited for the determination of total sulphur in such products as the syntans, and the only one which was actually used by the writer, involved the oxidation of the sample with nitric acid, the precipitation of the sulphuric acid by means of barium chloride, and weighing the precipitate so obtained. The sample of syntan (3 to 8 cc of solution, depending on its concentration) is weighed out into a 400 cc beaker, diluted with about 25 cc of water, filtered from insoluble matter if present (since we are chiefly interested only in the soluble components of the solution), treated with 20 to 25 cc of concentrated

nitric acid (68 per cent), and evaporated to dryness, or nearly so, on a steam bath. The residue is then treated with a further portion (about 35 to 40 cc) of the concentrated nitric acid and heated to incipient boiling in the covered beaker as long as brown fumes are evolved. The beaker is then uncovered and the solution concentrated to a volume of about 10 to 12 cc, diluted with water to about 150 cc, heated to near boiling (preferably on the steam bath), and treated with an excess of a hot solution of barium chloride. The heating is then continued for about half an hour longer, after which the precipitate is filtered off, washed, dried, ignited, and weighed according to the well-known methods for handling barium sulphate in gravimetric analyses.

The results thus obtained, expressed as sulphuric acid, should represent the total original sulphuric acid used in the sulphonation or other process during the manufacture of the syntan, unless some of this acid has been subsequently lost through reduction and volatilization as sulphur dioxide, or removed in some other manner. In the case of some syntans where the amount and composition of the sulphuric acid used in the preparation of the material are accurately known, and where it is known that there has been no loss of the acid during the process of manufacture, it may not be necessary to determine the total sulphuric acid present (both free and combined) in the final product, except to confirm other data.

IV. TOTAL INORGANIC MATTER

In the case of synthetic tanning materials which are sulphonated condensation products, such as those for which these methods are intended, the inorganic matter will be present entirely in the form of sulphates or sulphonates, unless small amounts of other inorganic materials are introduced either as impurities in the raw materials or from the corrosion of the vessels used in the manufacturing process. Furthermore, since the free sulphuric acid in syntans is usually neutralized by means of sodium hydroxide or carbonate, the inorganic matter present will be mostly or entirely in the form of sodium sulphate. It can, therefore, be determined by a method similar to that in common use for the determination of sodium or potassium in organic compounds. A slight modification of the ordinary procedure, however, is recommended for the syntans. Instead of heating the dried material with concentrated sulphuric acid, it has been found preferable to first char it by gentle ignition and then moisten with sulphuric acid. Ashing the material completely before applying the sulphuric acid is not recommended because of the extensive reduction of the inorganic matter under these conditions and the resulting losses due to volatilization. The use of a platinum crucible,

as generally recommended in similar work, has the advantage, chiefly, of permitting stronger ignition in the final stages of the operation, and thus shortening the time required. Such operations as the one here described, however, are hard on platinum ware. Moreover, it is not necessary to use platinum if speed is not essential, since very good results may be obtained with the use of a porcelain crucible, provided the ignition in the final stages of the operation is not carried to the melting point of the sodium sulphate. Finally, it is not necessary to add ammonium carbonate to the contents of the crucible in order to remove the sulphuric acid, as recommended by some.

The following procedure is recommended: Weigh out a sample of the syntan into a weighed porcelain crucible (previously ignited) having a capacity of about 25 cc, and evaporate to dryness. The main portion of water may be evaporated on the steam bath, and the residue then dried in an oven at 105 to 110° C. for about an hour or two. The dry material is then charred by gently igniting over a free flame, and after cooling somewhat, the sintered mass is treated with about 15 drops of concentrated sulphuric acid. It is then heated gently over a small flame, care being taken to avoid spattering. The heating is gradually intensified, as the evaporation of the acid will permit, until a moderate red heat is reached. It is not desirable, in most cases, to attempt complete oxidation of the carbonaceous matter at this point, but after the outside of the mass has been nearly freed from the carbonaceous matter, the material is again allowed to cool somewhat, moistened with concentrated sulphuric acid, and once more heated as before. This is repeated, if necessary, until all carbonaceous matter is completely oxidized, when the residue is again cooled and moistened with just a drop or two of concentrated sulphuric acid and ignited, at first moderately until no more sulphuric acid fumes are visible, then more strongly but without melting the final product until constant weight has been reached. The removal of the last traces of sulphuric acid may be hastened by keeping the crucible covered during the last part of the heating, uncovering it only for a few seconds from time to time in order to permit the escape of fumes which may have accumulated.

As already stated, the residue thus obtained will, in most cases, consist largely or entirely of sodium sulphate. However, if it is known, or if the appearance of the residue indicates, that other metals are present, or if there is any doubt as to the composition of the residue, this may now be analyzed according to well-known methods for the determination of metals. Should iron or other metals whose sulphates decompose on heating be present in appreciable quantities, the equivalent quantity of sulphuric anhydride should be computed and added to the weight of the residue, in order

to obtain the correct weight of the inorganic matter in the form of sulphates. In most cases, however, no serious error will be committed if the entire residue as obtained is regarded as sodium sulphate.

It will be found most convenient to express the final result in terms of sulphuric acid.

V. FREE SULPHURIC ACID AND SULPHATES

Having determined the acidity, the total sulphur content, and the total inorganic matter in the syntan, it is now possible to estimate the amounts of free sulphuric acid or of sulphates, as well as the equivalent of the sulphonic acid in terms of sulphuric acid. The method of calculation will vary in different cases, depending upon the circumstances, as outlined below. In this scheme "A" represents the total acidity, "T" represents the total sulphur content, and "S" represents the total inorganic matter, all expressed in terms of sulphuric acid.

1. NO SOLUBLE INORGANIC MATTER PRESENT

(a) T is less than 2A—

Free sulphuric acid is present as well as sulphonic. The free sulphuric acid is equal to $2A - T$, and the acidity due to sulphonic acid is equivalent to $T - A$ in terms of sulphuric acid. The sulphuric acid combined as sulphonic acid is twice the last amount, or $2(T - A)$.

(b) T is equal to 2A—

No free sulphuric acid is present, and all of the sulphonic acid is free.

2. SOLUBLE INORGANIC MATTER PRESENT

(a) $(T - S)$ is equal to 2A—

No free sulphuric acid is present (for all practical purposes), and all of the sulphonic acid is potentially free.

(b) $(T - S)$ is less than 2A—

Free sulphuric acid is present in addition to soluble sulphates. The amount of the free sulphuric acid is equal to $2A + S - T$, and the combined sulphates and free sulphuric acid are equal to $2A + 2S - T$. The acidity due to sulphonic acid (expressed in terms of sulphuric acid) is equal to $T - S - A$, and the amount of sulphuric acid combined in this form is equal to twice this amount, or $2(T - S - A)$.

(c) $(T - S)$ is greater than 2A—

No free sulphuric acid is present (for practical purposes), and part of the sulphonic acid is also neutralized. The neutralized sulphonic acid is equivalent to $(T - S - 2A)$ in terms of sulphuric acid, and the sulphuric acid combined in the form of such neutralized sulphonic acid is twice the last amount, or $2(T - S - 2A)$. The soluble sulphate present in the syntan solution are equivalent to $(2A + 2S - T)$ in terms of sulphuric acid.

In the above it is assumed that no acids are present (either free or combined) except sulphuric and sulphonic. If other acids are present, of course their amounts would have to be determined and the necessary corrections applied.

VI. NONVOLATILE MATTER

By "nonvolatile matter" is here meant practically everything in the syntan except water, and it, therefore, also includes any free sulphuric acid which may be present. To determine this nonvolatile matter it is not sufficient simply to evaporate a sample of the syntan to dryness and weigh the residue not only because any free sulphuric acid which might be present would attack the organic matter as the solution became concentrated, but also because many sulphonic acids are more or less hydrolyzed when heated with water, even though no other acids may be present. This hydrolysis would result not only in the combination of water with other components of the solution, but also in the liberation of a certain amount of sulphuric acid, which in turn would again attack the organic matter as just mentioned, so that a whole series of errors would be introduced. In some cases these difficulties may be overcome by exactly neutralizing the sample of syntan before evaporating by adding the required amount of standard sodium hydroxide solution, and then correcting the weight of the final residue for the difference between the weights of sodium introduced and the hydrogen thus displaced. Unfortunately, however, even this expedient does not suffice in all cases, for it has been found that some syntans will be hydrolyzed when heated in aqueous solution even though they have been previously neutralized as just described. In such cases it is practically impossible to bring the residue to constant weight, each successive heating producing a further loss. Furthermore, the residue then fails to dissolve completely in water, and the resulting solution has a strong acid reaction instead of being neutral. It has been found, however, that if the solution is evaporated to dryness at ordinary temperatures (as in a vacuum desiccator over sulphuric acid), all of the above difficulties are overcome; the residue is readily dried to constant weight, it is then easily and completely dissolved in cold water, and the resulting solution is neutral and in every way like the original. Furthermore, as might be expected, it has also been found that when most of the water has been evaporated so that the residue appears dry the residue may be heated in an oven to a temperature of 105 to 110° C., for the purpose of removing the last traces of moisture and hastening the drying, without noticeable decomposition or other apparent effect.

Hence the procedure for the determination of total nonvolatile matter is as follows: Place the sample of syntan (about 5 to 10 cc depending upon its concentration) into a weighed, wide-mouthed weighing bottle of about 50 to 75 cc capacity, and weigh. Then, the

acidity of the syntan having been previously determined, add from a burtte the required amount of standard sodium hydroxide solution to exactly neutralize the sample, shake the bottle carefully with a rotating motion to mix the contents thoroughly, place into a vacuum desiccator over sulphuric acid and exhaust with any suitable suction apparatus. During this exhaustion of the desiccator care must be taken to avoid excessive foaming of the solution in the weighing bottle. This can be controlled by regulating the vacuum as circumstances may require. When the maximum vacuum attainable or permissible has been reached, the desiccator may be closed and allowed to stand undisturbed while the evaporation of the solution is taking place. With an internal pressure of 15 to 20 mm the bulk of the water is generally removed from the sample in 24 hours. Owing to the dilution of the sulphuric acid in the desiccator by the water which is absorbed from the solution and the consequent decrease in its dehydrating power, in cases where a considerable number of such determinations are to be made it is desirable to use two vacuum desiccators, one for the preliminary evaporation and the other to complete the drying. To hasten the removal of the last traces of moisture, the nearly dry residue may be heated in a vacuum oven. If this is not available the residue may be heated for two or three hours in an ordinary oven at a temperature of 105 to 110° C., then again placed into the vacuum desiccator and, while still hot, subjected to reduced pressure for several hours. This treatment is repeated until the residue has attained constant weight. The weight of the residue is now corrected for the difference between the weight of sodium which was introduced in the standard sodium hydroxide solution to neutralize the sample and the weight of the hydrogen displaced thereby. The result represents the total nonvolatile matter in the sample, including free sulphuric acid, assuming that no other acids are present in the syntan.

In case the syntan contains any insoluble matter it is desirable to determine the latter by filtering, washing, drying, and weighing, and to subtract the amount of this from the total nonvolatile matter, since we are usually interested only in the soluble constituents of the syntan.

VII. TOTAL ORGANIC MATTER

It is sometimes desirable to know the amount of organic matter present in the syntan. This can be readily calculated by subtracting the amount of inorganic matter (as sulphates, principally or entirely sodium sulphate) and the amount of free sulphuric acid, if any, from the total nonvolatile matter.

VIII. TANNING MATERIAL

The amount of actual tanning material in a syntan may be determined by a modification of the official method of the American Leather Chemists' Association. For this purpose it will be necessary

to dilute the original solution of the syntan to a suitable concentration for the treatment with the hide powder, and also to remove any free sulphuric acid or soluble sulphates. This can be accomplished by taking a weighed quantity of the syntan containing about 5 g of organic matter (see preceding determination), adding thereto a solution of barium acetate containing a quantity of this salt just equivalent to the amount of soluble sulphates and free sulphuric acid in the sample taken, and diluting with water to 1 liter. The barium sulphate formed under these conditions will be too finely divided to permit its separation from the solution by filtration, and it is not desirable to heat the solution in order to make the precipitate coarser because of the danger of splitting off more sulphuric acid by hydrolysis of the sulphonic acid. Hence the solution is allowed to stand overnight to allow the barium sulphate to settle, and the supernatant clear liquid is then used for the determination of tanning material. It sometimes happens that the barium sulphate will not settle out completely even after several days. In such cases it is better to proceed without separating it from the solution or after separating only the greater part of it, and then making correction for any barium sulphate which may be present in the final solution as will be described later.

The hide powder, which is used for removing the tanning material from the above-dilute solution of syntan, is prepared exactly as described in the official methods of the American Leather Chemists' Association for the analysis of vegetable tanning materials, and hence the details will not be given here. After determining the moisture content of the moist, chromed hide powder, a weighed quantity of the latter containing from 12 to 13 g of dry substance is placed into a bottle of from 500 cc to 1 liter capacity, together with 200 cc of the above-prepared solution of syntan, and the mixture shaken in a suitable shaking machine for 10 minutes. Usually this length of time is sufficient to "detannize" the solution, but in case it is not the shaking must be continued for a longer time. To determine whether or not all tanning material has been absorbed by the hide powder, 2 or 3 cc of the solution may be withdrawn by means of a pipette, taking care to obtain a sample as free as possible from hide powder, placed into a test tube, and treated with a drop or two of a fresh gelatin-salt solution, containing 1 per cent of gelatin and 10 per cent of sodium chloride. If a precipitate is formed on the addition of the gelatin solution, the tanning material has not been completely removed. If the tanning material has been completely absorbed, the main portion of the solution is separated from the hide powder by squeezing through a linen bag and immediately filtered through filter paper into an Erlenmeyer flask, taking care to prevent evaporation of the solution as much as possible during the filtration by keeping both funnel and

flask covered. The flask may be conveniently closed by means of a rubber stopper having a hole slightly larger than the stem of the funnel through which the latter passes.

One hundred and fifty cc of the filtrate are now evaporated to dryness in an evaporating dish capable of holding 50 cc of solution at a time, the solution being added in 50 cc portions as evaporation permits. The evaporation proper may be carried out on a steam bath and the final residue may then be dried to constant weight in an oven at 105 to 110° C. If any barium sulphate has come through in the filtrate, the amount of this must now be determined and subtracted from the weight of the residue just mentioned. If the syntan contained no inorganic matter and the evaporation of the filtrate was carried out in a platinum dish, the barium sulphate in the residue may be determined by merely moistening the latter with a few drops of concentrated sulphuric acid and heating gently until all fumes of sulphuric acid cease to come off, then igniting, cooling, and weighing. On the other hand, if the syntan has been previously shown to contain inorganic matter (which will usually be the case with commercial products), the residue from the filtrate must be redissolved by warming with a little dilute hydrochloric acid, the solution and barium sulphate washed upon a quantitative filter, and the latter washed thoroughly, dried, ignited (with the addition of a few drops of concentrated sulphuric acid), and weighed according to the usual methods for handling barium sulphate. The difference between the weight of the residue actually found and the weight of barium sulphate will give the corrected weight of residue from 150 cc of filtrate. Correcting the volume of the latter for the water introduced with the wet hide powder, the unabsorbed residue in the entire solution resulting from the treatment of the hide powder with 200 cc of diluted syntan solution may be calculated, and multiplying this by five we obtain the corresponding value for the original sample of syntan which was used for the preparation of the diluted solution for this determination.

This last value does not represent the weight of "nontans" in the sample, since the free sulphuric acid has been removed and the soluble sulphates were converted to acetates by treatment with barium acetate. However, the difference between the weights of the soluble sulphates and of the acetates formed therefrom can be calculated easily, and correcting the above value for this difference, and adding the weight of free sulphuric acid present in the syntan (if any), the weight of "nontans" in the sample is obtained. If now we subtract this quantity from the amount of total nonvolatile matter, we obtain the amount of "tanning material" in the sample.

WASHINGTON, March 2, 1926.

