

Thesis by
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The Practical Estimation of
the Value of Tanning Materials,
with Points on Tanning.
By W^m E. Stickerson. 1876.

The methods for the estimation of
of the tanning powers of different sub-
stances, heretofore published, have pur-
ported to be simply for the estimation
of tannic acid. In the practical
tanning of leather however, the hide
not only takes up tannic acid, but it
also absorbs, and incorporates into the
leather, other bodies, which certainly
add weight and give color to the leather,
even though they may not pre-
serve or strengthen it.

Those therefore, who are concerned with
tanning, are not so particular about
the amount of pure tannic acid, as
they are about the amount of sub-
stance, which will enter into the

leather, and add to its weight and firmness.

But moreover, these methods must fail, if they aim at the estimation of pure tannic acid itself; for in all of them, the reagents which are used, not only precipitate tannic acid, but also precipitate, with more or less of completeness, other bodies which occur in tanning materials.

Wagner has distinguished ^{two} kinds of tannic acid, one of which he calls the physiological, and the other the pathological tannic acid. He holds, that although both varieties unite with the corium of the hide, yet the physiological only can preserve it.

So therefore, both kinds of tannic acid, if such there be, enter into the leather, and increase its weight and firmness. And, since the pathological variety, only occurs in small

quantities, and that only in particular kinds of plants, and the great excess of the real preserving acid, renders the preservation of the leather sure, it seems hardly important to distinguish between the two varieties, in a practical estimation of the value of tanning materials.

If we knew that the reagents used in these methods, precipitated the same bodies occurring in the tanning materials, which the hide itself absorbs; then, any one of them which might be used with ease, would answer the purpose of the present search.

But this we do not know, with the exception of one case, that in which hide itself, is used as the reagent. The method in which hide is used as the reagent, was used with complete success, after the unsuccessful trial of one other, that of Dr Wagner,

in which, the tannic acid is precipitated with sulphate of cinchonia. Since the hide method proved to be entirely satisfactory, the other methods were not tried, on account of obvious weaknesses, so far as the practical estimation of the value of tanning materials is concerned. In the case of using hide itself as the reagent, we must necessarily get at, what really goes into the leather.

The more important of the methods for the estimation of tannin, which have been published are as follows:

By Fehling, Dingl. Polyt. Journal, CXXX page 5-3, or Wagner's Jahresbericht-1858 p. 512

The tannin solution is precipitated by a titrated solution of glue.

By G. Müller, Wagner's Jahresbericht, 185-8, page 5-10, and 185-9, page 5-73,

In this method the tannin is precipitated with a titrated solution of glue and alum.

By E. Morier, *Dingl. Polyt. Journal*, CXVIII, page, 209. The tannin solution is titrated with permanganate of potash.

By Löwenthal, *Jour. of Pract. Chemistry*, LXXXI, page 150. The tannin solution is titrated with permanganate of potash, with sulphurindigotic acid as an indicator.

By H. Fleck, *Wagner's Jahresbericht*, 1860, page 531. The tannin is precipitated with acetate of copper, and the amount of oxide of copper in the precipitate, determined volumetrically.

By E. Wolff, *Wagner's Jahresbericht*, 1861, page 624. The tannin is precipitated with acetate of copper, and determined from the weight of the oxide of copper, after the ignition of the precipitate.

(page 782.)

By Carpené, Bolley's Handbook of Tech. Chem. Analysis.

In this method, a solution of acetate of zinc in a solution of ammonia, is used. This reagent, is said to precipitate pure tannate of zinc, but not to precipitate pectin, glycerine, albumen, tart rates of calcium or potassium or organic salts of iron.

This precipitate of tannate of zinc is filtered from the other bodies, washed with hot water, dissolved in dilute sulphuric acid and titrated with a solution of permanganate of potassium.

It seems probable that this method, which is a new one will prove very use-ful in estimating pure tannic acid.

By R. Handtke. Jour. Pract. Chemistry,
LXXXII p. 345. The tannin is precipitated
with a solution of the acetates of sodium
and iron.

By H. Risler. Fresenius Zeitschrift, 1863,
page 137. The tannin is precipitated by
a solution of chloride of zinc, and
determined by the amount of oxide
of zinc, in the ignited precipitate.

By Gerland. Fresenius Zeitschrift, 1863,
page 419. The tannin is precipitated
with a titrated solution of chloride
of ammonium, and tartrate of an-
timony and potassium.

By M. Wittenzwey. Jour. Pract. Chem.
XCI, page 81, or Fresenius Zeitschrift, 1864,
page 484. The estimation of the tannin,
is based on its absorption of oxygen, in
an alkaline solution.

By Commaille. Fresenius Zeitschrift,
1864, page 488. The estimation of the
tannin is based on its oxidation in

presence of prussic acid, by iodic acid.
By R. Wagner. Fresenius Zeitschrift
Volume No. 5: 1st Article. The tannic acid is pre-
cipitated with neutral sulphate of
cinchonia, with acetate of ros aniline
as an indicator. As been stated, this
method was tried without success.

The process is conducted as follows:
The tanning material is weighed and
leached thoroughly with water, and the
solution made up to a known bulk.
4,523 grammes of sulphate of cinchonia,
0,5^{grm} of sulphuric acid, and 0,1^{grm} of acetate
of ros aniline, are dissolved in water, and
made up to one litre. One cubic centimetre
of this solution precipitates 0,001 gramme
of tannic acid. To make the determin-
ation, 50 cubic centimetres of the tannin
solution are taken, and the standard
solution of sulphate of cinchonia run
in. The color due to the ros aniline
is, theoretically, all thrown down with

the tannin precipitate, until all the tannin is precipitated, when a very slight excess of the cinchonia solution, imparts a pink color to the clear solution, after the precipitate has settled. The number of cubic centimetres of the cinchonia solution used, multiplied by 0,001, gives the number of grammes of tannic acid, in the 50 cubic centimetres of the tannin solution.

The difficulties encountered in working this method are these, Although the directions of the original paper were followed as closely as possible, yet, the coloring matter was not all precipitated with the tannic acid, but even the first few cubic centimetres of the cinchonia, produced a coloration of the tannin solution, although the point of saturation was not nearly reached. Also

as all the tanning solutions have a strong color of their own, which the cinchonia does not seem able to remove, another difficulty is introduced; for this color interferes with that of the indicator.

This method was tried faithfully, following the directions of the original paper, but without success.

It was then tried, with such modifications as were suggested, but to no purpose. On account of the failure to work this method in a satisfactory manner, it was decided, that it was not a process, to be offered for general and practical use, though it may have proved satisfactory in the hands of Dr Wagner.

By G. Hammer. Jour. Pract. Chem. LXXXI, page 159. This method appears to be the most rational, for practical

purposes, inasmuch as it shows precisely how ^{much} the hide takes up.

The method of procedure is as follows:-

Pieces of hide are obtained & prepared for immersion in the tan liquor.

These are washed, till they give up little or nothing to the wash water.

They are then stretched over a cylindrical piece of wood, and held by tacks. They are now put in a warm place and left until perfectly dry.

When dry, the hide is hard and brittle, and being stretched over a cylindrical form, is in a convenient shape for fine division. The division of the hide, is best accomplished by means of a flat wood rasp, with which it can be cut into fine shavings. The hide thus finely divided acts very quickly on the tanning material.

This prepared hide, a very delicate

hydrometer, or a specific gravity flask and a pair of balances which will weigh to one milligramme, a few beakers, apparatus for filtering, a half litre flask, and a thermometer, are the implements required for the determination.

The manipulation of the method is conducted as follows:-

If the substance containing the tannin is a solid, from 5 to 20 grammes according to richness of the material, are weighed out, after being pulverized, then placed in a beaker, and a little more than covered, with distilled water. The beaker is then placed in hot-water, and mixture in it stirred until it is quite hot.

It is then allowed to stand for 5 or 10 minutes, after which the liquor is poured off, through a filter, and some hot-water again turned on to the substance.

This water is also poured through the filter, and so on until the substance gives no more soluble matter.

That portion of the substance which possesses tanning power, is now in the filtrates, which together, are made up to the bulk of a half litre, in the half litre flask.

If the tanning material is already in solution, from 5 to 20 grammes of it, according to its apparent strength, are weighed out in a beaker, diluted with pure water, filtered, and made up to a half litre.

The tannic acid and other bodies, which enter into the composition of the leather, when dissolved in water, impart to it a higher specific gravity. The present process is based on the determination of the difference in specific gravity, between a solution holding tannin and the solution

after the tannin has been removed. Tables containing the percentage of pure tannic^{acid} dissolved in water, which corresponds to any given specific gravity, have been accurately constructed.

So, if the difference in specific gravity between a solution holding tannin, and the solution after the tannin has^{been} removed, is known, it can be referred to such a table as is described above, and the percentage of tannin found.

Here the method shows its weak point; for since a table concerning pure tannic acid is referred to, it might be advanced, that nothing but pure tannic acid should be determined by it. But a similar objection is open to all the rest of the methods, only in most of them the objection is stronger. In the present method, the hide does remove all that would

be taken up by the leather, and though all of the removed bodies are not tannic acid, still tannic acid forms, without doubt, by far the larger part, and the other bodies of like nature, would increase the specific gravity of a solution, approximately by the same amount as tannic acid itself.

To estimate the percentage of tannin in the solutions, as prepared above, the specific gravity is taken at 15° centigrade, either by the hydrometer, or better by the specific gravity flask. The specific gravity flask is used in the following manner:— First the wt of the dry flask is found; then its weight—filled to the mark on its neck, with distilled water at 15° C. The latter weight minus the first is the weight of the water held by the flask at 15° C. Next the weight of the flask filled with

the tannin solution, This weight minus the weight of the dry flask, and divided by the weight of the water, gives the specific gravity of the tannin solution. Of course the weight of the flask, and of the flask full of water, have to be determined but once.

After the specific gravity of the solution has been determined, a portion of it, rather larger than would be barely sufficient to fill the flask, or float the hydrometer, is treated with the hide as follows:— About five or six grammes of the prepared hide, for every gramme of tannin, which that portion of the solution taken might be expected to contain, are placed in a beaker and covered with water. The hide is allowed to soak until it is thoroughly saturated with water, which takes 5 or 10 minutes. The water is then poured off, and the hide is

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pressed between folds of filter paper,
until the paper is not wet by it.

When so treated the hide neither di-
lutes nor concentrates the tannin solu-
tion, to any appreciable extent. The
lump of hide, without being broken
open, for if broken open, it would be apt
to dry too much, is now transferred with
the tannin solution, to a flask of such
size, as to be about two thirds filled by
the mixture, and shaken, after which
it is allowed to stand, with frequent
shaking, for five minutes. The
flask may be closed with a clean
rubber stopper, while being shaken.

The flask is now immersed in hot water,
until the temperature of the contents has
reached about 50°C . It is then removed
from the hot water and ^{allowed} to stand with
frequent shaking until fifteen min-
utes ^{shall} have elapsed from the introduc-
tion of the hide. The tanning prop-

erties of the solution are now entirely removed. The solution is filtered as quickly as possible, to avoid loss by evaporation, and the specific gravity of the filtrate taken. This latter specific gravity subtracted from the first one, gives the loss in specific gravity. This loss corresponds to the loss of a certain amount of tannin.

To find what percent of the solution was available tannin, the amount of specific gravity lost, is referred to a table like the annexed.

This table gives the percent of tannin in the solution. To find the percent of tannin in the original substance, the total amount of it in the half litre, is found, and this, divided by the weight of the substance taken, gives the percent.

The main point of difference between the method here layed down, and that of Hammer's paper is this: He adds the

Percent of Tannin.	Spec. Grav. at 15°C.	Percent of Tannin.	Spec. Grav. at 15°C.
0,0	1,0000	2,8	1,0112
0,1	1,0004	2,9	1,0116
0,2	1,0008	3,0	1,0120
0,3	1,0012	3,1	1,0124
0,4	1,0016	3,2	1,0128
0,5	1,0020	3,3	1,0132
0,6	1,0024	3,4	1,0136
0,7	1,0028	3,5	1,0140
0,8	1,0032	3,6	1,0144
0,9	1,0036	3,7	1,0148
1,0	1,0040	3,8	1,0152
1,1	1,0044	3,9	1,0156
1,2	1,0048	4,0	1,0160
1,3	1,0052	4,1	1,0164
1,4	1,0056	4,2	1,0168
1,5	1,0060	4,3	1,0172
1,6	1,0064	4,4	1,0176
1,7	1,0068	4,5	1,0180
1,8	1,0072	4,6	1,0184
1,9	1,0076	4,7	1,0188
2,0	1,0080	4,8	1,0192
2,1	1,0084	4,9	1,0196
2,2	1,0088	5,0	1,0201
2,3	1,0092	6,0	1,0242
2,4	1,0096	7,0	1,0283
2,5	1,0100	8,0	1,0325
2,6	1,0104	9,0	1,0367
2,7	1,0108	10,0	1,0409

hide in the dry state and afterward makes up the solution to the bulk that was started with, while in the present method the hide is satisfied with water before it is added to the tannin solution which does not require to be made up to a known bulk again, thus saving considerable time. That this latter way does not involve any considerable amount of error, is shown by the fact, that solutions, from which the tannin has been removed by the hide, do not show any appreciable gain or loss in specific gravity on being again treated with more of the hide.

This test also shows that the removal of the tannin was complete.

The following are among the determinations made with the adopted method.

Substance	% of Tannin.	% found by other Chemists.
Hemlock Bark.	7,8 %	Wagner 7,3 % Fesser 5 to 15 %
Oak Bark.	7, %	Wagner 10, % Büchner 6, to 7, %
Best-Sumach.	18,8 %	? 12, to 17, %
Valonia.	39,8 %	Wagner. 40, % Rothe 43, %
1 st Quality of Gambir.	20,2 %	
2 nd " " "	10,25 %	
Cutch.	31, %	Wagner 30, to 40, %
Dividivi.	38,5 %	Wagner 26 % Fleck 32 % Müller 49, %
Miller's Hemlock Ext.	18, %	
Fresh Liguor, Tannery No. 1. (1)	0,5 %	
Fresh Liguor, Tannery No. 1. (2)	0,5-25 %	
Fresh Liguor, Tannery No. 2.	0,7 %	
Nearly spent Liguor, Tannery No. 1.	0,205 %	
Spent Liguor, Tannery No. 1.	0,1 %	
Spent Liguor, Tannery No. 2.	0,12 %	
Liguor pressed from spent bark.	0,2 %	

At present, about the only method that the tanner makes use of, for testing the value of a tanning material, is the trial of it on a large scale, and judges of its value by the amount of leather he can tan with it; A very good way, but since it takes weeks or months to execute it; it is not at all convenient for a ready estimation. The method used in this research, can be executed in less than one and a half hours, if the substance is in the solid state, and if it is already in solution, in less than an hour. For testing the strength of the liquors used in tanneries, hydrometers are often used, But these indicate nothing whatever, as far as the tanning power of the liquor is concerned; since almost any substance which may happen to be dissolved in the water, would

increase its specific gravity.

Some liquors were met with in this work which possessed a very high specific gravity but contained very little tannin. The use of hydrometers in this way can do little but deceive.

In fact the tanners themselves say, that they can tell the strength of a liquor, much better by the taste, than by the hydrometer. But any tanner of ordinary capability, can with a very little practice, tell with exactness, by means of the method here layed down, the tanning power of any substance or solution.

And so, without doubt, make improvements in the working of the tan liquors.

It has been believed by many people, that much tannic acid is lost during the process of tanning, by being oxidized, and changed to gallic acid and glucosides. An attempt has been made to discover the facts of the case, as far as a very limited amount of time would permit.

In the method of tanning in liquor, which is used at the present time, the hides after being prepared, are placed in tanks which are filled with water, in which is dissolved the soluble portion of the bark. The tanks are placed side by side and so connected together by spouts and openings, that the liquor from the leaches flows through them, beginning with the tank in which the hides are most nearly tanned, and the spent liquor flowing off from

the tank in which the fresh hides are placed, to be carried back again to the leaches. Thus the same water is used over and over, only enough new water being added, to replace that, lost by evaporation and other causes. The liquor which runs from the leaches, has a bitter, astringent taste, similar to that of bark, but no sour taste. When it has passed through the tanks, it has a more or less fetid odor, and a sour, disagreeable taste. The sour taste is generally supposed, to be owing to gallic acid, but from the following tests, it would seem to be otherwise.

In the first place, gallic acid does not possess a very sour taste, and the comparatively small amount in the solution would not be sufficient to produce so much acidity.

Two litres of a sour and spent

tan liquor were placed in a retort with a small amount of sulphuric acid, and distilled until only about 50 cubic centimetres, remained in the retort. This residue was neutralized with carbonate of barium, thus removing the sulphuric acid. This residue, which should have contained the gallic acid, gave only a very, only a very slight precipitate of galate of lead, when treated with lead acetate, showing conclusively that the acidity of the solution, was not owing to gallic acid. There was considerable gummy matter, in this residue and possibly a little lactic acid and sugar. (having considerable opalescence,)

The distillate, which measured nearly two litres, and which was quite strongly acid, and possessed a strong odor of butyric and acetic acids, was neutralized with carbonate

of soda and evaporated till near dryness, when on cooling, crystals like those of acetate of soda, were formed. One of these crystals on being treated with alcohol and sulphuric acid gave the characteristic odor of acetic ether, mingled with a slight smell of butyric acid. The evaporated mixture of carbonate acetate and butyrate of soda, was redissolved in a small quantity of water, made acid with sulphuric acid and redistilled in a small retort. The distillate contained a few small drops of an oily liquid not miscible with water, which had the appearance of being turpentine, or some such body. This distillate, which now possessed a very powerful smell of butyric and acetic acids, was shaken up, with about one half its bulk of ether. The ether was decanted and evaporated, and a thick oily looking liquid having the appearance of a mixture of

acetic and butyric acids remained. This residue was again mixed with the water from which it had been extracted by the ether, and the amount of acidity of the mixture approximately determined. 5.75 grammes of solid fused caustic potash were required to neutralize this acid, for the most part acetic, which had distilled off, from the two litres of sour tan liquor. This amount is fully sufficient, to account for the sour taste and smell, of the spent tan liquor.

When this sour liquor is again run through the leaches, all of the butyric and a part of the acetic acid is retained by the bark. This explains why the concentration of these acids in the tan liquors, is not increased indefinitely. ^{this} Fact was shown by the distillation of a portion of fresh tan

liquor. This distillate did not smell of butyric acid, but contained considerable acetic acid, though not so much as the sour liquor. This seems to show, that sour tan liquor instead of owing its acidity to gallic acid, formed at the expense of the tannic acid, owes it to volatile acetic and butyric acids, which are the products of the fermentation of the tannic acid, or of some other substance in the liquor.

Since the acetates and butyrates are all soluble in water, they cannot be precipitated out, but they might be neutralized in the sour liquor, should it be shown, that they are injurious to the tanning process.