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BEHAVIOR OF  
SYNTHETIC TANNING MATERIALS  
TOWARD HIDE SUBSTANCE

BY

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*Bureau of Standards*

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# BEHAVIOR OF SYNTHETIC TANNING MATERIALS TOWARD HIDE SUBSTANCE

By Edward Wolesensky

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## ABSTRACT

A study has been made of the solvent (hydrolytic) action of syntans on hide substance during tanning, the rate of fixation of the tanning material in the hide, and the maximum which may be thus combined under various conditions of concentration and length of treatment. The solvent action on the hide varies with the individual syntan, but no relation has yet been found between this and other characteristics of the tanning material. As regards the fixation of the tanning material in the hide, the syntans may be divided into two groups, corresponding to the two general methods of preparation. Those which are obtained by first sulphonating an aromatic compound and then condensing the sulphonic acid with an aldehyde, combine with the hide rapidly but to a very limited extent, and the combination is apparently little influenced by the concentration of the solution. The second group, in the preparation of which the order of the sulphonation and condensation with aldehyde is reversed, possesses much greater filling power, requires longer time to reach a maximum, and the time required for maximum combination is more dependent on the concentration of the solution. In the first group the combination with the hide seems to be of a chemical nature. In the second group there is evidence of both chemical reaction and some combination of a colloidal nature. High concentration of solution and long treatment are unnecessary, especially in the first group of syntans, and in many cases may actually be harmful.

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## I. INTRODUCTION—PURPOSE OF THIS STUDY

In the manufacture of heavy leathers, especially sole leather, tanning solutions of high concentration are applied to the leather in the last stages of the tanning process. It is therefore natural to think that if heavy leathers are to be obtained with the use of synthetic tanning materials these may also have to be applied

in concentrated form; but whereas the natural tanning materials are only feebly acidic in character, the synthetic tanning materials, such as those most commonly found on the market, viz, the sulphonated condensation products known as "syntans," are all strong acids. It is well known that hide substance is more or less hydrolyzed by active acids, especially if they are present in high concentrations. The question, therefore, arose as to the extent to which the hide substance of the hide is hydrolyzed during the tanning process by syntans of the above type in solutions of different concentrations and during periods of different length, and whether or not any tanning material containing a strongly acidic group, such as the sulphonic acid group, is suitable at all for the production of heavy leathers. Closely related are also the questions of the extent to which these syntans can combine with the hide substance under different conditions of concentration and duration of treatment, as well as the concentration of solution and the duration of treatment required to produce the best results. It was thought that possibly more or less general answers to these questions might be obtained, particularly those relating to the hydrolytic action of these syntans on hide substance, which would be more or less applicable to all syntans of this type. In particular, it was hoped that a certain maximum acid concentration might be found which would be more or less uniform for all sulphonated tanning materials, below which tanning could be carried on without much loss of hide substance, but above which the hydrolysis would be excessive.

These questions have such an important bearing upon the commercial value of this class of tanning materials that it was deemed desirable to have some fairly definite answers to them before launching upon a prolonged and exhaustive study of such materials. Accordingly, a study of the hydrolytic action of some typical sulphonated tanning materials on hide substance was undertaken. Incidentally, as will be shown later, the results of this study also threw some light on the rate of fixation of the tanning material by the hide substance as well as on the maximum amount of the material that can combine with the hide substance. The study was therefore extended so as to obtain some more direct and definite information on these latter points.

## II. METHOD OF PROCEDURE

The most natural and the simplest method of determining the loss of hide substance from the leather during tanning would seem to be the direct determination of the "organic nitrogen" in the bath after the tanning—by the Kjeldahl method. This, however, proved to be impracticable in most cases because of the small amount of nitrogenous matter present in solution, the relatively large amount

of other organic matter (the excess of the syntan) usually present, and the difficulty of oxidizing the latter in the Kjeldahl process.

An indirect method of determining this loss was therefore adopted, which involved the determination of the total amount of hide substance in a piece of cowhide both before and after treatment with a solution of syntan. The piece of hide used for this purpose was first slightly pretanned for each experiment with a 2 per cent solution or less of the same syntan with which it was to be subsequently treated. The object of this pretanning was partly to make it possible to dry the hide for weighing and analysis and still leave it in such a condition that it could subsequently be brought as nearly as possible to the condition in which it was before being dried, and partly to make it possible to then place it directly into a relatively concentrated solution of syntan without affecting the normal rate of penetration of the syntan for that particular concentration. The hide, thus pretanned, was then thoroughly washed in running water for about eight hours at ordinary temperature, dried, analyzed for nitrogen, weighed, treated with syntan under definite conditions, and again washed, dried, weighed, and analyzed as before. From the weight of the dried leather and its content of nitrogen the total amount of "hide substance" present in each case could be calculated, and the difference in this amount of hide substance present before and after treatment with the syntan solution represented the amount of hide substance dissolved.

The method thus involved the making of several measurements for a single determination of loss and resulted in the accumulation of all errors on the final result. The natural variation in the character of the hide and the difficulty of always washing and drying the leather to the same condition further enhanced the possibilities of error. Nevertheless, this method was preferable to the more direct method, for the reasons already given, and by taking all possible precautions to reduce errors to a minimum, results were obtained which are believed to reliably represent the behavior and possibilities of those particular syntans which were studied in this way.

### III. EXPERIMENTS AND RESULTS—SOLVENT ACTION ON HIDE SUBSTANCE

In the first series of experiments, owing partly to the difficulties just mentioned and partly to the fact that these experiments were carried out on a very small scale, somewhat erratic results were obtained which will, therefore, not be reported in detail. The results, however, did show certain tendencies which may be stated briefly.

This series of experiments dealt with two syntans. One was prepared from phenolsulphonic acid by treating the concentrated sulphonation mixture (including unchanged sulphuric acid) with formaldehyde at a temperature of 30 to 35° C. The other was obtained from

sulphonated cresylic acid by heating the diluted sulphonation mixture with formaldehyde in a closed vessel at a temperature of 90 to 100° C. Sodium hydroxide was added to the final solution in each case in an amount equivalent to the unchanged sulphuric acid present, as is generally done in the commercial manufacture of such syntans, so that the final acidity of the syntan solution is presumably due, largely at least, to the sulphonic acid rather than to the sulphuric acid. The leathers used in these experiments represented two degrees of tannage in each case; that is, in each case there were used two pieces of leather, one of them being very lightly tanned (barely struck through), while the other was more fully tanned. Each of these leathers was treated for two different periods of time (two days and seven days, respectively) with solutions of the syntans representing four different concentrations of acid in each case, viz, one-tenth normal, one-fourth normal, one-half normal, and normal.

As was to be expected, the more lightly tanned leather in each case showed a larger increase in weight due to fixation of tanning material than did the more fully tanned leather, but the loss of hide substance was of about the same order of magnitude for both kinds of leather. This latter result is undoubtedly due to the fact that as soon as the syntan comes into contact with the raw hide substance it immediately combines with the latter, so that in reality we are dealing with leather instead of raw hide, whether we start with fully tanned or only slightly tanned material. Also, as might be expected, the longer treatment and the higher concentrations of acid (syntan) resulted in greater hydrolytic action than the shorter treatment and the lower acid concentrations. Finally, the results indicated that for these two particular syntans the loss of hide substance was small, or even negligible in some cases, when the acid concentration was one-half normal or less. Even in solutions of normal acid concentration one of the syntans used (the one derived from cresylic acid) showed very little hydrolytic action on the hide substance; but the other one at this concentration, particularly after seven days' treatment, showed a very appreciable increase in its destructive action.

In the second series of experiments six different syntans were used, two being the same as those of the first series and two of the remaining four being commercial products. These will be more fully described presently. Only two different concentrations of solution were used in this series, viz, one-half normal and normal acid concentrations. The leather used was lightly pretanned, but only one degree of tannage was employed, and only one period of treatment (seven days) was used in each case. The amount of leather used for each individual test was considerably larger than in the first series of experiments, and every precaution was taken to reduce all possible errors to a minimum. Otherwise the general procedure was the same as in the first series of experiments.



The results are given in Table 1. In this table the different syntans are designated by Roman numerals in the first column. The first two syntans were the same as those already described in the first series of experiments, Number I being derived from phenolsulphonic acid and Number II from cresylic acid. Number III is a commercial product whose derivation is not definitely known, but it is probably made from cresylic acid in much the same manner as Number I was obtained from phenol, while Number IV is another commercial product obtained by condensing naphthalenesulphonic acid with formaldehyde. Number V was obtained by condensing phenol with paracetaldehyde, removing the bulk of the unchanged phenol by evaporation with steam and sulphonating the resulting resin. Number VI was similarly obtained from cresylic acid by condensation with formaldehyde in a closed vessel at a temperature of 90 to 100° C. in the presence of 25 per cent sulphuric acid and sulphonating the resin so obtained.<sup>1</sup> The letters "b" and "c" in the first column of the table designate the leathers which were treated with solutions of one-half normal and normal acid concentration, respectively.

TABLE 1

Syntans	Original weight of dry leather	Hide substance in original leather	Weight of hide substance in original leather	Final weight of leather (dry)	Hide substance in final leather	Weight of hide substance in final leather	Loss of hide substance
	<i>Grams</i>	<i>Per cent</i>	<i>Grams</i>	<i>Grams</i>	<i>Per cent</i>	<i>Grams</i>	<i>Per cent</i>
I-----fb-----	8. 1530	81. 75	6. 6651	9. 0670	73. 45	6. 6597	0. 08
I-----fc-----	7. 3557	-----	6. 0133	7. 7706	72. 50	5. 6337	6. 31
II-----fb-----	8. 8423	85. 74	7. 5814	9. 7292	77. 87	7. 5781	. 04
II-----fc-----	10. 2095	-----	8. 7536	11. 2330	77. 87	8. 7494	. 05
III-----fb-----	9. 9978	77. 62	7. 7603	10. 1221	74. 33	7. 5238	3. 05
III-----fc-----	10. 7297	-----	8. 3284	-----	-----	-----	-----
IV-----fb-----	10. 1683	81. 55	8. 2922	-----	82. 19	-----	-----
IV-----fc-----	9. 8002	-----	7. 9921	-----	81. 68	-----	-----
V-----fb-----	13. 8578	78. 69	10. 9047	16. 3102	66. 40	10. 8300	. 68
V-----fc-----	13. 3626	-----	10. 5150	-----	-----	-----	-----
VI-----fb-----	15. 8221	81. 43	12. 8839	18. 0018	68. 73	12. 3726	3. 97
VI-----fc-----	15. 6913	-----	12. 7774	17. 1852	69. 60	11. 9609	6. 39

The results show a much greater divergence between the various syntans, as regards their hydrolytic action on leather, than had been expected from the previous results, although insofar as the previous experiments were repeated in this series their results were confirmed. It will be seen that whereas some syntans produce negligible hydrolysis of the leather even in solutions of normal acid concentration, others will practically destroy the leather in solutions of one-half this concentration. The normal solutions of Syntans III and V converted the leather in one week's time into a soft, pasty mass which had lost all fibrous structure and which could not be washed. Full data in these cases, therefore, were unobtainable. Syntan IV, on the other hand, produced a very extensive disintegration of the

<sup>1</sup> The preparation of all of these syntans, except the commercial products, was described in detail in an earlier report on Investigation of Synthetic Tanning Materials. B. S. Tech. Paper No. 302.

leather in both the solutions of half normal and normal acid concentration, causing the outer portions of the leather to slough off, so that full data again were unobtainable, but enough of the interior portion of the leather remained to permit a nitrogen determination.

#### IV. FIXATION OF TANNING MATERIAL IN THE HIDE

Because of the indirect procedure adopted for the determination of the solvent action of syntans on the hide substance of leather during tanning, the results also give some interesting information on the rate of combination of the syntans with the hide, as well as on the maximum amount of syntan that can combine with the hide, and from this information it is also possible to make certain deductions as to the concentrations of the solutions and the length of time required to obtain maximum or optimum tannage. For this purpose the data obtained in the above series of experiments were arranged so as to show the proportion of syntan fixed in the leather. This is expressed as a percentage of the weight of the dry, raw hide as prepared for tanning (that is, dehaired and delimed), which went to form each piece of leather. The amount of the dry hide was not obtained by direct weighing, since it would obviously be inconvenient to dry the hide after dehairing and deliming before proceeding with the experiment, but was calculated from the amount of hide substance present in the final leather, assuming that the hide substance constituted 98 per cent of the dry hide after it had been dehaired and delimed. This latter assumption is based on the fact that a number of analyses of such hide gave a result close to 98 per cent hide substance. "Dry," here as elsewhere in this report, means not air dried, but dried in an oven at 105° C. to constant weight.

TABLE 2

Syntans	Original concentration of syntan	Duration of treatment	Hide substance in final leather	Increase in weight over dry hide	Ratio of syntan in solution to hide substance	
					Original	Final
	<i>g/liter</i>	<i>Days</i>	<i>Per cent</i>	<i>Per cent</i>		
I.....	a.....	5	81.75	19.9	(0.3)	(0.1)
	b.....	7	73.45	33.4	1.59	1.45
	c.....	7	72.50	35.15	3.18	3.11
II.....	a.....	5	85.74	14.3	(.25)	(.1)
	b.....	7	77.87	25.8	1.01	.90
	c.....	7	77.87	25.8	2.03	1.91
III.....	a.....	2	77.62	26.25	(.5)	(.2)
	b.....	7	74.33	31.8	2.81	2.80
	c.....	7	242.8		5.63	
IV.....	a.....	2	81.55	20.2	(.5)	(.3)
	b.....	7	82.19	19.2	2.53	2.53
	c.....	7	81.68	20.0	5.06	5.06
V.....	a.....	5	78.69	24.5	(.7)	(.4)
	b.....	7	66.40	47.6	2.83	2.34
	c.....	7	247.0		5.65	
VI.....	a.....	5	81.43	20.3	(.6)	(.4)
	b.....	7	68.73	42.6	2.46	2.03
	c.....	7	69.60	40.8	4.92	4.60

The results of these calculations are given in Table 2. In this table, in addition to the data on the leathers which were treated with solutions of half normal and normal acid concentration (designated, respectively, by "b" and "c" as before), there are also given the corresponding data for the original leather, designated by "a," for each syntan. In the case of this last leather the results represent the pretannage of the raw hide, whereas in the case of "b" and "c" they represent the further effect of subsequent treatment of the already partly tanned material with fresh solutions of syntan. For example, when the raw hide was pretanned with Syntan I under the conditions given, it took up a quantity of tanning material equal to 19.9 per cent of the weight of the dry raw hide, but when subsequently further treated with a fresh solution of the syntan the proportion of tanning material which combined with the hide was increased to 33.4 per cent of the weight of the dry raw hide, when the last solution of syntan was of one-half normal acid concentration, or to 35.15 per cent when the last solution was of normal acid concentration. The last two columns in this table show the ratio of syntan in the solution to the hide substance in the leather at the beginning and end of the treatment. These data are given merely to show that, except in the case of the pretanning, the concentration of the syntan at the end of the experiment was not very much lower than at the beginning. The figures in parentheses represent only approximate values, since the weight of hide was not accurately determined in those cases.

By comparing the amount of syntan fixed in the leather during the pretannage with the total quantity of tanning material in the leather after subsequent treatment with fresh solutions of syntan (see fourth column of figures, Table 2) a general idea of the rate of fixation may be gained, as well as of the maximum quantity of tanning material that is capable of combining with the hide. It is realized that much dependence can not be placed on these results, since, in the first place, no attempt was made in these experiments to attain the maximum fixation of tanning material, and, secondly, in most of the experiments a dry, lightly tanned leather was placed directly into a strong solution of the syntan, a procedure which is not calculated to bring about the most rapid penetration of the leather and may even result in effects which may considerably interfere with this process. The latter explanation may account for the discrepancy in VI, c, where a considerably larger proportion of tanning material should have combined with the hide, as will be shown later. Nevertheless, the results show that the amount of tanning material that is capable of combining with the hide is far less in the case of these syntans than in the case of vegetable tanning materials where the maximum is sometimes as high as 140 to 145 per cent of the weight of the dry raw hide. Furthermore, it will also be observed that in most cases more than half of the

final amount of combined tanning material was combined during the pretanning when the concentration of tanning material in the tanning bath was not more than one-fifth to one-tenth of what it was during the subsequent treatment, and the length of treatment was likewise shorter. The most striking example of this is syntan IV, in which case the pretanning with a 2 per cent solution for two days completely saturated the hide, and subsequent treatment with much stronger solutions and for considerably longer periods of time failed to increase the amount of combined tanning material. In general, the above results indicate that the tanning material in a solution of syntan is very rapidly taken up by the hide, that the maximum amount of this tanning material which can combine with the hide is relatively small as compared with vegetable tanning materials, and that a high concentration of solution and long treatment of the hide with the solution are not necessary to attain this maximum.

In order to obtain more definite and conclusive information on these points, a further series of experiments was carried out. Pieces of cowhide, containing from 4 to 5 g of air-dry hide, were tanned in solutions of definite concentrations of the various syntans for periods of one, two, and three weeks, then each piece was thoroughly washed in running water for 8 hours, pressing and kneading the pieces of leather in the hands occasionally to facilitate the removal of the syntan solution from the interior of the leather, after which the leather was dried and analyzed for organic nitrogen by the usual method. From this result the weight of hide substance in the leather, the weight of dry raw hide (dehaired and delimed) which went to form this leather, and finally the increase in weight due to combined tanning material were calculated. The same syntans were used in these experiments as in the last series. Two different concentrations of solutions were used in each case, viz, 20 and 40 g per liter, respectively, except in the case of Syntan V, where, in addition to the above, a solution containing 60 g per liter was also used.

The raw hide was not placed directly into solutions of the above concentrations, but was first placed into a solution containing 5 g of tanning material per liter (using 200 cc of solution for each piece of hide), and the concentration of the solution was then brought up by degrees to the required value. Thus, in the case of the pieces of hide which were to be subjected to concentrations of 20 g per liter, they were started in a solution of 5 g per liter; after about 8 hours this concentration was increased to 10 g per liter; at the end of 24 hours this was increased to 20 g per liter, and at the end of 48 hours the hide was placed into a fresh solution containing 20 g per liter for the remainder of the week. Those pieces of hide which were to be subjected to a concentration of 40 g per liter were similarly started in a concentration of 5 g per liter, which was increased at

the end of 8 hours to 10 g per liter, to 20 g per liter at the end of 24 hours, and to 40 g per liter at the end of 48 hours. At the end of 72 hours the hide was placed into a fresh solution containing 40 g per liter of tanning material for the remainder of the week. The pieces of hide which were to be subjected to a concentration of 60 g per liter were started in a concentration of 5 g. per liter, which was increased to 10 g per liter at the end of 8 hours, to 20 g per liter at the end of 24 hours, to 40 g per liter at the end of 48 hours, and to 60 g per liter at the end of 72 hours. In all of these cases at the end of the first week the pieces which were to be subjected to longer treatment were placed into fresh solutions of the same syntans of the proper concentrations, and the same was done at the end of the second week. The purpose of thus replacing the old solution with a fresh one of the same concentration is, of course, to prevent the concentration of the tanning material in the solution from dropping too far below the desired value.

TABLE 3

Syntan	Concentration of solution	One week		Two weeks		Three weeks	
		Hide substance in final leather	Increase in weight over dry hide	Hide substance in final leather	Increase in weight over dry hide	Hide substance in final leather	Increase in weight over dry hide
	<i>g/liter</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
I.....	20.....	75.35	30.0	74.93	30.8	74.55	31.4
	40.....	75.82	29.2	73.69	33.0	73.52	33.3
II.....	20.....	76.81	27.6	75.52	29.7	74.57	31.4
	40.....	74.95	30.7	74.62	31.3	73.28	33.7
III.....	20.....	75.15	30.4	74.57	31.4	74.61	31.3
	40.....	75.78	29.3	75.44	29.9	74.24	32.0
IV.....	20.....	80.27	22.1	79.83	22.7	80.69	21.4
	40.....	79.45	23.4	81.25	20.6	80.74	21.4
V.....	20.....	71.32	37.4	66.30	47.8	61.25	60.0
	40.....	67.49	45.1	60.42	62.2	50.99	92.1
VI.....	60.....	63.85	53.5	52.82	85.5	50.00	96.0
	20.....	77.08	27.1	63.48	54.4	60.83	61.1
	40.....	65.68	49.2	56.95	72.0	52.35	87.2

The percentage of hide substance in each piece of leather thus obtained from the various syntans at the end of one, two, and three weeks, respectively, and the corresponding increase in weight over the weight of the dry hide, are shown in Table 3. The syntans are again designated by Roman numerals as before; the second column gives the concentration of solution used in each case, and the remainder of the table explains itself. Each value given here is the average of two closely agreeing analyses, as is true also of the results given in the preceding tables. In spite of this, a few discrepancies will be observed in the results, which are evidently due to causes other than the usual errors of measurement involved in such work. Possibly these may be taken as a measure of the degree of accuracy which may be expected in work of this kind. Considering the fact that each result was obtained on a different piece of leather, and considering, furthermore, the variation in the thickness, texture,

and other properties of the hide from different portions of the animal, it is not surprising that such discrepancies as the above are encountered. After all, the irregularities here observed are not vital, and the results obtained point to some very definite conclusions.

In the first place, it may be observed, as the entire table is surveyed, that the six syntans may be divided into two groups according to their behavior toward hide, both as regards the maximum quantity of tanning material that ultimately combines with the hide as well as the rate at which this maximum is attained. The first four syntans, it will be remembered, were all prepared by processes which are alike in that they involved, first, the sulphonation of an aromatic compound followed by the condensation of the resulting sulphonic acid with formaldehyde, while in the case of the last two syntans the order of the sulphonation and condensation was reversed. At first thought it might appear that this should not make very much difference, but it evidently does. The first four syntans, which for the sake of brevity we will designate as type A syntans, are evidently not capable of combining with hide substance to the same extent as are the last two syntans, which we will designate as the type B syntans.

This difference in behavior of the two types of syntans may readily be accounted for if we assume that the tanning process in the case of these syntans consists of the chemical combination of the syntan with the hide substance, and that this combination takes place through the sulphonic acid groups of the syntan and some basic groups (most probably the amino groups) of the hide protein. For, since sulphonation preceded condensation with aldehyde in the type A syntans, each aromatic nucleus or residue in the final product would be linked to one sulphonic acid group, whereas in the type B syntans, since sulphonation followed condensation with aldehyde and, as has been shown by other work done in this laboratory, in this sulphonation only one molecule of sulphuric acid is required to every two molecules of the original aromatic compound, there is only one sulphonic acid group for each two aromatic nuclei. In other words, the type A syntans contain twice as many sulphonic acid groups per molecule of final product as do the type B syntans, assuming that the condensation with the aldehyde is of the same degree of complexity in both cases, and the facts seem to warrant this assumption, since the proportion of aldehyde molecules to the aromatic nuclei is the same in both cases. Hence the combining capacity of the type A syntans per molecule would be twice that of the type B syntans, and each sulphonic acid group in the type B syntans would carry twice as much material with itself into the hide as would be the case in the type A syntans. This explanation, it will be observed, does not make any assumptions as to the nature of the reactions with the aldehyde in the preparation of the syntans and is equally valid

whatever may be the nature of these reactions. The results thus tend to confirm not only the idea that the tanning process, in the case of synthetic tanning materials, such as those used in this work, is chiefly if not entirely a strictly chemical combination, but also the view that this combination takes place through the sulphonic acid groups of the syntan and probably the amino groups of the hide protein.

Referring again to Table 3, it will be noticed that, in the case of the type A syntans, the amount of combined tanning material in the leather almost reaches its maximum by the end of the first week, although, it will be recalled, the hide was not subjected to the full concentration of the solution during the first part of this period. Furthermore, the concentration of the solution seems to have little or no effect on the maximum amount of tanning material fixed in the hide and but little on the time required to reach this maximum. These facts again furnish support for the view that in tanning with these syntans we are dealing with a true chemical reaction rather than with colloid phenomena.

On the other hand, the type B syntans show a steady and rapid increase in the proportion of combined tanning material throughout the three weeks of these tests and only begin to show an approach to a maximum in the more concentrated solutions at the end of the third week. The concentration of the solution likewise has a decided influence on the length of time required for maximum fixation of the syntan if not on the amount ultimately taken up. These facts suggest that in the case of this type of syntans the tanning process is also at least in part colloidal. This explanation is not, of course, inescapable, but it is also upheld by the fact that the difference in the amounts of syntans of the type A and those of the type B which are capable of combining with hide substance is much greater than can be accounted for by the difference in their relative content of combined sulphuric acid; that is, the difference in the relative number of sulphonic acid groups present in the two types of syntans. Thus, in Syntan I the amount of tanning material found by actual analysis was 1.88 times the quantity of sulphuric acid combined in the material to form sulphonic acid groups, while in Syntan V this ratio was 2.52.<sup>2</sup> Hence, if the tanning process in both types of syntans con-

<sup>2</sup> The exact composition and structure of the tanning materials in these syntans is not definitely known, but an approximation to their percentage composition may be arrived at from a consideration of their methods of preparation. Syntan I was obtained by condensing 2 molecules of phenol-sulphonic acid with 1 of formaldehyde, and its essential component, may, therefore, be assumed to be dihydroxydiphenylmethanedisulphonic acid or something having a similar percentage composition, while Syntan V was obtained by condensing 2 molecules of phenol with 1 of acetaldehyde and then sulphonating with somewhat more than 1 molecule of sulphuric acid, and may, therefore, contain the monosulphonic acid of dihydroxydiphenylmethane or something having a similar composition. The first would require a yield of 1.84 parts of tanning material for every part of sulphuric acid actually combined therein as sulphonic acid groups, while the second would similarly require a yield of 3 parts of tanning material. The discrepancy between these theoretical yields and those actually obtained may be accounted for in the case of Syntan I by the known fact that some of the sulphonic acid is hydrolyzed, while in the case of Syntan V some disulphonic acid is probably formed.

sisted only of a chemical combination through the sulphonic acid groups, as already described, the maximum amount of tanning material combined with the hide in the case of Syntan V should be 1.34 times as large as that obtained in the case of Syntan I. As a matter of fact, the ratio is practically 3 instead of 1.34. This can be explained if we assume that, in addition to the component which combines with the hide substance through its sulphonic acid group, there is also another component which is fixed in the hide in some other manner.

Indeed, in the appearance of the cross section of the hide during tanning we have positive proof of the presence in Syntan V of two components which behave toward the hide in a strikingly different manner. One of these components penetrates the hide very rapidly, striking through in a few days and leaving the fiber nearly white or pale yellowish, very much as do some of the syntans of type A. The other component colors the leather a dark brown and penetrates very slowly, requiring three or more weeks to strike through completely. A similar behavior is observed in tanning with Syntan VI, although in this case the difference in the rates of penetration of the two components is not as marked as in Syntan V.

The small amount of tanning material which is capable of combining with the hide, in the case of the type A syntans, and the conditions under which this maximum is attained show conclusively that this type of tanning material is only suitable for the production of light leathers, unless used in connection with other filling materials. Furthermore, it is obvious that high concentration of solution and long treatment with such syntans are not only unnecessary but futile. On the other hand, the type B syntans possess marked filling properties of their own, and both the length of time required for maximum fixation of the tanning material in the hide as well as the maximum increase in weight that is thus attained are much more dependent on the concentration of the solution and the length of treatment than is the case with the preceding class of products. But even here it is clear from the results shown in Table 3 that high concentration of the tanning solution is not necessary, and that the maximum increase in weight may be nearly, if not quite, attained in three or four weeks' time in a solution having a concentration of 4 to 6 per cent. A comparison of the concentrations of the solutions used in the last series of experiments with those used in the preceding experiments will show that the concentrations required to attain the maximum fixation of tanning material in the hide are far below those which exhibited any excessive solvent or other destructive action on the leather.



## V. SUMMARY AND CONCLUSIONS

The various synthetic tanning materials vary very much in the extent of their solvent (hydrolytic) action on the hide substance of leather during tanning, some showing negligible hydrolysis in solutions of normal acid concentration, while others, in solutions of half this concentration, produce a practically complete destruction of the leather as such. No relation has yet been found between this behavior and other characteristics of the syntans.

As regards the fixation of the tanning material in the hide, the syntans may be divided into two groups corresponding to the two general methods of preparing these products. Those which are obtained by first sulphonating an aromatic compound and then condensing the sulphonic acid with an aldehyde (designated as type A syntans) combine with the hide rapidly, but to a limited extent, and the maximum of combined tanning material, as well as the time required to reach this maximum, are but little affected by the concentration of the solution. The second group of syntans, in the preparation of which the order of sulphonation and condensation with aldehyde is reversed (type B), possesses much greater filling power, requires longer time to reach a maximum, and the time required to reach this maximum is more dependent on the concentration of the solution.

The tanning process, in the case of the type A syntans, appears to be a true chemical combination of the tanning material through its sulphonic acid groups with the hide substance, probably through amino groups of the hide protein, while in the case of the type B syntans, in addition to this chemical combination, the tanning process appears to include also some other mode of fixation, possibly adsorption.

The type A syntans are suitable only for the production of light leathers, unless used in connection with other filling materials, while the type B syntans are capable of producing a full, firm leather, such as is required for soles, without the aid of other tanning materials.

Concentrations of solutions in excess of 2 to 4 per cent in the case of type A syntans and 4 to 6 per cent in the case of type B syntans, as well as long periods of treatment, in excess of a week to 10 days in the case of the first group and three to four weeks in the case of the latter group, are unnecessary to attain the best results and may even be injurious.

WASHINGTON, November 30, 1925.



PROCEEDINGS OF THE YAMATO

The first day of the expedition was spent in the  
 morning and in the afternoon. The day was  
 very hot and the wind was from the east.  
 The second day was spent in the morning  
 and in the afternoon. The day was  
 very hot and the wind was from the east.  
 The third day was spent in the morning  
 and in the afternoon. The day was  
 very hot and the wind was from the east.  
 The fourth day was spent in the morning  
 and in the afternoon. The day was  
 very hot and the wind was from the east.  
 The fifth day was spent in the morning  
 and in the afternoon. The day was  
 very hot and the wind was from the east.  
 The sixth day was spent in the morning  
 and in the afternoon. The day was  
 very hot and the wind was from the east.  
 The seventh day was spent in the morning  
 and in the afternoon. The day was  
 very hot and the wind was from the east.  
 The eighth day was spent in the morning  
 and in the afternoon. The day was  
 very hot and the wind was from the east.  
 The ninth day was spent in the morning  
 and in the afternoon. The day was  
 very hot and the wind was from the east.  
 The tenth day was spent in the morning  
 and in the afternoon. The day was  
 very hot and the wind was from the east.