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INVESTIGATION OF SYNTHETIC TANNING MATERIAL

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I. INTRODUCTION—IMPORTANCE OF THE SUBJECT

A large and increasing proportion of the vegetable tanning materials used in the United States is imported. A tanning-materials survey by the United States Department of Commerce (1)¹ shows that 39.6 per cent of the vegetable tanning materials consumed in the United States in 1922 were imported. From this same source we learn that "the most important natural sources of vegetable tannins" are the following:

Root.—Canaigre.

Wood.—Chestnut and quebracho.

Barks.—Oak, hemlock, wattle, mangrove, and larch.

Fruits.—Myrobalans, valonia, and divi-divi.

Leaves.—Sumac and terra japonica (gambier).

"Of these materials the ones indigenous to the United States are chestnut wood, oak and hemlock barks, larch, sumac, and canaigre." Of these latter by far the most important is chestnut, as shown by the

¹ The figures inclosed in parentheses here and throughout the text relate to the numbered references in the bibliography at the end of this paper.

relative percentages of the various domestic vegetable materials of all kinds consumed in the United States in 1922 (1):

Chestnut extract.....	47. 6
Hemlock bark and extract.....	27. 0
Oak bark and extract.....	23. 3
Spruce extract.....	1. 6
All other domestic materials.....	. 5

Including imported materials as well, the percentages are as follows (1):

Quebracho extract.....	29. 1
Chestnut extract.....	28. 7
Hemlock bark and extract.....	16. 3
Oak bark and extract.....	14. 1
All other extracts and materials.....	11. 8

From the last table it will be noted that quebracho and chestnut form nearly 60 per cent of all the vegetable tanning materials of all kinds consumed in the United States, yet the first one (quebracho) is a foreign product, while the second one (chestnut) is rapidly disappearing from the United States. On this last point the above-mentioned bulletin has the following to say:

In 1904 the chestnut blight, a fungus importation from Japan and China, was recognized as a serious disease around New York City. Since that year the disease has spread rapidly, until at the present time it has killed 80 per cent of the available chestnut north of Virginia and penetrated western North Carolina, eastern Tennessee, and Georgia, the vital centers of the remaining stands of chestnut timber. The effect of this blight from the point of view of its economic consequence has not yet been fully determined, but it now appears certain that any estimate of our resources based upon an inexhaustible supply of chestnut wood must be subject to radical modifications.

From the foregoing it will be clear that, while at the present time there exists no immediate danger of a shortage of tanning materials, the future is by no means so secure. We are becoming more and more dependent upon foreign countries for our supplies of tanning materials. This alone should be a matter of concern to our leather industry in particular and to our Government and people in general, but when we consider the importance of leather to the comfort and convenience of every individual, not only in peace time but also in war, the matter of our growing dependence upon foreign countries for our supplies of vegetable tanning materials assumes a much more serious aspect.

It is not only because of our dwindling resources of vegetable tanning materials and our increasing dependence upon foreign countries for these products that the development of satisfactory synthetic tanning materials is desirable. Another matter which is quite as important, and one which has not been sufficiently stressed heretofore, is the replacement of chromium in tanning.

Regarding the proportion that chrome-tanned leather bears to the total amount of leather produced in the United States, the Department of Commerce in a survey of "World Trade in Chromite" (2) states that "on the basis of the surface measurement of the output for 1923 a conservative estimate places that of chrome-tanned leather at from 40 to 45 per cent of the total production." This proportion is increasing at the present time. It has been estimated that the tanning industry requires about 13 per cent of the total quantity of chromium ore consumed in the United States for all purposes, and this proportion is likewise steadily increasing; but this industry, while one of the two chief users of chromium products in this country, is not the principal one by any means. It has been estimated that the steel industry consumes in the manufacture of various forms of steel about one-half of the total quantity of chromium ore consumed in this country, and if we include also the chromite used in the manufacture of refractories, used in the lining of basic open-hearth steel furnaces, the proportion used by the steel industry is about three-fourths of the total. The quantity of chromium ore consumed in this country as well as in other countries for the various metallurgical purposes is rapidly increasing at the present time, and this increase is likely to continue in the future.

While this country is the principal consumer of chromium ore in the world, it produces practically none at the present time, importing more than 99 per cent of its requirements, chiefly from Africa, India, and New Caledonia (French Oceania). Although there are deposits of chromium ore in the United States, these are neither extensive nor of high grade, and they are, furthermore, not conveniently located with reference to other materials that are required in working up the ore. It has been estimated that our domestic sources of chromium ore could supply our normal annual requirements of this material for about 12 years. While this might suffice to meet our most urgent needs during times of an emergency, such as the recent war, it is clear that it is wholly inadequate to meet our normal demands for any extended period of time and at reasonable cost.

The above information seems to establish the importance and wisdom of beginning at this time to investigate other sources for materials which will become available to the tanning industry for supplementing and replacing the vegetable tannins and chromium now used.

II. PLAN AND SCOPE OF INVESTIGATION

On casting about for a substitute for the ordinary tanning materials one will be struck with the number and variety of substances which possess tanning properties to a greater or less degree and which have been proposed for use in this manner. The numerous suggestions

range from the practicable to the fantastic and cover a wide range of materials—from those which are capable of producing true tannage to those which merely act as preservatives. These substances include inorganic compounds, such as various salts or mixtures of these with each other or with vegetable tanning materials; organic compounds, such as aldehydes (particularly formaldehyde), quinones, phenols, fatty acids, fats, oils, tars, pitches; products derived from various constituents of coal tar, from petroleum products, including the so-called "acid resins" or "acid sludges" obtained in the washing of crude petroleum or its various fractions with sulphuric acid; and, finally, products obtained by various processes from the sulphite cellulose waste liquors of the paper mills. Many of these materials are of doubtful value in tanning. In some cases they are valuable only when used with other tanning materials, while in other cases they are impracticable because of manufacturing or other difficulties. Nevertheless, the list undoubtedly includes substances which are capable of being developed into valuable tanning materials.

It is the purpose of this investigation, therefore, to first determine, by a careful and critical experimental study, the value and possibilities of some of the most promising suggestions that have been advanced up to the present, and then, with the information thus gained as a groundwork, in case no satisfactory substitute for our present tanning materials is found, to extend the investigation to new fields, covering raw materials similar to those which have been previously proposed as well as those yielding related products, and also any other products which have the desired effect on raw hide.

III. PRESENT STATUS OF COMMERCIAL SYNTHETIC TANNING MATERIALS

Of the various classes of materials which have been proposed as possible substitutes for the usual tanning materials those which have found the most extended use are products derived from the sulphite cellulose waste liquors and sulphonated condensation products of aromatic compounds with formaldehyde, the latter being generally known to the trade as "syntans." However, neither of these two classes of materials, at least as represented on the market to-day, has been accepted by the tanning trade as a satisfactory and complete substitute for the vegetable tanning materials. In fact, the sulphite cellulose products are used chiefly as fillers for sole leather, and the manufacturers of the so-called syntans frankly state that their products are not suitable for tanning by themselves and recommend that they be used in connection with vegetable tanning materials, partly for the purpose of hastening the tanning process and partly to solubilize and make more available the insoluble

components of the vegetable tanning extracts. Some have also been used for the bleaching of vegetable tanned leather.

Although statistics are not available on the subject, it is well known that these sulphonated condensation products are being used to a considerable extent in European countries, particularly in England and Germany. In the latter country especially their use was stimulated during and since the war. On the other hand, only a few of such products have been placed on the market in the United States, and most of these have again been withdrawn. Although this may have been due in part to the high cost of manufacture of these products and in part to the conservatism of the leather manufacturers, there seem to have been other grounds for objection to the use of these syntans, based on the properties of these materials themselves.

Perhaps the most serious of these objections was the injurious action of some of these syntans on the leather produced. In some cases where this injury was not apparent at once it developed on aging of the leather. Whether this injury was due to excess of unchanged sulphuric acid which was left in the product or to the inherent character of the syntans themselves, and whether and how this injury might be prevented, are questions which appear not to have been definitely answered up to the present.

Another disadvantage of the present-day commercial syntans is the fact that they possess little or no filling qualities; that is, the power to give fullness and weight to leather. This quality is desired for the manufacture of the heavy leathers not only because such leathers are sold by weight, but more particularly because for certain purposes (for example, for the soles of shoes) a leather is required which possesses a certain amount of firmness and rigidity, together with a moderate amount of flexibility. These qualities in leather have been attained up to the present only by "filling" the leather and incidentally giving it weight.

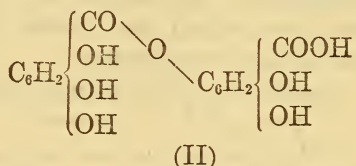
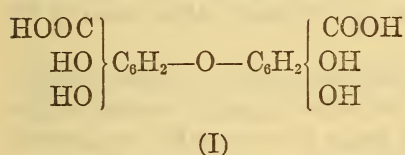
IV. HISTORICAL

In 1805 Hatchett (3) found that "tanninlike substances" may be obtained by the action of sulphuric or nitric acid on wood charcoal (evidently incompletely carbonized and still containing tarry material) and on many other substances rich in carbon, and these results were confirmed by Chevreul and later by Berzelius. These "so-called artificial tannins" obtained from nitric acid were later identified as picric acid and other nitro-derivatives of phenols, and Schiff thinks that those obtained by the action of sulphuric acid were anhydrides of sulphonic acids, the sulphuric acid itself acting, at high temperatures, as the dehydrating agent. During the next 60 years a great deal of study was devoted to the problem of the nature and con-

stitution of the natural tannic acid, but evidently little or no attempt was made either to reproduce this compound artificially or to produce any other synthetic compounds having similar properties.

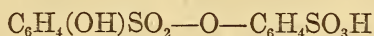
In 1867, however, Löwe (4) reported that by the action of silver nitrate on gallic acid or its barium salt he was able to obtain a water-soluble material having an acid reaction and an astringent taste, and which not only gave precipitates with gelatin, alkaloids, and various salts, but actually converted raw hide into leather. This product he believed to be identical with the natural tannic acid which he, therefore, considered to be an oxidation product of gallic acid, and he speculated on the possibility of increasing the tannin content of various natural tanning materials (as sumac) by oxidizing the gallic acid which they contained.

In 1871 Schiff (5), by condensing gallic acid with itself in the presence of phosphorus oxychloride at 100 to 110° C., obtained a digallic acid which showed all the reactions, solubilities, physical properties, etc., of tannic acid. He first gave it the formula (I) given below, but later (6) concluded that it had the constitution represented by formula (II):



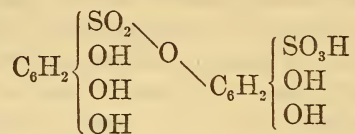
He subsequently found (7) that this compound can be prepared in much better yield by boiling the gallic acid in aqueous solution with arsenic acid. This enabled him to obtain it in purer form and to prove conclusively, as he thought, that it was digallic acid, and he stated, furthermore, that its acetyl derivative was "identical with that of the natural tannic acid" (8); but while Löwe (9) claimed that under these conditions the arsenic acid oxidizes the gallic to ellagic acid, Schiff claimed that the arsenic acid is unchanged, merely acting as a catalytic agent, and that a small amount of it is capable of completely converting a large amount of gallic acid into the digallic acid.

By the action of phosphorus oxychloride on phenolsulphonic acid (10) Schiff obtained a condensation product to which he ascribed the constitution:



This compound, he claimed, with the exception of the iron reaction, gives all the reactions of tannic acid, such as the precipitation of albumins, alkaloids, metal salts, etc. In a similar manner he ob-

tained from pyrogallolsulphonic acid (which he called sulphogallic acid) a condensation product (11) of the following constitution:



This, it will be noticed, is exactly analogous to the constitution of the digallic acid (II, above). He stated, furthermore, that the reactions and solubilities of this product, which he called sulphotannic acid, are exactly like those of tannic acid. Similar products were also obtained from phloroglucinolsulphonic acid (12) as well as from trichlorohydroquinolsulphonic acid (13). By heating phenolsulphonic acid by itself (14) he again obtained a tanning material having the composition $\text{C}_6\text{H}_4\text{SO}_2$ or $\text{C}_{12}\text{H}_{10}\text{S}_2\text{O}_4$, but differing in behavior from the product obtained from phenolsulphonic acid by the action of phosphorus oxychloride. Finally, he also claimed that among the products of decomposition of citric acid by means of phosphorus oxychloride he found a substance giving the tannin reactions, which also stands close to the ordinary tannic acid in its percentage composition.

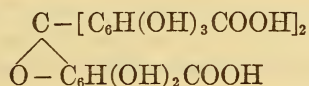
Baeyer in 1872 (15) found that by the interaction of formaldehyde with pyrogallol in the presence of hydrochloric acid, besides an insoluble product, he was also able to get a water-soluble compound which "precipitates gelatin and behaves generally like tannin." However, he did not try its action on raw hide, and apparently was not specially interested in the synthesis of tanning materials.

Böttinger in 1884 (16), by heating gallic acid or its ethyl ester with pyrrocemic acid (or glyoxylic acid) in the presence of sulphuric acid, obtained a water-soluble substance which was capable of precipitating gelatin from its solutions. It contained no sulphur and apparently no portion of the pyrrocemic or glyoxylic acids, and its analysis indicated the formula $\text{C}_{14}\text{H}_{10}\text{O}_9 + 2\text{H}_2\text{O}$. It lost water at 100°C . without any apparent change in properties. Böttinger called it a digallic acid and considered it "an isomer of tannin," meaning evidently Schiff's digallic acid.

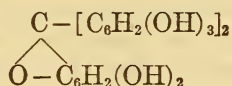
After Baeyer's first work on the condensation products of aldehydes with other compounds the action of aldehydes, in general, on various other organic compounds was studied by a considerable number of investigators during the next 30 years, chief among whom were the following: Zeidler and others in 1874 (17); Fabinyi and also Steiner in 1878 (18); Michael, together with Comey, in 1883 (19); Claisen, together with others, in 1884 to 1887 (20); Claus and Trainer in 1886 (21); J. R. Geigy & Co., in 1889 (22); Kleeberg in 1891 (23); Caro in 1892 (24); Möhlau and Koch in 1894 (25); Kahl,

together with Möhlau, in 1898 (26); and Goldschmidt in 1903 and 1904 (27). These investigators, however, did not note any tanning properties in the compounds which they prepared and, indeed, did not appear to be interested in this matter.

In 1905 Nierenstein (28), who appeared to be chiefly interested in establishing his theory of the tannophore in tanning materials (29), repeated Baeyer's work with pyrogallol as well as with gallic acid. In each case, in addition to the insoluble diphenylmethane derivative, he also found a water-soluble gelatin-precipitating compound. The latter compound, in the case of the gallic acid derivative, he identified as Caro's hexahydroxyaurintricarboxylic acid (I below), and that from pyrogallol as the hexahydroxyaurin (II).



(I)



(II)

Later (30) he found that in all condensation reactions between formaldehyde and phenols or hydroxycarboxylic acids, in addition to the insoluble diphenylmethane derivative, there was also formed the corresponding aurin derivative which contains a decided tannophore group and therefore gives a precipitate with gelatin solution and acts like a tannin.

Stiasny in 1905 (31), in seeking a method for the determination of tannins, studied the action of formaldehyde on various natural tannins, and, for the sake of comparison, also studied the reactions of formaldehyde with a number of definite organic compounds (dihydroxyphenols, pyrogallol, the three monohydroxybenzoic acids, and a few methylated phenols). He confirmed Nierenstein's finding that in addition to the precipitates these reactions also yield soluble products which in turn are capable of precipitating gelatin from its solutions and therefore possess a tannin-like character. He found this behavior especially pronounced in the case of gallic and protocatechuic acids, pyrogallol and hydroquinol and suggested this reaction as a possible basis for the preparation of artificial tanning materials.

Kauschke in 1906 (32), in describing some new developments in the dyeing of leather, also mentioned the fact that both soluble and insoluble products are formed by the interaction of formaldehyde with the pyrogallol tannins, and that when this reaction is allowed to take place in the leather the soluble products so formed are not lost, but act like tannins and likewise become fixed in the leather. He thus confirmed the findings of Nierenstein and Stiasny.

Weinschenk in 1905 (33) tried to make practical use of Baeyer's discovery, but since pyrogallol and other phenolic compounds occurring in vegetable tannins are too expensive, he tried the action of a solution of a naphthol, together with formaldehyde, either simultaneously or alternately, on raw hide. He claimed to have obtained in this way (using alpha-naphthol) a leather which even experts could hardly distinguish, by a superficial examination, from vegetable-tanned leather. Stiasny (34), Ricevuto (35), and Nierenstein (36), disputed these claims of Weinschenk's, arguing that under the conditions given there would be very little reaction between the formaldehyde and the naphthol; that any methylenedinaphthol formed would be insoluble in any case and therefore could not act as a tanning material; and that any tanning action of the mixture must be ascribed to the independent action of the formaldehyde alone. Weinschenk, however, stoutly maintained his claims (37) and was granted patents covering his discovery (38).

The study of the natural tannins up to this point indicated that the most common components of these were various hydroxybenzoic acids, especially gallic and protocatechuic acids, and that these were probably largely if not entirely combined with each other in the form of ester anhydrides by the interaction of the carboxyl group of one molecule with the hydroxyl of another in strings of two or more such molecules. Fischer and Freudenberg (39) proposed to call such compounds "depsides." Such compounds had already been prepared by various investigators. Thus, some of the compounds prepared by Gerhardt in 1852 to 1854 (40) were undoubtedly of this type, particularly his so-called salicylic anhydride. Other compounds of this character were later prepared from salicylic acid by Prinzhorn in 1868 (41) and from *p*-hydroxybenzoic acid by Klepl in 1883 (42). None of these earlier investigators, however, noted any tanning properties in any of their compounds; besides, all of these earlier compounds of this type were insoluble in water, and therefore, even if they did possess tanning properties, they would hardly be available for such use on a commercial scale.

In 1908 Emil Fischer, later in cooperation with others, started a series of investigations on the synthesis of various polydepsides (43) and later of gallotannic acid itself as well as other closely related compounds. They succeeded in preparing a number of compounds which were soluble in water, precipitated gelatin from its solutions, and possessed other properties of tannins, and they furthermore showed that ordinary gallotannic acid, if not actually identical with pentadigalloylglucose, is at least very closely related to the latter compound; but all of these compounds are still too difficult of preparation to serve as practical substitutes for the natural tannins in the commercial manufacture of leather.

In the meantime (1911) Stiasny had applied for his first patents (44) on the condensation products of phenol or cresolsulphonic acids with formaldehyde, which he proposed for use as tanning materials. A product derived according to these patents from crude cresols (cresylic acid) was placed on the market under the name of "Neradol D," and later a product similarly derived from naphthalene was also marketed under the name of "Neradol ND." These were probably the first synthetic organic products to be used with any degree of success by the tanning industry as substitutes, in part at least, for the vegetable tanning materials or as aids in tanning with the latter, but the success of even these products was far from what might be desired, for they were incapable of completely replacing the natural, vegetable tanning materials. Even as partial substitutes for the latter, or as mere aids in tanning, they were not entirely satisfactory, for reasons which have already been mentioned in an earlier part of this report. Nevertheless, such success as Stiasny attained with his products proved to be a great stimulus to the further investigation and development of other synthetic tanning materials of a more or less related type, and during the years that followed a large number of materials and processes for tanning were proposed and patented in the leading industrial countries of the world, and the number of such suggestions is still increasing. Unfortunately, the majority of these have never been thoroughly investigated. Many have been entirely barred from commercial use because of the high cost of the raw materials or of the process of manufacture, and those which can be manufactured at sufficiently low cost to enable them to compete with the ordinary tanning materials have not yet been developed to the point where they are satisfactory, except, perhaps, in a minor capacity.

V. EXPERIMENTS AND RESULTS

1. GENERAL

Although the present commercial syntans of the type of sulphonated condensation products possess a number of disadvantages, and in the past serious objections have been raised to their use (except in limited quantities in connection with vegetable tanning materials), nevertheless they do possess a number of characteristics of undoubted value, and on the whole they have shown themselves to be the most promising of the numerous proposed substitutes for the vegetable tanning materials. It has, therefore, seemed advisable to investigate this class of substances with a view to eliminating their objectionable characteristics, if possible, particularly their injurious action on the leather produced, and also developing their filling qualities. The latter does not mean that a deliberate attempt is going to be made to find something that will give weight to leather. If a substance

can be found which will give to leather the necessary firmness and rigidity or other characteristics required to make it suitable for soles or other purposes, this will be considered satisfactory, even though it may not give the maximum weight to the leather.

The first work carried out in the course of this investigation, and indeed the only work included in this report, was chiefly of a qualitative nature, the purpose being to gain first-hand information on a considerable number and variety of products derived from some of the cheaper raw materials, and especially on the quality of leather which they are capable of producing, if any. This work involved the preparation of the condensation products by various methods and under various conditions and then subjecting them to actual tanning tests on a small scale.

The bases of these products were chiefly the simpler and more common of the aromatic compounds, namely, the hydrocarbons, benzene, toluene and naphthalene, and the corresponding monohydric phenols; that is, ordinary phenol, cresylic acid, and α - and β -naphthols, although a number of experiments were also made with resorcinol and pyrogallol. These raw materials were either sulphonated first and then condensed with an aldehyde (usually formaldehyde, although in some cases the ordinary acetaldehyde in its polymerized form was used instead, and in a few cases furfural) under various conditions, or the aromatic compound was first condensed with the aldehyde and the condensation product subsequently sulphonated. In the case of the polyhydric phenols (resorcinol and pyrogallol) the products were not sulphonated. In a number of cases the condensation of the sulphonic acids by the action of heat alone (that is, without the use of an aldehyde or other compound) was tried, and in the case of naphthalenesulphonic acid condensation with glycollic acid was also attempted.

No attempts have been made thus far to isolate and purify any of these condensation products or to determine their constitution and structure, neither was the sulphuric acid in most cases removed from the solution of the sulphonic acid, either before or after condensation with the aldehyde, although in a few instances the sodium sulphonates were first purified and then treated with the aldehyde and an acid. Of course, the excess of free sulphuric acid was always neutralized before the product was used for tanning. The object of this procedure was to determine the value of the material as a tanning agent in the condition in which it would most likely be manufactured and applied on a commercial scale.

2. TANNING TESTS

(a) WHAT CONSTITUTES "TANNING."—In the pages which follow a great deal will be said about the tanning properties of various substances and whether or not they possess any tanning properties

at all, but the terms "tannin" and "tanning" have not always been used in the same sense by different authorities, and there exists a considerable difference of opinion, even among persons who should know, as to just what these terms mean. Nevertheless, it is obviously necessary to have some standard whereby we may measure the tanning properties of any given agent and determine whether or not a piece of hide has been tanned. It is also obvious that such a standard must necessarily be more or less arbitrary.

For the purpose of the present paper we shall consider tanning as the conversion of raw hide into a permanent, nonputrescible material which can not again be converted by washing with water at ordinary or slightly elevated temperatures (not over 60° C.) into the original raw hide. It is realized that this is a rather broad and general statement and that it may allow the classification of certain materials as "tanned" which would constitute a very unsatisfactory kind of leather, if, indeed, they could be called leather at all, in the ordinary sense. However, it is also believed that any attempt to draw the lines closer and to make finer distinctions would only lead to greater difficulties and uncertainties, and therefore more detailed definition will not be attempted at present.

(b) METHOD OF MAKING TANNING TESTS.—The tanning tests were generally carried out in one of two ways. One method was to partially neutralize the solution of the sulphonated condensation product with sodium hydroxide, as already stated, so as to convert the free sulphuric acid to its sodium salt, and then dilute a portion of the resultant solution with enough water to reduce the remaining free acid (sulphonic) to a concentration of about one-tenth normal or less. This dilute solution was then used directly for the tanning test, more of the tanning agent being added when the hide was nearly or entirely penetrated. The second method was to completely neutralize the solution of the sulphonated condensation product, then dilute a portion of this solution to a concentration of about 5 per cent organic matter (usually estimated as free sulphonic acid), and finally acidify to about one-tenth normal acid concentration, using a weak acid like acetic and adding more of this acid when the hide was nearly or entirely penetrated by the syntan.

As might be expected, in the first method the hide was somewhat more plumped than in the second, though not excessively, and the rate of penetration was therefore correspondingly diminished. In the second method, in the case of several of the syntans at least, it was found that hydrochloric acid could be substituted for the acetic acid in exactly equivalent concentrations (up to one-tenth normal) with practically identical results, both as to the course of the tanning as well as the quality of the final leather. Another interesting observation in this connection was the fact that the

neutral syntans (that is, the sodium salts of the sulphonated condensation products), which in this form have no tanning action, have a very pronounced plumping action. This is quite appreciable even in a 1 per cent solution, and in a 5 per cent solution this effect is excessive. As a result, if, in the second method of applying the tanning test, an insufficient amount of acid is added to the neutral syntan the small amount of sulphonic acid thus liberated will be very quickly taken up by the hide (mainly on its surface), leaving essentially a solution of neutral syntan which then plumps the interior of the hide excessively, and thus materially slows down the tanning process, if not practically stopping it, on the subsequent addition of more acid.

3. PRODUCTS DERIVED FROM AROMATIC HYDROCARBONS²

The sodium sulphonates of benzene, toluene, and naphthalene were treated with equivalent proportions of a 10 per cent solution of hydrochloric acid and then heated in tightly closed bottles at a temperature of 95 to 100° C., with varying proportions of a 37.5 per cent solution of formaldehyde. In no case was any appreciable condensation noted. If any condensation takes place under these conditions, it is very slow. As will be noted in a later portion of this report, the sulphonic acids of the corresponding phenols condense with formaldehyde very readily under similar conditions. However, if the formaldehyde is heated with the sulphonated hydrocarbons in concentrated form, the condensation will again take place quite readily.

(a) **TOLUENESULPHONIC ACID AND FORMALDEHYDE.**—Toluene was sulphonated with 1.5 moles of 93 per cent sulphuric acid and the sulphonation mixture was then treated directly with 1 mole of a 37.5 per cent solution of formaldehyde, the latter being added slowly (during six hours) to the sulphonation mixture melted on a water bath. The product dissolved readily in water and precipitated gelatin from its solutions. A tanning test indicated that the product possessed very little, if any, tanning properties. No attempt was made to analyze the hide after treating with this condensation product to determine whether or not any combination had taken place.

(b) **NAPHTHALENESULPHONIC ACID AND FORMALDEHYDE.**—Two hundred grams of crystallized naphthalene were sulphonated by heating for seven hours on an oil bath at about 160° C. with 206.2 g of 95.75 per cent sulphuric acid, this quantity of acid representing about 1.29 moles. The flask was at first kept loosely covered with a watch glass to prevent loss of naphthalene, but during the last

² A part of the experimental work dealing with the hydrocarbons and the naphthols was performed by Samuel I. Gertler; also, some of the tanning tests were made by Everett L. Wallace.

portion of the heating it was left uncovered to permit escape of the unchanged naphthalene. The reaction mixture was allowed to cool to about 100° C., 40 cc of water were added, and then, while maintaining the temperature at 95 to 100° C., and with constant stirring, there were added drop by drop 60 cc of 37.5 per cent formaldehyde solution, representing about 0.52 mole of the aldehyde per mole of original naphthalene. The addition of the formaldehyde required about two hours, and the heating was continued for about two and one-half hours longer. A stiff, dark-colored paste was obtained which dissolved readily and completely in warm water. A tanning test carried out with this solution gave a product which on drying had all of the characteristics of a piece of dry, raw hide, except that it was white and opaque instead of the dark, horny and translucent material obtained by drying dehaired raw hide. It was very thin, hard, stiff, and could not be bent without cracking. However, a determination of nitrogen in this material indicated that the hide substance had combined with about 20 per cent of its own weight of the condensation product, which could not be washed out by water at ordinary temperature, even after eight hours of washing. A determination of tanning materials in the original solution of the condensation product by the official method of the American Leather Chemists' Association indicated a total of 299.5 g of "tans" produced.

The above experiment was repeated with twice the proportion of formaldehyde. The results were similar to the above, except that a stiffer paste was obtained in the reaction with the formaldehyde, and there was an excess of the latter reagent even after six additional hours of heating at 120° C. The "leather" produced by this second condensation product was also similar to that obtained in the previous experiment, but the total amount of tans produced in this case from 200 g of original naphthalene was only 158.3 g, or little more than a half of what was obtained in the first case. Evidently a higher condensation product is obtained when the proportion of formaldehyde is greater than 1 mole of the latter to 2 of original naphthalene, but this condensation product apparently is not capable of combining with hide substance.

When the condensation was conducted in a tightly closed bottle (the formaldehyde being added all at once, instead of drop by drop, and in the same proportions as in the first experiment) in order to prevent loss of formaldehyde, the results were again practically the same as those first obtained when the condensation was carried out in an open flask. The total amount of "tans" obtained in this case from 200 g of naphthalene was 303 g, or only about 1 per cent more than in the first case.

The products obtained above are essentially the same as those described in German patent, 290965/1917 (45), which have been sold in Europe under the name of "Neradol N" or "Neradol ND." A similar product is also being marketed in this country but under a different name. It is not recommended as a complete tanning material by itself but is used in connection with other tanning materials.

(c) NAPHTHALENESULPHONIC ACID, FORMALDEHYDE, AND OXIDIZING AGENTS.—It is claimed in various patents (46) that improved tanning agents may be obtained from sulphonated condensation products of hydrocarbons and of phenols by treating these with various oxidizing agents. Accordingly, the naphthalenesulphonic acid-formaldehyde condensation product above described was heated in dilute solution with varying quantities of nitric acid chromic anhydride, or hydrogen peroxide, but in no case was any improvement in the tanning properties of the product observed.

(d) CONDENSING NAPHTHALENESULPHONIC ACID BY HEATING.—It has also been claimed that tanning agents may be obtained by merely heating various sulphonic acids by themselves or in the original sulphonation mixture at various temperatures, as 130 to 180° C., either at ordinary atmospheric pressure or in vacuum, or with a stream of air bubbling through the hot mixture to carry off the water (47); but while these products (which are probably sulphones) will precipitate gelatin from its solution, tanning tests with these materials failed to produce anything resembling leather.

(e) CONDENSING NAPHTHALENE WITH NAPHTHOLSULPHONIC ACID BY MEANS OF HEAT.—Twenty grams of α - or β -naphthol were sulphonated with 10 cc of 93 per cent sulphuric acid (about 1.25 moles) and then heated for six hours on an oil bath at 165 to 170° C. with 18 g (about 1 mole) of naphthalene. The reaction mixture was then treated with water and the aqueous solution filtered off. A considerable proportion of the naphthalene had gone into combination, either by reacting with excess of sulphuric acid and the formation of naphthalenesulphonic acid or by reacting with the naphthol-sulphonic acids (probably partly disulphonic acids) and forming a sulphonated sulphone. However, in each case a considerable insoluble residue also remained, consisting chiefly of unchanged naphthalene, but also containing some black, partly carbonized material. The aqueous solution obtained from the reaction mixture was black and opaque. It precipitated gelatin from its solutions and evidently possessed some tanning properties, but it was far from being a satisfactory tanning agent. The solution derived from α -naphthol produced a nearly black, light, spongy leather of rather low tensile strength, while that derived from β -naphthol had a decidedly destructive action on the hide substance, producing a material in which

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the fibrous structure had almost entirely disappeared and which had the appearance of having been carbonized.

(f) CONDENSING NAPHTHALENESULPHONIC ACID WITH PHENOLSULPHONIC ACID.—One mole of naphthalene was treated with 3 moles of 93 per cent sulphuric acid and the mixture heated for three hours on an oil bath at 140° C. Then there were added 1.36 moles of phenol, and the heating was continued at 140° for 14 hours. The product on cooling was treated with water and the solution filtered. Most of the material dissolved, but a small amount of insoluble residue remained. The solution was dark and opaque and possessed very little, if any, tanning properties. A piece of calfskin treated with the solution was colored a dirty gray, and on drying yielded a very dark thin, hard, and stiff material.

Attempts were also made to condense naphthalenesulphonic acid and phenolsulphonic acid with each other by means of formaldehyde, but the attempts proved unsuccessful and were discontinued.

(g) CONDENSING NAPHTHALENESULPHONIC ACID WITH GLYCOLLIC ACID.—It has been claimed (48) that a tanning agent can be obtained from naphthalene, sulphuric acid, and glycollic acid, which, in addition to the tanning properties, also possesses the property of "filling" the skins "to a surprising degree." As the filling property of a tanning material is very important in the production of heavy leathers, and since this property is conspicuously lacking in the ordinary syntans, it was considered to be desirable to try out this process, even though one of the materials called for (the glycollic acid) is prohibitively expensive for use in the manufacture of tanning materials.

Fifty grams of naphthalene were placed into an Erlenmeyer flask and heated on an oil bath to 160° C. Then a warm mixture of 76.2 g of 95.75 per cent sulphuric acid and 15.3 g of glycollic acid was added and the heating was continued at 160° for 20 minutes. Active effervescence soon set in, and for a few minutes the mixture foamed strongly. On cooling the reaction mixture was extracted with hot water and filtered, yielding a nearly black filtrate which strongly precipitated gelatin and a considerable quantity of a porous, black insoluble material apparently consisting chiefly of carbon. This residue on drying weighed about 6 g.

The above experiment was repeated, but the heating was conducted at a temperature of 120° instead of the higher temperature. This time there was no foaming, and the effervescence was quite moderate. After 20 minutes the odor of sulphur dioxide was very prominent in the escaping gases. Heating was discontinued after 25 minutes. The reaction mixture while still hot separated into two layers—a black upper layer and a lighter colored purple lower layer. On cooling the mixture was treated with hot water. Naphthalene sublimed in the neck of the flask. Filtering gave a dark greenish solution and an

insoluble, black residue. This residue weighed 6.7 g, and on heating at 100 to 105° C. it lost 63 per cent of its weight which was recovered as naphthalene. The filtrate precipitated gelatin strongly, even when completely neutralized. The neutral solution, however, had no tanning power, but it plumped the hide strongly. The acid solution, on the other hand, converted raw hide into a very thin, hard, stiff material of dark color and low tensile strength, which broke on bending.

Since the naphthalene was not completely sulphonated in the last two experiments, the procedure was modified by first sulphonating the naphthalene in the usual way and then adding the glycollic acid to the reaction mixture and continuing the heating at atmospheric pressure. At 160° the reaction takes place very vigorously, with some foaming and evolution of sulphur dioxide. When the reaction with glycollic acid is allowed to take place at 110° (slightly above the melting point of the mixture), there is less effervescence and evolution of sulphur dioxide, but it requires longer heating to convert all of the naphthalenesulphonic acid. In either case, however, a dark greenish mass is obtained which dissolves completely to a dark green solution which resembles the solution obtained in the last experiment above. It also precipitates gelatin either in the acid or neutral condition. When partly neutralized (to convert the free sulphuric acid to sulphate), it will after a time deposit a light, flaky, crystalline precipitate which again redissolves on warming or on adding more water. The acid solution appears to have tanning properties, but it also has a very destructive action on the hide, causing complete disintegration in a few days.

(h) SULPHONATED HYDROCARBON FORMALDEHYDE RESINS.—It has been claimed in various patents (49) that the resinous condensation products of naphthalene or other aromatic hydrocarbons with formaldehyde (50) when sulphonated yield tanning agents. Attempts to prepare such material by heating with sulphuric acid the condensation products obtained by the reaction of formaldehyde with toluene or naphthalene in the presence of concentrated sulphuric acid, however, proved unsuccessful because of the difficulty of the sulphonation. Even prolonged heating of such condensation products with ordinary concentrated sulphuric acid at temperatures up to 140° C. proved insufficient to bring more than a very small amount of the resin into solution, while, on the other hand, there was considerable oxidation and charring of the undissolved portion. In addition, great difficulty was also experienced in filtering the soluble portion of the reaction mixture from the insoluble portion.

Thus, although it can not be claimed that these compounds have been studied exhaustively, the simple aromatic hydrocarbons have failed thus far to yield anything like satisfactory tanning agents.

4. PRODUCTS DERIVED FROM PHENOL

While the simpler aromatic hydrocarbons do not yield satisfactory tanning materials by mere sulphonation and condensation with formaldehyde, the situation is very different when one or more hydroxyl groups are introduced into the molecule and joined directly to the benzene ring. Not only are sulphonated condensation products, as a general rule, readily produced from the simple phenols and formaldehyde or other aldehydes, but these products generally possess the properties of true tanning materials and are capable of converting raw hide into a true leather. Not all of them will produce a satisfactory leather; but many of them are capable of producing a leather of excellent quality as regards softness, flexibility, and strength, although lacking fullness, and there are some which even possess filling qualities to a marked degree, though not to the extent that these are possessed by the vegetable tanning materials.

(a) PHENOLSULPHONIC ACID AND FORMALDEHYDE.—Phenolsulphonic acid reacts with formaldehyde readily. In concentrated solution and in the presence of sulphuric acid the reaction takes place with the evolution of considerable heat. In dilute solutions it takes place very slowly but may be hastened by raising the temperature. Although this reaction can be carried out in an open vessel, when heat was required it was deemed preferable to heat the reacting substances together in a closed vessel in order to prevent the loss of formaldehyde, since otherwise it would be impossible to control the proportions of the reagents. In most cases pure reagents were not used, but in the first experiments with phenolsulphonic acid, in order to avoid the presence of unchanged phenol or sulphuric acid, the sodium salt of *p*-phenolsulphonic acid, containing 2 molecules of water of crystallization, was acidified with the equivalent quantity of dilute hydrochloric acid and then treated directly with the formaldehyde solution. The following is a typical experiment of this kind.

One hundred and thirty grams of $C_6H_4(OH)SO_3Na + 2H_2O$, 197.5 cc of dilute hydrochloric acid (containing 0.1033 g per cc), and 21 cc of a 37.5 per cent solution of formaldehyde solution were placed into a tightly stoppered bottle and heated on a steam bath at 95 to 100° C., with frequent shaking. The above quantities of reagents are in the proportions of 1 mole formaldehyde to 2 moles phenolsulphonic acid. The heating was continued for one hour after all of the sodium sulphonate had gone into solution. As will be shown in another place, the condensation is completed, and the reagents apparently reach complete equilibrium under these conditions within one hour. A dark-colored solution was obtained which, on cooling overnight, deposited a small amount of an amorphous, white solid. This solid

readily dissolved on the addition of a small amount of cold water and was evidently the condensation product. The final acidity of the solution was equivalent to 25.21 g of hydrochloric acid, or about 23.5 per cent higher than the amount of hydrochloric acid used (20.40 g). It also gave a very finely divided, white precipitate with barium chloride. Evidently the sulphonic acid had been hydrolyzed to this extent. The solution strongly precipitated a solution of gelatin and, after partial neutralization, could be used directly for tanning. It produced a very light colored, nearly white leather which was firm but pliable, long-fibred and strong, but lacking fullness.

The hydrolysis of the sulphonic acid during condensation with formaldehyde is a phenomenon which was repeatedly observed in the course of this work, not only in the case of phenolsulphonic acid but also in the case of other sulphonic acids, particularly those of the cresols and naphthols, and this hydrolysis is not due merely to the large amount of water present or the high temperature employed, for a considerable amount of hydrolysis was also observed even when the condensation was carried out at ordinary temperatures, with the concentrated sulphonation mixture containing the excess of unchanged sulphuric acid, with only a very small amount of water added. On the other hand, when sodium phenolsulphonate is heated with dilute solutions of hydrochloric acid or sulphuric acid it shows no increase in acidity, indicating that the phenolsulphonic acid itself is not hydrolyzed. The tendency to hydrolysis of the sulphonic acid which takes place during the reaction with formaldehyde must, therefore, be a property of the condensation product. These results confirm those observed by Croad (51), who found that the cresol-sulphonic acids when condensed with formaldehyde were hydrolyzed, splitting off sulphuric acid, in some cases to the extent of 2.75 per cent.

When the sodium phenolsulphonate, formaldehyde, and hydrochloric acid are taken in equimolecular proportions, the other conditions being the same as in the last experiment, the solution after being heated 15 to 20 minutes begins to become viscous, then to gelatinize, and at the end of an hour or so forms a firm, semitransparent, jellylike mass which is insoluble in water. This product after being dried does not dissolve in concentrated sulphuric acid, either hot or cold, and when heat is applied the material becomes carbonized. If the proportion of formaldehyde to sulphonic acid is between 1 and 2 molecules (that is, in the neighborhood of 1.5 molecules) of the former to 2 of the latter, we naturally obtain a mixture of the soluble and insoluble products, as might be expected. The insoluble product, however, is not separated but is held in colloidal suspension by the soluble one, and the resulting solution is more or

less viscous, depending upon the proportions of the two products formed, which, in turn, depends upon the proportions of formaldehyde and sulphonie acid taken and the length of heating.

It was thought that a partly colloidal solution such as this might be employed for the production of heavy leathers, on the theory that the colloidal component of the solution might be carried by the water soluble component into the hide where it would be then deposited by adsorption (somewhat as suggested in United States Patent 1399510/1921), but such did not prove to be the case. The leather produced by this solution was practically identical with that obtained by the use of the one described in the next preceding experiment, in which the molecular ratio of formaldehyde to phenolsulphonie acid was 1:2. In other words, the colloidal product obtained when the proportion of formadehyde is doubled apparently has no tanning value. This same fact is indicated, also, by the amounts of "tans" absorbed by chromed hide powder from the two solutions in the official method of the American Leather Chemists' Association.

Instead of using pure sodium phenolsulphonate or attempting to isolate in any way the phenolsulphonie acid, the crude sulphonation mixture obtained by heating phenol with concentrated sulphuric acid may be simply diluted with water and treated directly with the formaldehyde, as in the preceding experiments. The results are exactly the same as when the pure materials are used, except that when the diluted sulphonation mixture is being heated with formaldehyde a white precipitate separates out, later turning pink, which is due to the presence of a small amount of unchanged phenol in the sulphonation mixture. This phenol, under the conditions existing in the solution, evidently reacts with the formaldehyde more readily than does the sulphonie acid. The solid product, however, can be readily removed by filtration, and the resulting filtrate is then practically identical with the solution obtained with the use of sodium phenolsulphonate, as far as the essential component is concerned. The unchanged sulphuric acid in this solution may be neutralized by the addition of the corresponding amount of sodium hydroxide and the solution after proper dilution may be used directly for tanning.

The following experiment will show what results may be expected from this method of procedure. Ninety-two and three-tenths grams of crystallized phenol and 110.8 g of 95.7 per cent sulphuric acid were heated together for three hours on a steam bath, care being taken to prevent the entrance of water vapor into the flask during this heating. After cooling the sulphonation mixture was dissolved in 231 cc of water (2.5 times the weight of phenol taken) and heated on the steam bath for two hours in a tightly closed bottle with 38 cc

of 37.5 per cent formaldehyde solution. This proportion of formaldehyde represents 1.05 moles of formaldehyde to 2 moles of original phenol. Six and three-fourths grams of air-dried precipitate were filtered off from this reaction mixture, representing about 7.3 per cent of the original weight of the phenol. The filtrate now had a total acidity equivalent to 68.127 g of sulphuric acid as compared to 106.035 g of actual sulphuric acid originally taken. The difference, or 37.908 g of sulphuric acid, would be the equivalent of the actual sulphonie acid formed, and twice that would be the amount of combined sulphuric acid, whence the amount of free sulphuric acid is found to be 30.219 g. Hence, the amount of sodium hydroxide required to neutralize the free sulphuric acid would be about 24.7 g.

Incidentally, the degree of hydrolysis of the sulphonie acid may also be approximately calculated from the above data. Assuming that the precipitate which was formed during the condensation was methylenediphenol, this would represent about 6.3 g of phenol which escaped sulphonation. The remaining phenol (86 g) would require 89.65 g of sulphuric acid for conversion to the monosulphonie acid, whereas the above figures indicate that actually only about 75.82 g of sulphuric acid remained combined after the condensation. The difference between the last two quantities would indicate a hydrolysis of about 15.4 per cent.

Instead of neutralizing the free sulphuric acid with sodium hydroxide, a portion of the product was treated with the theoretical amount of a solution of barium acetate to remove the sulphuric acid, and the resulting solution was then analyzed for "tannin" by the official method. The result indicated a total of 142.8 g of tanning material in the entire preparation, or about 89.2 per cent of the estimated total organic matter.

The leather obtained with this solution is identical in every way with that obtained with the solution prepared as above described from sodium phenolsulphonate. The presence of the sodium sulphate appears to have no visible effect on the tanning process or on the quality of the finished leather, unless the slight amount of sulphuric acid which is formed by reaction of this salt with the sulphonie or other acid in the solution should remain in the leather and affect the life of the latter. It is well known that sulphuric acid will combine with hide substance, and experiments in this laboratory have shown that chromed hide substance will remove sulphuric acid from a solution containing nothing but sodium sulphate and acetic acid and convert a large proportion of the sodium sulphate in this way to sodium acetate, but whether the sulphuric acid will remain combined with the hide substance in the presence of a tanning material, particularly such a tanning material as those here described, is a question which can not be answered at the present time. This is one of the

questions which are now under investigation in the course of the present work.

Instead of condensing the phenolsulphonic acid with the formaldehyde in dilute solution at an elevated temperature as was done in the above-described experiments, the reaction can be carried out at ordinary room temperature in concentrated solution, only enough water being added to keep the reaction mixture sufficiently fluid to permit efficient stirring. Under these conditions a great deal of heat is evolved, and the mixture must be thoroughly stirred and cooled while the formaldehyde is being slowly added if the temperature is to be kept within control. This is essentially the original method of Stiasny (52). Under these conditions, furthermore, there is no precipitate formed by the interaction of the unsulphonated phenol with the formaldehyde, so that there is no need of filtering the final product. On the other hand, however, there is a red coloring material formed in the solution which colors the leather a deep red, and the amount of this coloring matter, as well as the dyeing effect on leather, seem to increase with the age of the solution, probably due to absorption of oxygen from the air. The following experiment will illustrate this method.

Two hundred and seventy-two and three-tenths grams of crystallized phenol and 334 g of 95.75 per cent sulphuric acid were heated together on a steam bath for seven hours. After cooling the reaction mixture, add 65 cc of water and then very slowly and with constant stirring 121 cc of 37.5 per cent formaldehyde solution, keeping the temperature meanwhile between 30 and 35° C. These proportions represent 1.1 moles of formaldehyde for 2 moles of original phenol. The mixture was allowed to stand for four days at room temperature to insure complete reaction of the formaldehyde. The total acidity of the product was now equivalent to 205.6 g of sulphuric acid, and a separate test on another portion of the original sulphonation mixture showed that not over 1.85 per cent or 5.04 g of the original phenol had escaped sulphonation. By a calculation similar to the one already described it was determined that in this case about 18.0 per cent of the original sulphonic acid had been hydrolyzed during the condensation.

Stiasny in his patents claims that unless the temperature during the condensation is kept down to approximately room temperature insoluble products are formed instead of the soluble tanning materials. This, however, was not found to be the case. Thirty-seven and six-tenths grams of crystallized phenol were heated on the steam bath for two and one-half hours with 46 g of 95.75 per cent sulphuric acid. The cooled sulphonation mixture was treated with 7.5 cc of water, and then 16 cc of 37.5 per cent formaldehyde solution were added all in one portion. The temperature began to rise rapidly, and the mixture finally became very hot. On the first addition of the formaldehyde the mixture assumed a deep, rose-red color, which later became a

dark red, but there was no precipitate visible at any stage of the reaction or at any time after. The final acidity of the reaction product was equivalent to 28.15 g of sulphuric acid, as compared with 44.05 g of actual original acid. A simple calculation will show that at least 31.8 g of the sulphuric acid, or 81.15 per cent of the theoretical, remained combined after the condensation, thus indicating that under these conditions the hydrolysis is no greater than when the temperature is carefully controlled. The coloring matter in this product also dyes the leather a deep red.

The last two products have no advantage as tanning agents over those obtained by carrying out the condensations in dilute solutions and at an elevated temperature. Except for the fact that the former give a highly colored leather whereas the latter yield a practically white leather, there is no appreciable difference in the quality of the leather produced in the two cases. The condensation of the formaldehyde with the sulphonation mixture directly in concentrated solution, particularly when this is done without temperature control, would undoubtedly have the advantage in commercial manufacture over the other method if the presence of the dye in the final product were of no consequence, since this method would require no filtration of the final product and, in addition, it would yield a more concentrated tanning agent. The method of condensation in dilute solution with artificial heating, on the other hand, although being more expensive both as regards the manufacture and transportation of the product, has the advantage of yielding a product which gives a nearly white leather.

It is claimed (53) that phenol sulphonic acid can be condensed to a tanning material with formaldehyde in an alkaline solution; that is, using the sodium salt of the sulphonic acid. This condensation was attempted, both with the neutralized sulphonation mixture as described in the first example of the above-mentioned patent as well as with a solution of pure sodium phenolsulphonate to which a small amount of sodium hydroxide had been added. The heating with formaldehyde was carried out at 140 to 150° C., as specified in the patent, and also, in the case of the pure sodium phenolsulphonate, at 100° C. Although the disappearance of the formaldehyde was noted, the product in no case gave evidence of being able to convert raw hide into leather. In this connection it may be added that it was repeatedly noted that when sodium phenolsulphonate is heated with formaldehyde the resulting solution has an acid reaction, even though it may have been distinctly alkaline at the beginning, unless the amount of sodium hydroxide added is sufficiently large to more than neutralize any acid that may be formed in the reaction. This is probably due to a splitting off of the sulphonic group, not from the sodium phenolsulphonate, but from the condensation product.

(b) **SULPHONATED PHENOL-FORMALDEHYDE RESINS.**—Phenol and formaldehyde may be condensed with each other by heating in the presence of acids or alkalies, which act as “condensing agents,” to form insoluble, resinous products. Such condensation products, under the name of bakelite, condensite, etc., are the basis of the plastic resins used in the manufacture of various molded products and in this form are familiar to all. The sulphonation of these resins and their use as tanning agents has been suggested in various patents (54). Products of this kind have been regarded by some as the same, or nearly the same, as those just described; namely, products obtained by first sulphonating a phenol and then condensing the sulphonic acid with an aldehyde. It is more likely, however, that they are quite different from the latter, at least in chemical structure. As a general rule, they are more difficult to prepare, and often the yields are lower. Their preparation involves, first of all, the preparation of the resin, separating this from more or less water or aqueous solution, and, finally, sulphonating it.

The character of the resin obtained will vary considerably according to the proportions of reagents used and the temperature and length of heating. These same conditions will also determine the extent to which the phenol and formaldehyde react and therefore the yield of resin. The reaction will take place under ordinary atmospheric pressure; that is, in an open vessel. But under these conditions considerable amounts of both phenol and formaldehyde will be lost by vaporization, and if ammonia is used as the catalyst this will also be gradually removed from the reaction mixture. This difficulty may, of course, be largely overcome by heating the reagents under a reflux condenser, but a closed vessel will be the most satisfactory for this purpose. The following experiments will serve to show what results may be expected.

Fifty-two and thirty-two one-hundredths grams of phenol (2 moles), 22.27 cc of a 37.5 per cent solution of formaldehyde (1 mole), and 0.4 cc of a concentrated solution of ammonia (about 28 per cent) were heated together in a tightly stoppered bottle on a steam bath at 95 to 100° C. for two and one-half hours. On cooling an amber colored, sirupy liquid was obtained in which unchanged phenol and formaldehyde could both be detected by their odors. On shaking with water this solution yielded an emulsion which separated into two layers—a colorless aqueous layer and an amber colored sirupy oil. Distillation in a vacuum removed considerable phenol along with water and some formaldehyde, and repeated extraction with hot water finally left an insoluble yellow, amorphous substance which, when dried under reduced pressure, weighed about 13 or 14 g, or not over 25 per cent of the theoretical yield of condensation product.

If the heating in the above experiment is continued for eight hours, the yield of insoluble resin is about 60 per cent. About the same yield may be obtained either by increasing the proportion of formaldehyde by 50 per cent or by increasing the duration of heating in the same ratio. An increase in the amount of ammonia about tenfold likewise increases the yield to about 60 per cent. On the other hand, if the proportion of formaldehyde is increased by one-half (that is, taking 1.5 moles of the aldehyde to 2 moles of phenol), and the amount of ammonia is simultaneously increased to about one-tenth by weight of the amount of phenol (that is, about fourteen and one-half times the proportion given in the first case above, or 10 cc of the concentrated ammonia solution to 90 g of phenol), the condensation is practically complete in about seven hours. Again, if the temperature is raised to 150° C., 2 moles of phenol and 1.5 moles of formaldehyde with but a very small proportion of ammonia (about 0.75 cc of the concentrated solution per 100 g of phenol) will yield a solid product, representing practically complete condensation in one and one-half hours.

The solid resin obtained under the last-mentioned conditions does not appear to be well suited to the preparation of synthetic tanning agents. It is difficult to sulphonate, requiring a large excess of sulphuric acid, and while a portion of the resin is left unacted upon by the sulphuric acid other portions are partially oxidized, yielding a nearly black mass which, when dissolved and used as a tanning agent, produces a very thin, dark colored, hard and stiff leather of low tensile strength. On the other hand, the mixture of condensation product with unchanged phenol, such as may be obtained by the incomplete condensation of phenol with formaldehyde as described above, is much better suited for such purposes. Such a mixture containing about 60 per cent of condensation product can be readily sulphonated, requiring little more than the theoretical amount of sulphuric acid, and the sulphonation product dissolves readily and completely in water. The following experiment will illustrate this procedure.

Four hundred and six and three-tenths grams of crystalized phenol (2 moles), 161.5 cc of a 37 per cent solution of formaldehyde (1 mole) and 2.85 cc of a concentrated solution of ammonia were placed into a tightly stoppered bottle and heated on the steam bath with frequent shaking for 11 hours. The reaction mixture was then transferred to a tared beaker, the water first evaporated as much as possible on the steam bath, and the product then dried further by heating in an oven at 115 to 120° C., for one and one-half hours. Four hundred and twenty-six and three-tenths grams of an amber-colored, sirupy liquid were obtained, giving off considerable phenol vapors while hot. This material while still warm was treated with 170 cc of ordinary con-

centrated sulphuric acid (about 95 per cent), the mixture thoroughly stirred, and then heated in an oven at 120° for about one and one-half hours. On cooling a dark-colored, pasty mass was obtained which was dissolved by warming with 800 cc of water, yielding 1,240 cc of a dark, rather viscous solution. This product, when properly diluted and partially neutralized, yielded a firm, pliable, and strong leather which was rather strongly colored (pink), although other similar preparations produced a less highly colored leather. This product also showed considerable "filling" properties, but no quantitative determinations were made of this characteristic of the material.

An attempt was made to improve the filling properties of the above material by a process of "double condensation," as described in British patent 182824/1922. One-half of the solution of the sulphonated material obtained in the last-described experiment—that is, 620 cc of the solution—was treated with 65 cc of a 37 per cent solution of formaldehyde and the mixture heated on the steam bath for one and one-fourth hours. The solution became very viscous and on cooling formed a jelly-like mass which, however, readily redissolved in cold water to a partly colloidal solution. The tanning properties of this solution did not seem to be improved any by this treatment, however, since the leather produced with it was practically identical with that obtained with the previous preparation.

It has been claimed (55) that insoluble resins such as those described above may be dissolved as colloids by means of solutions of various kinds, including phenolsulphonic acid. Accordingly, a quantity of the phenol-formaldehyde resin obtained as above described, but separated from excess of unchanged reagents, was finely pulverized and mixed with about twice its weight of 91 per cent phenolsulphonic acid, and the mixture was then heated for four hours on the steam bath. But when water was subsequently added it was found that very little, if any, of the resin had been dissolved. It is possible that the resin used in this case had been heated too long before treatment with the sulphonic acid, or that other dispersing agents might have been used more successfully. It is also possible that the more fluid, less completely condensed mixture containing unchanged phenol, if treated with some sulphonated product might more readily pass into solution, although such was not found to be the case when a similarly prepared derivative of cresylic acid was so treated, as will be seen later. Finally, even if this resin were brought in solution by such methods, it is probable that in its tanning properties it would be very little different, if at all, from other partly colloidal products already described.

The condensation product of phenol and formaldehyde in the presence of dilute sulphuric acid is somewhat different from that

obtained by condensing in the presence of ammonia, being nearly transparent and colorless or slightly pink or rose colored instead of amber colored. This product was obtained by following, in general, the directions given by Stiasny (56). Here, as in the case of the condensation in presence of ammonia, the extent of the reaction was found to vary considerably with the proportions of reagents and the temperature and duration of heating. The proportions which seemed to give the best results were as follows: 2 parts by weight of phenol, 4 parts water, 1 part concentrated sulphuric acid, and about 0.86 part of 37 per cent formaldehyde solution, representing 2 moles of phenol to 1 of aldehyde. Stiasny recommends heating for a few hours at from 40 to 50° C., but this requires very long heating or gives a very low yield of condensation product. At 100° for 11 hours and under reflux the above proportions gave, after washing repeatedly with fresh portions of hot water to remove sulphuric acid and unchanged phenol and then drying in an oven at 100°, 1.79 parts of condensation product. This represents about 85 per cent condensation, assuming that the product is methylenediphenol (or dihydroxydiphenylmethane). Heating the same proportions of reagents in a closed vessel at 150° for three hours gives a yield of about 88 per cent. Hydrochloric acid in the same equivalent concentration appears to be somewhat more efficient as a catalyst than sulphuric acid, but the difference is not important. The dry product is of a waxy consistency and rather hard when cold but is quite fluid at 100° C. It can be readily sulphonated by treating 100 parts of the melted resin with 57 parts of concentrated sulphuric acid and heating at 100° for about one to one and one-half hours, with frequent stirring. During this treatment the resin becomes deep rose red in color at first, somewhat darker at the end of the operation. It yields a sirupy fluid while hot and a hard, tough mass when cold, which readily and completely dissolves in cold water. The leather obtained by the use of this sulphonated resin is, in general, like that obtained with the use of materials similarly prepared from the resins obtained by using ammonia as a condensing agent; that is, more or less pink colored, strong and pliable, but not possessing sufficient weight or "fullness."

When the proportion of formaldehyde is doubled—that is, when equimolecular proportions of phenol and formaldehyde are heated together in a closed vessel in the presence of 25 per cent sulphuric acid, as above described—a white, doughlike mass soon separates out from the solution and on cooling hardens to a brittle, porcelain-like mass. An attempt was made to sulphonate this material, but the same difficulties were encountered as in the previous attempts to sulphonate such resins, namely, a large amount of sulphuric acid was

required, and while much of the material remained unacted upon other portions were more or less carbonized.

(c) **SULPHONATED PHENOL-ACETALDEHYDE RESIN.**—Attempts to condense phenol with acetaldehyde (the latter in the form of its polymer, known as paraldehyde) in the presence of ammonia, as had been done with phenol and formaldehyde, proved unsuccessful. Even at temperatures up to 150 to 155° C. the results were unsatisfactory. Likewise, attempts to condense these reagents in aqueous solution in the presence of a small amount of dilute sulphuric acid, as has been recommended for the condensation of aldehyde with polyhydric phenols (57), were unsuccessful.

On the other hand, when the phenol and paraldehyde are brought together directly, without the use of a solvent, and treated with a very small amount of dilute sulphuric acid (58) better results are obtained. The condensation will take place even at ordinary temperatures, although very slowly. Heating under reflux, at temperatures up to 100° C., appears to be as satisfactory as heating in a closed vessel, so far as the character of the product and the yield are concerned. In most cases, however, the yield of resin obtained is rather low, being generally about 60 to 61 per cent, even after 12 hours heating at 100°, although in one case a yield of 73.4 per cent of the theoretical was obtained. Heating to a higher temperature was not attempted in this reaction. While the condensation product is insoluble in water, the remainder of the reaction mixture can be dissolved out with water or removed by volatilization with steam. The resin is a dark-colored, gummy material, rather stiff and hard at ordinary temperatures, but melting readily when heated on the steam bath. It can be readily sulphonated, after it has been thoroughly dried, by heating with slightly more than the theoretical amount of ordinary concentrated sulphuric acid. The sulphonated product dissolves readily in water, yielding a brownish black, opaque solution, which becomes a deep violet or purple when neutralized with sodium hydroxide. The acid solution strongly precipitates gelatin from its solutions and can convert raw hide into a true leather. This material also possesses considerable filling properties, and, in fact, is the most promising in this respect of all of the sulphonated products thus far prepared in this laboratory.

The entire process of condensation and sulphonation may be illustrated by the following example: Two hundred and seventy-one and six-tenths grams of crystallized phenol were mixed with 69.3 cc of 95 per cent paraldehyde (representing about 1.1 moles of aldehyde to 2 moles of phenol), treated with 2 cc of a 10 per cent solution of sulphuric acid, and then heated for about 15 hours in a tightly stoppered bottle on a steam bath at 95 to 100° C. The reaction mixture was then transferred to a tared beaker with a half liter of water and

placed on the steam bath for evaporation, during which time it was frequently stirred. After evaporating down thus three successive times with fresh portions of water, and then drying in the oven at 100° for about one and one-half to two hours, the resin weighed 188.65 g, or about 61 per cent of the theoretical yield of dihydroxy-diphenylethane. The molten resin was then mixed with 54 cc of 95.75 per cent sulphuric acid added slowly with thorough stirring, and the heating continued at 110° with frequent stirring for one hour. The product was then treated with about one-half liter of water and warmed to dissolve. The bulk of the material dissolved, but about 15 g of material remained undissolved as a pasty mass which hardened on cooling to a brittle solid. The solution was filtered and treated with 15 g of 95 per cent sodium hydroxide to neutralize the unchanged sulphuric acid.

Analysis of this solution by the official method indicated 162 g of tanning material, or approximately 75 per cent of the organic matter present. The solution as prepared above was used directly for tanning. A piece of cowhide tanned with this material in a bath in which the concentration of tanning material was gradually raised in the course of 19 days from 0.25 to about 7 per cent, at the end of 27 days, after being thoroughly washed and then "bleached" and fat liquored in the usual way, yielded a thick, firm leather of a light brownish color, with a tight, smooth grain, and possessing a strength and flexibility equal to that of the ordinary vegetable tanned sole leather. The weight of tanning material fixed by the hide substance, however, was only about 57 per cent of that of the dry, raw hide, as compared with the 140 to 145 per cent which is possible with some vegetable tanning materials; but, as has already been stated in another part of this report, although the manufacturer demands weight in his sole leather, this has no special value to the consumer, provided the same properties can be produced in the leather by other methods. Furthermore, it is also quite possible that the results obtained in the above case could be materially improved upon with further study and with careful control of the manufacturing processes.

5. PRODUCTS DERIVED FROM CRESOL

The cresols can be substituted for phenol in the preparation of synthetic tanning materials by processes such as are described in the preceding pages and in most cases yield similar products, possessing similar tanning properties. In the present work the mixed cresols, obtainable on the market under the name of cresylic acid, were used almost entirely. Since this material contains not only the three isomeric cresols but also higher homologues of phenol, as the xylenols, and possibly also a slight amount of ordinary phenol, it is obvious that the final product obtained after sulphonation and

condensation with aldehyde must necessarily be a very complex mixture; and, furthermore, since the composition of the commercial cresylic acid is more or less variable, according to its source, the conditions of its production, etc., the results obtained therewith would also necessarily be correspondingly variable. The material used in this work was the crude cresylic acid, described as "straw colored," and containing 97 per cent of coal-tar acids and 3 per cent of inert matter.

(a) **SULPHONATED CRESYLIC ACID AND FORMALDEHYDE.**—The cresols, like ordinary phenol, are all readily sulphonated, and the sulphonic acids all readily condense with formaldehyde, either at ordinary temperatures in concentrated solution, or at elevated temperatures in dilute solution. However, when cresylic acid is sulphonated in the ordinary way—that is, by heating with slightly more than the theoretical quantity of concentrated sulphuric acid—there is always a considerable proportion of unsulphonated material present in the reaction mixture, consisting chiefly of the xylenols, and when this sulphonation product is then treated with formaldehyde, either in the cold or at elevated temperatures, a considerable quantity of insoluble solid product is always formed, due to the reaction of the formaldehyde with the unchanged phenolic compounds. This same result was encountered in treating the diluted sulphonation mixture of phenol and sulphuric acid directly with formaldehyde at elevated temperatures, but in that case the amount of solids separating out of the solution generally amounted to only a small percentage of the quantity of phenol taken, whereas in the case of the sulphonated cresylic acid the amount of solids separating out on treatment with formaldehyde sometimes runs up as high as 25 per cent of the weight of cresylic acid taken. There is also a further difference in the behavior of phenol and cresylic acid under these conditions, namely, that in the case of the former the formation of an insoluble condensation product may be avoided even when sulphonation is incomplete, provided the condensation takes place in the concentrated solution, whereas in the case of the sulphonated cresylic acid mixture there is an insoluble precipitate formed under all conditions whether the condensation takes place in dilute or concentrated solution, hot or cold. Of course, the amount of this insoluble product may be decreased by taking a larger excess of sulphuric acid for the sulphonation, or using a stronger acid, such as fuming sulphuric acid, or heating to a higher temperature; but all of these expedients would add more or less to the cost of the manufacture.

The first condensations with cresolsulphonic acid were carried out, not with the crude sulphonation mixture of cresylic acid and sulphuric acid, but with sodium cresolsulphonates, as had been done in the case

of phenolsulphonic acid. In the present case the cresolsulphonates were not pure, but a mixture was used, containing the salts derived from *m*- and *p*-cresols, chiefly the latter. This mixture was obtained by sulphonating cresylic acid by heating it with ordinary concentrated sulphuric acid, pouring the product into water, extracting the aqueous solution with carbon tetrachloride to remove the unsulphonated portion of the cresylic acid, and finally salting out the cresolsulphonic acids with sodium chloride and recrystallizing the sodium cresolsulphonates thus precipitated. In this way the sulphonate derived from *o*-cresol would be eliminated, since this is very soluble, and the product would contain only the other two cresols, especially *p*-cresol.

Twenty-five grams of the dried sodium cresolsulphonates were treated with 42 cc of a solution of hydrochloric acid, containing 0.1033 g HCl per cc, then with 4.45 cc of a 37 per cent solution of formaldehyde (1 mole of aldehyde to 2 moles of sulphonates), and the mixture heated in a tightly stoppered bottle on the steam bath for two hours. On cooling a heavy white precipitate separated out but redissolved again on the addition of cold water. The solution as thus obtained was nearly black in color and resembled in all outward appearances the solution obtained in a similar manner from sodium phenolsulphonate. It required 5.644 g of sodium hydroxide to neutralize the entire solution after the condensation, or about 18.5 per cent more than would have been required for the original hydrochloric acid used. Evidently the cresolsulphonic acids were hydrolyzed to this extent during the reaction with the formaldehyde, just as was the case with the phenolsulphonic acid. The leather produced by this product was also very much like that obtained with the corresponding phenol derivative. It was of a very light color, nearly white, flexible, and very tough, but lacking fullness.

When the proportion of the formaldehyde in the above experiment is doubled—that is, when equimolecular proportions of the aldehyde and sulphonate are used—an insoluble product is formed, just as in the case of phenolsulphonic acid under similar conditions. In this case, however, the product is not gelatinous and more or less transparent, but is opaque, of a greenish color, and earthy character.

Results similar to the above are also obtained when, instead of using sodium cresolsulphonate and hydrochloric acid, we use directly the crude sulphonation product obtained by heating cresylic acid with sulphuric acid, except that in this case, as already mentioned above, a precipitate is obtained, due to presence of unsulphonated phenolic compounds, which is insoluble in water. If the proportion of formaldehyde is intermediate between 1 and 2 molecules of the aldehyde to 2 of the sulphonic acid, we obtain a partly colloidal solution, owing to the formation of more or less of the insoluble condensation product which is kept in suspension by the soluble product, just as

was the case with phenolsulphonic acid under similar conditions. Here, again, we find that the colloidal component of the solution apparently is incapable of combining with hide substance to form leather, since determination of tanning material by the official method shows a smaller amount of material capable of being absorbed by the chromed hide powder in products where the proportion of formaldehyde was considerably in excess of 1 molecule per 2 molecules of the cresolsulphonic acid.

An important difference was noted between the product obtained by condensing sulphonated cresylic acid in dilute, hot solution with formaldehyde and that obtained in a similar way from phenolsulphonic acid. It was repeatedly observed that the former tanned a piece of hide more slowly than the latter. It was also repeatedly observed that in the determination of tanning material in the syntan by the official method it was practically impossible to completely detannize the solution of the syntan derived from cresylic acid. The filtrate from the hide powder always remained faintly acid and always gave more or less precipitate with gelatin solutions, usually a very heavy one. Even a double extraction with hide powder—that is, taking the filtrate from one treatment with hide powder and shaking it with another fresh portion of hide powder—failed to detannize the solution completely or to show a materially larger indicated amount of tanning material. Shaking for one hour with hide powder likewise was unsuccessful; but when a more dilute solution of the syntan was taken (about one-half the concentration called for in the official method), and the quantity of hide powder was simultaneously increased by one-half, and the duration of shaking was increased to six hours, the filtrate was not only neutral to litmus but was of a lighter color than had been obtained from the same preparation on previous occasions and gave no precipitate with gelatin solution. In the last case, also, the amount of tanning material indicated was 75 per cent of the amount of total organic matter present, whereas the official method indicated only about 55 per cent.

Condensation of the sulphonated cresylic acid with formaldehyde in concentrated solution and in the presence of strong sulphuric acid—that is, using the sulphonation mixture directly, without dilution with water, or diluting only very slightly—both at room temperatures (30 to 35° C.) and also without temperature control, was tried. The results were, in general, like those obtained in the condensation of phenolsulphonic acid under similar conditions, except that, whereas the latter under these conditions produced no insoluble products, the sulphonated cresylic acid always gave more or less of a precipitate. The amount of this precipitate was about the same, irrespective of how the condensation was brought about, whether in dilute or concentrated solution, and whether at room temperatures or at elevated

temperatures. This difference is apparently due to the presence in the cresylic acid of xylenols or other higher homologues of phenol which remain largely unchanged in the sulphonation mixture and later unite with the formaldehyde to form the insoluble products.

(b) CRESYLIC ACID-FORMALDEHYDE RESINS, AND THEIR SULPHONATION PRODUCTS.—Cresylic acid may be condensed with formaldehyde in the presence of very small amounts of ammonia (59) in the same manner as phenol, which has already been described in the preceding pages, and a similar product is obtained. This product is also insoluble in water and may be converted by sulphonation into a soluble product which possesses tanning properties. This sulphonation may be accomplished in the same manner as that of the phenol resin. In this case, however, the sulphonation does not appear to take place quite so readily, probably due to the presence here of the xylenols and higher phenols. While a portion of the resin remains unattacked, other portions are oxidized in part, and the product always yields black solutions. The leather produced with these solutions is more or less pinkish in color, soft and spongy, and possessing moderate strength.

Much better results were obtained by condensing cresylic acid with formaldehyde in the presence of dilute sulphuric acid, according to Stiasny's method (60). The condensation product obtained here was very similar to the corresponding phenol derivative obtained under similar conditions. Fifty cubic centimeters of 97 per cent cresylic acid were treated with a solution consisting of 13.6 cc concentrated sulphuric acid (one-half of the weight of cresylic acid) and 18.7 cc of 37.5 per cent formaldehyde solution in 100 cc of water. The above proportions represent 1.1 moles of formaldehyde to 2 moles of cresylic acid. The mixture was heated in a tightly stoppered bottle on a steam bath, with frequent shaking, for two hours. The condensation product separated from the aqueous solution in the form of a soft, thick, "sticky" mass, which was quite fluid while hot, becoming more pasty on cooling. This was removed to a tared beaker, the aqueous layer poured off, and the resin dried by first heating on the steam bath and then for one hour in an oven at 120° C. Fifty-one and nine-tenths grams of a dark reddish, gummy resinous mass were obtained. This was melted and then treated with 28.4 cc of ordinary concentrated sulphuric acid (about 95 per cent), the acid being slowly added with constant stirring. A great deal of heat was evolved, and the mixture became dark colored (nearly black) and opaque. On cooling it formed a hard, horny material. After about one-half hour this was treated with water and warmed to dissolve and the solution filtered. Practically the entire solid had passed into solution. The solution now had an acidity equivalent to 37.5 g of sulphuric acid, whereas the original weight of actual sulphuric

acid used for sulphonation was about 49.65 g, indicating that 24.3 g of sulphuric acid had reacted with the resin. Hence, if we consider the resin to be methylenedicrosol—that is, dimethyldihydroxydiphenylmethane—only about 1.09 moles of sulphuric acid had reacted with 1 mole of the resin.

This product when partially neutralized, produced a leather which was at first of a rather dirty grayish color, but which later turned to a light brown or yellowish brown color. It was fairly thick, tight-grained, firm, pliable, and very strong, and apparently quite permanent. After 16 months it had not lost any of its flexibility and was apparently unchanged. Although tanned in a solution which did not have a concentration of over 3 per cent in tanning material, the leather showed an increase of over 48 per cent on the weight of the dry hide.

An attempt was also made here, as in the case of the phenol-formaldehyde resin, to use the solution of the condensation product of sulphonated cresylic acid and formaldehyde as a dispersing agent for bringing into colloidal solution the resin obtained by condensing cresylic acid with formaldehyde in the presence of ammonia. A similar process is described in the first part of example 15 of United States Patent, 1399510/1921 (46). However, in this case, as in the one previously described under the phenol-formaldehyde resin, very little, if any, of the water insoluble resin was dissolved by the soluble condensation product.

6. PRODUCTS DERIVED FROM THE NAPHTHOLS

α - and β -naphthols were also studied as possible sources of synthetic tanning materials and for this purpose were treated with formaldehyde both in the form of free naphthols as well as in the form of their sulphonic acids. The attempts to prepare tanning materials by first condensing the free naphthols with formaldehyde, however, proved unsuccessful. This was partly because the free naphthols do not condense with formaldehyde as readily as do the cresols and ordinary phenol, at least under certain conditions, and partly also because such products as were obtained were too difficult so sulphonate.

When heated in a closed vessel with equimolecular proportions of formaldehyde, in the presence of very small amounts of ammonia, as was done with both phenol and cresol, very little, if any, condensation was obtained. The products were crystalline, and their melting points were nearly the same as those of the original naphthols. Even in the presence of considerable quantities of 25 per cent sulphuric acid, α -naphthol gave very little evidence of the formation of condensation products. On the other hand, β -naphthol, when heated with formaldehyde in equimolecular proportions in the presence of

25 per cent sulphuric acid, gave a pink or rose colored solid. This probably contains more or less unchanged naphthol, but whereas β -naphthol is readily sulphonated by ordinary concentrated sulphuric acid at 100° C. this red product is only slightly attacked by concentrated sulphuric acid even after prolonged heating at 120 to 130° C.

The condensation of formaldehyde with naphtholsulphonic acid takes place quite readily, both in dilute and concentrated solutions, and in most cases soluble products are obtained which possess tanning properties.

(a) ALPHA-NAPHTHOLSULPHONIC ACIDS AND FORMALDEHYDE.—

When the sulphonation mixture obtained by heating 1 mole of α -naphthol with 1.5 moles sulphuric acid at 60 to 70° C., and containing mainly the monosulphonic acid, is heated in dilute solution with approximately one-half mole formaldehyde, an insoluble condensation product is obtained.

Twenty-five grams of α -naphthol were heated for three hours at 60 to 70° with 15 cc of 93 per cent sulphuric acid, the mixture on cooling was dissolved in 70 cc of water, treated with 7 cc of a 37.5 per cent solution of formaldehyde, and heated in a tightly stoppered bottle on the steam bath, with frequent shaking, for one hour. The formation of the insoluble dark brown product began soon after heating was started, and after cooling 21.5 g of the precipitate were obtained. An attempt was made to further sulphonate this condensation product, but this was unsuccessful.

However, if the sulphonation is carried out at a higher temperature (130 to 140° C.), either with the same or a larger proportion of sulphuric acid, in which case a part or all of the naphthol is converted to a disulphonic acid, and the condensation then carried out as above, a soluble product is obtained. The solution is dark brown or nearly black, and after being partially neutralized can be used for tanning. It produces a dark-colored leather, firm and moderately "filled," but flexible and possessing fair strength.

When the sulphonation was conducted as in the first case mentioned above and the condensation carried out in concentrated solution and at ordinary temperature, a soluble product was again obtained. Twenty-five grams of α -naphthol were heated with 15 cc of 93 per cent sulphuric acid for three hours at 60 to 70° C., the mixture then treated with 10 cc of water (just enough to keep the mixture from solidifying when cold), and 7 cc of 37.5 per cent formaldehyde were slowly added with stirring, while the temperature was kept down by immersing the beaker into a dish of water. The reaction mixture was then allowed to stand over night, after which it was dissolved in 150 cc of water and filtered. Practically all of the solid had gone into solution. This solution was very dark colored and when partially neutralized produced a reddish brown leather,

of fair thickness, firm and flexible, but weak and appearing burned in the interior.

(b) BETA-NAPHTHOLSULPHONIC ACID AND FORMALDEHYDE.—Beta-naphthol is not quite so readily sulphonated as is *α*-naphthol. Even when heated for five hours at 100° C. with twice the theoretical quantity of 93 per cent sulphuric acid, the bulk of it is still in the form of monosulphonic acid. The proportion of sulphuric acid used in sulphonating *β*-naphthol, however, was ordinarily about 1.25 moles per mole of the naphthol. This sulphonation mixture, when treated with formaldehyde, either in dilute solution at elevated temperature or in concentrated solution at ordinary temperature, and whether the molecular proportions of formaldehyde to original naphthol were 1:1 or 1:2, always yielded a soluble product. These solutions were in all cases a very dark brown. The condensations were carried out as already described under *α*-naphthol.

When the condensation was carried out in concentrated solution at ordinary temperature, using 1 molecule of formaldehyde to 2 of naphthol, the product, after being partially neutralized, yielded a brown leather, rather thick and firm, but flexible and possessing great strength. When the condensation was carried out in dilute solution and at 100°, the proportions of reagents being the same, the product produced a leather of a peculiar light pink or reddish color, somewhat thinner than the last one described above, but quite firm and flexible and possessing fair strength. If the condensation is carried out as in the last case, but with double the proportion of formaldehyde, a soluble product is again obtained, whereas with phenol or cresolsulphonic acids, under similar conditions, an insoluble resin was produced. This last solution produces a leather of light brown color which is thin and rather stiff at first, but which is tough and strong and can be worked into a soft pliable condition.

(c) BETA-NAPHTHOLSULPHONIC ACID AND FORMALDEHYDE CONDENSATION PRODUCT WITH OXIDIZING AGENTS.—An attempt was also made here to make use of the principle claimed in certain patents (61) for improving the tanning qualities of syntans by treating them with various oxidizing agents. In these experiments *β*-naphtholsulphonic acid containing excess of sulphuric acid was condensed with formaldehyde in the proportion of 1 molecule of the latter to 2 of original naphthol by heating in dilute solution at 100° C. The oxidizing agents used were nitric acid, chromic acid, and hydrogen peroxide.

When nitric acid was used as the oxidizing agent, the solution of condensation product was always first diluted to a concentration of about 12 to 15 per cent (calculated as naphtholsulphonic acid), and the nitric acid was then added to the solution heated on the steam bath. The heating was then continued for several hours after all

nitric acid had been added. A small amount of a rather light yellow insoluble solid was always formed, and more or less unchanged nitric acid always remained in the final solution, depending upon the proportion of nitric acid originally taken. When the proportion of nitric acid was 0.45 mole per molecule of original naphthol, about 4.2 per cent of the nitric acid taken remained unchanged. This solution, after being neutralized to the correct acidity, yielded a brown leather which was unusually firm, but flexible and very strong, whereas without the nitric acid treatment a pink and somewhat more flexible leather was obtained. The treatment with nitric acid, however, did not appear to give the syntan greater filling qualities as had been expected, although this was not determined quantitatively. When the proportion of nitric acid used was 1.1 moles per molecule of original naphthol, the other conditions being the same as in the last case, about 3.9 per cent of the original nitric acid remained unchanged. In other words, the final solution contained about twice as much unchanged nitric acid as before. This solution after partial neutralization produced a dark and very hard and stiff leather which was short fibered and weak and which broke on bending.

When chromic anhydride was used as the oxidizing agent, in the proportion of one molecule per molecule of original naphthol, the chromium being then removed by adding sodium hydroxide and filtering, the product yielded a brown leather of very good appearance, unusually firm but flexible, tough and strong, although still lacking the "fullness" desired in heavy leathers.

Using hydrogen peroxide as the oxidizing agent, the other conditions being the same as before, a product was obtained which produced a very dark, reddish brown leather which was rather thin, very hard, stiff, short fibred and weak, and broke on bending.

7. NONSULPHONATED DERIVATIVES OF POLYHYDRIC PHENOLS

All of the products described thus far in the present report have been sulphonated, chiefly to make them soluble, although it is also possible that to a certain extent the tanning properties of the products may be dependent upon the sulphonic acid groups in the molecule. However, this group or any other strongly acidic group is not necessary to confer tanning properties upon the condensation products of aldehydes with other compounds, as will be shown in the following pages. It has been shown (62) that water soluble condensation products can be obtained from aldehydes and polyhydric phenols, which possess tanning properties, although they are not sulphonated. Indeed, some of these products appear to be superior to sulphonated products, not only in the fact that they contain neither any strongly acidic group nor a group which is capable by hydrolysis

of giving rise to any product, such as sulphuric acid, which would have a highly destructive action on leather, but also in possessing filling qualities to a greater degree than any sulphonated products encountered in the course of the present investigation.

(a) RESORCINOL AND FORMALDEHYDE.—Resorcinol will condense readily with formaldehyde on heating to about 100° C., especially in the presence of acids, even though these are present only in traces. In fact, in the presence of acids, the reaction will take place at ordinary temperatures, although, of course, more slowly than at an elevated temperature, but the temperature will rise spontaneously, due to the heat of reaction, thus increasing the rate of reaction until the latter is complete. If the proportions of reagents are 2 moles of resorcinol to 1 of the aldehyde, an amber-colored, sirupy, water soluble product is obtained. If the proportion of aldehyde considerably exceeds that given above, there will be formed more or less of an insoluble product.

Seventy grams of crystallized resorcinol were dissolved in 35 cc of water by warming and the solution then cooled to room temperature. Then 25.6 cc of a 37.5 per cent solution of formaldehyde (representing 1.1 moles per 2 moles of resorcinol) were added, together with five drops of a 10 per cent solution of sulphuric acid, and the temperature of the solution was slowly raised by heating on a steam bath. When the temperature reached approximately 70° C., a violent reaction set in, the temperature rising spontaneously to the boiling point of the solution. The heating was then continued for about half an hour.

The amber-colored sirup dissolves readily in water, and the resulting solution may be used for tanning directly, without the addition of any acid or other reagent. In fact, it appears to be able to tan raw hide with equal facility whether the solution is neutral or slightly acid, or even slightly alkaline, although the resulting leather appears to be firmer in neutral or feebly acid solution than in the alkaline solution. The finished leather is of a pale pinkish or lavender color when freshly prepared, but turns gradually to a light brown. It is moderately firm but not hard, very flexible, and stronger than vegetable-tanned leather. A piece of leather prepared in a tanning bath containing not more than 2.75 per cent of the tanning material obtained in the manner just described contained an amount of fixed tanning material equal to 79.8 per cent of the weight of the dry raw hide. If the solution is allowed to stand for a long time in contact with air, it becomes somewhat darker in color, and the leather prepared therefrom is also slightly more highly colored, but in other respects the results are the same as with the fresh solution. Otherwise the solution appears to be entirely stable.

(b) RESORCINOL AND ACETALDEHYDE.—Acetaldehyde (in the form of the polymer, paraldehyde) may be substituted for formaldehyde

in the above-described experiment, and the results obtained are practically the same. Twenty grams of crystallized resorcinol and 4 cc of 95 per cent paraldehyde were heated together in an open flask on a steam bath for two hours. No water or acid was added, but it was found advantageous during the heating to add a few cubic centimeters of alcohol to aid in dissolving the resorcinol. When cooled, a thick, sirupy mass of pale amber color was obtained, which dissolved readily and completely in water. The solution, strongly precipitates gelatin from its solutions and tans raw hide in the same way as the resorcinol-formaldehyde condensation product described above; in fact, the two leathers produced by these two products are practically indistinguishable from each other.

(c) RESORCINOL AND FURFUROL.—Furfurol does not react as readily with resorcinol as do the other two aldehydes used, and the problem of preparing condensation products from furfurol is also complicated by the fact that it is less stable than formaldehyde or paraldehyde. Nevertheless, under the proper conditions it can be made to react with resorcinol and will yield a product possessing similar tanning properties.

When 2 moles of resorcinol and 1 mole of furfurol are heated together at 100° C., without the addition of any solvent or other agent, the mixture gradually becomes dark colored and finally black. If cooled after being heated for a half hour, almost the entire mixture becomes a solid mass of long, slender crystals. Further heating for an hour produces no apparent change. The product dissolves in a small amount of water to a dark solution, which becomes clouded on the addition of a larger amount of water but again clears up on further dilution. Distillation of this solution shows the presence of a large proportion of unchanged furfurol; in fact, in the first fraction of the distillate a portion of the furforol separates out from the aqueous solution. Evidently there has been very little, if any, reaction between the furfurol and resorcinol.

In the presence of acids, however, there is considerably more action. Ten grams of resorcinol were dissolved in 23 cc of water with the addition of 4.5 cc of a 25 per cent solution of sulphuric acid. To this solution were added 3.8 cc of furfurol (specific gravity, 1.1515), representing 1 mole for 2 moles of resorcinol. In a few minutes the solution began to take on a deep green color, which later changed to a deep purple. After having been allowed to stand at ordinary temperature for 48 hours the solution had become black in color and had deposited a large proportion of a thick, black, gummy mass which was insoluble in either cold or hot water. The solution which was filtered off from this black pitch was green in color, and was capable of precipitating gelatin from its solutions, but the bulk of the original materials was in the form of the black pitch.

If a mixture of 10 g of resorcinol and 3.8 cc of furfural is warmed until melted into a homogenous liquid and then treated, while hot, with three drops of a 10 per cent solution of sulphuric acid, an intense blue color is immediately formed, which on further heating changes to a dark green. After heating thus on the steam bath for half an hour and then cooling a dark, stiff, pasty mass is obtained, which on warming with water yields a dark, brownish solution and a black, insoluble tar. The aqueous solution strongly precipitates gelatin and is capable of converting hide into a true, permanent leather of a pinkish, gray color, smooth grain, soft and tough. The solution on further standing slowly deposits additional small quantities of the black tarry product.

Better results are obtained when the furfural and acid are added to a cold solution of resorcinol and the temperature slowly raised. Ten grams of resorcinol were dissolved in 5 cc of water by warming, and the solution was then cooled to room temperature. Three and eight-tenths cubic centimeters of furfural were now added along with one drop of a 10 per cent solution of sulphuric acid and the mixture slowly warmed on the steam bath. The original orange color gave place, first, to a dark green, then to a dark, yellowish brown. After heating for about 20 minutes and cooling a dark brown, viscous, sirupy liquid is obtained, which dissolves readily and completely in cold water. This solution also deposits a small amount of a black tar, on prolonged standing, but the bulk of the material remains in solution apparently indefinitely. If the black tar is allowed to deposit on the leather during tanning, it will naturally color the leather black; but the tar can be readily removed by washing with alcohol.

(d) PYROGALLOL AND FORMALDEHYDE.—Pyrogallol condenses with formaldehyde in the presence of very small amounts of acids in much the same way as does resorcinol and with similar results. Ten grams of crystallized pyrogallol were dissolved by warming with 5 cc of water, and the solution was cooled; then added 2.95 cc of a 37.5 per cent solution of formaldehyde (1.013 moles per 2 moles of pyrogallol), and finally two drops of a 10 per cent solution of sulphuric acid. The mixture was heated in a closed bottle for one and one-half hours on the steam bath. Except for a slight darkening of the solution there was no apparant change. On cooling a white, amorphous solid separated out, the entire contents of the bottle becoming practically solid. This material dissolves in cold water rather slowly but dissolves readily on warming. The solution thus obtained strongly precipitates gelatin and tans hide in very much the same way and under the same conditions as does the resorcinol-formaldehyde condensation product. The leather produced is also similar to that obtained with the latter solution but somewhat darker in color, being a dark brown.

(e) **PYROGALLOL AND ACETALDEHYDE.**—Acetaldehyde (in the form of paraldehyde) and pyrogallol will react with each other, both in the absence and presence of acids, to yield a water soluble condensation product which possesses tanning properties. Twenty grams of crystallized pyrogallol, 10 cc of water, and 3.5 cc of 95 per cent paraldehyde were heated together on the steam bath for about an hour. An amber-colored, sirupy liquid was obtained, which dissolved readily and completely in water. The solution thus obtained precipitates gelatin.

The same experiment was repeated, but with the addition of six drops of a 10 per cent solution of sulphuric acid. The results were exactly like those obtained in the last experiment. The product produces a rather soft, very pliable and tough leather, which is brown on the grain side but orange-colored in the interior. An interesting observation made in connection with this product is the fact that hide which has been treated with it is colored an intense indigo blue by indigotin solution, even on the outer surface, which is ordinarily taken as an indication of the absence of tanning. However, neither washing with cold water nor treatment with a hot fat liquor at 65° C. succeeds in reproducing the raw hide, although the latter treatment does produce a marked shrinkage of the product.

VI. SUMMARY AND CONCLUSIONS

A study was made of the tanning properties of the sulphonated condensation products of the simple aromatic hydrocarbons (benzene, toluene, naphthalene) and the corresponding monohydroxy phenols with aldehydes, particularly formaldehyde, and to some extent with acetaldehyde and furfural, as well as a few condensation products obtained from sulphonic acids by mere application of heat, or from the condensation of polyhydroxy phenols with aldehydes without sulphonation. The sulphonated condensation products were prepared, in general, either by first condensing the aromatic compound with the aldehyde and then sulphonating the resulting resin, or by first sulphonating the aromatic hydrocarbon or phenol and then condensing the sulphonic acid with the aldehyde.

The simple sulphonic acids of the aromatic hydrocarbons or of the corresponding phenols, as far as studied in this investigation, possess no tanning properties.

The sulphonated condensation products derived from the hydrocarbons (containing no phenolic groups) were found to be generally unsatisfactory as tanning agents. The resins obtained by condensing naphthalene or toluene with formaldehyde were found to be too difficult of sulphonation by direct treatment with concentrated sulphuric acid, and the condensation products of the sulphonic acids of toluene or naphthalene with formaldehyde were found to possess

only inferior tanning properties, if any, and when applied to hide produced a very thin, hard, and stiff product which possessed little or no resemblance to ordinary leather.

The products obtained by condensing the sulphonic acids of the monohydroxy phenols with formaldehyde possess true tanning properties and are capable of producing leathers of light weight, which are soft, pliable, and very strong, but such tanning materials are not suitable for the production of heavy leathers when used independently of other tanning materials, since they lack the necessary filling qualities. These condensations can be carried out either in dilute solutions at elevated temperatures, or in concentrated solutions with or without cooling. When the phenol or cresolsulphonic acids are condensed with formaldehyde in dilute, hot solutions, the resulting syntan produces a nearly white leather, but if the condensation is carried out in concentrated solution the product is more or less highly colored (rose red) and colors the leather correspondingly. The syntans derived from the naphtholsulphonic acids always produce dark-colored leathers.

The phenol or cresol formaldehyde resins, if not too highly condensed, can be readily sulphonated by means of concentrated sulphuric acid, but this operation requires greater care and skill than the sulphonation of the original phenol or cresylic acid in order to obtain complete sulphonation without carbonization. These sulphonation products are also good tanning agents, and while they generally color the leather more or less they also possess better filling properties than the last-mentioned group.

Formaldehyde was replaced by acetaldehyde in a sulphonated phenol-aldehyde resin with good results as regards the tanning properties of the product. In fact, this particular product was the most promising of all the sulphonated products encountered thus far in the present investigation, so far as their filling properties are concerned, but the yield of condensation product was low.

Very interesting nonsulphonated condensation products possessing tanning properties may be obtained from resorcinol or pyrogallol by condensation with formaldehyde or acetaldehyde. These were found to possess filling properties to a greater degree than any of the sulphonated products described and, in general, are capable of producing a very good quality of leather for some purposes.

The experience gained in this study of synthetic tanning materials has been such as to encourage the belief that such materials can be produced which are not only suitable for use in connection with other tanning materials but which are capable of producing a good quality of leather for certain purposes without the aid of any other tanning materials. This applies particularly to the production of light leathers, in which case there is a possibility of replacing chromium,

if not other tanning materials, for tanning purposes, but there is also reason to believe that it may be possible to develop similar materials which are capable of producing leathers which are suitable for soles.

Further work is necessary to determine the value as well as the best methods of manufacturing and utilizing syntans of this type, and work along these lines is in progress.

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