Our invention relates to sulphonated compounds for tanning leather, and in particular to tanning compounds prepared by treating monohydric phenolic bodies with aldehydes containing one or more carbon atoms under certain conditions, and then sulphonating the material thus formed so that a soluble sulphonic acid compound is formed. The term, phenolic body is used herein to refer to the monohydroxy aromatic compounds in which the hydroxyl group is attached directly to a ring carbon atom, and includes not only phenol but also related compounds having one or more than one closed chain or benzene radical.

It is desirable to have a material that will tan hides to a white or light color in a shorter time and with a less expenditure of tanning material than that required with the commonly used tanning materials. When a vegetable tan is used, the tanning of the light weight leathers usually requires two to four days, while heavy leathers usually require four weeks or more. The tanning solutions must be discarded while they still contain approximately 12% of the original tanning material. Various synthetic tanning materials are known which require less time than the vegetable materials, but these materials frequently make yellowish or brownish leathers and such leathers often have a horny or "tinny" feel and do not have the full body that is required in commercial leathers.

We have discovered a group of excellent tanning materials which complete this action in one-half to one-fourth the time required by vegetable materials. Solutions of these materials can be used until the tanning material is practically completely consumed because even the dilute solutions have the desired rapid action on skins. The leathers tanned with these materials are light colored. The lighter skins such as sheep and calf can be tanned to a white or nearly white color and they have a good full body and a soft silky feel.

Broadly our process consists in using amounts of the phenolic body and aldehyde such that more than one phenolic radical is present and capable of condensing with an aldehyde radical; carrying out the reaction in the presence of a condensing agent; and then sulphonating; the condensation product may be carried out in the presence of a small amount of acid but larger amounts of acid may be present. The entire process is preferably carried out at temperatures between 45° and 55° C. but temperatures between 40° and 65° can be used in the process without seriously affecting the properties of the products. Phenol or cresols and paraaldehyde or acetaldehyde in proportions such that two phenol radicals will combine with one aldehyde radical are preferred, but the other phenolic bodies and aldehydes of higher and lower molecular weight may be used in equivalent proportions.

We have prepared a tanning material by pouring it into 100 parts of phenol to which has been added 0.25 parts of concentrated sulphuric acid and then slowly adding 23.4 parts of paraaldehyde. The mixture was stirred and maintained at a temperature of 45° to 55° C. for about two hours or until the reaction was complete.

This product was then sulphonated by pouring it into 100 parts of concentrated sulphuric acid maintaining the temperature of the mixture between 45° and 55° C. The mixture was stirred at this temperature until the sulphonated product was soluble or until the sulphonation was complete and it was then diluted with water and the uncombined sulphuric acid neutralized. The sulphonated product is itself an acidic material. A product prepared as described is preferred for making most tanning baths on account of its degree of acidity and because the alkali sulphonate is useful for plumping the leather, but solutions of less or greater acidity will tan hides satisfactorily and may be prepared accordingly for special purposes.

It is not necessary to complete the condensation before sulphonating. We have mixed phenol and paraaldehyde in the proportions given in the above example and before the reaction was complete, poured the mixture with stirring into the above named excess of concentrated sulphuric acid at a rate such that the temperature was maintained at 45° to 55° C. When the condensation and sulphonation were complete the mixture was diluted and the excess of sulphuric acid was neutralized.

The product is a water soluble material and usually forms clear slightly yellow solutions. The solution may be used alone for making baths for tanning hides or it may be
used in conjunction with other tanning materials. Most of the lighter hides come out white when tanned in a bath made solely of a solution of this material but some of the heavier hides are slightly colored, depending upon the nature of the hide.

A temperature of 40° to 65° C. should not be departed from in preparing the material and the best products are made at temperatures of 45° to 55° C. Temperatures materially below 40° to 45° C. make a crystalline product that sulphonates with difficulty, and temperatures materially above 65° C. form materials that color the leather. When the material is sulphonated by pouring the product obtained by mixing the phenolic body and aldehyde into the acid, the mixture is liquid permitting efficient temperature control, and the sulphonated product makes light colored leathers, but when the acid is added to the condensed product the mixture becomes pasty, the sulphonation is difficult to control due to local overheating, and the sulphonated product makes dark colored leather.

The higher molecular weight phenolic bodies such as the cresols, xylanols and naphthols tend to make a material that colors the leather. When the product is made of such materials or when such materials are present, we carry out one or more of the steps of the process in the presence of a small amount of zinc. Other means for producing nascent hydrogen, such as the presence of an amalgam or electrolysis, will also diminish the coloring properties of the material. The reducing agent may be and is preferably used in making all of these tanning materials as there is a tendency to form products that color the leather slightly, but it is sometimes not necessary to use the zinc in order to make a satisfactory product when paraaldehyde and phenol are used and when the temperature is closely controlled. The zinc may be added during the condensation, during the sulphonation or after the sulphonated compound is formed but we prefer to have the zinc present during the sulphonation. The addition of 1 to 4 parts of zinc per 100 parts of the phenolic body is usually sufficient to make a light colored tanning material.

We claim as our invention:

1. The process of making a tanning material which comprises condensing a phenolic body containing one hydroxyl group and an aldehyde containing one or more carbon atoms at a temperature of 40° to 65° C. in the presence of a small amount of a condensing agent and adding the condensed material to an excess of sulphuric acid at said temperature to form a soluble product.

2. The process of making a tanning material which comprises condensing a phenolic body containing one hydroxyl group and an aldehyde containing one or more carbon atoms at a temperature of 40° to 65° C. in the presence of a small amount of a condensing agent and adding the condensed material to an excess of sulphuric acid at said temperature to form a soluble product.

3. The process of making a tanning material which comprises condensing a phenolic body containing one hydroxyl group and an aldehyde containing one or more carbon atoms at a temperature of 40° to 65° C. in the presence of a small amount of a condensing agent and adding the condensed material to an excess of sulphuric acid at said temperature to form a soluble product, one or more of the steps being carried out in the presence of a small amount of nascent hydrogen.

4. The process of making a tanning material which comprises condensing a phenolic body containing one hydroxyl group and an aldehyde containing one or more carbon atoms at a temperature of 40° to 65° C. in the presence of a small amount of a condensing agent and adding the condensed material to an excess of sulphuric acid at said temperature to form a soluble product, one or more of the steps being carried out in the presence of a small amount of zinc.

5. The process of making a tanning material which comprises condensing a phenolic body containing one hydroxyl group and an aldehyde containing one or more carbon atoms at a temperature of 40° to 65° C. in the presence of a small amount of a condensing agent, adding the condensed material to an excess of sulphuric acid at said temperature to form a soluble product, the sulphonation being carried out in the presence of a small amount of zinc.

6. The process of making a tanning material which comprises reacting a phenolic body containing one hydroxyl group and an aldehyde containing one or more carbon atoms in the presence of a small amount of a condensing agent at a temperature of 40° to 65° C., the proportion of phenolic body to aldehyde being substantially two phenol radicals to each aldehyde radical and then sulphonating the product of condensation by adding the same to an excess of sulphuric acid.

7. In the process of making a tanning material which comprises condensing an amount of a phenolic body containing one hydroxyl group and an aldehyde containing one or more carbon atoms so that one aldehyde radical is linked with more than one phenol radical and then sulphonating the material, the step consisting of adding the condensed material to an excess of sulphuric acid for sulphonating the condensed compound whilst the reaction mixture is maintained at 40° to 65° C.

8. In the process of making a tanning material which comprises condensing an amount
of a phenolic body containing one hydroxyl group and an aldehyde containing one or more carbon atoms so that one aldehyde radical is linked with two phenol radicals and then sulphonating the material, the step consisting of adding the condensed material to an excess of sulphuric acid for sulphonating the condensed compound whilst the reaction mixture is maintained at 40° to 65° C.

2. The sulphonated condensation product which forms an almost colorless solution in water and which tans skins and hides giving white or nearly white leather, obtainable when a monohydroxy aromatic hydrocarbon containing one or more benzene radicals is condensed with an aldehyde containing one or more carbon atoms in the proportion of one aldehyde radical to two hydroxyl compound radicals and the condensation product is sulphonated, the condensing and sulphonating being carried out at 40° to 65° C.

10. The sulphonated condensation product which forms an almost colorless solution in water and which tans hides giving light colored leather, obtainable by treating 100 parts phenol and a small amount of sulphuric acid with 25.4 parts of paraaldehyde at a temperature of 40° to 65° C. to form a condensation product, pouring the condensation product into an excess of concentrated sulphuric acid while maintaining the reaction mixture at 40° to 65° C. and then neutralizing the excess of free acid.

11. The process of making a tanning material which comprises adding a phenolic body containing one hydroxyl group and an aldehyde containing one or more carbon atoms to an excess of sulphuric acid and maintaining the temperature between 40° and 65° C.

In testimony whereof, we affix our signatures.

CLARENCE J. HERRLY.
A. MARSHALL MATHESON.