The present invention relates to the production of synthetic tanning agents.

I have found that a new group of valuable synthetic tanning agents can be obtained by condensing a methylol compound of a monohydric phenol with resorcinol at a temperature below 50°C. in the presence of water and, preferably, of small amounts of a condensing agent either of acid or alkaline nature. The amount of condensing agent to be employed varies with the temperature employed, smaller amounts being employed on working at a higher temperature whereas on working at a lower temperature the amount of condensing agent can be increased without producing water-insoluble products. The products obtained according to this invention have very good tanning properties and differ from most of the artificial tanning materials hitherto known, by the absence of the sulfite group.

The methylol compounds of a monohydric phenol employed as initial materials may be prepared in any convenient manner, for example, according to the particulars given in the U.S.A. Patents Nos. 626,786 and 568,975, by condensing a monohydric phenol of the benzene series with formaldehyde in the presence of neutral or alkaline condensing agents; thus, for instance, an aqueous solution containing up to 5 or 6 molecular proportions of formaldehyde may be allowed to act upon 1 molecular proportion of phenol. According to the process of the present invention the methylol compounds of a monohydric phenol obtained by a process of this kind need not be isolated from the aqueous solution as the solution may be brought directly into reaction with resorcinol. The amount of resorcinol to be employed per each molecular proportion of the methylol compound of a monohydric phenol is preferably chosen so as to be sufficient to provide 1 molecular proportion of resorcinol for each methylol group present in the phenol alcohol, but it may also be smaller.

This method of operation furnishes a variety of products which, according to the nature and amount of the initial materials, depending, for example, on the amount of the resorcinol on the one hand and on the amount of formaldehyde employed in the preparation of the methylol compound of a monohydric phenol on the other hand, differ among themselves by the degree of their solubility in water. The tanning agents prepared with larger amounts of resorcinol and with methylol compounds of a monohydric phenol which are richer in methylol groups, are readily soluble in water, and produce a light coloured leather of good body and in a high yield, which is practically equivalent to that obtained with the aid of weight-giving vegetable tanning extracts. The tanning agents prepared from smaller quantities of resorcinol and from methylol compounds of a monohydric phenol with fewer methylol groups are less soluble in water and are comparable with the sparingly soluble quebracho extract. The last-named condensation products in particular are preferably employed for tanning in the presence of the well known dispersive-sulfonic acids, such as aromatic sulfonylic acids of high molecular weight or condensation products of sulfonic acids with formaldehyde and the like, which may also possess tanning properties, in which case also a firm, compact and weighty leather of excellent character is produced. The new tanning agents may also be used, with advantage, in admixture with other tanning or non-tanning substances usually employed in tanning processes, such as vegetable tanning agents, fillers or buffer substances.

The following examples further illustrate the nature of this invention which however is not restricted thereto. The terms “parts by weight” and “parts by volume” as herein-after used, are to mean for instance metric tons and cubic meters, or kilograms and liters respectively.

**Example 1**

A solution of 94 parts by weight of phenol in 400 parts by volume of a 10 per cent solution of caustic soda, is treated with 220 parts by weight of a 30 per cent aqueous solution of formaldehyde, and diluted with water to make 1100 parts by volume. After standing for several days, during which time the form...
aldehyde disappears, the solution is exactly neutralized with dilute sulfuric acid, whereupon a solution of 220 parts by weight of resorcinol in 280 parts by weight of water and 10 parts by volume of concentrated hydrochloric acid is added. After again standing for several days, the water is driven off to a large extent by moderate heating in vacuo, the reaction product separating out in the form of a pale reddish-yellow, wax-like mass, which is only partially soluble in water.

400 parts by weight of this substance are next triturated with 800 parts by weight of a 50 per cent aqueous solution of the sulfonic acid, obtained in accordance with the Example 1 of U. S. Patent No. 1,557,844 and bleached in the manner described. The resulting viscous paste can be diluted with water in any proportions and, when employed for tanning, produces a pale yellow-brown leather of good body which is satisfactorily compact and weighty. The analysis of the tanning agents by the agitation method shows an increase of 110 per cent of tanning agent calculated on the content of the sulfonic acid in the tanning matter.

**Example 2**

A solution of 94 parts by weight of phenol in 400 parts by volume of a 10 per cent caustic soda solution, is treated with 330 parts by weight of a 30 per cent aqueous solution of formaldehyde, and diluted to 1200 parts by volume with water, and after standing for several days, is neutralized with dilute sulfuric acid. It is then treated with an additional 530 parts by weight of resorcinol, dissolved in 400 parts by weight of water and 10 parts by volume of concentrated hydrochloric acid; after standing again for several days, most of the water is eliminated in vacuo and a product similar in character to that described in Example 1 is obtained.

Triturating 400 parts by weight of this substance with 1200 parts by weight of the not wholly neutralized sulfonic acid prepared in accordance with Example 1 of U. S. Patent No. 1,237,405 results in the formation of a syrupy mass, which is readily soluble in water and, when employed for tanning, produces a light reddish leather of good body which is firm and compact and weighty. The analysis of the tanning agent by the method of agitating with hide powder shows an increase of 54 per cent of tanning agent calculated on the content of the sulfonic acid in the tanning matter.

In the place of hydrochloric acid, sulfuric or acetic acid or acid sodium sulfate or sodium hydroxide can be employed as condensing agent.

**Example 3**

158 parts by weight of finely powdered barium hydroxid are introduced into a solution of 94 parts by weight of phenol in 600 parts by weight of 30 per cent aqueous solution of formaldehyde. After standing for several days, the barium hydroxide is precipitated by a current of carbon dioxide, the deposited barium carbonate is filtered off, and the filtrate is treated with a solution of 550 parts by weight of resorcinol in 600 parts of water and 10 parts by volume of concentrated hydrochloric acid. After again standing for several days, the solution is concentrated in vacuo to the consistency of a tanning extract, a pale reddish syrupy mass being obtained which can be readily diluted with water. The tanning analysis, by the filtration method, of a product with a density of about 92° Bé., shows tanning matter 50.4 per cent, non-tanning matter 15.6 per cent; insolubles in water 6.2 per cent. When used for tanning, a pale reddish leather of good body is obtained in a high yield.

What I claim is:

1. The process of producing water soluble synthetic tanning agents which comprises condensing a methyol compound of a monohydric phenol with resorcinol at a temperature below 50° C. in the presence of water and of a small amount of a condensing agent.

2. The process of producing water soluble synthetic tanning agents which comprises condensing an aqueous solution of a methyol compound of a monohydric phenol with resorcinol at a temperature below 50° C. and in the presence of water and of a small amount of a condensing agent.

3. The process of producing water soluble synthetic tanning agents which comprises condensing at a temperature below 50° C. and in the presence of water and of a small amount of a condensing agent a methyol compound of a monohydric phenol with an amount of up to one molecular proportion of resorcinol per each methyol group contained in the aforesaid methyol compound.

4. The process of producing water soluble synthetic tanning agents which comprises condensing at a temperature below 50° C. and in the presence of water and of a small amount of an acid condensing agent a methyol compound of a monohydric phenol with an amount of up to one molecular proportion of resorcinol per each methyol group present in the aforesaid methyol compound.

5. The process of producing water soluble synthetic tanning agents which comprises condensing at a temperature below 50° C. and in the presence of water and of a small amount of a condensing agent a methyol compound of phenol with an amount of up to one molecular proportion of resorcinol per each methyol group present in the aforesaid methyol compound.

6. As new articles of manufacture synthetic tanning agents comprising a water soluble...
condensation product of a methylol compound of a monohydric phenol with resorcinol.

7. As new articles of manufacture synthetic tanning agents comprising a water soluble condensation product of a methylol compound of a monohydric phenol with an amount of up to one molecular proportion of resorcinol per each methylol group present in the aforesaid methylol compound.

8. As new articles of manufacture synthetic tanning agents comprising a water soluble condensation product of a methylol compound of a monohydric phenol with resorcinol and an organic sulfonic acid possessing dispersive properties.

9. As new articles of manufacture synthetic tanning agents comprising a water soluble condensation product of a methylol compound of a monohydric phenol with resorcinol and an organic sulfonic acid possessing dispersive and tanning properties.

In testimony whereof I have hereunto set my hand.

HERMANN SCHUETTE.