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PROCESS OF MAKING LIGHT COLORED AND LIGHT STABLE PHENOLIC SYNTANS

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This invention relates to synthetic phenolic tanning agents and more particularly, to phenolic syntans which are relatively light in color and/or which are stable against discoloration upon storage under normal conditions.

A number of different types of synthetic tannins have in the past been derived from phenol. These agents have met with considerable success in tanning processes where they have been used either alone or in combination with other tanning agents such as vegetable tannins, mineral tans, and the like. Two of the most widely used phenolic syntan products are the nuclearly sulfonated phenol-formaldehyde resins and the condensation products of phenol and formaldehyde with an alkaline salt of sulfurous acid. One great disadvantage in the use of these products for tanning skins and hides, however, has been their initial dark color and their tendency to darken upon standing under normal conditions of storage. Thus, an unattractive commercial product which will rapidly darken on the shelf of either the supplier or the ultimate consumer, i. e., the tanner, has been offered. Moreover, the deep color of these phenolic syntans is in part transferred to the tanned leather so that a discolored leather, usually pink darkening to red during tanning, is obtained.

Attempts to remedy this situation have resulted in the development of initially light colored phenolic syntans, some of which are stable against discoloration. Phenol-acetaldehyde condensation products and formaldehyde condensation products of sulfones such as dihydroxy diphenyl sulfone are examples of such syntans. These products, however, possess certain disadvantages including increased costs which have made it desirable to turn back to the sulfonated and sulfited phenol-formaldehyde syntans.

I have discovered, as described in my copending application entitled "Light Stable Phenolic Syntans," Serial No. 109,428 filed August 9, 1949, now U. S. Patent No. 2,592,587 issued April 15, 1952 that admixture of a very small amount of a vegetable tannin with a normally light unstable phenolic syntan will prevent formation of color in the syntan solutions upon storage and the so-stabilized syntans, either before or after storage, will produce uniformly light colored tanned leather although they themselves are generally relatively dark in color.

It is an object of the present invention to provide a phenolic syntan which is itself light in color.

It is another object of the present invention

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to provide a phenolic syntan which is light in color and which is stable against discoloration upon storage under normal conditions.

A further object of the present invention is to so modify a phenolic syntan which discolors upon storage under normal conditions that it will become stable against such discoloration.

Another object of the present invention is the stabilization of a nuclearly sulfonated condensation product of phenol and formaldehyde against discoloration upon storage under normal conditions.

Still another object of the present invention is the stabilization of a phenolic syntan which is a condensation product of phenol, formaldehyde and an alkaline salt of sulfurous acid against discoloration upon storage under normal conditions.

It is a further object of the present invention to prepare a sulfited phenol-formaldehyde syntan which is light in color.

The above and other objects are attained by providing a phenolic syntan containing a quantity of free SO_2. The free SO_2 may be present throughout the preparation of the syntan in which case a light colored and light stable product is obtained, or it may be added after preparation of the phenolic syntan in which case a product which may or may not be light colored initially but which is stable against discoloration upon storage under normal conditions is obtained.

The invention will be described in greater detail in conjunction with the following specific examples in which proportions are given in parts by weight. It should be understood that the examples are given for purposes of illustration and the scope of the invention is not to be measured by the details therein set forth.

Example 1

(1) 107 parts (1.0 mol) of phenol containing 12% water
(2) 44.6 parts (0.55 mol) of 37% aqueous formaldehyde
(3) 28.5 parts (0.15 mol) of sodium metabisulfite
(4) 28.4 parts (0.35 mol) of 37% aqueous formaldehyde
(5) 12.9 parts (0.22 mol) of 68% aqueous sodium hydroxide

Mol ratio (4)/SO_2—1.17
Free SO_2—3.9 parts per thousand

(1) and (2) are heated together in the presence of 5.2 parts of 10% aqueous hydrochloric acid, (3) and (4) and (5) are then added and the con-

densation is continued by heating at 90° C. for about 15–18 hours. The alkaline syntan is then neutralized with sulfuric acid to a pH of 5 to 7, followed by addition of acetic acid equivalent to 4% of its final weight. The syntan is then diluted with water to a concentration of 30% active solids by weight, "active solids" including the phenol, the methylene group from the formaldehyde, and the SO_3 group from the sulfite.

The syntan so produced is orange yellow in color and it remains orange yellow upon standing. Leather produced therewith is soft, full and white.

Example 2

The procedure of Example 1 is repeated using varying proportions of the reactants and, in one case, sodium sulfite in place of sodium metabisulfite with alkali. Results are as follows:

Phenol mols	CH_2O(2) mols	$Na_2S_2O_5$ mols	CH_2O(4) mols	NaOH mols	Mol ratio (4)/SO_2	Free SO_2 pts./th.
1.0	0.55	0.4 (Na_2SO_3)	0.54	------	1.33	5.2
1.0	0.55	0.2	0.485	0.119	1.21	4.3
1.0	0.55	0.3	0.70	0.175	1.17	3.1
1.0	0.55	0.2	0.585	0.119	1.46	1.0
1.0	0.55	0.3	0.6	0.175	1.0	13.0
1.0	0.55	0.1	0.325	0.175	1.6	0

Color		Color of Tanned Leather
Original	On standing	
orange	orange	off white.
yellow	yellow	
lemon	lemon	off white.
yellow	yellow	
lemon	lemon	off white.
yellow	yellow	
orange	orange	tan.
yellow	yellow	
light lemon	light lemon	off white.
yellow	yellow	
red brown	bright red	pink.

Example 3

(1) 1395 parts (14.9 mols) of phenol
(2) 720 parts (8.9 mols) of 37% aqueous formaldehyde
(3) 38.6 parts of 10 N sulfuric acid
(4) 288 parts of acetic anhydride
(5) 670 parts of 100% sulfuric acid

(1) and (2) are heated together at 95° C. in the presence of (3). Water and unreacted phenol are removed by vacuum distillation, and the viscous resin is diluted with (4). It is then sulfonated with (5) by heating for 5 hours at 70°–75° C., diluted with water, neutralized with ammonia to a pH of 3.0, and further diluted with water to a 30% resin solids solution.

The solution of sulfonated phenol-formaldehyde resin is divided into two portions and to one portion is added 0.15% by weight of sodium metabisulfite. Pickled calfskin squares are tanned with a portion of each of the syntans by tumbling in 100% of the syntan diluted with water to 400% and containing 2.5% salt. The remaining portions of the syntans are then allowed to stand in the sunlight at about 20°–30° C. for 2.5 months, after which the tanning tests are repeated. Results observed appear below:

Additive	Original		After Storage	
	Color of Soln.	Color of Tanned Skin	Color of Soln.	Color of Tanned Skin
None (control)	red	pink	deep red	dark pink.
$Na_2S_2O_5$	light amber	pink white	amber	pink white.

Thus, the sulfite not only prevents the usual darkening of the syntan on storage but it also bleaches much of the color originally present.

Examples 1 and 2 above are concerned with the preparation of phenol-formaldehyde-sulfite condensation products which are not only stable against discoloration upon storage under normal conditions but are initially light in color. In order to achieve this initial light color it is necessary to condense a condensation product of phenol and formaldehyde in a molar ratio of about 1.1:1 to 2.5:1, and preferably about 2:1, with sulfurous acid or a water soluble salt thereof and formaldehyde under alkaline conditions. Free SO_2 must be present in the reaction mixture throughout the reaction and this may conveniently be provided for by adjusting the molar ratio of formaldehyde and source of SO_2 in the second step of the reaction to between about 1:1 and 1.5:1. If more formaldehyde is used the free SO_2 will be combined and the product will become dark in color as it is formed.

My idea of providing free SO_2 in normally light unstable phenolic syntans is also applicable to preformed nuclearly sulfonated phenol-formaldehyde resins as exemplified in Example 3 above. In this case the syntan will normally be dark in color. Addition of bisulfite to the phenolic syntan may bleach the initial color somewhat but, of more importance, it will prevent discoloration upon storage under normal conditions.

There is no real upper limit on the amount of free SO_2 present during the preparation of the phenolic syntan and/or in the finished product, but any amount above about 15 parts per thousand will be undesirable because of the odor. Good practical limits for the amount of free SO_2 are from about 0.5 to about 8 parts per thousand. These concentrations are based on the finished syntan solution, not merely on the active material therein.

The process of my copending application referred to above may be conveniently applied to syntans which contain, according to the process of the present invention, free SO_2. ' In such an event the free SO_2 may be removed from the syntan solution prior to addition of vegetable tannin or it may be allowed to remain in the solution. A combination of the two processes for producing light stable syntans is particularly advantageous because the influence of the sulfite treatment of the present invention does not necessarily extend

to the tanned skins as does that of the vegetable tannin treatment of the copending application.

If desired, my stabilized syntan solutions may be dried by any suitable conventional means and stored in the dry form. In such a case it is only necessary to dissolve the dry syntan in water prior to its use.

In the present specification and claims when it is stated that a syntan solution is "light stable" or that it will not discolor appreciably "upon storage under normal conditions" it is meant that the syntan solution will not discolor appreciably upon standing in the sunlight at temperatures of from about 10°–40° C. for at least two months. It should be understood, of course, that I am referring only to light stability against discoloration due to the syntan itself. Obviously discoloration of the leather resulting from the presence of impurities such as iron cannot be arrested by the present invention, so the absence of such extraneous color forming impurities in the syntan solution is assumed.

Similarly, the term "free SO_2" as used in the description of the present invention includes not only SO_2 as sulfur dioxide, either in gaseous form or in aqueous solution, but also the SO_2 of anions derived from sulfurous acid which are uncombined, i. e., form no part of the structure of the syntan. These anions will include sulfite, bisulfite, metabisulfite, etc., depending upon their source or upon the pH of the syntan solution. Since my invention is effective at pH values ranging from about 2 to 11, its effect is apparently due to free SO_2 as defined above and not solely to sulfur dioxide, but I do not wish to be limited to any particular theory of mechanism.

My invention is applicable to any and all phenolic syntans which tend to discolor on standing or upon storage under normal conditions as defined above and hence produce discolored leathers. Such phenolic syntans are termed for the sake of convenience "light unstable." My invention is particularly applicable to those syntans of the specific examples but analogous products in which the phenols are replaced wholly or in part by either of the naphthols, by any of the isomers of monoalkylated phenols in which the alkyl group contains from 1–5 carbon atoms such as the o-, m-, and p-cresols, the o-, m- and p-tertiary butyl phenols, or the o-, m- and p-amyl phenols and the like, or by dihydric phenols such as resorcinol and catechol, etc., may be stabilized with free SO_2 according to my invention.

The sodium metabisulfite and sodium sulfite used in Examples 1 and 2 serve a dual function. They take part in the formation of the basic syntan structure, i. e., they act as sulfiting agent, and they serve the stabilizing purpose of the present invention. Other alkali metal salts of sulfurous acid such as sodium bisulfite, potassium sulfite, potassium metabisulfite, potassium bisulfite, and the like may be substituted in the preparation of the sulfited type phenolic syntan. In addition, sulfur dioxide and other salts of sulfurous acid may be used to stabilize pre-formed sulfited or sulfonated phenolic syntans. It is only necessary that such salts be sufficiently water soluble to produce a concentration of free SO_2 of at least 0.5 part per thousand in the final syntan solution. Thus in addition to the alkali metal sulfites, bisulfites and metabisulfites I may use certain of the alkaline earth metal salts of sulfurous acid, the ammonium salts of sulfurous acid, etc.

The stabilized phenolic syntans of the present invention may be used alone or in conjunction with other tanning agents such as ligno-sulfonate, vegetable tannins, mineral tanning agents, formaldehyde, other synthetic tanning agents and the like. In the latter case my new tanning agents may be used to after-tan leather already pretanned with another agent or agents, or skins and hides may be first tanned with a new agent and then with a tanning agent of another type.

I claim:

1. A process which consists of mixing a sulfonated product of the condensation of phenol and formaldehyde with a sufficient quantity of a substance of the group consisting of sulfur dioxide, sulfurous acid and water-soluble salts thereof to provide a free SO_2 concentration of at least about 0.5 part per thousand whereby the resulting composition is stable against discoloration upon storage under normal conditions.

2. A process according to claim 1 in which said substance is sodium metabisulfite.

3. A process according to claim 1 in which said SO_2 concentration is between about 0.5 and about 8 parts per thousand.

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