

# UNITED STATES PATENT OFFICE

1,938,022

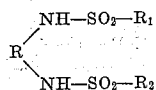
## TANNING AGENT

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2 Claims. (Cl. 260-129)

The present invention relates to new tanning agents. According to this invention the materials to be tanned in accordance with tanners practice are treated with a water soluble compound of the general formula:

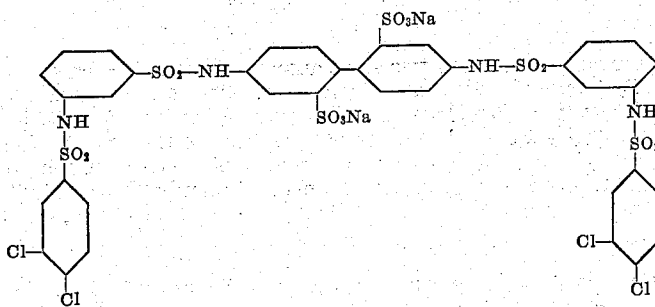


wherein R stands for an aromatic radical of the benzene, naphthalene or diphenyl series or two similar aromatic radicals of the benzene series which are linked with each other or by means of a bridge, for example, for the grouping  $\text{C}_6\text{H}_5\text{CH}_2\text{-CH}_2\text{-C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_5\text{CH=CHC}_6\text{H}_5$ ,  $\text{C}_6\text{H}_5\text{-O-C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_5\text{-NH-CO-NH-C}_6\text{H}_5$ , and  $\text{R}_1$  and  $\text{R}_2$  stand for the same or different sub-

### Example 1

Drenched, unhaired goats' skins (free from lime) are treated with 25% of almost completely neutralized but still acetic acid reacting bis-(1:2-dichlorobenzene-4-sulfonyl-3'-aminobenzene-1'-sulfonyl)-benzidine-m-m'-disulfonic acid with the addition of 3.3% of lactic acid in 300% of water until completely tanned. (All the figures given refer to the weight of the unhaired skins.)

The tanning agent is obtainable by condensing bis-(3-amino-benzene-sulfonyl)-benzidine-m-m'-disulfonic acid (compare British Letters Patent No. 333,559, Example 6) with 1,2-dichlorobenzene-4-sulfochloride analogously to the process as described in Example 5 of the said Letters Patent and corresponds to the formula:



stituted or unsubstituted bi- or polynuclear aryl-sulfone-arylamide derivatives of the benzene or naphthalene series with chain-like linkage in which the sulfone imide groups combining the aryl nuclei may be partly replaced by aliphatic or aromatic carboxylic acid amide groups, at least one of the nuclei containing a sulfonic acid group. These new tanning agents are generally colorless powders being easily soluble in water. They are obtainable according to methods described in the British Letters Patent No. 333,559, Examples 5 to 7.

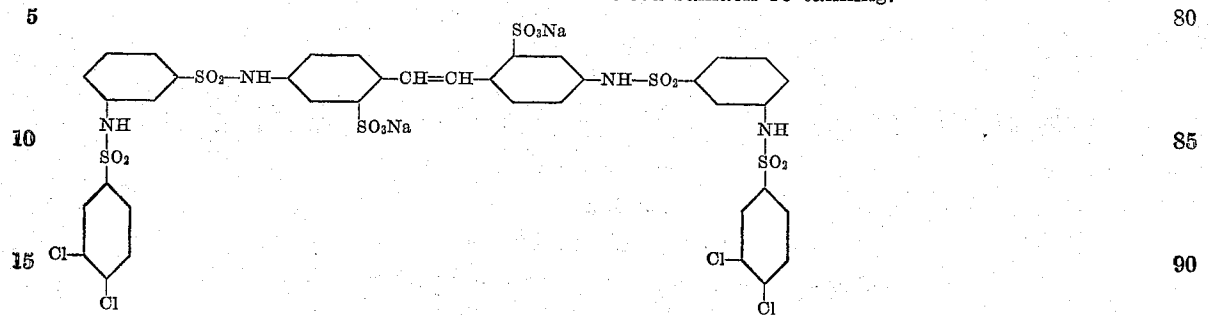
The following examples illustrate the invention but without limiting it thereto:

According to the thickness of the skins the tanning requires three to five days. After tanning the skins are well rinsed and oiled from the grain. The finished curried leather is soft, plump and long fibered and shows great similarity to leather tanned with vegetable tanning agents. It differs, however, advantageously from the latter in its pure white color and practically complete fastness to light.

### Example 2

Unhaired skins pickled with a pickle consisting of:—1% of commercial formic acid, 8% of sodium chloride, and 100% of water are tanned in

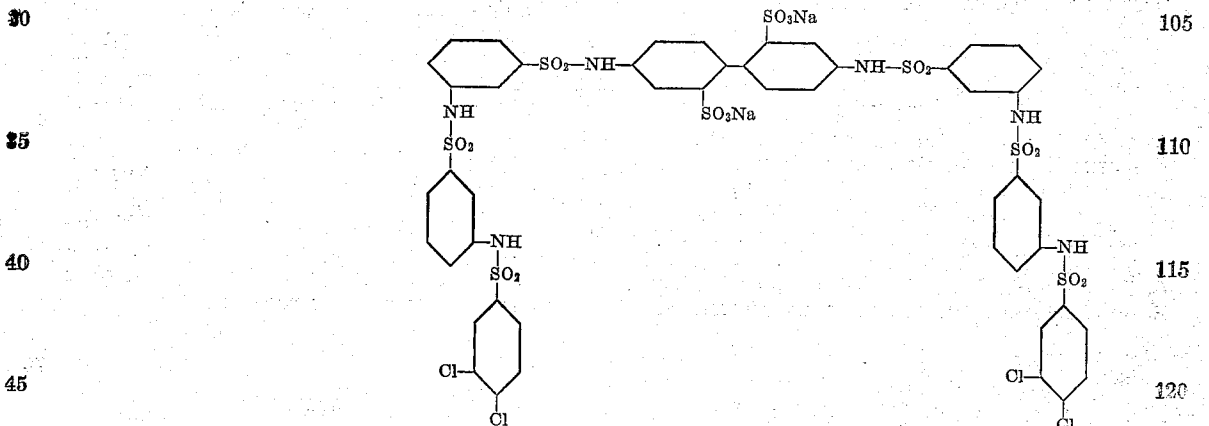
a fulling vessel with 15% strength of partly neu- This re-tanning confers upon the leather a re-  
tralized bis-(1:2-dichlorobenzene-4-sulfonyl-3'- remarkable fullness. The color of the leather is  
aminobenzene-1'-sulfonyl)-diamino-stilbene-di- lighter than that obtained by the often prac-  
sulfonic acid of the formula:



20 having a weakly acid reaction to Congo red  
in 100% bath without further addition. The  
bis - (1.2 - dichlorobenzene-4-sulfonyl-3'-amino-  
benzene-1'-sulfonyl) -diamino-stilbene-disulfonic  
acid may be produced analogously to the process  
described in Example 1 of British Letters Patent  
No. 333,559, by causing one molecular proportion  
of 4.4'-diamino-stilbene-disulfonic acid to react  
with two molecular proportions of 3-nitro-ben-  
zene-sulfochloride, reduction of the resulting con-  
densation product and condensation of the di-

*Example 4* 95

One-bath chromium calf leather, thoroughly  
freed from acid, is fulled for one hour in 150%  
of water (all the quantities are calculated on  
the shaving weight) containing 3% of the sodium  
salt of bis-(1:2-dichlorobenzene-4-sulfonyl-3'-  
aminobenzene-1'-sulfonyl-3''-aminobenzene-1''-  
sulfonyl)-benzidine-m-m'-disulfonic acid (Brit-  
ish Letters Patent No. 333,559, Example 7) of  
the formula:



50 amino compound with two molecular proportions  
of 1.2-dichlorobenzene-4-sulfochloride. The tan-  
ning agent dissolved in a little water is added  
in three portions in the course of six hours.  
The tanning is complete after two days. The  
finished pure white leather is very similar to  
that of Example 1.

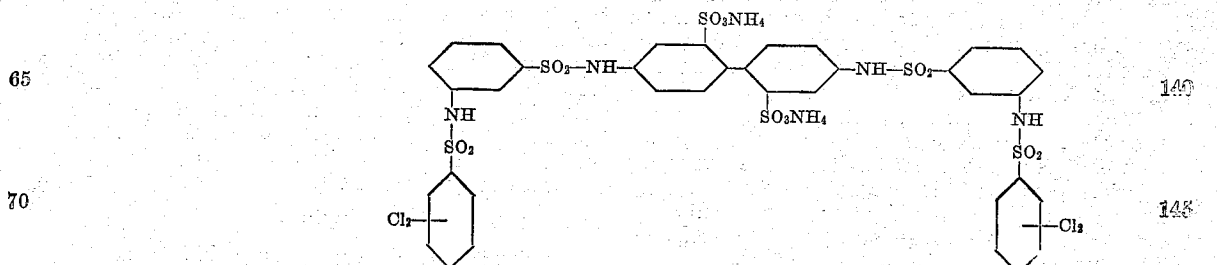
125 1.5% of oxalic acid is then added and fulling con-  
tinued for three quarters of an hour longer.  
After that the leather is rinsed in running water  
for half an hour and well stuffed with 3%  
of sulfonated neat's-foot oil, at 50° C. The chro-  
mium leather thus bleached is almost pure white  
and possesses almost complete fastness to light.

55 *Example 3*

60 East Indian sheep skin leather is well fulled  
in the customary manner and rinsed in running  
water. Re-tanning follows in 150% of water  
with 10% of the tanning agent of Example 1  
and 1.3% of lactic acid. The time of tanning

130 *Example 5*

Degreased sheep skins (free from lime) treat-  
ed with a pickle consisting of: 0.5% of formic acid,  
6% of sodium chloride, and 100% of water are  
tanned with a synthetic tanning agent of the  
probable formula:



75 amounts to three hours. The quantities speci-  
fied are calculated on the striking out weight,

150 which is obtained by the condensation of bis-(3-  
aminobenzene - sulfonyl) -benzidine-m-m'-disul-

fonic acid (compare British Letters Patent No. 333,559, Example 6) with a mixture of 1,2-dichlorobenzene-4-sulfochloride and 1,4-dichlorobenzene-2-sulfochloride. Therefore it consists of a mixture of symmetrically and asymmetrically constructed compounds of the above mentioned formula. 2.5% of this product are used, and 22

In the examples the tanning agents specified can be replaced by other representatives of the compounds denoted by the general formula. Such products are, for example, the sodium salt of bis-(1:4-dichlorobenzene-2-sulfonyl-3'-aminobenzene-1'-sulfonyl)-benzidine-m-m'-disulfonic acid.

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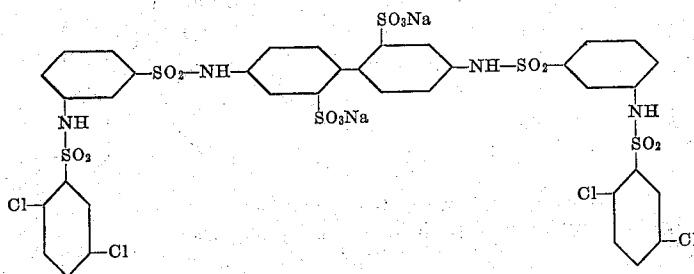
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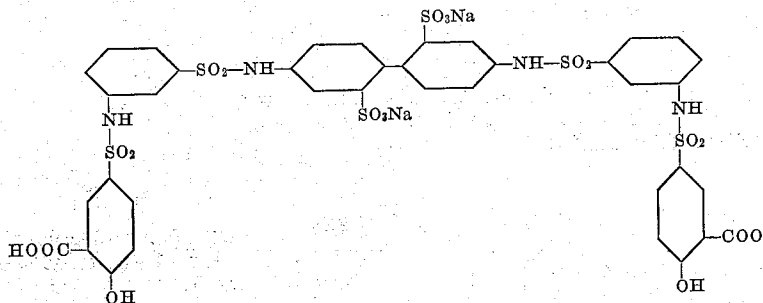
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parts by weight of a technical 30% acetic acid are added for each 100 parts by weight of the tanning agent.

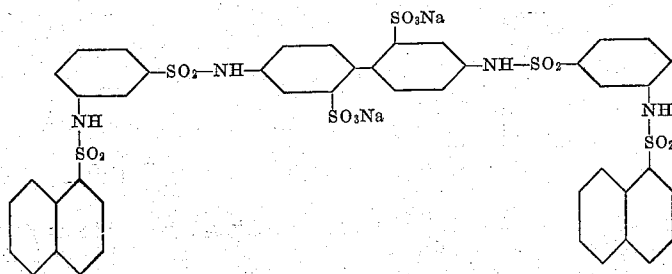
After some hours the tanning is performed with the addition of 10% of the tanning agent, 25 parts by weight of 30% acetic acid and 3 parts by weight of 100% formic acid for each 100 parts by weight of the dry ware.

or of bis-(4-chlorobenzene-1-sulfonyl-3'-aminobenzene-1'-sulfonyl)-benzidine-m.m'-disulfonic acid or of bis-(toluene-4-sulfonyl-3'-aminobenzene-1'-sulfonyl)-benzidine-m.m'-disulfonic acid or of bis-(benzenesulfonyl-3'-aminobenzene-1'-sulfonyl)-benzidine-m.m'-disulfonic acid or of bis-(salicylic acid-sulfonyl-3'-aminobenzene-1'-sulfonyl)-benzidine-m.m'-disulfonic acid:



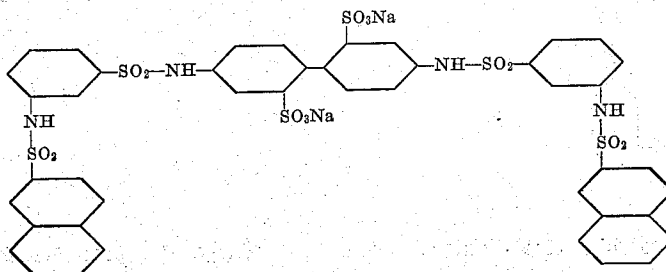
The acidified concentrated aqueous solution of the tanning agent is added in several portions in the course of one day. Then it is fuled until

or of bis-(naphthalene-1-sulfonyl-3'-aminobenzene-1'-sulfonyl)-benzidine-m.m'-disulfonic acid:

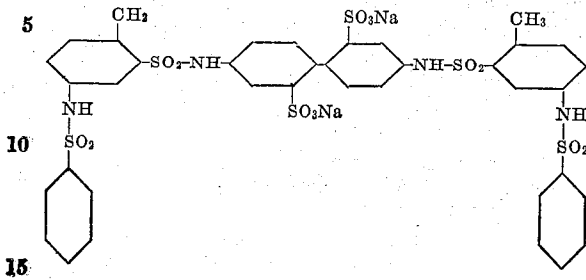


completely tanned and after a short rinsing it is carried in the customary manner. The leather thus obtained shows the same excellent properties as mentioned in Example 1.

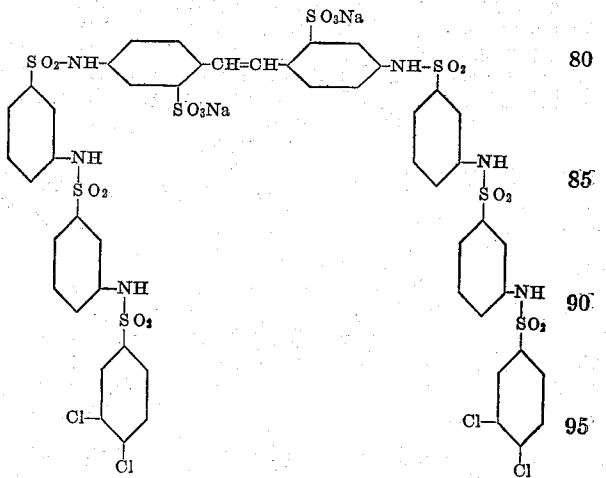
or of bis-(naphthalene-2-sulfonyl-3'-aminobenzene-1'-sulfonyl)-benzidine-m.m'-disulfonic acid:



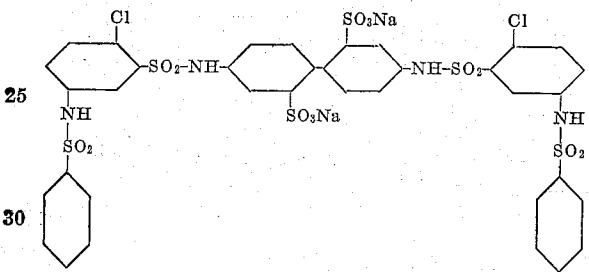
or of bis-(benzenesulfonyl-4'-amino-1'-toluene-2'-sulfonyl)-benzidine-m.m'-disulfonic acid:



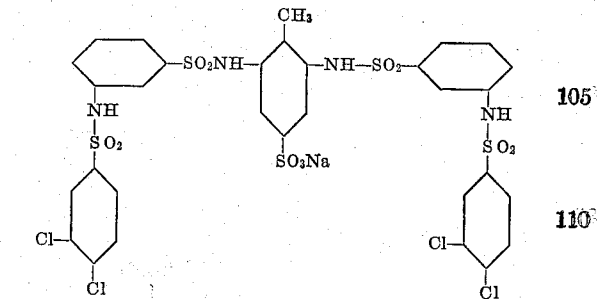
aminobenzene-1'-sulfonyl-3''-aminobenzene-1''-sulfonyl)-diaminostilbene-disulfonic acid:



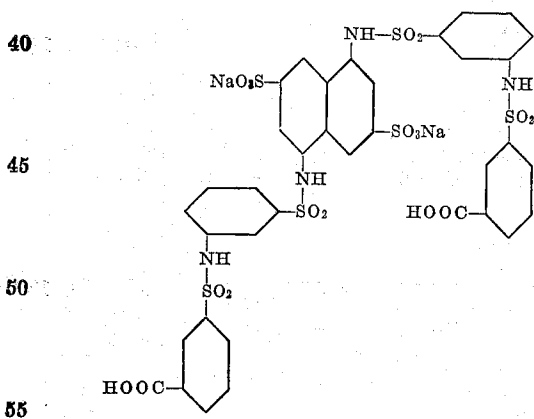
or of bis-(benzenesulfonyl-4'-amino-1'-chlorobenzene-2'-sulfonyl)-benzidine-m.m'-disulfonic acid:



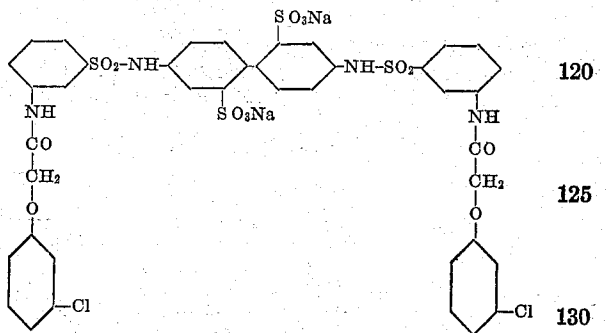
or of bis-(1:2-dichlorobenzene-4-sulfonyl-3'-aminobenzene-1'-sulfonyl)-2'''.6''-toluylenediamine-4''-disulfonic acid:



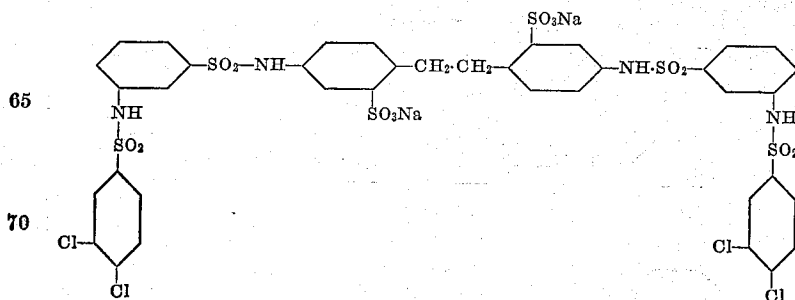
or of bis-(benzoic acid-sulfonyl-3'-aminobenzene-1'-sulfonyl)-1'''.5''-naphthalenediamino-3'''.7''-disulfonic acid:



or of bis-(3-chlorophenoxyacetyl-3'-aminobenzene-1'-sulfonyl)-benzidine-m.m'-disulfonic acid:



or of bis-(1,2-dichlorobenzene-4-sulfonyl-3'-aminobenzene-1'-sulfonyl)-4'''.4''-diaminodibenzyl-2''-2''-disulfonic acid:



obtainable by condensing one molecular proportion of the sodium salt of bis-(3-aminobenzene-sulfonyl)-benzidine-m.m'-disulfonic acid (com-

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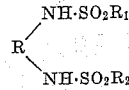
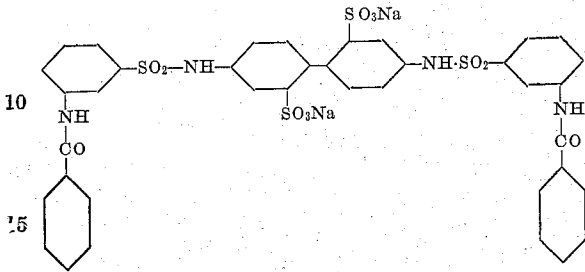
75 or of bis-(1:2-dichlorobenzene-4-sulfonyl-3'-aminobenzene-1'-sulfonyl)-diaminostilbene-disulfonic acid: compare British Letters Patent No. 333,559, Example 150

6) with two molecular proportions of 3-chloro-  
phenoxy-acetylchloride according to the methods  
described in the British Letters Patent 313,110,  
or of bis-(benzoyl-3'-aminobenzene-1'-sulfonyl)-  
benzidine-m-m'-disulfonic acid:

also mixtures of the same among themselves or  
with other synthetic or vegetable tanning agents.

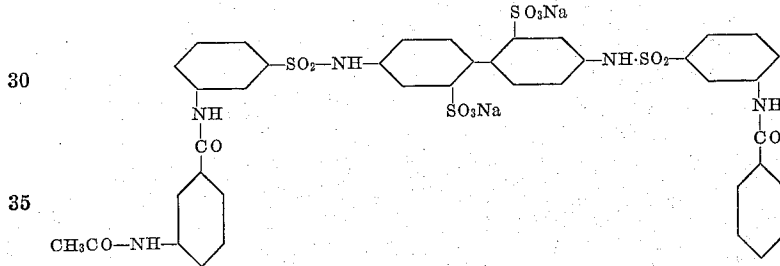
We claim:

1. A tanning composition, the active con-  
stituent of which is a condensation product of  
the probable formula:



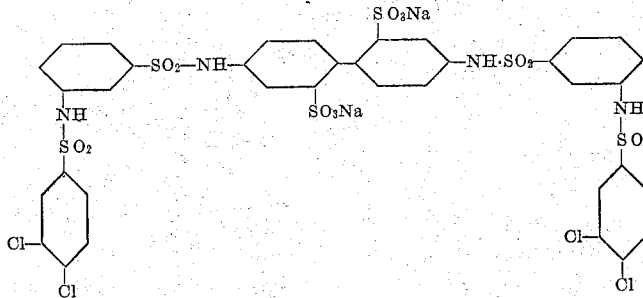
wherein R stands for a benzene, naphthalene or  
diphenyl radical, both nuclei of the diphenyl  
radical being linked together directly or by means  
of a bridge, and R<sub>1</sub> and R<sub>2</sub> represent di- or poly-  
nuclear aryl-sulfone-arylamide derivatives of the  
benzene or naphthalene series with chain-like  
linkage in which the sulfone-imide groups combin-  
ing the aryl nuclei may be partly replaced by  
aliphatic or aromatic carboxylic acid amide  
groups, and wherein at least one nucleus contains  
a sulfonic acid group, and wherein all nuclei may  
be further substituted by halogen or alkyl- or  
hydroxy- or carboxylic- or alkylacetyl-amino  
groups.

obtainable by condensing one molecular propor-  
tion of bis-(3-aminobenzene-sulfonyl)-benzidine-  
m-m'-disulfonic acid (compare British Letters  
Patent 333,559, Example 6) with two molecular  
proportions of benzoylchloride in a known man-  
ner, or of bis-(3-acetylaminobenzene-1-sulfonyl-  
3'-aminobenzene-1'-sulfonyl)-benzidine-m-m'-  
disulfonic acid:



obtainable by acetylating the sodium salt of bis-  
(3-aminobenzene-1-sulfonyl-3'-aminobenzene-  
1'-sulfonyl)-benzidine-m-m'-disulfonic acid

2. A tanning composition, the active con-  
stituent of which is a condensation product of  
the probable formula:



(British Letters Patent 333,559, Example 7) in an  
aqueous solution with an excess of acetic an-  
hydride at a temperature of 40° C. in the presence  
of chalk and many other compounds of the like  
constitution. All these products are distinguished  
by their strong tanning properties as, accordingly,

being a colorless powder easily soluble in water.

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