This invention relates to novel compounds of the abietene family. More particularly this invention relates to novel condensation products obtained by reacting sulfonic acids of the abietene family with aldehydes.

By the term "sulfonic acids of hydrocarbons of the group consisting of abietene, abietone and abietane" we mean the products obtained by sulfonating a compound containing the abietene nucleus, such as abietene, abietone, or abietane. The first two, abietene and abietone, are derivate by pyrogenic decomposition of rosin, abietic acid, or abietyl chloride. Abietane is obtainable by hydrogenating abietene. Methods of preparing these compounds as well as their sulfonation products, are described in the copending application of Gubelmann and Henke Serial No. 431,626, filed Feb. 26, 1930, and in U. S. Patents Nos. 1,853,446, 1,853,452, and 1,853,553. However, our invention is not limited to the particular derivatives obtainable by the particular methods disclosed in said copending applications. Many varieties of abietene or abietone are known in the art, (see for instance, Rudzka, Helv. Chim. Acta, vol. 6, pages 658-640). The sulfonation products of any of these derivatives, obtainable according to the above mentioned copending applications or according to any well known method, are suitable for our invention.

We have now found that the above defined sulfonic acid compounds of the abietene, abietone and abietane hydrocarbons combine readily with aldehydes to give novel and useful, water-soluble compounds. The chemical nature of these compounds is not quite understood, but it is probable that they belong to the family of polyarylmethanes, and are formed, for example, according to the following equations:

\[
\begin{align*}
\text{abietene} & \rightarrow \text{SOH} \\
(1) & \quad 2 \text{abietene} + \text{SOH} + O = \text{CH} \rightarrow \text{CH}_2 + \text{H}_2 \text{O} \\
(2) & \quad 2 \text{abietone} + \text{SOH} + O = \text{CH} \rightarrow \text{O} + \text{CH} \rightarrow \text{R} + \text{H}_2 \text{O} \\
\text{abietene} & \rightarrow \text{SOH}
\end{align*}
\]

In Equation 2 "R" stands for a hydrogen atom or an alkyl or aryl group.

Our novel condensation products are in the form of their free acids, soluble in water and in benzene, but insoluble in 50% sulfuric acid. Upon evaporation from a benzene solution they form a black pasty material. Their sodium salts are quite stable and may be stored indefinitely without decomposition.

The aldehyde condensation products, like the uncondensed sulfonic acid derivatives of the abietene, abietone and abietane hydrocarbons, form excellent wetting, dispersing and tanning agents both in the form of the free acids, or in the form of their alkali metal salts. They are therefore very useful commercially both in the textile and leather industries. Thus the addition of our novel compounds to any aqueous treatment bath for textile fibers, for instance in dyeing, bleaching, scouring and cleansing fiber, yarn or cloth, facilitates the penetration of the fiber by the liquid, improves the uniformity of the treatment, shortens the time of the treatment, and in general increases the efficiency of the entire operation. Addition of these compounds to tanning baths reduces the amount of natural tanning agent required, accelerates the time of tanning, and improves the color and texture of the leather.

The preparation of our novel products may be effected by dissolving the particular abietene, abietone or abietane sulfonic acid body in concentrated sulfuric acid and adding the particular aldehyde chosen. It is more advantageous, however, to add the aldehyde directly into the sulfonation mass in which the sulfonic acid body is formed, thereby saving the step of isolating the intermediate sulfonic acid body. Upon the addition of the aldehyde a vigorous reaction takes place with liberation of heat. After a few hours the entire mass becomes so viscous that it is difficult to stir. Dilution of the entire mass with water at this point, causes a separation of the mass into layers, the upper layer containing the condensed sulfonic acid body, while the lower layer contains the aqueous sulfuric acid.

The following examples will serve further to illustrate our invention, without however, limiting the same. Parts given are parts by weight.

**Example 1**

1000 parts of sulfuric acid monohydrate are placed in a sulfonation vessel fitted with an agitator, and cooled to about 10° C. 500 parts of abietene, such as for example, the product ob-
tained from grade B or grade FF wood rosin, by heating the same at reflux temperatures until its acidity substantially disappears as is more fully described and claimed in the copending appli-
cation of Henke, Serial No. 540,007, filed of
even date herewith and in U. S. Patent 1,653,353,
and then dropped slowly over a period of 4
hours, and the agitation continued for about 20
hours more. The entire mass is maintained at a
temperature of 5 to 10°C. by means of external
cooling during this treatment. 100 parts of a 40%
aqueous solution of formaldehyde are next added,
and the stirring is continued for about 2 hours.
The reaction mass is now poured into 1000 parts
of water, stirred thoroughly, and allowed to set-
tle. The lower, aqueous, acid layer is discarded.
The upper layer, which contains the formalde-
hyde-abiitene-sulfonic-acid condensation pro-
duct, is dissolved in water, neutralized with caustic
soda, filtered, and evaporated to dryness. The
yield of the condensation mass is about 700 parts.
If desired, instead of evaporating the neutral-
ized filtration mass the latter may be extracted
with benzene, and the extracted aqueous mass
may be dried over calcium chloride. The prod-
tected for dryness thus ob-
tained is considerably purer and better in its
practical qualities than the product obtained
without benzene extraction. The latter step ap-
parently removes any residual unsulfonated oil.
Instead of the 100 parts of a 40% formaldehyde
solution above specified, 30 parts of paraformal-
dehyde may be used, all other conditions remain-
ing the same. The product is similar in prop-
ties to the product above described.

Example 2

The procedure is the same as in Example 1, ex-
cept that instead of 500 parts of abietane therein
mentioned, 500 parts of abietane are used. The
latter may be obtained by the hydrogenation of
abiitene in the presence of a catalyst as is more
fully described and claimed in the copending ap-
lication of Gubelmann and Henke, Serial No.
431,638, filed Feb. 28, 1930. The final product has
substantially the same properties as the product
of Example 1, and like the products of
Example 1 may be further improved by extract-
ing its aqueous sodium salt solution with benzene.

Example 3

110 parts of benzaldehyde are used instead of
100 parts of 40% formaldehyde as described in
Example 1 and all the other details of Example 1
are maintained. The product is similar to that
obtained in Example 1. It is evidently a con-
densation product of 2 mol of abietane and 1
mol of benzaldehyde.

Instead of using 110 parts benzaldehyde, 155
parts of benzal-chloride may be used. In this
case hydrochloric acid is liberated during the re-
action, which either escapes as a gas or finds
its way into the aqueous layer in the dilution
step. The products obtained in Examples 1, 2, and 3,
especially after extraction with benzene, are ex-
cellent "Sintans", that is synthetic tanning agents,
and are very useful as assistants to the
natural tanning agents used in the ordinary pro-
cesses of tanning hide. The tanning process
when mixtures of our novel condensation prod-
ucts and natural tanning agents are used, is con-
siderably simplified and accelerated. Moreover, the
resultant leather excels in color and texture.

Example 4

28 parts of the benzene-extracted product ob-
tained in Example 1 are dissolved in 84 parts of
water. 448 parts of sumac extract are added, and
the mixture is diluted with 1500 parts of
water. 1000 parts of pickled sheepskin are now
introduced, and the entire mass is agitated in a
drum for about 3 to 4 hours. At the end of this
period the sheepskin becomes converted into
leather of lighter color and better texture than
leather obtainable by the use of sumac extract
alone. It will also be noted that the time re-
quired for tanning has been reduced to about 1/3
of that normally required when using sumac ex-
tract alone, and that the quantity of the sumac
extract necessary has been reduced by about 20%
compared to what would be required to produce
the same tanning effect, if it were used alone.
The process of using our novel compounds in
tanning is claimed in the copending application
of Henke and Orthune, Serial No. 540,009, filed
of even date herewith.

The tannin equivalent of our novel condensa-
tion products, when determined by the Ameri-
Can Leather Chemists Association method, runs
about 40 to 50% of the weight of the product.
Other and further modifications may be in-
troduced in our invention without departing from
the spirit of the same.

Besides aldehydes in general, compounds which
react like aldehydes in condensation reactions
may be used in our process such as, for example,
parafomaldehyde and benzal-chloride.

We claim:

1. The process of producing water soluble com-
 pounds which comprises condensing a sulfonic
acid body of hydrocarbons of the group consist-
ing of abietane, abietine and abietane with a mem-
ber of the group consisting of aldehydes and com-
 pounds which react like aldehydes.

2. The process of producing water soluble com-
 pounds which comprises reacting a sulfonic acid
 body of a hydrocarbon selected from the group
 consisting of abietane, abietine and abietane in
 concentrated sulfuric acid with a member of the
 group consisting of aldehydes and compounds
 which react like aldehydes.

3. The process of producing water soluble com-
 pounds which comprises condensing sulfonic
 acids of hydrocarbons of the group consisting of
abietane, abietine and abietane with formalde-
hyde.

4. The process of producing water soluble com-
 pounds which comprises condensing sulfonic
 acids of hydrocarbons of the group consisting of
abietane, abietine and abietane with benzalde-
hyde.

5. The process of producing water soluble com-
 pounds which comprises reacting upon a hydro-
carbon of the group consisting of abietane, abie-
tine and abietane with sulfonic acid, adding a
member of the group consisting of aldehydes and
compounds which react like aldehydes to the sul-
fonation mass and recovering the reaction prod-
uct.

6. A water soluble condensation product of a
 sulfonic acid body of hydrocarbons selected from
the group consisting of abietane, abietine and abie-
tane with a member of the group consisting of
aldehydes and compounds which react like
aldehydes.

7. A water soluble condensation product of sul-
fonic acids of hydrocarbons of the group consist-
ing of abietane, abietine and abietane with for-
maldehyde.

8. A water soluble condensation product of a
 sulfonic acid body of hydrocarbons selected from
the group consisting of abietene, abietine and abietane with benzaldehyde.
9. A water soluble compound having most probably the following formula:

\[ \text{Abietene} - \text{SO}_2 \text{H} \]
\[ \text{H}_2 \text{R} \]
\[ \text{Abietene} - \text{SO}_2 \text{H} \]

in which R stands for a hydrogen atom or an alkyl or aryl group.
10. The process of producing water soluble compounds which comprises condensing a sulfonic acid body of hydrocarbons selected from the group consisting of abietene, abietine and abietane with benzal-chloride.
11. A water soluble condensation product of a sulfonic acid body of hydrocarbons selected from the group consisting of abietene, abietine and abietane with benzal-chloride.

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