ROSIN COMPOUNDS OF IMPROVED COLOR AND STABILITY

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No Drawing. Continuation-in-part of applications Ser. No. 579,819 and Ser. No. 579,851, filed on November 18, 1966. Title of applications: 579,819, Serial No. 579,851 is a continuation-in-part of Serial No. 496,660, filed October 15, 1965, which became abandoned after the continuation-in-part application was filed. Application Serial No. 579,819 is a continuation-in-part of Serial No. 496,667, filed on October 15, 1965 and Serial No. 560,566, filed June 27, 1966, both now abandoned.

This invention relates to methods for improving the color and color retention of tall oil, tall oil fractions predominating in fatty acids, tall oil fractions predominating in rosin acids, rosins and rosin compounds including tall oil rosin, wood rosin and gum rosin and compounds thereof. The invention includes methods wherein these materials are subjected to heat treatments at bleaching temperatures within the range of about 180° C. to about 350° C. in the presence of small quantities of a particularly defined class of phenol sulfide bleaching and color stabilizing agents and for times such that improvements in color characteristics are obtained. The invention also includes the improved tall oils, tall oil fractions, rosins and rosin compounds obtained by these methods, all of which are characterized by a lighter color and an enhanced color stability as compared with the raw materials from which they were obtained.

Tall oil is a mixture of rosin and fatty acids released by acetylation of the "black liquor soap" skimmed off the "black liquor"—the concentrated alkaline digestion liquor washed out of paper pulp in the sulfate or "kraft" process for manufacture of paper. The crude tall oil is then commonly fractionally distilled to provide various cuts ranging from rosin-fatty acid mixtures having a fatty acid content as low as about 1% by weight and rosin content as high as about 99% by weight, usually up to about 90% by weight. To other such mixtures wherein the rosin content is below about 1% by weight, e.g., 0.3% by weight, and the fatty acid content is as high as about 99% by weight, e.g., 39.3% by weight.

The term "tall oil fractions predominating in fatty acids" is employed herein to mean crude, solvent/acid-refined, and distilled tall oil portions as well as tall oil fractional distillation products, each having a fatty acid content of at least about 50% by weight, the balance being mainly rosin acids in admixture with minor amounts of unsaponifiable materials of complex chemical constitution. The fatty acids consist mainly of a mixture of oleic, linoleic, conjugated linoleic, palmitic, and stearic acids together with lesser amounts of palmitoleic, higher molecular weight saturated acids such as arachidic (C20), behenic (C22), acids, higher molecular weight unsaturated and polyunsaturated acids, and low boiling monobasic and dibasic acids.

Preferred tall oils treated according to the present invention are the commercially available acid/solvent-refined tall oils. Typically, these are crude tall oils which have been slurried in a hydrocarbon solvent such as hexane, in a weight ratio of about 40 parts tall oil to 60 parts hexane, then treated with about 8-12% by weight of 96-100% concentrated sulfuric acid at about 35°C, and separated. Such refined tall oils generally contain about 50% by weight or more of fatty acids, the balance being rosin acids, dimerized rosin acids, and unsaponifiable materials.

Other preferred tall oils are the commercially available tall oil fractions containing a minimum of 90% by weight fatty acids and a maximum of 5% by weight rosin acids, the balance being minor amounts of complex unsaponifiable materials.

Light color and color stability are important characteristics for commercial acceptance of tall oil fatty acids and end products prepared therefrom. Thus, tall oil fatty acids are conventionally saponified, amidated, aminated, condensed with ethylene oxide and esterified to provide a host of household and industrial products such as soaps, synthetic detergents, disinfectants, wax emulsions, paper chemicals, coating compositions, epoxy esters and other well-known products.

A method commonly employed to improve, i.e., to lighten, the color of tall oil fatty acids involves dry-blending and heating the fatty acid fraction with an adsorbent material such as activated clay. Fuller's earth, activated carbon or the like are, the use of color bodies. The tall oil fatty acid is thereafter separated by filtration and the clay discarded.

To stabilize the resulting improved color, it has become conventional to add known oxidation inhibitors.

While effective, the prior art methods of bleaching and stabilizing tall oil fatty acids have serious deficiencies. Thus, some of the fatty acids will be adsorbed with color bodies onto the adsorbent materials and subsequently lost when the adsorbed material is discarded, thereby adding to the expense of the recovered bleached product. Furthermore, a second treatment with an oxidation inhibitor is often required to stabilize the improved color. This further increases the expense of the final product.

An object therefore of the invention is to provide a method of bleaching tall oil fractions predominating in fatty acids while simultaneously substantially stabilizing the improved color.

A further object is to provide a method of bleaching, and substantially stabilizing the resulting improved color of tall oil fractions predominating in fatty acids by a simple treatment which avoids fatty acid loss and eliminates or substantially reduces the expense of prior art multi-step methods.

Another object is to provide tall oil fractions predominating in fatty acids having improved color and color stability.

By "rosins and rosin compounds" is meant abietyl compounds, i.e., hydrophilenethrene radical-containing materials, including but not limited to the following: tall oil rosin, tall oil fractions predominating in rosin acids, i.e., containing at least about 50% by weight of rosin acids; wood rosin; and gum rosin; modifications of these products such as hydrogenated rosins, formaldehyde-treated rosins (such as described in U.S. Patent 2,934,468 and 3,135,127). Diels-Alder reaction products such as fumarated rosins and maleated rosins; and the use of such rosins including rosin esters, rosin amines, rosin amides, rosin alcohols, rosin-alkylene oxide adducts; and the nu-
numerous well-known equivalents of the foregoing materials. The term “rosinyl,” as defined in U.S. Patent 2,154,629, is a convenient representation for the “rosins and rosin compounds” of the present invention.

Rosin esters include reaction products of rosin and mono- and polyhydroxy alcohols such as methanol, ethan-

ol, butanol, ethylene glycol, propyleneglycol, glycerol, and the like. Among the many well-known rosin amides may be mentioned the products prepared by dehydrating the ammonium salt of rosin to the nitrile which is then re-
duced by hydrogen to the amine. Rosin amides are con-
ventionally prepared either by decomposing ammonium salts of rosin or by reacting rosin with primary amines. Rosin alcohols are conventionally prepared by reducing the corresponding rosin esters. Rosin-alkylene oxide adducts include the known reaction products of rosin and ethylene oxide and the like.

It is important in many end uses of rosin compounds that the starting material be light-colored and that the color remain stable under normal conditions of use. Thus, rosin compounds are widely employed in the manufac-
ture of paper size, as plasticizers for films such as poly-

ethylene and polypropylene, and for the manufacture of rosin used in paint and varnish. In these and other end uses the industry desires a light colored product which also exhibits color stability. Hence, industry looks for these properties in the rosin compound intermediates used to make these products since good color and stability is normally retained in the end product.

It is known that rosin compounds may be bleached somewhat by heating at elevated temperatures or by treatment with sulfur, sulfur dioxide and similar sub-
stances. However, the degree of bleaching often is poor
and the treated compounds do not exhibit good color stability. Furthermore, substantial amounts of the treat-
ing agent, e.g., sulfur, are often required, thus adding to the expense of treatment. Distillation and crystalliza-
tion are also employed to achieve bleaching but these
methods require elaborate apparatus and extended proc-
essing time and thus substantially increase the expense
of the treated products. Other problems encountered in prior art bleaching methods include retention of the odor
of the treating agent in the rosin compounds (particularly objectionable if sulfur) and tendency to form unsaponifi-
able materials during the treatment.

An object of the present invention is to provide light
colored rosin compounds which also exhibit color sta-

bility.

A further object is to provide a method of bleaching
and stabilizing rosin compounds without substantial ef-

fect on other properties of the compounds, particularly
formation of unsaponifiable materials.

A still further object is to provide a low cost method
of bleaching and stabilizing rosin compounds which re-
quires only catalytic amounts of a treating agent.

These and other objects, features, and advantages of
the invention will become more apparent from the de-
scription which follows:

The rosin compounds are bleached and stabilized by

treatment with minor amounts of a treating compound of

Formula I at elevated temperatures for a time suf-

ficient to effect bleaching. Very small amounts of the
additive are effective and may be termed “catalytic
amounts,” e.g., from about 0.01% to 1.0%, preferably 0.02% to 0.5%, by weight of the treating compound based on the weight of the rosin compound.

The amount of temperature and time of treatment will vary depending on the type of rosin, modified rosin or rosin derivative employed. Little or no bleaching is ob-
served in the absence of heating or if the rosin compounds are heated in the absence of the treating compound.

Normally, the rosin compound is heated in the presence
of the treating compound at a temperature in the range of from about 180°C. to 350°C. for up to about 18
hours, the longer times corresponding to the lower tem-

peratures and vice versa. A maximum bleach of tall oil rosin is observed in 30 minutes at a temperature range of about 250°C. to 275°C. at a treating compound concentration of 0.1% and substantially instantaneous bleach is observed at or above 300°C. The higher temperatures generally promote lighter colors when the treating com-
pound concentration is held constant but excessive tem-
peratures should be avoided since degradation and ex-
cessive formation of unsaponifiable materials may result
therefrom. Optimum bleaching and color stability is ob-
tonied for most of the rosin compounds when the same
are treated with about 0.1% to 0.5% of the treating agent
at 240°C. to 275°C. for about 30 minutes to one hour.

To avoid oxidation, the treatment is generally conduct-
ed under a blanket of inert gas such as nitrogen, carbon
dioxide, steam and the like.

In accordance with the invention the above and other
objects are accomplished when the tall oil or fraction
thereof or rosin or rosin compound is heated at an effec-
tive temperature within the range of about 180°—350°
C. hereinafter sometimes called a bleaching temperature, in the presence of effective amounts of a treating compound of the formula

$$\text{R}_m\text{Ar}_n$$

$$\text{R}\text{Ar}_m\text{Ar}_n$$

$$\text{R}\text{Ar}_m\text{Ar}_n$$

where n is an integer from 1 to 3 inclusive, p is an integer from 0 to 100 and preferably about 5 to 20 inclusive, and the sum of m and n on each Ar is preferably between 1 and 5 inclusive. R is a hydrocarbon group, e.g., alkyl,

cycloalkyl and substituted alkyl, e.g., C1-C6 wherein the substituents are cycloalkyl, aryl, alkyaryl, and the like

desirably contains from 1 to 22 carbon atoms inclusive.

Preferred alkyl groups are straight chain second-
ary and tertiary alkyl groups containing up to 8 carbon atoms inclusive. Preferred Aryl groups are those containing
6 to 18 carbon atoms inclusive typically phenyl, naphthyl and anthracyl. Typical cycloalkyl groups contain
3–8 carbon atoms in the ring, e.g., cyclopentyl, cyclo-

pentyl and cyclohexyl.

In Formula I when Aryl is phenyl it will be apparent
when p is 0 that the sum of m and n on each phenyl ring will not be more than 5 and when p is 1 or higher the
sum of m and n on each phenyl ring will not be more than
4. It will also be apparent, however, that the values for n and
m may range higher, when Aryl is naphthyl or anthracyl,
only when p is 0 or at least 1 more than 5 or 4 sites,
respectively, are available for OH and R substituents.
The values for m, n, p and p, except when 0, are positive,
whole numbers.

Included are compounds and position isomers having
R groups of mixed character, i.e., the R group or groups
on one aryl ring may differ from the R group or groups
on the other aryl rings; m and n may be the same or
different for each aryl ring; and when more than one R


vously, a polymer of such high molecular weight as to be unmanageably tacky or glassy is to be avoided in the practice of the invention. From the viewpoint of economy and ease of preparation and use according to the invention, preferred treating agents are those which are soluble in the material treated, e.g., components of Formula I wherein \( p \) is in the range of 5 to about 20. As typical and non-limiting examples of the treating agents may be mentioned:

Thiobis naphthols, e.g.:  
1,1'-thiobis(8-naphthol)  
2,2'-thiobis(α-naphthol)  
2,2'-thiobis phenols, e.g.:  
2,2'-thiobis(4-methyl-6-tert.-butylphenol)  
2,2'-thiobis(4,6-dimethylphenol)  
2,2'-thiobis(4,6-di-tert.-butylphenol)  
2,2'-thiobis(4-ethyl-6-tert.-butylphenol)  
2,2'-thiobis(4-n-propyl-6-ethylphenol)  
2,2'-thiobis(4-methyl-6-octylphenol)  
2,2'-thiobis(4-amyl-6-tert.-octylphenol)  
2,2'-thiobis(4-methyl-6-n-decylphenol)  
2,2'-thiobis(4-methyl-6-laurylphenol)  
2,2'-thiobis[4-methylene-(1-methylcyclohexyl)phenol]  
2,2'-thiobis[4-methylene-(1-methylbenzyl)phenol]  
2,2'-thiobis(4,6-diarylphenol)  
2,2'-thiobis(4,6-di-tert.-butylphenol)  
2,2'-thiobis(4,6-diketophenyl)  
2,2'-thiobis(4,6-dieisaryphenol)  
3,3'-thiobisphenols, e.g.:  
3,3'-thiobis(methyl-6-(1,1,3,3-tetramethylbutyl)phenol)  
3,3'-thiobis(methyl-6-4-decylphenol)  
3,3'-thiobis(pentadecyl-1-butylphenol)  
4,4'-thiobis phenols, e.g.:  
4,4'-thiobis(3-methyl-6-tert.-butylphenol)  
4,4'-thiobis(3-methyl-6-(1-methylcyclohexyl)phenol)  
4,4'-thiobis(2-methyl-6-tert.-butylphenol)  
4,4'-thiobis(3,5-dimethylphenol)  
4,4'-thiobis(3,6-di-tert.-butylphenol)  
4,4'-thiobis(3-ethyl-6-tert.-butylphenol)  
4,4'-thiobis(3-n-propyl-6-amylphenol)  
4,4'-thiobis(3-methyl-6-n-octylphenol)  
4,4'-thiobis(3-amyl-6-tert.-octylphenol)  
4,4'-thiobis(3-methyl-6-n-decylphenol)  
4,4'-thiobis(3-methyl-6-laurylphenol)  
4,4'-thiobis(3,6-diallylphenol)  
4,4'-thiobis(3,6-diarylphenol)  
4,4'-thiobis[3-methylene-(1-methylcyclohexyl)phenol]  
4,4'-thiobis[3-methylene-(1-methylbenzyl)phenol]  
4,4'-thiobis(2-tert.-butylphenol)  
4,4'-thiobis(2-methyl-6-(1-methylcyclohexyl)phenol)  
4,4'-thiobis[2-methyl-6-(1-methylbenzyl)phenol]  
4,4'-thiobis(2,6-tert.-butylphenol)  
4,4'-thiobis(2,6-laurylphenol)  
4,4'-thiobis(2,6-diarylphenol)  
4,4'-thiobis(2,6-diethylphenol)  
4,4'-thiobis[2,6-di(α-methylbenzyl)phenol]  
4,4'-thiobis[3-(α-methylbenzyl)-6-(α,α-dimethylbenzyl)phenol]  

Thiobis-polyhydroxy compounds, e.g.:  
4,4'-thiobis(resorcinol), 5,5'-thiobis(pyrogallol)  
the di- and tri-thiobis variants of any of the foregoing, and higher molecular weight materials corresponding to the repeating unit of any of the foregoing. These and other like compounds are disclosed, for example, in U.S. Patents 2,670,382; 2,670,383; 2,841,619; 3,060,121; 3,069,384; 3,157,277; 3,173,798 and Compt. rend. 195, 1791-1793 (1934), said disclosures being incorporated herein by reference.  

Particularly preferred are the polyhydroxy compounds such as 4,4'-thiobis(resorcinol) and 5,5'-thiobis(pyrogallol), the so-called "hindered" thiobisphenols, e.g., those wherein each aromatic ring is substituted by one hydroxy group, one bulky group, e.g., secondary or tertiary alkyl group, and one short straight chain (C\(_2\)-C\(_4\)) alkyl group, and higher molecular weight compounds wherein \( p \) is in the range of 5 to 20. Typical of the "hindered" thiobisphenols are 2,2'-thiobis(4-methyl-6-tert-butylyphenol); 4,4'-thiobis(6-tert-butylyl methyl cresol); and 4,4'-thiobis(6-tert-butylyl ortho cresol). Of the thiobisphenols, the first shows best results and it would appear that as the sulfur atom is shifted away from a position ortho to the hydroxyl and the methyl group is shifted toward the ortho from the para position, bleaching efficiency decreases. Typical of the higher molecular weight compounds is polythio-(resorcinol) wherein \( p \) is 6 to 9.  

The conditions of treatment may be varied over fairly wide ranges and are therefore not particularly critical. Likewise, sequence of admixture of treating compound and fatty acid fraction is non-critical. Very small amounts of the additive are effective and may be termed "catalytic" amounts, e.g., from about 0.01% to 1.0%, preferably 0.02% to 0.5%, by weight of the treating compound based on the weight of the tall oil or resin or compound thereof.  

The treating compounds may be employed singly or in mixtures of two or more.  

Good bleaching and color stability of tall oil fatty acid fractions is generally achieved by treating them for from about 5 minutes to 5 hours over a temperature range of about 200° C. to 300° C., the lower temperature corresponding to the longer time and vice versa. Preferred conditions are a treatment for from about 15 minutes to one hour over about 240° C. to 275° C., time and temperature being inversely related. Little or no bleaching and color stabilization is noted below about 200° C., and above about 300° C., decomposition and polymerization sets in, particularly in tall oil fractions containing higher proportions of fatty acids, e.g., 75% to 99%. The process may be conducted at atmospheric, sub- or superatmospheric pressure if desired, with corresponding temperature adjustments. Procedures may be batch, semi-continuous or continuous.  

To avoid oxidation, the treatment is conducted under a blanket of inert gas such as nitrogen, carbon dioxide, steam or the like. Additional treatment of tall oil fatty acid fractions to obtain further bleaching and color stability is unnecessary for most end product uses of these fatty acids. However, if desired, bleaching with clay in the conventional manner may be employed as a supplemental treatment to further reduce the color. Other stabilizing treatments likewise may be employed if desired, such as the addition of oxidation inhibitors and the like.  

From the foregoing description, and also from the examples appended hereto, it will be seen that the present invention is based on the discovery that tall oil and tall oil ingredients, including particularly resins and resin compounds, can be bleached to lighter and more color-stable products by heating them in the presence of the phenol sulfide bleaching agents described. The present inventor, jointly with Joseph James McBride, has also discovered that these same phenol sulfides are also disproporionation accelerators or catalysts so that disproporionated resins can be obtained when resins containing them are heated at from about 250° C. to 350° C. until their abietic acid content is reduced to less than 15%. It will be understood that this discovery is not claimed as such herein as it is the claimed subject matter of a copending application Serial No. 579,817 filed Sept. 16, 1966 now Patent No. 3,377,324 dated Apr. 9, 1968.  

The following is a summary of the subject matter of that application.  

Use more stringent conditions of treatment, such as heating rosin at 300° C. or higher in the presence of catalytic amounts (as defined hereinabove) of treating
agent, disproportionation occurs simultaneously with bleaching. Generally, disproportionation may be achieved with bleaching when rosin is heated at from about 250°C to 350°C for from about 1 to 8 hours, preferably from 290°C to 320°C for from about 3 to 6 hours. A consequence of disproportionation is greatly improved resistance of the rosin to oxidation. For purposes of disproportionation, "rosin" includes the treated samples in air at 110°C (oven) for 1 hour. The color and stability of the feed were 7* and 7*, respectively.

As compared to the colors of the control after each sampling, maximum bleaching was not more than about two points (7* to 5*) on the color scale. However, this is a considered a good result in the art, particularly in view of the substantial stability of the improved color.

### Table I

<table>
<thead>
<tr>
<th>Example</th>
<th>Control</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
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<td>7</td>
<td>6</td>
<td>7</td>
<td>6</td>
</tr>
</tbody>
</table>

### Table II

Table II below shows the results of treating substantially the same tall oil fatty acid fraction as in Examples 1–8 and another commercially available tall oil fatty acid fraction (Example 10) of typical analysis 97.0% fatty acid mixture, 1.4% rosin acids and 1.6% unsaponifiables.

The treatment comprises heating the samples under nitrogen at 275°C for 30 minutes in the presence of 0.1% of TBP, i.e., 2,2'-thiobis(4-methyl-6-t-butylphenol), cooling to 60°C, and then treating the bleached products for 1 hour with clay in the conventional manner. The thiobiphenol treatment shows good bleaching with substantial stability as compared with the feed. As also shown, further bleaching and stability is achieved by subsequent clay treatment. The colors are based on Gardner 1933 standards.

<table>
<thead>
<tr>
<th>Example</th>
<th>Feed</th>
<th>Color</th>
<th>Stability</th>
<th>Color</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>TBP-treated</td>
<td>5°</td>
<td>5°</td>
<td>5°</td>
<td>5°</td>
</tr>
<tr>
<td>19</td>
<td>Clay-treated</td>
<td>2°</td>
<td>4°</td>
<td>3°</td>
<td>5°</td>
</tr>
</tbody>
</table>

### Examples 11–13

Table III demonstrates bleaching, and stabilization of the resulting improved color, of solvent/acid-reified tall oils by treatment at 250°C under nitrogen with 0.1% by weight of 2,2'-thiobis(4-methyl-6-t-butylphenol) for the indicated times essentially as described in Examples 1–8. The tall oils were three grades (Examples 11–13) of "Facoil" solvent refined tall oils obtained by heating a hexane slurry of crude tall oil with concentrated sulfuric acid and separating the resultant refined oil. The color scale is the same as Examples 1–8. The color is improved (lightened) by the acid treatment and further improved by the method of the invention as a comparison of the feed color and stability shows.

<table>
<thead>
<tr>
<th>Example</th>
<th>Time (min.)</th>
<th>Color</th>
<th>Stability</th>
<th>Color</th>
<th>Stability</th>
<th>Color</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>9</td>
<td>7*</td>
<td>10</td>
<td>7</td>
<td>10</td>
<td>8</td>
<td>13</td>
</tr>
<tr>
<td>12</td>
<td>13</td>
<td>6*</td>
<td>14*</td>
<td>5</td>
<td>7</td>
<td>6</td>
<td>11</td>
</tr>
<tr>
<td>13</td>
<td>30</td>
<td>6*</td>
<td>15*</td>
<td>5</td>
<td>7</td>
<td>6</td>
<td>11</td>
</tr>
<tr>
<td>14</td>
<td>30</td>
<td>6*</td>
<td>15*</td>
<td>5</td>
<td>7</td>
<td>6</td>
<td>11</td>
</tr>
<tr>
<td>15</td>
<td>9</td>
<td>7*</td>
<td>10</td>
<td>7</td>
<td>10</td>
<td>8</td>
<td>13</td>
</tr>
<tr>
<td>16</td>
<td>13</td>
<td>6*</td>
<td>14*</td>
<td>5</td>
<td>7</td>
<td>6</td>
<td>11</td>
</tr>
</tbody>
</table>

### Examples 14–16

Under substantially the same conditions as described in Examples 1–13 above, good bleaching and stabilization of the resulting color is obtained by treatment of high...
fatty acid tall oil fractions, including solvent/acid refined tall oils, with 4,4'-thiobis(resorcinol), 1,1'-thiobis(p-naphthol), and a poly(thio(resorcinol)) compound of Formula I above wherein p is 6.

The poly(thio(resorcinol)) is prepared by slowly adding sulfur dichloride to a solution of resorcinol in dibutyl ether and holding the reaction at 10–15°C, for a half hour after the addition. Sodium hydroxide solution is then added to dissolve the resulting polymeric black precipitate and the dibutyl ether is stripped by steam distillation. The polymer is then precipitated by addition of hydrochloric acid and collected by filtration.

Group B—Bleaching and stabilizing rosin compounds

In all of the examples of this group S–1 rosin is tall oil rosin conforming to the Naval Stores Act (February 8, 1952) and Federal Specification LLL-R–6266, Class C (May 27, 1957). S–2 rosin is substantially the same as S–1 rosin except that it contains less bottoms than S–1 rosin. N rosin is an N-colored S–1 tall oil rosin and SH rosin is a heat-treated S–1 tall oil rosin.

A suitable reaction vessel equipped with thermometer, inert gas inlet and means for agitation. When steam is employed as the inert gas, a suitable condenser is attached. The treating agent is then added to the vessel and heat is applied. The contents are reacted under an inert gas blanket, such as nitrogen or steam, while maintaining the temperature at a preselected level. Colors are determined following this treatment. Samples are then tested for color stability after aeration. The samples are aerated by drawing over them for 10 minutes a volume of air equal to 2 milliliters per gram of rosin compound which has been heated to 180–200°C under agitation. The vessel containing the treated rosin compound is then closed and agitator continued for 20 minutes at 180° C. to 200°C. Aeration and color sampling is repeated as required.

Table I below shows a number of runs representing batches of several types of rosin compounds treated as above. For comparison, the results of treatment with several commercially available antioxidants are shown in section 4 of the table.

TABLE I Treatment Color

<table>
<thead>
<tr>
<th>Table section</th>
<th>Run (batch)</th>
<th>Type rosin compound</th>
<th>Temp., °C.</th>
<th>Additive</th>
<th>Weight, per cent</th>
<th>Feed</th>
<th>After treatment</th>
<th>After aeration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 hour</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>S–1, SH</td>
<td>180</td>
<td>I</td>
<td>0.1</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>S–1, SH</td>
<td>180</td>
<td>1</td>
<td>0.1</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>S–1, SH</td>
<td>180</td>
<td>I</td>
<td>0.4</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>S–2, SH</td>
<td>220</td>
<td>I</td>
<td>0.1</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>S–2, SH</td>
<td>220</td>
<td>I</td>
<td>0.1</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>S–2, SH</td>
<td>220</td>
<td>I</td>
<td>0.1</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>S–2, SH</td>
<td>275</td>
<td>I</td>
<td>0.1</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>S–2, SH</td>
<td>275</td>
<td>I</td>
<td>0.1</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>S–2, SH</td>
<td>275</td>
<td>I</td>
<td>0.1</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td>4</td>
<td>19</td>
<td>S–2, SH</td>
<td>275</td>
<td>III</td>
<td>0.1</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>S–2, SH</td>
<td>275</td>
<td>IV</td>
<td>0.1</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>S–2, SH</td>
<td>275</td>
<td>V</td>
<td>0.1</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>S–2, SH</td>
<td>275</td>
<td>VI</td>
<td>0.1</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>S–2, SH</td>
<td>275</td>
<td>VII</td>
<td>0.1</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>S–2, SH</td>
<td>275</td>
<td>VIII</td>
<td>0.1</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>S–2, SH</td>
<td>275</td>
<td>VIII</td>
<td>0.1</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>S–2, SH</td>
<td>275</td>
<td>VIII</td>
<td>0.1</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td>5</td>
<td>26</td>
<td>N</td>
<td>275</td>
<td>I</td>
<td>0.1</td>
<td>X</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>W</td>
<td>275</td>
<td>I</td>
<td>0.1</td>
<td>X</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>Gum</td>
<td>275</td>
<td>I</td>
<td>0.1</td>
<td>X</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
<tr>
<td></td>
<td>29</td>
<td>S–2</td>
<td>275</td>
<td>I</td>
<td>0.1</td>
<td>Y</td>
<td>NW</td>
<td>WW-WG</td>
</tr>
</tbody>
</table>

*0.05% added at the start of the bleach and 0.05% added after 1/2 hour.

Unless otherwise indicated, the color values are those of the conventional USDA and French scales.

The French Rosin Standards (Bordeaux Scale) are obtainable from Tintometer, Ltd., Salisbury, England, and in the United States from Hayes G. Shimp, Inc., 866 Willis Ave., Albertson, N.Y. They are often used to grade rosins which are lighter in color than X, the lightest color of the USDA scale.

The additives of Tables I to III are identified as follows:

I = 2,2'-thio bis(4-methyl-6-tertiary-butylphenol)
II = 2,2'-methylenebis(4-methyl-6-tertiary-butylphenol)
III = 4,4'-thiobis(6-tertiary-butyl-meta cresol)
IV = 4,4'-thio bis(6-tertiary-butyl-ortho cresol)
V = thiiodipropionic acid
VI = distearyltithiodipropionate
VII = 2,5-diphenyl-p-benzoquinone
VIII = sulfur

Example 1

In a typical treatment, a rosin compound is charged to

Although the non-thiobisphenol sulfur-containing additives show some bleaching, it will be noted that additive I gives a better bleach and less color loss after two aeration than the others. Also notable is the absence of bleaching with additive II which has the same structure as I except that sulfur is replaced by —CH=.

Table II belowshows the effect of treatment, as in the foregoing runs, on analytical values of S–2 tall oil rosin samples. It will be seen that abietic acid content is only slightly reduced and the color values are negligibly affected if at all. Loss of abietic acid, i.e., disproportionation, can be minimized by not heating over 300°C. and by shortening the time of treatment. The analytic methods are those identified or described in "Acintol Tall Oil Products," Arizona Chemical Company, New York, November 1964, pages 23–26 except that the percent abietic acid is measured by the Rubber Reserve Method and hardness is determined by reading the depth of penetration in 0.1 mm. units of a standard needle into a solid sample, employing a Universal Model Penetrometer.
Table II

<table>
<thead>
<tr>
<th>Run (batch)</th>
<th>Additive, weight percent</th>
<th>Temp., °C</th>
<th>Time, hours</th>
<th>Acid number</th>
<th>Racemic acids percent</th>
<th>Unstable, percent</th>
<th>Fatty acids, percent</th>
<th>Specific rotation</th>
<th>Hardness, mm.</th>
<th>S-P, %</th>
<th>Acetic acid, percent</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 (feed)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>175.6</td>
<td>90.8</td>
<td>3.3</td>
<td>4.0</td>
<td>+1.1</td>
<td>0.5</td>
<td>79.5</td>
<td>29.9 X</td>
</tr>
<tr>
<td>31</td>
<td>0.1</td>
<td>275</td>
<td>1</td>
<td>174.5</td>
<td>90.7</td>
<td>4.1</td>
<td>3.1</td>
<td>+11.5</td>
<td>0.1</td>
<td>83.0</td>
<td>26.7</td>
<td>2A</td>
</tr>
<tr>
<td>32</td>
<td>0.1</td>
<td>275</td>
<td>1</td>
<td>174.8</td>
<td>90.7</td>
<td>4.0</td>
<td>3.3</td>
<td>+8.8</td>
<td>0.1</td>
<td>80.0</td>
<td>28.3</td>
<td>4A</td>
</tr>
<tr>
<td>33</td>
<td>0.1</td>
<td>275</td>
<td>1</td>
<td>173.5</td>
<td>90.8</td>
<td>3.7</td>
<td>3.9</td>
<td>+11.9</td>
<td>0.1</td>
<td>78.0</td>
<td>23.0</td>
<td>2A</td>
</tr>
<tr>
<td>34</td>
<td>0.1</td>
<td>240</td>
<td>1</td>
<td>176.7</td>
<td>90.4</td>
<td>2.5</td>
<td>3.5</td>
<td>+7.4</td>
<td>0.0</td>
<td>81.9</td>
<td>21.0</td>
<td>2A</td>
</tr>
</tbody>
</table>

Example 2

Table III below shows the effect of treating tall oil rosin with thiophenol additive I under nitrogen as in Example 1 except that the mixture was held at 180° C. for 5 minutes (only to insure uniform dispersion before aeration) rather than for 30 minutes or longer. By contrast with the examples of Table I, it will be seen that no bleaching occurred and the color actually darkened slightly after aeration. The data thus shows the importance of bleaching and color stability of extended heat treatment at lower temperatures as well as use of the thiophenol.

<table>
<thead>
<tr>
<th>Color</th>
<th>WGT Percent of Additive I</th>
<th>WGT Percent of Additive II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>1 Aeration</td>
<td>WW, WW, WW, WW, WW, WW, WW</td>
<td>WW, WW, WW, WW, WW, WW</td>
</tr>
<tr>
<td>2 Aeration</td>
<td>WW, WW, WW, WW, WW, WW, WW</td>
<td>WW, WW, WW, WW, WW, WW</td>
</tr>
<tr>
<td>3 Aeration</td>
<td>WW, WW, WW, WW, WW, WW, WW</td>
<td>WW, WW, WW, WW, WW, WW</td>
</tr>
</tbody>
</table>

Example 3.—Formaldehyde-treated tall oil rosin

Part (A).—An S-1 tall oil rosin sample was first treated with paraformaldehyde in a conventional manner. This product was thereafter bleached as follows:

The formaldehyde-treated rosin was charged to a 1-litter, 3-neck flask with attached agitator, thermometer, gas inlet tube, and condenser. The rosin was heated to 260° C. under a nitrogen blanket and 2,2'-thiobis(4-methyl-6-t-butyphenol) was added and heating was continued for ½ hour. At this time the color was Y. The reaction mixture was then cooled over 40 minutes to 225° C. Color was then 3A. Paraformaldehyde was then introduced at 148° C. and the resulting formaldehyde treated rosin had a color of K.

At the end of the formaldehyde treatment, the pressure was vented. A color of I (dark) resulted. After heating to 275° C., a color of I (light) was obtained which lightened still further to K when the heating was continued at 275° C. for ½ hour. Cooling was applied and, after 45 minutes, a temperature of 210° C. was reached. A color of M was obtained.

Part (D).—The procedure of Part (A) was repeated with 0.02% of the same thiophenol additive except that the additive was charged before heating the formaldehyde-treated rosin (which had an H color). The mixture was then heated to 275° C. to give a color of I and after 30 minutes (only to insure uniform dispersion before aeration) rather than for 30 minutes or longer. By contrast with the examples of Table I, it will be seen that no bleaching occurred and the color actually darkened slightly after aeration. The data thus shows the importance of bleaching and color stability of extended heat treatment at lower temperatures as well as use of the thiophenol.

Example 4.—Fumaric acid adds of tall oil rosin

Part (A).—In a 1000-ml., 3-neck flask equipped with agitator, thermometer, gas inlet port and reflux condenser, S-1 rosin (color WW) and 2,2'-thiobis(4-methyl-6-t-butylphenol) was added and heating was continued for 2 hours under nitrogen.

A color of N resulted. The resulting rosin was then bleached 30 minutes at 275° C. with 0.1% 2,2'-thiobis(4-methyl-6-t-butylphenol). A color of 3A resulted. This color was maintained after an additional 30 minutes treatment at 275° C.

Part (B).—In the same equipment as in Part (A), S-1 rosin (color WW) was bleached 30 minutes at 275° C. with 0.1% of the same thiophenol under nitrogen. A color of 6A resulted. The rosin was then cooled to 200° C. and 4% by weight fumaric acid was added. Heating was continued for 2 hours. After this time, a color of 3A was obtained.

Example 5.—Maleic anhydride adducts of tall oil rosin

In the equipment described in Example 4, S-1 rosin and 3.6% by weight maleic anhydride were heated at 190° C. for 1 hour under nitrogen. A color of M resulted. This adduct was then heated 1 hour at 275° C. with 0.1% 2,2'-thiobis(4-methyl-6-t-butylphenol), resulting in WG color.

Examples 6–8

In substantially the same manner as in Example 1, the following thiobis additives were employed to bleach S-1 rosin. The conditions of treatment were 0.1% by weight thiophenol and 275° C. for 1 hour. A control rosin sample treated under the same conditions except for the presence of the thiophenols had a color in the range Y–2A. Afdic acid content of the control was about 27%. The additive of Example 1 is included for comparison. Substantial bleaching and good color stability was obtained in each case as demonstrated in Table V.

TABLE V

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Additive</th>
<th>Color after treatment</th>
<th>Abietic acid, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2,2'-thiobis(4-methyl-6-t-butylphenol)</td>
<td>15.0</td>
<td>2A</td>
</tr>
<tr>
<td>7</td>
<td>4',4''thiobis(ferulic acid)</td>
<td>15.0</td>
<td>2A</td>
</tr>
<tr>
<td>8</td>
<td>2,2'-thiobis(4,5-dimethylphenol)</td>
<td>15.0</td>
<td>2A</td>
</tr>
</tbody>
</table>

Examples 9–10

Essentially as described in Example 1, S-2 rosin was treated at 275° C. for 1 hour with 0.1% of the thiophenol indicated in Table VI to obtain substantial bleaching as shown. The samples were thereafter cooled to 190–200° C. and aerated as described in Example 1. These tests show good color stability.
TABLE VI

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Additive</th>
<th>Color</th>
<th>Feed color</th>
<th>After bleaching</th>
<th>After aeration (stability)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>2,7-thiobis(4,6-dimethylphenol)</td>
<td>X-WW</td>
<td>6A</td>
<td>4A</td>
<td>3A</td>
</tr>
<tr>
<td>10</td>
<td>4,4'-thiobis(resorcinol)</td>
<td>WW</td>
<td>6A</td>
<td>5A</td>
<td>3A</td>
</tr>
</tbody>
</table>

B. Bleaching action

Essentially as described in Example 1, various samples of S-tall oil resin were heated at 275° C. under nitrogen for 30 minutes with 0.02% by weight of the polymeric product of part A above with the good bleaching shown in Table VII below.

TABLE VII

<table>
<thead>
<tr>
<th>Run</th>
<th>Feed color</th>
<th>Product color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>2</td>
<td>N</td>
<td>X</td>
</tr>
<tr>
<td>3</td>
<td>N</td>
<td>WW</td>
</tr>
<tr>
<td>4</td>
<td>N</td>
<td>WW</td>
</tr>
</tbody>
</table>

The color of these products was nearly the same, i.e., product of run 3 was slightly darker than X and the product of run 4 was slightly lighter than WW.

I claim:

1. A method of improving both the color and the color stability of a material of the group consisting of tall oils and resin compounds which comprises heating said material in the presence of an effective amount within the range of about 0.01% to 1% of a phenol sulfide of the formula:

   \[
   (\text{HO})_x \left[ \text{Ar} \right] \left[ \text{Ar} \right] \left[ \text{S} \right] \left[ \text{S} \right] \left(\text{OH}\right)_x
   \]

2. The method of claim 1 wherein the phenol sulfide is a poly(thio(resorcinol)) wherein \( p \) is in the range of 5 to 20.

3. A method of improving both the color and the color stability of a tall oil containing at least 50% by weight of fatty acids which comprises heating said tall oil at a temperature of about 200° C. to 300° C. in the presence of about 0.01% to 1% of a phenol sulfide for about 5 minutes to 5 hours, said phenol sulfide being a compound of the formula:

   \[
   \left(\text{HO}\right)_x \left[ \text{Ar} \right] \left[ \text{Ar} \right] \left[ \text{S} \right] \left[ \text{S} \right] \left(\text{OH}\right)_x
   \]

   wherein \( n \) is an integer from 1 to 3, \( p \) is an integer from 0 to 100, \( x \) is 1 to 3 inclusive, the sum of \( m \) and \( n \) on each \( \text{Ar} \) is from 1 to 5 inclusive, \( \text{Ar} \) is phenyl, naphthyl or anthracyclic, and \( R \) is a hydrocarbon radical of 1 to 22 carbon atoms, the heating being at about 180° C. to 350° C. for a time ranging from instantaneous to 18 hours and such that a substantial lightening in color of the material is obtained but the abietic acid content is not reduced by the heating to less than 15%.

4. The method of claim 5 wherein said phenol sulfide is 2,2'-thio-bis-(4-methyl-6-t-butyl-phenol).

5. The process of bleaching and stabilizing the color of a material selected from the group consisting of resin containing at least 50% of resin acids and resin compounds derived therefrom which comprises heating said material in the presence of about 0.01% to 1% of a phenol sulfide of the formula:

   \[
   \left(\text{HO}\right)_x \left[ \text{Ar} \right] \left[ \text{Ar} \right] \left[ \text{S} \right] \left[ \text{S} \right] \left(\text{OH}\right)_x
   \]

   wherein \( n \) is an integer from 1 to 3 inclusive, \( p \) is an integer from 0 to 100, \( x \) is 1 to 3 inclusive, the sum of \( m \) and \( n \) on each \( \text{Ar} \) is from 1 to 5 inclusive, \( \text{Ar} \) is phenyl, naphthyl or anthracyclic, and \( R \) is a hydrocarbon radical of 1 to 22 carbon atoms, the heating being at about 180° C. to 350° C. for a time ranging from instantaneous to 18 hours and such that a substantial lightening in color of the material is obtained but the abietic acid content is not reduced by the heating to less than 15%.

6. The method of claim 6 wherein said phenol sulfide is 2,2'-thio-bis-(4-methyl-6-t-butyl-phenol).

7. A method of treating a resin comprising heating said resin at a temperature of about 200° C. to 350° C. for about 1 to 8 hours in the presence of about 0.01% to 1% of a phenol sulfide of the formula:

   \[
   \left(\text{HO}\right)_x \left[ \text{Ar} \right] \left[ \text{Ar} \right] \left[ \text{S} \right] \left[ \text{S} \right] \left(\text{OH}\right)_x
   \]

   wherein \( n \) is an integer from 1 to 3; \( p \) is an integer from 0 to 100; \( x \) is a number from 1 to 3; the sum of \( m \) and \( n \) on each \( \text{Ar} \) is from 1 to 5 inclusive, \( \text{Ar} \) is selected from the group consisting of phenyl, naphthyl, and antracylic, and \( R \) is a hydrocarbon radical containing from 1 to 22 carbon atoms, the heating being for a time such that a substantial lightening of the material is obtained but the abietic acid content is not reduced by the heating to less than 15%.

8. The method of claim 7 wherein said phenol sulfide is 4,4'-thio-bis-(resorcinol).

9. The process of bleaching and stabilizing the color of a material selected from the group consisting of resin containing at least 50% of resin acids and resin compounds derived therefrom which comprises heating said material in the presence of about 0.01% to 1% of a phenol sulfide of the formula:

   \[
   \left(\text{HO}\right)_x \left[ \text{Ar} \right] \left[ \text{Ar} \right] \left[ \text{S} \right] \left[ \text{S} \right] \left(\text{OH}\right)_x
   \]

   wherein \( n \) is an integer from 1 to 3; \( p \) is an integer from 0 to 100; \( x \) is a number from 1 to 3; the sum of \( m \) and \( n \) on each \( \text{Ar} \) is from 1 to 5; \( \text{Ar} \) is selected from the group consisting of phenyl, naphthyl, and antracylic, and \( R \) is a hydrocarbon radical containing from 1 to 22 carbon atoms, the heating being for a time such that a substantial lightening of the material is obtained but the abietic acid content is not reduced by the heating to less than 15%.

10. The process of bleaching and stabilizing the color of a material selected from the group consisting of resin containing at least 50% of resin acids and resin compounds derived therefrom which comprises heating said material in the presence of about 0.01% to 1% of a phenol sulfide of the formula:

11. The process of claim 8 wherein said phenol sulfide is 4,4'-thio-bis-(resorcinol).

12. The process of claim 8 wherein said phenol sulfide is 2,2'-thio-bis-(4-methyl-6-t-butyl-phenol).
A method of improving both the color and the color stability of a tall oil containing at least 50% by weight of fatty acids which comprises heating said tall oil at 200° C. to 300° C. under a blanket of inert gas and at substantially atmospheric pressure in the presence of an effective amount, within the range of about 0.01% to 1%, of a phenol sulfide for a time, within the range of about 5 minutes to 5 hours, until a substantial lightening of its color is obtained, said phenol sulfide being a compound of the formula

\[
\left(\text{Ar}y\right)_{n}\left(\text{Ar}y\right)_{m}
\]

where  \(n\) is an integer from 1 to 3 inclusive,  \(p\) is an integer from 0 to 100,  \(x\) is 1 to 3, the sum of  \(m\) and  \(n\) on each  \(\text{Ar}y\) is from 1 to 5 inclusive,  \(\text{Ar}y\) is phenyl, naphthyl or anthracyl and  \(R\) is a hydrocarbon radical of 1–22 carbon atoms.

A method according to claim 13 in which the tall oil is a commercial fraction containing about 94.2% mixed saturated and unsaturated fatty acids, about 4.2% rosin acids and 1.6% unsaponifiables, the phenol sulfide is 2,2’-thiobis(4-methyl-6-butyphenol), and the heating is at about 240° C. to 275° C. for from about 15 minutes to two hours.