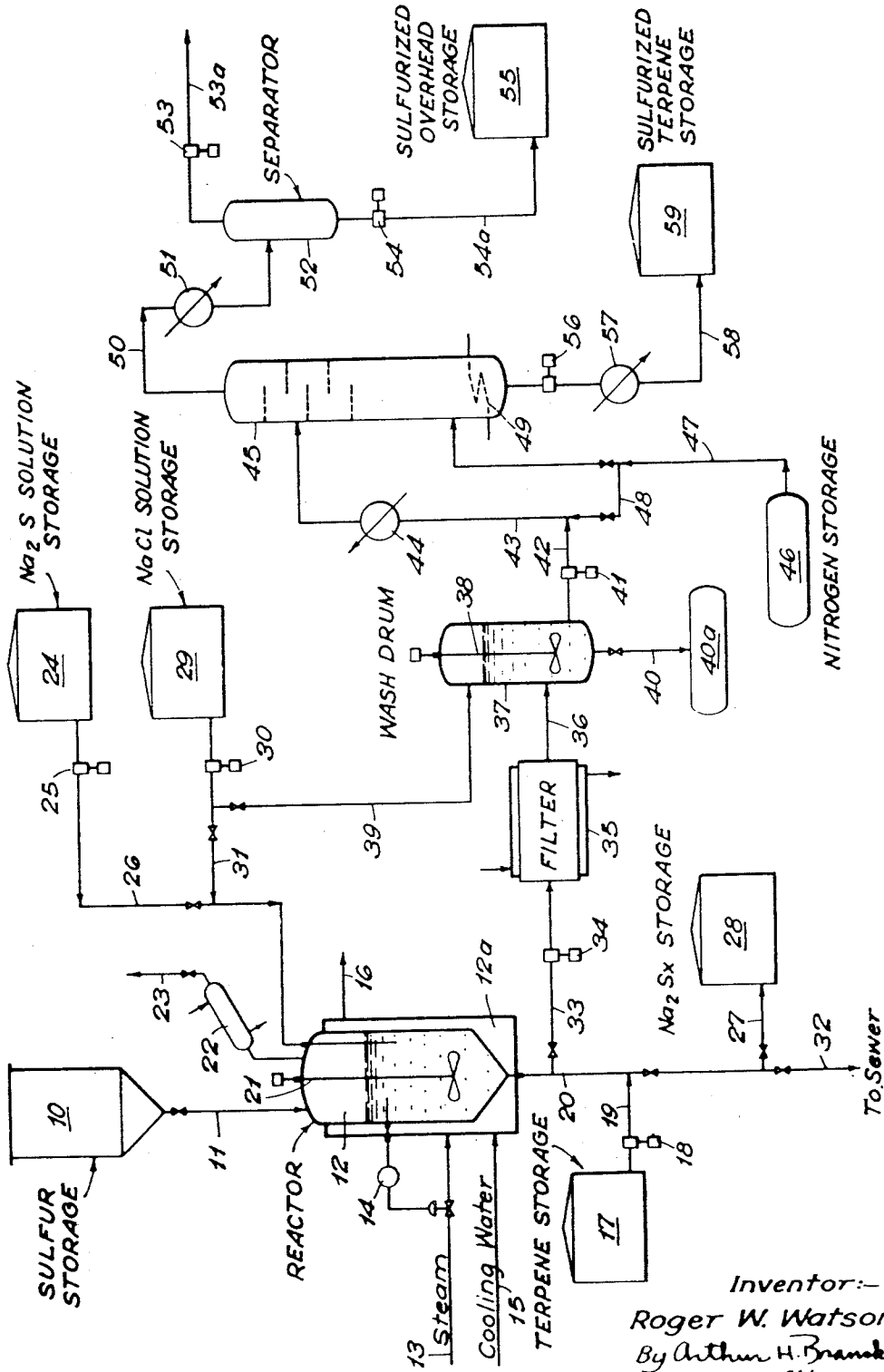


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METHOD OF SULFURIZING TERPENES

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METHOD OF SULFURIZING TERPENES

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The present invention relates to an improved method of sulfurizing terpenes with elemental sulfur.

Terpenes have heretofore been sulfurized with elemental sulfur by mixing the terpene and the sulfur and heating the mixture to the desired reaction temperature. Another method commonly employed is to heat the terpene to the reaction temperature while adding thereto small amounts of the sulfur until the required amount of sulfur has been added. These methods of sulfurizing terpenes have the disadvantage in that it is extremely difficult, if not impossible, to regulate the temperature or to control the rate of reaction due to the exothermic nature of the reaction. The incremental or continuous addition of sulfur to the reaction involves many difficulties since the light hydrocarbons reflux at the reaction temperature and the condensate impedes the addition of dry sulfur. Because of difficulties encountered in controlling the exothermic reaction when terpenes are sulfurized in the manner described, the sulfurized terpenes are very dark in color.

It is an object of the present invention to provide a method of sulfurizing terpenes in which the exothermic reaction can be controlled. Another object of the invention is to provide a method of sulfurizing terpenes which avoids excessive polymerization and color formation. Another object of the invention is to provide a method of sulfurizing terpenes which results in improved yields. Other objects and advantages of the present invention will become apparent from the following description thereof read in conjunction with the accompanying drawing, which is a flow diagram of a preferred method of carrying out the present invention.

I have discovered that the foregoing objects can be attained by a method of sulfurization in which the terpene is added in the liquid phase to a body of molten sulfur maintained at a certain optimum temperature. Terpenes which can be sulfurized by the herein-described method, including the monocyclic, bicyclic and acyclic terpenes, as well as polyterpenes. Examples of species falling within these classes of terpenes are pine oil, turpentine, cymene, alpha-pinene, beta-pinene, allo-ocimene, fenchenes, bornylenes, menthadienes such as limonene, dipentene, terpinene, terpinolenes and $\Delta^{2,4(8)}$ -p-menthadiene, sesquiterpenes, diterpene, and polyterpenes having the general formula $(C_5H_8)_x$. Mixtures of such terpenes can also be employed in the invention. In accordance with the present invention,

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elemental sulfur is stirred at a temperature above its melting point, for example at a temperature of from about 325° F. to about 400° F., and preferably at a temperature of from about 350° F. to about 375° F., and the terpene slowly added in the liquid phase to the molten sulfur. To facilitate adequate stirring, it is advantageous to add a small amount of the terpene, preferably when the molten sulfur has reached a temperature of about 310° F.-340° F., and the temperature then raised to the desired reaction temperature, for example 375° F. before the remaining portion of the terpene is added. Usually, the addition of about 5% of the terpene will be found adequate to facilitate adequate stirring; the remaining 95% of the terpene being then added at the desired reaction temperature.

The sulfurized terpenes contain some active sulfur, as evidenced by the darkening of a copper strip submerged in about 0.5% solution of the sulfurized terpenes in a hydrocarbon oil maintained at a temperature of about 210° F. For certain uses such as lubricating oil additives, the presence of such active sulfur compounds in the sulfurized terpenes is undesirable. These so-called active sulfur compounds can be deactivated by treating the same with an alkali metal sulfide, such as sodium sulfide or with a mixture of an alkali metal sulfide and a small amount of an alkaline material such as for example sodium hydroxide.

After the sulfurization reaction is completed, which will take from about 5 minutes to about 60 minutes or more, and usually about 15 minutes, the sulfurized terpene is rendered non-corrosive by deactivation by the addition of an alkali metal sulfide, such as sodium sulfide, preferably added as an 18% aqueous solution. It will be understood that the time of sulfurization is dependent largely upon the rate of refluxing and other cooling means for controlling the exothermic reaction. During the deactivation stage the reaction mixture is maintained at a temperature from about 200° F. to about 260° F., and preferably at about 230° F. It is desirable during the deactivation stage to maintain the reaction mixture under a pressure sufficient to retain the light ends of the product, usually a pressure of about 7 pounds will be found to be sufficient for this purpose. While it is desirable to carry out the deactivation at a preferred temperature at about 230° F. and a pressure of about 7 pounds, higher or lower temperatures and pressures may be employed. After the sulfurized terpene reaction product is deactivated, such as by treatment with

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the sodium sulfide, the reaction mass is permitted to separate into an upper layer comprising the sulfurized terpenes and a lower layer comprising sodium polysulfide solution. After the sodium polysulfide solution layer is separated from the sulfurized terpene product the latter is washed at a temperature of from about 200° F. to about 250° F., and preferably at about 220° F. with a 20% sodium chloride solution. The brine solution is then settled and drawn off. The washed deactivated sulfurized terpene product is then filtered and again washed with a 20% sodium chloride solution to remove the last traces of alkali metal polysulfide from the sulfurized product. If desired, the sulfurized terpene product can then be flash distilled, preferably under reduced pressure, to remove any unreacted hydrocarbons or slightly sulfurized lighter boiling terpenes, preferably using an inert gas, such as nitrogen for stripping. In order to avoid the darkening of the sulfurized terpene product, it is essential that the material be held at a temperature of from about 250° F. to about 350° F., and preferably at about 300° F. for a period of time no longer than about 30 to 35 minutes.

The following description of sulfurizing dipentene according to the present invention to obtain a product suitable for use as a lubricant additive is given by way of example only and not intended as limiting the scope of the invention.

Referring to the accompanying drawing, sulfur forming about 40% by weight of the sulfurization reaction mixture from sulfur storage tank 10 is introduced through a line 11 to the jacketed reactor 12 provided with heating means, such as superheated steam introduced through a line 13, and temperature control means 14. If desired, reactor 12 may be provided with a Dowtherm boiler to supply the necessary heating. The jacketed reactor 12 is also provided with cooling means such as for example water inlet and outlet 15 and 16, respectively. After the sulfur is added to the reactor 12, it is heated to a temperature of about 325° F. to 330° F. at which time about 5% of the required amount of dipentene from storage tank 17 is introduced in the liquid phase into the reactor 12 through pump 18 and lines 19 and 20, and the mixture stirred by means of stirrer 21 or other suitable means. The temperature of the reactor contents is then increased to a temperature of about 375° F. and the balance of the liquid dipentene introduced into the reactor as rapidly as possible. The quantity of dipentene employed amounts to about 60% by weight of the sulfur-dipentene reaction mixture. During this period the temperature within the reactor is maintained at approximately 375° F. suitably by means of a reflux condenser 22. The hydrogen sulfide formed is vented from the reactor 12 through condenser tube 23.

After the completion of the sulfurization reaction, the temperature in the reactor 12 is lowered to about 230° F. by introducing water through line 15 into reactor jacket 12a.

The sulfurized dipentene is then deactivated by treatment with an 18% aqueous solution of sodium sulfide from tank 24 introduced into the reactor 12 via pump 25 and line 26. From about 10% to 20%, and preferably 14% to 15% by weight of sodium sulfide is usually sufficient to deactivate the sulfurized dipentene product. During the time the sulfurized dipentene reaction product is being deactivated with the sodium sulfide, a temperature of about 230° F. is maintained in the reactor by passing steam into the

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jacket 12a. The mixture of sulfurized dipentene reaction products and sodium sulfide is stirred at the proper temperature for a period of about two hours while maintaining a pressure of about 7 pounds upon the reactor to retain the light ends. At the end of the two hour deactivation period, the reaction mass in reactor 12 is permitted to stratify into an upper layer, comprising the deactivated sulfurized dipentene product, and a lower layer of sodium polysulfide solution, and the latter drawn off through lines 20 and 27 to a sodium polysulfide storage tank 28.

After the sodium polysulfide solution is withdrawn from the reactor 12, the deactivated sulfurized dipentene is washed with a 20% sodium chloride solution introduced into the reactor 12 from tank 29 through pump 30 and lines 31 and 32. The washed deactivated sulfurized dipentene is then settled and the sodium chloride drawn off through lines 20 and 32 to the sewer.

The solid sodium polysulfide remaining in the washed deactivated dipentene, together with any other solid or colloidal impurities, are removed by introducing the sulfurized dipentene via lines 20 and 33 and pump 34 to a suitable filter 35, which may be a Sparkler type filter. Filter 35 is maintained by suitable means at a temperature of about 320° F. and operated at a pressure of about 20 pounds per square inch. It has been found that a filter rate of 12½ gallons per hour per square foot is suitable. Lower or higher pressures or temperatures can of course be employed, but with some sacrifice in efficiency.

The filtrate from the filter 35 is passed via line 36 to a wash drum 37, provided with stirring means 38 wherein the filtered sulfurized dipentene is washed one or more times with a 20% sodium chloride solution from tank 29 via pump 30 and lines 31 and 39 to remove the last traces of sodium polysulfide. The sodium chloride solution in wash tank 37 is withdrawn via line 40 to tank 40a. The used sodium chloride solution may be dumped to the sewer, or if a plurality of washes are used, the last wash may be recycled to the wash drum for the washing of the next batch.

The washed filtered sulfurized dipentene from wash tank 37 is passed via pump 41 and lines 42 and 43 to a preheater 44 in which the sulfurized dipentene is heated to a temperature of about 300° F. and then introduced into a stripping tower 45, wherein the heated sulfurized dipentene is flash distilled at about 50 mm. pressure and with sufficient nitrogen purge gas, introduced from nitrogen supply tank 46 via line 47 to reduce the sulfurized dipentene product to a bottoms fraction having the desired sulfur content. If desired, a portion of the nitrogen from tank 46 may be introduced via lines 47 and 48 to line 43 and introduced into the stripping tower 45 together with the sulfurized dipentene. The stripping tower 45 may be provided with heating and/or cooling coils 49.

The amount of nitrogen used is that necessary for maintaining agitation within the stripper 45 and for removing the light ends entrained in the bottoms. An overhead fraction is taken from the stripper 45 via line 50 and condenser 51 to a separator drum 52, from which uncondensables are withdrawn via vacuum pump 53 and line 53a. Unreacted hydrocarbons and sulfurized light products recovered as overhead from the stripping tower 45 are removed from separator drum 52 via pump 54 and line 54a to the storage tank 55. The bottoms from the stripper 45 are withdrawn via

pump 56, passed through a cooler exchanger 57 and through line 58 to storage tank 59.

The filtered sulfurized dipentene after the sodium chloride wash may be used as such; however, for use as a lubricant additive, it is desirable to remove the light ends of the product and concentrate the bottoms to a sulfur content of from about 30% to about 50%, and preferably about 40%. Sulfurized terpenes, particularly sulfurized dipentene having a sulfur content within this range, are suitably employed as lubricant additives to inhibit corrosion, particularly corrosion of alloy bearings and as extreme pressure agents.

Depending upon the intended use of the sulfurized terpene, any amount of sulfur can be employed in the sulfurization of the terpene by the herein-described method. However, for the preparation of sulfurized terpenes as a lubricant additive, the sulfur-terpene reaction mixture should contain from about 25% to about 50%, and preferably about 40% by weight of sulfur, and from about 50% to about 75%, and preferably about 60% by weight of the terpene.

The improvement obtained by sulfurizing terpenes in the manner herein-described is illustrated by the data in the following table in which color and sulfur content comparisons are made between terpenes sulfurized in accordance with the present invention, indicated as method A, and terpenes sulfurized by heating a mixture of sulfur and terpene, indicated as method B.

Test No.	Per Cent Sulfur in Charge	Method of Preparation	True Color ¹ After Deactivation	Per Cent Sulfur After Deactivation
1	25	A	97	21.5
2	25	B	133	19.3
3	33	A	133	24.3
4	33	B	180	23.8
5	40	A	140	28.3
6	40	B	160	27.3
7	40	B	180	26.8

¹ Determined by the method described in Industrial and Engineering Chemistry, vol. 18, p. 164 (1926).

The above data demonstrate the improvement in color and increase in sulfur content of deactivated sulfurized terpenes obtained in changing from the usual method of sulfurizing terpenes to the sulfurization method in accordance with the present invention. The color improvement in the method of the present invention is about 30%. The increase in sulfur in the deactivated sulfurized terpene is an improvement which reflects directly in cost of production. In addition to these advantages, the important advantage of the herein-described method is in the simplicity of operation. Other advantages are that the heat taken up by the incoming terpene, such as dipentene, helps to control the speed of the reaction; further, the dipentene reacts almost instantly with the sulfur so that substantially no polymerization or resinification takes place. This results in improved color and yields.

While I have described in detail a preferred embodiment of my invention, it should be understood that the invention is not limited to any of the details hereinabove set forth, except as defined by the appended claims.

I claim:

1. The method of sulfurizing terpenes comprising heating sulfur to a temperature above its melting point, but not above about 400° F., introducing liquid terpene in said molten sulfur and maintaining said temperature for a time suffi-

cient to substantially complete the sulfurization of said terpene.

2. The method of sulfurizing a terpene comprising heating sulfur to a temperature of from about 325° F. to about 400° F., introducing a terpene in the liquid phase into said molten sulfur and maintaining the reaction mixture at a temperature within the range of about 325° F. to about 400° F. for a time sufficient to complete the sulfurization of said terpene.

3. The method of sulfurizing a terpene comprising heating sulfur to a temperature of 310° F. to 340° F., introducing a small amount of the terpene into said heated sulfur, increasing the temperature of the sulfur-terpene mixture to a temperature of about 350° F. to 375° F., introducing the remainder of the terpene in the liquid phase into the sulfur-terpene mixture and maintaining the reaction mixture at a temperature of about 350° F. to about 375° F. for a time sufficient to substantially complete the sulfurization of said terpene.

4. The method of sulfurizing a terpene as described in claim 3 in which the terpene is a menthadiene.

5. The method of sulfurizing a terpene as described in claim 3 in which the terpene is dipentene.

6. The method of sulfurizing a terpene comprising heating sulfur to a temperature of about 350° F. to about 375° F., introducing a terpene in the liquid phase into said molten sulfur, maintaining the reaction mixture at a temperature of about 350° F. to about 375° F., for a time sufficient to substantially complete the sulfurization of said terpene, treating said sulfurized terpene with an alkali metal sulfide, separating the alkali metal sulfide from the sulfurized terpene product and washing the sulfurized terpene product with a sodium chloride solution.

7. The method of sulfurizing a terpene comprising heating sulfur to a temperature of about 350° F. to about 375° F., introducing a terpene in the liquid phase into said molten sulfur, maintaining the reaction mixture at a temperature of about 350° F. to about 375° F. for a time sufficient to substantially complete the sulfurization of said terpene, treating said sulfurized terpene with an alkali metal sulfide, separating the alkali metal sulfide from the sulfurized terpene product, washing the sulfurized terpene product with a sodium chloride solution and distilling the washed sulfurized terpene product in the presence of an inert gas to remove unreacted hydrocarbons and low boiling sulfurized terpenes.

8. The method of preparing a sulfurized terpene lubricant additive comprising heating elemental sulfur to a temperature of 310° F.-340° F., adding a small amount of terpenes to the heated sulfur, heating the terpene-sulfur mixture to a temperature of about 350° F. to about 375° F., adding the remaining portion of the terpene to the heated mixture, maintaining the reaction mixture at a temperature of about 350° F. to about 375° F. for a time sufficient to substantially complete the sulfurization of the terpene, reducing the temperature of the sulfurized terpene reaction mixture to a temperature of from about 200° F. to about 250° F., adding an alkali metal sulfide to the sulfurized terpene reaction mixture to remove corrosive sulfur therefrom, separating the alkali metal sulfide from the sulfurized terpene reaction product, washing the sulfurized terpene reaction product with a so-

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dium chloride solution and distilling the washed sulfurized terpene reaction product in the presence of an inert gas at a temperature of from about 250° F. to about 350° F. to obtain a bottoms fraction containing from about 30% to about 50% sulfur.

9. The method of preparing a sulfurized dipentene lubricant additive comprising heating elemental sulfur to a temperature of about 325° F. to about 330° F., adding about 5% of the required dipentene in the liquid phase to said heated sulfur, heating said sulfur-dipentene mixture to a temperature of about 375° F., adding the remaining portion of the required dipentene in the liquid phase to said heated dipentene-sulfur mixture, maintaining the reaction mixture at a temperature of about 375° F. for a time sufficient to substantially complete the sulfurization of said dipentene, lowering the temperature of the reaction mixture to about 230° F., adding a sodium sulfide solution to the reaction mixture to deactivate the corrosive sulfur compounds in

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said sulfurized dipentene product, separating the sodium sulfide solution from the sulfurized dipentene reaction product, washing the deactivated sulfurized dipentene product with a 20% sodium chloride solution, filtering the washed sulfurized dipentene product and distilling the filtrate at a temperature of about 300° F. in the presence of nitrogen to obtain a bottoms fraction containing about 40% sulfur.

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