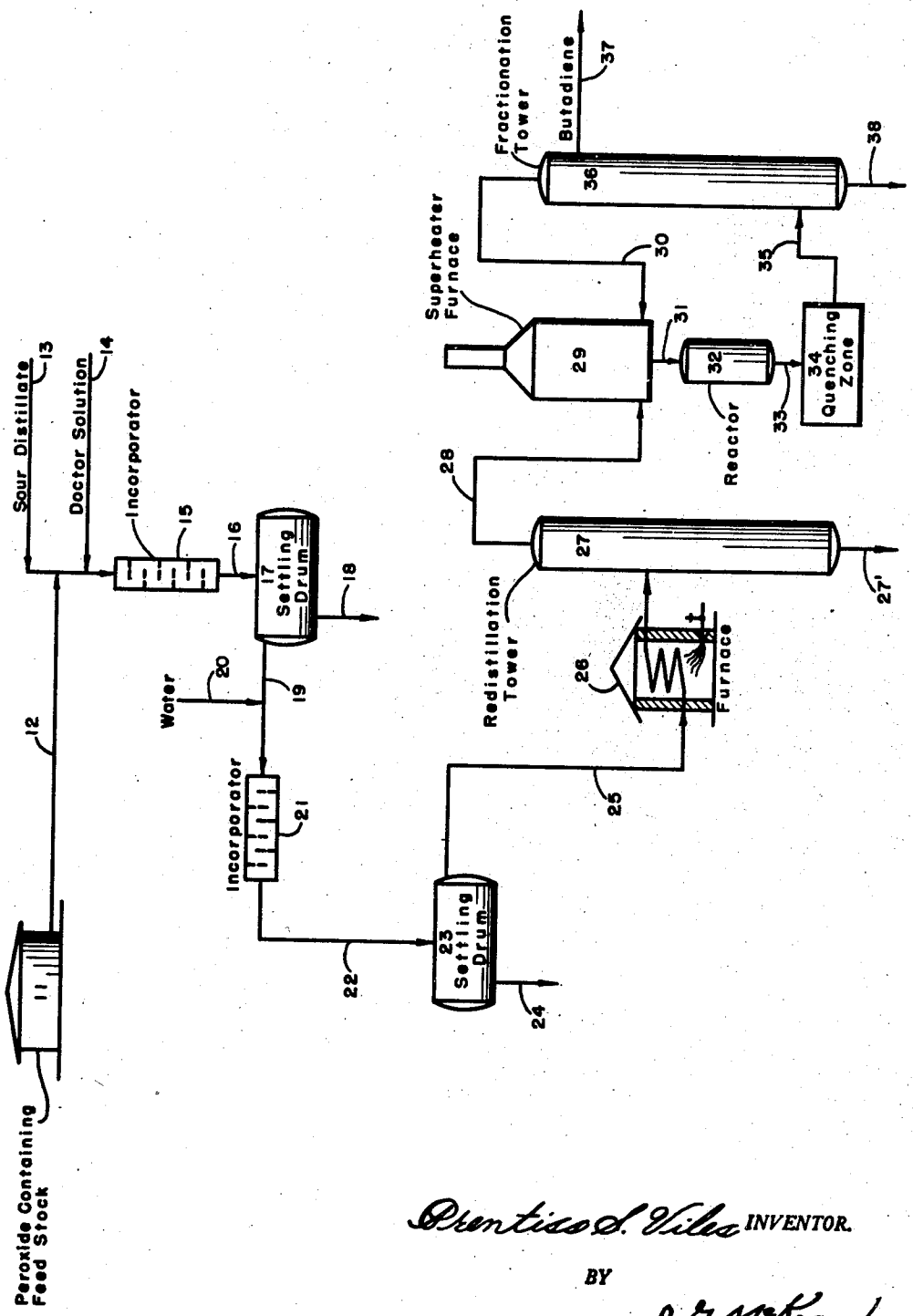
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PRODUCTION OF BUTADIENE

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PRODUCTION OF BUTADIENE

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5 Claims. (Cl. 260—680)

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This invention is concerned with a process for the production of butadiene by the high temperature vapor phase cracking of petroleum distillate.

When a distillate in the naphtha boiling range and containing peroxides is subjected to the high temperatures and other conditions necessary for the optimum production of butadiene by cracking, a severe corrosion problem is encountered. In furnaces, for example, rapid pitting and corrosion often occurs in the furnace tubes subjected to the high temperatures employed for the cracking operation. This corrosion usually leads to early failure of the furnace tubes.

It is believed that when petroleum distillate containing peroxides is subjected to a high temperature cracking operation in order to produce butadiene, such as a temperature of the order of 1300° F. or above, the peroxides are decomposed to form organic acids and perhaps combine with reactive sulfur compounds to form corrosive sulfur compounds and other corrosive products with the result that a rapid pitting and corrosion of the metal equipment occurs at the high temperature spots adjacent the point of formation of the corrosive materials. Prior to the present invention, furnace tube failures occurred in approximately 200 to 400 hours when processing stocks containing appreciable amounts of peroxides or peroxides and reactive sulfur compounds. In an operation in which the reactive materials are absent little or no difficulty is to be expected and furnace tube life should be more than 2,000 hours.

In accordance with the present invention a process is provided to produce butadiene from a peroxide-containing petroleum distillate fraction or a peroxide and reactive sulfur-containing petroleum distillate fraction in such a manner that the formation of materials such as organic acids, hydrogen sulfide and other corrosive compounds is reduced to a minimum thereby causing the corrosion of furnace tubes and other equipment to be substantially reduced or eliminated.

The process of the present invention may be described briefly as involving the steps of forming a peroxide-containing feed stock from a petroleum distillate fraction in the naphtha boiling range, bringing the feel stock into contact with lead mercaptides in a sufficient quantity to react with all of the peroxides and reactive sulfur compounds present in the feed stock, distilling to form a distillate fraction and cracking the distillate fraction at a temperature no less than 1300° F. to form butadiene.

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A preferred method for the practice of the invention will now be described in conjunction with the drawing in which the sole figure is in the form of a diagrammatic flow sheet.

Turning now specifically to the drawing, a container or tank 11 has present therein a charge of a petroleum distillate fraction in the naphtha boiling range and containing peroxides. A suitable charge stock is a naphtha boiling in the range of 180° to 350° F.; the feed stock may include appreciable amounts of aromatic and paraffinic materials or may be principally aromatic material or paraffinic material. Feed stocks in this boiling range and containing appreciable amounts of peroxides may be obtained by distilling a fraction in this boiling range and then allowing it to stand in a tank exposed to an oxygen-containing atmosphere for an interval of time which may be in the range of a few days to months. It is to be understood that the addition of peroxides as such to a feed stock is not usually practiced nor contemplated in the practice of the present invention but the production of a naphtha feed stock in a suitable boiling range and the accumulation of the feed stock in storage exposed to an oxygen-containing atmosphere over an interval of time which allows peroxides to be formed in the feed stock is conventional practice in some refining operations.

The feed stock in the naphtha boiling range and containing peroxides is withdrawn from tank 11 through line 12 and has added thereto a sour distillate fraction discharged into line 12 through inlet 13 and doctor solution which is discharged into line 12 through inlet 14. The mixture of feed stock, sour distillate and doctor solution passes through incorporator 15 where it is thoroughly admixed and the mixture flows through line 16 into settling drum 17. Before the feed stock is mixed with the sour distillate and doctor solution, the amount of peroxides and reactive sulfur material present in the feed stock is determined and the sour distillate and doctor solution is added to the feed stock in amounts sufficient to produce therein lead mercaptides in sufficient quantity to react with at least all of the peroxides and reactive sulfur compounds present in the feed stock withdrawn from storage tank 11. It is preferred that the sour distillate added to the system through inlet line 13 have a higher or lower boiling range but preferably higher than the feed stock. By way of example, as illustrating the practice of the invention, the feed stock may boil in the range of 180° to 350° F. and the

sour distillate may boil in the range of 350° to 550° F.

In settling vessel 17, the lead mercaptides react with the peroxides and reactive sulfur compounds of the feed stock to form insoluble reaction products. These insoluble reaction products settle under the influence of gravity to form a heavy layer which may be withdrawn from vessel 17 through outlet 18 while the remainder forms a light layer which is withdrawn through outlet 19. Water is added to the light layer through inlet line 20 and admixed therewith in incorporator 21, the mixture passing through line 22 to settling vessel 23. The step of contacting the hydrocarbon material with water insures the removal of excess doctor solution and other water insoluble impurities therefrom. The water with dissolved doctor solution and other water soluble materials settles to form a heavy layer in vessel 23 and is removed through outlet 24 and is discarded while the water washed hydrocarbons are withdrawn through outlet 25 to a distillation step.

The hydrocarbon fraction in line 25 is passed through a furnace 26 and thence to distillation tower 27 where it is distilled to form an overhead fraction removed through line 28 and a bottoms fraction removed through outlet 27'. It will be found convenient to withdraw as bottoms from tower 27 an amount equivalent to the heavy sour distillate added to the feed stock via line 13 although a larger or smaller bottoms fraction may be withdrawn, as desired. The distillation step performed in tower 27 is for the purpose of separating a bottoms fraction including peroxides and reactive sulfur compounds which have not been removed by the prior settling and water washing steps.

The overhead fraction passes from line 28 into furnace 29 where it is heated to a sufficiently high temperature to cause the formation of a substantial amount of butadiene. In a preferred operation, a recycle gas is added to the furnace through line 30 with the stream of recycle being separately heated in the furnace to a temperature of approximately 1370° F. before it is mixed with the feed. The feed may be withdrawn from tower 27 through line 28 in a vaporous condition and may be mixed with the hot recycled gas within furnace 29 and the mixture subjected to additional heating so that the mixture withdrawn from the outlet of furnace 29 may be at a temperature within the range of 1300° to 1450° F. The mixture is withdrawn from furnace 29 through outlet 31 to a reactor vessel 32. The vapors from vessel 32 pass through line 33 to quenching zone 34 where they may be quenched to a temperature of approximately 400° F. and pass thence through line 35 to distillation tower 36. In tower 36 a butadiene-containing fraction is separated and withdrawn through side stream 37, a light fraction containing an appreciable amount of C_2 and C_3 hydrocarbons is withdrawn as overhead through line 30 and recycled to furnace 29, while a heavier fraction is withdrawn as bottoms through line 38. The butadiene-rich fraction withdrawn through side stream 37 may be extracted and further purified by conventional methods.

It may be pointed out that the overhead fraction withdrawn from distillation column 27 through outlet line 28 passes the mercury test but is off doctor test. The mercury test consists simply in shaking a small amount of hydrocarbons with a small amount of chemically clean mercury for from 5 to 10 minutes and observing that a black precipitate has formed. If there is no black precipitate, the hydrocarbon sample passes the test; the lack of a black precipitate indicates the lack of peroxides and reactive sulfur compounds in the sample.

While in the drawing is shown a preferred mode for the practice of the present invention, various modifications will be obvious to a worker skilled in the art as within the scope of the invention. For example, while the lead mercaptides are formed within the feed stock by separately adding a mercaptan-containing fraction and doctor solution to the feed stock, the lead mercaptides may be formed by mixing the mercaptan-containing fraction with doctor solution and the resultant lead mercaptides added as such to the peroxide-containing feed stocks. Similarly, while a single water washing step has been shown, a plurality of such steps may be employed. It will also be evident that although the preferred boiling range of the feed stock is disclosed as 180° to 350° F., this boiling range is not intended as a limitation and either a lower or a higher boiling range material may be employed. In like manner, while the preferred boiling range of the mercaptan-containing material is given as within 350° to 550° F., this material may have a lower or higher boiling range, as desired.

Wherever used in this specification and the appended claims, the term "reactive sulfur" is intended to refer to free sulfur and those organic compounds of sulfur which readily react with metallic mercury.

Having fully described the present invention, what I desire to claim is:

1. A method for producing butadiene including the steps of forming a feed stock from a petroleum distillate fraction and including an appreciable amount of peroxides, bringing the feed stock into contact with lead mercaptide in an amount at least sufficient to react with substantially all peroxide and reactive sulfur compounds in the feed stock, subsequently redistilling to form a non-corrosive distillate fraction free of organic peroxides and reactive sulfur compounds and a bottoms fraction and heating the distillate fraction to a cracking temperature of the order of 1300° F. to form butadiene.

2. A method in accordance with claim 1 in which the feed stock boils in the range of approximately 180° to 350° F.

3. A method for forming butadiene including the steps of forming a feed stock from a petroleum distillate fraction boiling in the range of approximately 180° to 350° F. and containing peroxides, admixing with the feed stock a solution containing lead mercaptide in an amount at least sufficient to react with substantially all peroxides and reactive sulfur compounds in the feed stock, settling under the influence of gravity to form a heavy layer including insoluble reaction products and a light layer containing a major portion of the feed stock, washing the light layer, distilling the washed light layer to form a non-corrosive overhead fraction of approximately the same volume as the original feed stock said overhead fraction being free of organic peroxides and sulfur compounds reactive to mercury, and cracking the overhead fraction at a temperature of the order of 1300° F. to form butadiene.

4. A method for producing butadiene including the steps of forming a feed stock from petroleum distillate boiling within the range of 180° to 350° F. and containing peroxides, admixing the feed stock with mercaptans and doctor solution to

form sufficient lead mercaptides to react with substantially all peroxide and reactive sulfur compounds present in the feed stock, subsequently settling to form a heavy layer including insoluble reaction products and a light layer, washing the light layer with water, distilling the washed light layer to form a bottoms fraction and a non-corrosive, sour distillate fraction approximately equal in volume to the feed stock, said distillate fraction being free of organic peroxides and sulfur compounds reactive to mercury, cracking the distillate fraction at a temperature of the order of 1300° F. to form butadiene and recovering a butadiene fraction.

5. A method in accordance with claim 4 in which the mercaptans are added to the feed stock in the form of a sour distillate having a boiling range above that of the feed stock.

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