

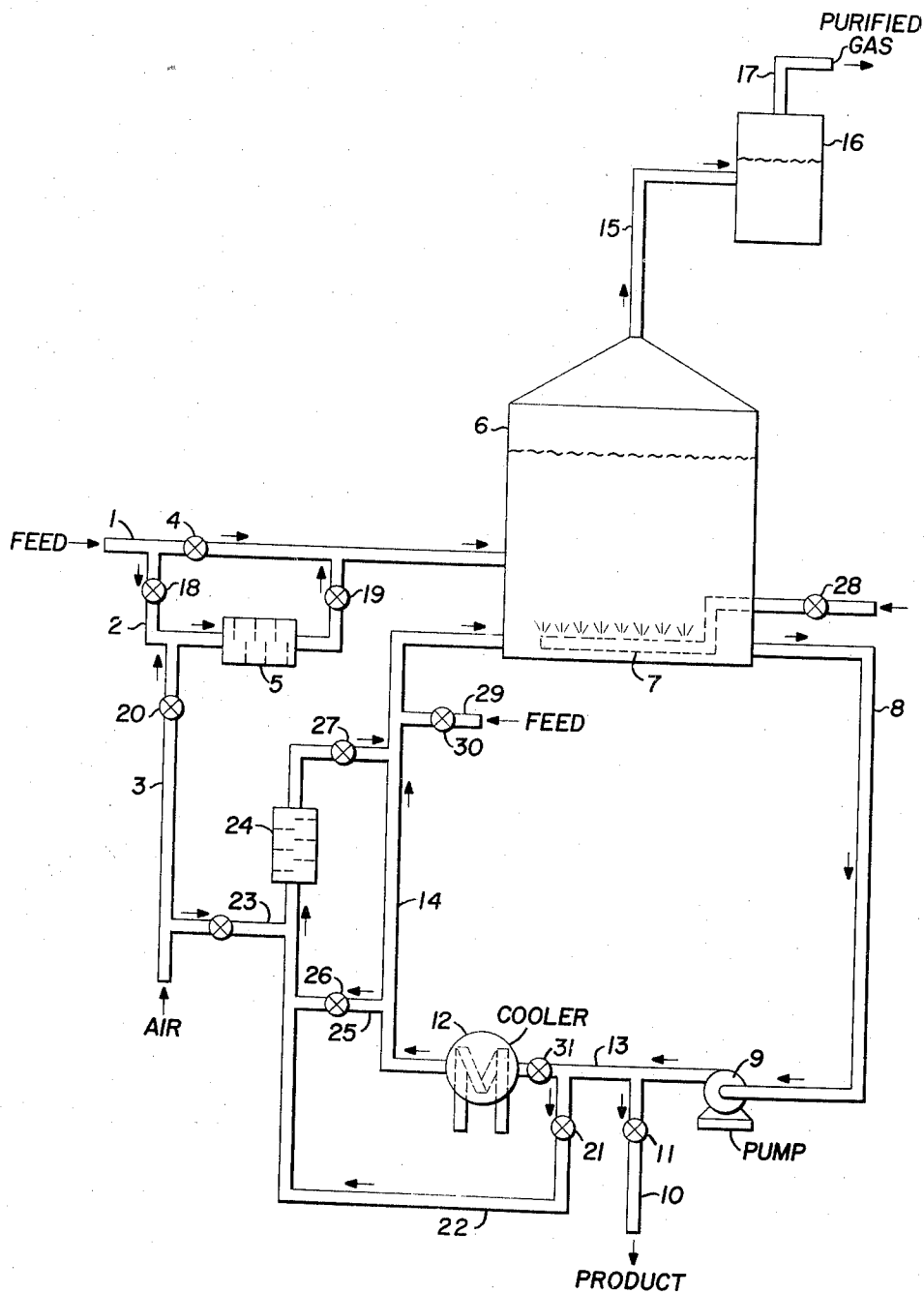
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ASHPALT OXIDATION

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ASPHALT OXIDATION

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The present invention relates to an improved process for oxidizing asphalts. More particularly, it relates to an improved process for oxidizing residual petroleum stocks by injecting an oxygen-containing gas into asphalt streams in a continuous asphalt oxidizing apparatus.

The production of oxidized asphalts by blowing air through a petroleum residue or straight run asphalt at elevated temperatures is well known. Air blowing asphalt serves to increase the hardness, softening point, pliability at low temperatures and weather resistance of the asphalt, and decrease its ductility and susceptibility to change in temperature. The hardness of a straight run asphalt may be greatly increased by steam or vacuum distillation of the asphalt, but the resulting product is generally very temperature susceptible. The air blowing technique, in comparison with the vacuum distillation method, produces a product of greater pliability yet having about the same hardness. In general, oxidized asphalts have softening points of about 100° F. to 250° F. or more and penetrations of about 200 down to about 10 (100 g./5 seconds/77° F.). Straight reduced asphalts are generally available with softening points of 100° to 170° F., having penetration values of the same magnitude as oxidized asphalts.

Up to the present time the conventional process for blowing asphalts involves forcing air through a tank of asphalt by means of an air spray located near the bottom of the tank. The asphalt is usually heated to between about 400° and about 550° F. During the oxidation step which is an exothermic reaction, the asphalt is dehydrogenated. The exhaust vapors are passed through a knockout drum, and the purified gases are permitted to escape into the atmosphere, while the malodorous material is trapped. In some continuous processes the asphalt is recycled as a pumparound stream to remove the exothermic heat of reaction. This permits removal of a portion of the oxidized asphalt through a line usually located downstream of the pump. Once the continuous operation is underway, it is only necessary to have the same feed and withdrawal rates and maintain a heat balance by removing the exothermic heat by means of the pump-around.

One embodiment of this invention involves injecting an oxygen-containing gas into the recycle stream to decrease the reaction time, and thereby increase the capacity of the apparatus.

This invention permits oxidation of asphalt at a higher temperature than would be possible by conventional processes. This is achieved by injecting the oxygen-containing gas into a small stream of asphalt, which has the effect of increasing its temperature about 60° to 200° F., and then rapidly quenching it by mixing it with a cool asphalt stream. A result of the quick quench is that there is little or no thermal degradation. By using the techniques herein described air requirements are reduced for a given softening point increase. This in turn reduces blower sizes and capacities of air handling equipment.

Another embodiment of the present invention is to in-

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ject the gas into the feed stream as well as the recycle stream. This serves a dual purpose. First it helps pre-heat the asphalt entering the tank since the reaction is exothermic, thus shortening the time to bring the asphalt up to the desired temperature. Second it partially oxidizes the asphalt, thereby reducing the reaction time.

In order that the invention may be more fully understood, reference is made to the drawing which diagrammatically illustrates a process for practicing this invention.

The asphalt to be oxidized is preheated to a temperature of about 400° to 450° F. and fed into the apparatus by means of line 1. The feed then passes through line 2, valve 4 being closed, and is mixed with an oxygen-containing gas issuing from line 3. The feed and gas are intimately mixed by means of a suitable mixer 5, for example an orifice mixer, and returned to line 1. The partially oxidized feed is introduced into tank 6 where it is further oxidized by means of oxygen-containing gas coming from spray 7. A portion of at least partially oxidized asphalt in tank 6 is withdrawn into line 8, by means of pump 9. About 1/2 of the partially oxidized asphalt stream is taken off as product through line 10, by opening valve 11. The remainder of the stream is either pumped through a cooling apparatus 12, in line 13, and cooled to between about 100° and 120° F. below the temperature of asphalt in the oxidation zone or it circumvents the cooler by flowing through line 22, valve 21 being open and valve 31 closed. The oxygen-containing gas flowing through line 23 is injected into the asphalt stream in line 22. The injected asphalt stream is then pumped through a mixer 24 where it is intimately contacted with the oxidizing gas. A part of the cooled asphalt stream may be diverted through line 25, by opening valve 26, and into line 22 where it is injected with the oxygen-containing gas from line 23, and mixed with the asphalt stream that by-passed the cooling apparatus. The gas injected asphalt is pumped to line 14 through valve 27, where it is quenched with the cooled asphalt stream in line 14 to a temperature between about 400° to 480° F. before returning to a point near the bottom of tank 6 through line 14. The exhaust vapors in tank 6 escape through line 15, being purified in drum 16, and the purified gas is allowed to escape by means of line 17.

Another embodiment of this invention is the process described above wherein no oxygen-containing gas is injected into the feed stream. This step is eliminated by closing valves 18, 19 and 20, and opening valve 4, thereby permitting the preheated feed to flow directly to tank 6 through line 1.

Alternatively, while injecting an oxygen-containing gas into both the feed and recycle streams the spray 7 may be shut off, by means of valve 28, or a relatively small amount of oxidizing gas may be employed to promote circulation within tank 6. Under these conditions the total or major portion of the asphalt is oxidized by the gas injections in the feed line and recycle stream. In this embodiment tank 6 serves mainly as a storage zone for the asphalt.

There are numerous advantages of this process over conventional tank blowing processes. For example, the quick quenching which takes place immediately after the injection of the oxidizing gas into the recycle stream permits oxidation of the asphalt at higher than normal temperatures, that is between about 500° and 700° F. In turn these higher temperatures increase the rate of oxidation and therefore allow a better utilization of the oxidizing gas. The residence time is short so that little or no thermal degradation takes place.

Another feature of this process is that varying quantities of recycle asphalt may be pumped through the cooling unit 12 or bypass it through line 22 before being oxidized by the oxygen-containing gas issuing from line

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23. The excellent temperature control afforded by this process gives a large temperature range from which to select the most suitable oxidizing temperature for the particular feed.

EXAMPLE 1

In order to more clearly illustrate the advantages of this invention over the prior art the following comparison was made. A conventional continuous asphalt oxidizing process having a cooling unit in the pumparound was used as standard for comparison to show the superiority of the novel process disclosed by this application over the known art. The results obtained in the standard process as compared with injecting air into the recycle stream (Process I) and injecting air into the feed stream as well as the recycle stream (Process II) are shown in the accompanying table.

Table

	Conventional Continuous Process	Process I Continuous Process with air injected in recycle stream	Process II Continuous Process with air injected in feed and recycle streams ¹
Maximum feed rate (barrels/stream day)	1,000	1,850	3,000
Maximum space velocity (volume/volume of reactor/hour)	5	9.3	15.0
Air requirements for a 38° F. change in softening point (standard cubic ft./barrel of asphalt)	380	260	193

¹ No air blowing in tank.

It will be noted that the throughputs of Processes I and II are from one and one-half to three times greater than that of the conventional continuous operation. Furthermore, the air requirements are reduced by from about 25 to 50% by injecting air in the pumparound and feed stream.

EXAMPLE 2

A typical operation of this invention involves injecting an oxygen-containing gas into both the feed stream and pumparound. The tank 6 is used as a reservoir for the asphalt. An asphalt feed having a softening point of about 117° F. was heated to between about 400° to 420° F. and introduced into feed line 1 at a rate of about one million pounds per stream day. Air was injected into the feed stream at a rate of about 0.29 million standard cubic feet per stream day, and the air and asphalt were intimately mixed by means of an orifice mixer prior to being introduced into tank 6. The temperature of the partially oxidized asphalt entering the tank was about 480° F. When the tank was about 80% full the recycling operation was commenced. About 40% of the recycled asphalt that was not withdrawn as product through line 10 was allowed to bypass the cooling unit and flow directly to the air injection point through line 22. The remaining 60% of this recycled asphalt was pumped through the cooling unit and cooled to about 360° F. About one-third to two-thirds of this cooled asphalt was mixed with the hotter asphalt in line 22 by means of line 25 and valve 26. The resulting mixture, which had a temperature of about 400° F. to about 420° F., was injected with air flowing at a rate of about 0.29 million standard cubic feet per stream day, and put through orifice mixer 24. During this oxidation step the temperature of the asphalt rose to from about 500° to 700° F. Upon returning to line 14 the hot asphalt was quenched with the remaining cooled asphalt, which was about 360° F. before it was introduced into tank 6, near the bottom. The quenching step drops the temperature of the oxidized asphalt from a range of about 500° to 700° F. to about 480° F., which is approximately the

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temperature maintained in the oxidizing tank. Once the operation was underway about one-half of the recycle material was removed as product. The product had a softening point of about 38° to 40° F. above that of the feed.

5 An alternate method of cooling or quenching the oxidized portion of the recycle stream is by introducing the asphalt feed through line 29 and valve 30. For example, asphalt preheated to between about 360° and 440° F. may be used to quick-quench the hot oxidized asphalt coming from line 22 into line 14.

EXAMPLE 3

In another embodiment of the present invention, the oxygen-containing gas is injected into the pumparound stream and the asphalt in tank 6. Asphalt feed having a softening point of about 117° F. was heated to about 420° F. and introduced into tank 6 through line 1 at a rate of about 650,000 barrels per stream day. The asphalt in the tank was oxidized by means of air flowing at a rate of about 0.24 million cubic feet per stream day through the sprays in the bottom of the tank. This resulted in an exothermic reaction which increased the temperature of the asphalt to about 480° F. When the tank was about 80% full the recycling operation was commenced. From this point on the process is similar to that described in the previous example. About half of the partially oxidized asphalt was withdrawn as product, while the remainder was pumped through a cooling unit and/or injected with air flowing at a rate of about 0.29 million standard cubic feet per stream day. The air-injected asphalt stream was intimately mixed by means of an orifice mixer. The exothermic reaction which occurred raised the temperature of the asphalt to from about 500° F. to 700° F. depending on the temperature of the asphalt before air was added through line 23. It was then quenched by means of the cooled asphalt stream which was about 100° to 120° F. below the temperature of the asphalt in the oxidizing tank. The quenched asphalt, which is a mixture of the cold and hot streams, was reintroduced into tank 6.

It will be understood that oxygen-containing gases other than air may be employed, for example ozone, oxygen or a mixture of air or oxygen with nitrogen dioxide. Also, catalysts, such as ferric chloride, potassium chlorate or sulfates of zinc, iron, copper or antimony may be employed. Furthermore, it will be appreciated that the present process may be modified in various respects without departing from the scope or spirit of the invention.

50 What is claimed is:

1. In a continuous process for the oxidation of asphalt wherein preheated asphalt is fed into an oxidation zone and oxidized asphalt is taken off as a product, and wherein the exothermic heat of reaction is removed by withdrawing a stream of at least partially oxidized asphalt from said oxidation zone, cooling said withdrawn stream and recycling said cooled stream to said oxidation zone, the improvement which comprises mixing an oxygen-containing gas with a cooled portion of said withdrawn stream, the resulting oxidation thereby raising the temperature to a level higher than that existing in said oxidation zone, rapidly quenching the resulting heated portion by admixing therewith sufficient cool asphalt to lower the temperature of the resulting mixture to about the temperature maintained in said oxidizing zone and recycling the quenched asphalt to said oxidizing zone.

2. A process as defined by claim 1 in which the oxygen-containing gas is air.

3. A process as defined by claim 1 including the steps of injecting into and mixing the preheated asphalt feed with an oxygen-containing gas prior to its passage into said oxidation zone.

4. Process as defined by claim 1 wherein said cool asphalt employed from quenching comprises an additional cooled portion of said withdrawn stream.

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5. Process as defined by claim 1 wherein said cool asphalt employed for quenching comprises a stream of fresh asphalt feed.

6. Process as defined by claim 1 wherein the temperature in said oxidation zone is in the range of 400° to 480° F., the temperature to which said cooled withdrawn portion is heated as a result of admixture with said oxygen-containing gas is in the range of 500° to 700° F. and the temperature of said cool quenching asphalt is from about 100° to 120° F. below the temperature in said oxidizing zone.

7. A continuous asphalt oxidation process comprising the steps of preheating the asphalt feed to between about 400° to 420° F. injecting air into said feed, mixing said air with said feed, passing said feed into a storage zone, withdrawing a portion of at least partially oxidized stream of asphalt from said storage zone, recycling said stream, taking off a portion of said withdrawn stream as product, cooling a portion of said withdrawn stream to about 360° F., injecting air into an asphalt mixture comprising

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a part of said cooled asphalt and a second portion of said withdrawn stream, mixing said air with said asphalt mixture, maintaining the temperature of said mixture between about 500° and 700° F. by adjusting the proportion of said cooled asphalt to said withdrawn stream, quenching said mixture with another part of said stream to a temperature between about 400° and 480° F. and returning said portions of said stream to said storage zone.

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