

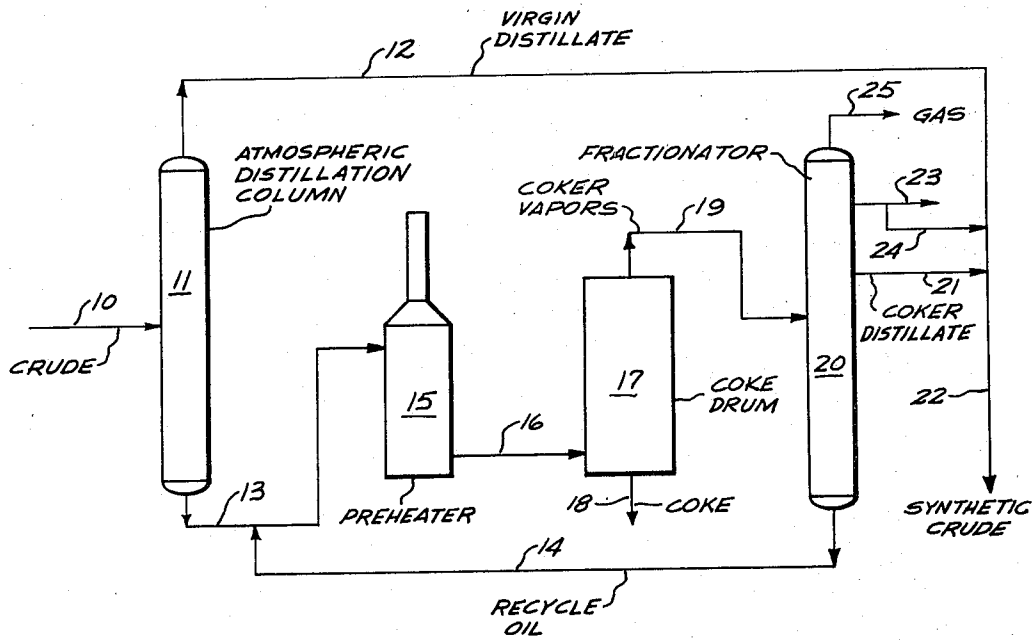
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A. M. HENKE ETAL

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LOW POUR POINT SYNTHETIC CRUDE OIL

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LOW POUR POINT SYNTHETIC CRUDE OIL

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11 Claims. (Cl. 208-14)

ABSTRACT OF THE DISCLOSURE

A wholly distillate low pour point synthetic crude oil produced from the virgin distillate and reduced crude from a high wax, high pour crude by mixing the virgin distillate with that fraction obtained by coking the reduced crude with a heavy recycle stream and fractionating the coker overhead volatile product into the heavy recycle stream and a coker distillate fraction for combination with the virgin distillate to produce the low pour point synthetic crude. The pour point of the synthetic crude is further reduced by the addition of minute amounts of pour point depressants.

This invention relates to the conversion of a high pour point crude oil into a low pour point oil, and more specifically it relates to the novel treatment of a high pour point crude oil to produce a synthetic crude oil of reduced pour point which may be transported by pipeline.

Untreated crude petroleum most frequently possesses a pour point in the range of about 10° to 40° F. Some crude oils possessing a pour point much higher than this have been discovered. Although such oils usually occur as a liquid at reservoir conditions, they may not be produced because of operational difficulties arising from the potential solidification of the oil during production. For example, well bore heating may be required to prevent the high pour point oil from congealing and plugging up the well or the production tubing on its way to the surface. And once the oil arrives at the surface, aboveground transportation problems begin. Economic considerations usually require the transporting of crude petroleum by pipeline from the well site to distant refinery locations or port facilities. Congelation of high pour point oil into a non-pumpable solid in a long-distance pipeline is an intolerable threat, particularly in areas which experience cold periods in which the ambient temperature drops substantially below the pour point of the oil.

This problem of transporting high pour point crude oils by pipeline has been recognized, and efforts have been directed to its solution with only limited or localized successes. In some areas a high pour point crude oil has been blended with a low pour point oil enabling the blend to be pipelined without the threat of solidification. However, this is a satisfactory solution only when sufficient quantities of the low pour point crude oil are locally available for adequate pour point reduction. Unfortunately, this proximate occurrence of high pour point and low pour point crudes is not common. Heating the crude oil and pumping it through a thoroughly insulated pipeline is another method which has been used, but this is prohibitively expensive for anything but short distances and relatively low volumes. Also, steam tracing of pipelines or transporting by truck are prohibitively expensive alternative solutions particularly where long distances and large quantities are involved.

Oil refineries frequently receive crude petroleum from several sources. Each crude is unique in that it possesses its own distinct chemical and physical characteristics. These various crudes are usually preblended prior to re-

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fining to give a composite crude rather than sequentially refining each separate crude. High pour point crude that is received at a refinery likely possesses the undesirable characteristic of being a downgrading blending constituent. Not only does it interfere with efficient refinery operation, but it also tends to degrade some of the refinery products that would be obtained without the inclusion of the high pour point crude in the blend.

By this invention, we have discovered a relatively inexpensive method of producing a synthetic crude oil from a high pour point crude oil, the synthetic crude oil having a pour point as low as or lower than normally occurring crude oils permitting it to be transported by pipeline for long distances without fear of solidification in the pipeline. Significantly, we have discovered that this synthetic crude oil can be blended with crude oils from other sources at the refinery without adversely affecting the overall refinery operation or the quality of the refinery products and in some respects with improvement in both the refinery operation and the quality of some of the refinery products.

In accordance with our invention, the crude oil of high pour point is separated by distillation into an overhead virgin distillate fraction of satisfactory pour point which is used directly in making the synthetic crude and a reduced crude fraction with a pour point greater than the parent crude. This reduced crude is subjected to a coking operation, such as delayed coking, producing a hard coke and vapors. These coker vapors are subsequently fractionated in a manner to obtain an overhead coker distillate product that possesses satisfactory pour point for pipeline transportation in admixture with the virgin distillate, while the bottoms product of the fractionator is recycled through the coking unit with the reduced crude to extinguish those constituents in the heavier portion of the crude oil which are the source of the high pour point.

In attempting to solve this high pour problem, we discovered that although visbreaking lowered the pour point of the crude oil, it introduced other serious disadvantages. For example, hydrocarbon entities resulting from the visbreaking tended to deposit out gums and tars, apparently through the process of slow polymerization, which would lower the quality of the refinery products. In addition, some refinery catalysts such as the reforming and cracking catalysts were poisoned much more quickly than occurred prior to the visbreaking operation. Furthermore, we discovered that the refinery asphalt product was substantially degraded when the visbroken crude was blended with other crudes in the refinery feed, apparently caused by substances created by the visbreaking.

Unexpectedly, we have discovered that despite the fact that our process involves coking, which is recognized as a more severe thermal conversion operation than visbreaking, none of the disadvantages experienced with visbreaking are encountered. Thus, the synthetic crude oil is eminently adapted to be used in admixture with other crudes and enhances the efficiency of certain refinery operations by reducing catalyst poisoning and decreasing the degradation of certain products such as the asphalt fraction than would otherwise result with untreated high pour point crude or the visbroken material. It was fortuitous that the process of this invention possessed these advantages since they serve as a partial compensation for the processing costs and for that portion of the coker crude which is represented by the gases and the coke. When the crude under treatment is a low sulfur material, the resulting coke is a high quality material in high demand and serves as an additional compensation for the processing costs. By our invention, we have consistently caused a pour point reduction in natural crudes having a pour point of about 95° F. to a synthetic crude having a

pour point of about 40° F. with less than 10 percent weight conversion to gases and coke.

As a result of our investigations, we have discovered that high pour point problems are essentially associated with waxy constituents in the crude oil and that addition of asphaltic materials to the crude in sufficient amount will eliminate the pour point problem. However, unless such asphaltic materials are available in close proximity to the high pour point crude, it is not economical to ship them to the wellhead in the amount required for adequate pour point depression. Unexpectedly and of great significance to this invention, we have discovered that the pour point of the synthetic crude oil produced by this process can be further reduced by as much as 50° F. or more by the addition of an asphaltic or other pour point depressing material in an amount so minute as to have no noticeable effect on pour point when added to the natural crude. Thus, it was discovered that 0.1 percent of a hard asphalt would reduce the pour point of a synthetic crude produced hereunder from 45° F. to -5° F., yet when added to the natural crude in much greater amount, it had no significant effect on its pour point.

Pour point depressants in these small quantities can be economically transported to the wellhead and used for additional pour point depression when required for severe winter conditions or to provide for design or operating flexibility by the appropriate interrelationship of the two pour point depressing techniques. That is, partial pour point depression can be obtained by the partial coking operation described herein in a smaller, less expensive plant with less conversion to gases and coke than required for complete pour point depression. Final pour point depression to the desired degree can then be obtained by the addition of a minute amount of a suitable pour point depressant at substantially no additional expense.

In our process, it is desired to produce a synthetic crude having a pour point low enough to prevent congelation in the pipeline particularly if flow should be interrupted. A pour point reduction to 40° F. or lower may be required during the winter season. This can be accomplished by a complete reduction of the pour point to the desired level by our distillation-coking operation. Or the desired pour point can be obtained by a partial reduction in the summertime by the distillation-coking operation and a final reduction during cold weather operation with a suitable pour point depressant. Within this latitude of operation, the atmospheric distillate may have an end point of between about 650° to 850° F. with a preferred range of about 700° to 800° F., the end point of the atmospheric distillate being determined by the character of the crude and the pour point desired in the atmospheric or virgin distillate. A higher cut point in the atmospheric column will increase the capacity of the plant by decreasing the load on the coking unit as well as enlarge the non-degraded fraction, but this is accomplished with a sacrifice in pour point reduction.

Vacuum tower bottoms having an initial boiling point of at least 950° F. is the usual feed to a coking unit. This material is asphaltic in nature and will exhibit a Ramsbottom carbon residue (ASTM D524-64) of at least 10 percent up to 40 percent or more which is a relative measure of its coke-forming potential. Our process is particularly adapted to crudes of over 50° F. pour point (ASTM-D97) containing greater than about 10 percent waxy constituents, only a minor amount of asphaltic substituents and having a carbon residue by the Ramsbottom method of less than about 5 percent. As a result and contrary to existing coking practices, the Ramsbottom carbon residue of the vacuum tower bottoms that are fed to the coker will be under 10 percent and more likely under 5 percent. Therefore, the yield of coke is much lower than in conventional coking processes being less than 10 percent by weight of the virgin crude.

When delayed coking is utilized in our process, the atmospheric bottoms are mixed with the cycle oil, then

preheated to a suitable temperature for coking and immediately introduced into the coking drum. Coking is carried out at a temperature between about 750° to 950° F., preferably between about 800° to 920° F. at a pressure of about 5 to 100 p.s.i.g. with about 15 to 50 p.s.i.g. being preferred. As the heated oils crack, coke deposits out in the drum, and the resulting vapors are quenched to about 600° F. as they leave the drum. These coker vapors are then fractionated to separate the noncondensable gases and heavy recycle oil from the distillate material. This coker distillate is added to the atmospheric distillate to produce the synthetic crude. It is usually desired that the Reid vapor pressure (ASTM D323-58) of a material that is pumped by pipeline does not exceed ten. If this figure is exceeded, the fractionation column may be operated to remove the C₃ and C₄ hydrocarbons for subsequent addition to the synthetic crude in an amount to bring it up to a Reid vapor pressure (RVP) of about ten. Other coking methods such as fluid coking may be employed in addition to delayed coking.

The pour point of the coker distillate is controlled by adjusting the cut point of the fractionator. This automatically determines the recycle rate to the coker; the lower the cut point, the higher the recycle rate and the lower the ultimate pour point. In our invention, the recycle rate may vary from about 10 to about 100 percent with a preferred recycle rate being about 20 to 40 percent. The recycle rate as used herein is the ratio, expressed as a percent, of the volume of recycle oil to the volume of atmospheric bottoms fed to the coking unit. Since the recycle rate is a significant factor in establishing the overall capacity of the coking unit, it is preferred for operating economy to use as small a recycle rate as practical within the ultimate objectives of the operation. Lower recycle rates are furthermore preferred since the pour point reduction becomes proportionately smaller with each incremental increase in recycle rate. It was surprising that the cracking of this high wax stock could be accomplished with this low recycle rate when experience has indicated that high wax materials require a high recycle rate, up to 200 percent or more, in order to obtain the desired cracking.

The figure schematically illustrates a procedure for carrying out our process. Crude oil 10 is fed to an atmospheric distillation column 11 to produce an overhead virgin distillate fraction 12 and a bottoms fraction 13. This bottoms fraction is mixed with recycle oil 14 and heated in preheater 15 to coking temperatures. The preheated mixture 16 is introduced into the coking drum 17 producing a hard coke 18 and coke vapors 19 which are introduced into fractionator 20. The coker distillate 21 from the fractionator is added to the virgin distillate 12 to produce the synthetic crude 22. A C₃ and C₄ fraction 23 is also removed from the fractionator with a portion 24 utilized to adjust the Reid vapor pressure of the synthetic crude. The non-condensable gases 25 and bottoms 14 for recycling are additional products of the fractionator.

Our invention will now be described in connection with the production of a synthetic crude from high pour points Wonsits crude obtained from the Red Wash Field in eastern Utah. This crude oil has a pour point of about 95° F. and contains about 25 percent wax. The crude was topped to a cut point of 720° F. to produce a distillate having a pour point of 45° F. Table I sets forth data on this atmospheric distillation.

TABLE I

	Crude	Distillate	Reduced Crude
Yields, percent by vol.			
Gravity, °API	29.7	31.4	68.6
Pour Point, °F.	+95	+45	+110
Nickel, p.p.m.	11		15
Nitrogen, percent	0.21		0.30
Sulfur, percent	0.14		0.14
Carbon Residue, Ramsbottom, percent	2.60		3.79

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The reduced crude was mixed with recycle oil and coked. The coker vapors were fractionated and the synthetic crude was made by mixing the atmospheric distillate with the coker distillate, C₄ hydrocarbons, and sufficient C₃ hydrocarbons to raise the Reid vapor pressure to ten. Table II shows data for three synthetic crudes which were made using recycle rates of 17, 28 and 55 percent.

TABLE II

Recycle Rate, Percent.....	17	28	55
Yields, Percent by Volume:			
Coker Distillate.....	62.3	62.5	62.8
Virgin Distillate.....	31.4	31.4	31.4
Butane-Butene.....	2.3	2.2	2.3
Propane-Propene.....	1.0	1.0	1.0
10 RVP Synthetic Crude.....	97.0	97.1	97.5
Gravity, °API.....	40.2	41.1	43.3
Pour Point, °F.....	50	45	40

Table III shows the yields of true boiling distillation fractions of the synthetic crudes using 17 and 55 percent recycle rates.

TABLE III

Recycle Rate, Percent.....	17	55
Yields, Percent by Volume:		
Light Gasoline.....	4.8	3.2
Naphtha.....	22.9	26.2
Kerosene.....	15.3	21.2
Heavy Furnace Oil.....	17.9	18.9
Gas Oil.....	32.8	24.7
Total.....	93.7	94.2

Table IV sets forth more detailed data regarding the fractions of the synthetic crude specified in Table III.

TABLE IV

Recycle Rate, Percent.....	17	55
Gasoline:		
Bromine Number.....	73	69
Octane Numbers:		
Motor, +3 cc. TEL.....	88.0	-----
Research, +3 cc. TEL.....	95.8	-----
Naphtha:		
Olefins, percent.....	25.5	18.5
Naphthenes, percent.....	29.3	25.5
Aromatics, percent.....	10.5	22.0
Nitrogen, p.p.m.....	40	30
Sulfur, p.p.m.....	370	400
Kerosene:		
Olefins, percent.....	21.5	19.0
Aromatics, percent.....	19.2	21.5
Nitrogen, p.p.m.....	180	260
Sulfur, p.p.m.....	540	600
Pour Point, °F.....	-40	-40
Heavy Furnace Oil:		
Olefins, percent.....	15.0	14.0
Aromatics, percent.....	12.4	19.5
Naphthenes, percent.....	24.5	22.4
Nitrogen, p.p.m.....	660	730
Sulfur, p.p.m.....	1,180	1,100
Gas Oil:		
Olefins, percent.....	1.9	1.3
Aromatics, percent.....	30.7	28.2
Nitrogen, p.p.m.....	2,000	1,600
Sulfur, p.p.m.....	900	1,000
Nickel, p.p.m.....	<0.1	<0.1
Vanadium, p.p.m.....	<0.1	<0.1

It was discovered that the yields of the synthetic crude were essentially independent of the recycle rate and constant at about 97 percent by volume of the Wonsits crude. The yields of C₁ and C₂ remained constant at about 2.5 percent by weight of the crude and the yield of coke was constant at about 7.1 percent by weight of the crude and did not vary with a change in recycle rate. In addition, the C₃ and C₄ hydrocarbons remained constant with variations in the recycle rate. Pour points decreased with higher recycle rates and as indicated by the gravity of the synthetic crudes in Table III, higher recycle rates caused a lowering in molecular weight of the liquid product without lowering the yield of synthetic crude.

As indicated by Table IV, the quality of the fractions did not change significantly with the recycle rate during coking. The naphtha fraction, after customary pretreatment to reduce sulfur and nitrogen, is suitable reformer charge stock. The higher boiling fractions are excellent charging stock for cracking since they are low on metallic

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catalyst poisons and will not produce significant coke on the cracking catalyst. Furthermore, since the synthetic crude contains no fraction boiling above gas oil, it contains no waxy or olefinic portions which would lower the quality of the asphalt obtained in the final refining of a blend of this synthetic Wonsits crude with crudes from other sources.

Table V provides an analysis of the low sulfur, electrode grade coke obtained in this operation.

TABLE V.—INSPECTIONS OF COKE

Moisture, percent.....	0.2
Volatile matter, percent.....	12.8
Ash, percent.....	0.4
Nickel, percent.....	200
Vanadium, p.p.m.....	4
Sulfur, percent.....	0.3

Fluidity Test, MIL-F-859D, which is a test designed for heavy fuel oils, was carried out on the three synthetic crudes of Table II to provide a general indication of their flowability. This test consists of a measurement of the pressure differential necessary to cause the oil to move in a U-tube. The results are shown in Table VI.

TABLE VI

Pour Point, °F.....	50	45	40
Fluidity Test, cm. Hg to Flow:			
At 32° F.....	14.1	7.4	0.8
At 40° F.....	9.8	2.4	0.2

Since a pressure differential of 15 or less cm. of mercury is considered to be passing under this test, each synthetic crude passed the tests at 32° and 40° F.

In pumping the synthetic crude from Wonsits, Utah to California through a pipeline buried three to six feet below the surface, a maximum pour point of about 30° to 40° F. is considered to be necessary. It has been established that, if solidified in the pipeline, flow can be initiated with the oil at a maximum temperature differential of 3° to 5° F. below the pour point; however, it is important that any possibility of solidification be avoided.

The pour point of the synthetic crude can be substantially reduced by the addition of a small amount of a suitable pour point depressant such as from about 0.01 to about 2.0 percent of the pour point depressant. Suitable pour point depressants include asphaltic materials such as 85/100 penetration asphalt, various hard asphalts, asphaltic tower bottoms, untaite commercially available as Gilsonite, and non-asphaltic materials such as Paradyne 20, sold by Enjay Co., Inc., New York, N.Y., which is a synthetic polymeric material, whose composition and method of making are disclosed in U.S. Patent No. 3,042,505. For example, 0.1, 0.2 and 0.5 weight percent of 85/100 penetration asphalt added to a synthetic Wonsits crude oil having a pour point of 45° F. reduced the pour point to 15° F., 5° F., and -15° F. respectively. In like manner, 0.02 and 0.04 weight percent of Paradyne 20 added to a synthetic Wonsits crude oil having a pour point of 55° F. reduced the pour point to 35° F. and 30° F. respectively, while five times the first amount of 0.1 weight percent produced no pour point reduction in virgin Wonsits crude having a pour point of 95° F. It is noted that the synthetic crude oil produced hereunder is wholly distillate material except for the minor amount of pour point depressant that may be added.

The pour point, i.e., flow point, of the synthetic crude produced by our distillation-coking operation may also be reduced by condensing the coker distillate under conditions of high shear such as by the use of vigorous agitation to prevent agglomeration of waxy materials or by chilling the synthetic crude under high shear conditions to break up the waxy crystals. In a related technique for flow point reduction, the synthetic crude is introduced into a pipeline under high shear conditions, as through an orifice.

It is to be understood that the above disclosure is by

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way of specific example and that numerous modifications and variations are available to those of ordinary skill in the art without departing from the true spirit and scope of our invention.

We claim:

1. A method of converting a high wax, high pour point oil into a pumpable low pour point synthetic crude oil for pipeline transportation which comprises separating the high pour point oil by distillation into a low-wax virgin distillate and a wax-rich reduced crude, mixing the wax-rich reduced crude with a heavy recycle oil, coking the wax-rich reduced crude-recycle oil mixture at a temperature between about 750° and 950° F. and a pressure between about 5 and 100 p.s.i.g. to produce coke and an overhead volatile product, fractionating the overhead volatile product into said heavy recycle oil fraction and a low-wax coker distillate, and combining the virgin distillate with the coker distillate to produce a low pour point synthetic crude oil adapted for pipeline transportation.

2. A process in accordance with claim 1 in which from about 0.01 to 2.0 percent of a pour point depressant is added to the synthetic crude oil.

3. A process in accordance with claim 2 in which the pour point depressant is an asphaltic material.

4. A process in accordance with claim 2 in which the pour point depressant is uinitaite.

5. A process in accordance with claim 2 in which the pour point depressant is a synthetic polymeric material.

6. A process in accordance with claim 1 in which said synthetic crude is subjected to conditions of high shear to lower its flow point.

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7. A process in accordance with claim 1 in which the cut point of the virgin distillate is between about 650° and 850° F.

8. A process in accordance with claim 1 in which the recycle oil is from about 20 to about 40 percent by volume of the reduced crude.

9. A process in accordance with claim 8 in which the initial boiling point of the heavy recycle oil is between about 700° and 850° F.

10. A low pour point synthetic crude oil produced from a high-wax, high pour point oil resulting from the process of claim 1.

11. A low pour point synthetic crude oil in accordance with claim 10 which contains from about 0.01 to about 2.0 percent of a pour point depressant.

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HERBERT LEVINE, *Primary Examiner*.

DELBERT E. GANTZ, *Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,369,992

February 20, 1968

Alfred M. Henke et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 55, for "low pour point lid" read -- low pour point oil --; line 56, for "solidifictaion" read -- solidification --; column 3, line 46, for "operaton" read -- operation --; column 4, line 50, for "coke vapors 19" read -- coker vapors 19 --; column 6, line 14, for "Nickel, percent" read -- Nickel, p.p.m. --; line 59, for "of 0.1" read -- or 0.1 --.

Signed and sealed this 29th day of April 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents