METHOD OF PUMPING WAXY CRUDE OIL

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References Cited

UNITED STATES PATENTS

2,204,967 6/1940 Moser ..................... 208/370 X
2,303,823 12/1942 Coberly .................. 208/370 X
3,776,248 12/1973 Titus ..................... 137/13

ABSTRACT

Crude oils containing at least 25% wax are transported by fractionating (e.g., by distillation) the crude oil into at least a relatively high pour point fraction, a relatively medium pour point fraction, and a relatively low pour point fraction. The medium pour point fraction is congealed (preferably by prilling), and slurred in a mixture of the relatively low pour point fraction and a portion of the high pour point fraction. The remaining high pour point fraction can be congealed with the medium pour point fraction. Diluents, e.g., crude oil, can be added to improve pumpability. This procedure reduces the formation of strong wax matrixes and creates a slurry with better pumpability characteristics.

14 Claims, No Drawings
METHOD OF PUMPING WAXY CRUDE OIL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an improved method of transporting "waxy" crude oils as a slurry containing congealed waxy particles.

2. Description of the Prior Art

It is difficult to pump viscous crude oils below their pour point. Chemical additives and heat transfer methods have been studied to improve pumpability. Also, the oil has been congealed, suspended in water and the resulting slurry pumped at temperatures below the pour point of the crude oil.

Tracer lines and large heat exchangers have been placed intermittently along the pipeline to maintain the crude oil above its pour point and thus facilitate pumping of the same. The main disadvantage of these methods is that the crude oil tends to "set up" during shutdowns.

Examples of patents representative of the art include:

Iberfell et al., in U.S. Pat. No. 2,526,966 teach transporting viscous crude oils by removing the light hydrocarbons (including straight-run gasoline), hydrogenating the residue to increase the fluidity thereof and then combining the hydrogenated product and the light hydrocarbons to obtain a pumpable mixture.

Scott et al in U.S. Pat. No. 3,269,401 facilitate the flow of wax-bearing oil by dissolving in the oil, at super-atmospheric pressure and while above its pour point, an inert gas, which prevents the precipitated wax from agglomerating to form strong wax structures.

Kane in U.S. Pat. No. 3,425,429 transports viscous crude oils by forming an oil-in-water emulsion and then pumping same. The water contains a nonionic surfactant.

Watanabe in U.S. Pat. No. 3,468,968 forms spherical particles of wax by dispersing melted wax droplets in a non-solvent liquid (e.g., water) and thereafter cooling the dispersed wax to form discrete solid particles which can be coated with finely divided coating solids such as calcium carbonate, etc. Watanabe teaches that it is known in the art to disperse waxy particles by molding, prilling, syrup drying, extruding, etc.

Allen in U.S. Pat. No. 3,548,846 transports waxy crude oils by admixing propane or butane within the crude oil.

This technology, except for heat transfer methods and crude oil-water suspension systems, is generally economically unattractive.

SUMMARY OF THE INVENTION

"Waxy" crude oils are transported more easily by fractionating the crude oil into at least a low pour point fraction, a medium pour point fraction, and a high pour point fraction, admixing a portion of the high pour point fraction with the low pour point fraction, congealing at least a portion of the medium pour point fraction and/or the high pour point fractions. Slurrying the congealed particles with the low pour point mixture and the slurry transported, preferably in a conduit.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hydrocarbon mixtures having average pour points above the seasonably ambient temperature of the transportation system and which contain at least about 25 percent wax are useful with this invention. Crude oils are particularly useful and especially those classified as "waxy" crude oils. Examples of the latter include crude oils containing about 25 percent to about 80% wax (wax is defined as the precipitate which forms after one part of crude oil is dissolved in 10 parts of methyl ethyl ketone at above 80°C, and the mixture chilled to 

-25°C.). Examples of average pour points of crude oils particularly useful with this invention include about 0°F to about 200°F, and preferably about 20°F to about 150°F, and more preferably having pour points greater than about 50°F.

The hydrocarbon mixture is fractionated into at least three fractions, an overheads fraction which has a relatively low pour point, a middle fraction which has a medium pour point and a bottoms fraction which has a relatively high pour point. For a typical crude, the low pour point fraction will generally have typical molecules containing up to about 25 carbon atoms, the medium pour point fraction will have molecules containing between about 15 to about 30 carbon atoms, and the high pour point fraction will have molecules containing greater than about 20-26 carbon atoms. For a typical "waxy" hydrocarbon mixture, the low pour point fraction can be about 20 to about 95 and preferably about 40 to about 95 and more preferably about 50 to about 70 percent of the original crude, the medium pour point fraction can be about 3 to about 30, preferably about 5 to about 20 and more preferably about 10 to about 20 percent of the original crude and the high pour point fraction can be about 5 to about 60 and preferably about 10 to about 40 and more preferably about 20 to about 30 percent of the original crude oil.

It is to be understood that more than the three above fractions can be obtained during fractionation. Also, other crude oil fractions or hydrocarbon(s) can be combined with the crude oil either before or after fractionation. For example, other hydrocarbon(s) or crude oil fractions can be combined with the medium pour point fraction before congelation thereof.

Fractionation can be accomplished by any process which will separate the hydrocarbon mixture into at least three fractions, e.g., distillation, solvent extraction, membrane fractionation, or crystallization. Of course, the original hydrocarbon mixture can be fractionated into an overhead fraction and a bottoms fraction and the bottoms fraction further fractionated into a medium pour point fraction and a high pour point fraction. Optionally, up to about 30 percent of the crude oil can be cracked, e.g., by thermal, hydrogenation, catalytic, or combinations thereof, prior to, during, or after fractionation.

The low pour point fraction should have a pour point at least about 1°F, preferably at least about 10°F, and most preferably at least about 20°F below the average of the minimum temperature range of the transportation system at the time the slurry is transported.

After the hydrocarbon mixture is fractionated, all or at least a portion (preferably at least about 80 percent) of the medium pour point fraction, preferably containing up to 98 percent of the high pour point fraction, is collected, congealed and comminuted to form substantially solid particles having an average diameter of about 0.05 or less to about 20 or more mm (millime-
ters) and preferably about 0.1 to about 5 mm and more preferably about 0.5 to about 3 mm. The particles can be of any shape such as tubular, spherical, or irregular, but are preferably spherical and can be of substantially uniform or random diameter sizes. Comminution is accomplished by prilling, extruding, molding, shredding, grinding, shearing, and like methods for dispersing or disintegrating the uncongealed or congealed material. Congealing as used herein includes solidification, crystallization, making into a consistency like a firm jelly, etc.

The medium pour point fraction is preferably about 1° to about 150° and more preferably about 10° to about 100°F above its average congealing temperature as it enters the congealing and/or comminution steps. “Medium pour point fraction” as used hereinafter, can include other fractions, e.g., high pour point fraction, etc.

Prilling can be accomplished by spraying the fraction into a prilling tower where the prill comes in contact with gas (e.g., air, N₂, CO₂, natural gas, or like gases) and/or water (liquid and/or vapor). Optionally, the prill is collected in a water bath at the bottom of the tower. Air is the preferred gas and is preferably moved through the prilling tower by natural or forced convection at velocities sufficient to not exceed the drop or settling rate of the prill falling through the prilling tower. Air velocities below about 20 ft/sec and preferably below 10 ft/sec and more preferably below about 5 ft/sec are useful. Temperature of the air entering the prilling tower is preferably about 1° to about 230° and more preferably about 10° to about 150°F, below the congealing temperature of the prill. Temperature of the air leaving the prilling tower is preferably about 230° below to about 150° above and more preferably about 100° below to about 10°F, above the average congealing temperature of the fraction entering the tower. Water is preferably sprayed into the tower along with the air, the water being at temperature at least about 5°F and preferably at least about 20°F below the congealing temperature of the medium pour point fraction.

Also, it is preferred that the water be sprayed into the tower as a mist.

Another method for congealing the medium pour point fraction is by extruding or spraying into water, the fraction preferably at about 5° to about 100°F and more preferably about 130° to about 220°F, above its average congealing temperature. Preferably the water is in turbulent flow at the introduction or injection point of the fraction in the water. The dispersed fraction is thereafter congealed by admixing cooler water, e.g., at about ambient temperature. The congealed fraction is then separated from the water, slurried in the low pour point fraction and then transported.

Surfactants or other additives such as bactericides, insecticides, etc., can be incorporated into the medium pour point fraction before congealing. Volume amounts of about 0.0001 to about 20 percent and preferably about 0.001 to about 10 percent, and more preferably about 0.01 to about 1 percent by volume, based on the fraction, are useful. A surfactant should be at least partially hydrocarbon soluble. It is postulated that the surfactant molecules tend to orient their hydrophilic portion radially at the droplet surface and thus impart a hydrophilic property to the prill which in turn inhibits solubilization of the prill in the low pour point fraction. Theoretically, this happens as the droplets of wax are formed. Examples of useful surfactants include fatty acids (e.g., those containing about 10 to about 20 carbon atoms) and preferably monovalent carboxy containing salts thereof. Sorbiton monolaureate is an example of a useful surfactant. Preferably the surfactant is a petroleum sulfonate and more preferably one having a monovalent cation, e.g., Na⁺, and preferably having an average equivalent weight of about 200 to about 600 and more preferably about 250 to about 500 and most preferably about 350 to about 420.

Chemical agents to facilitate suspension of the congealed fraction can be added to the slurry. Examples of such agents include high molecular weight polymers, including biopolymers and chemically synthesized polymers. Also, viscosity reducing agents, pour point reducers, drag reduction agents can be admixed with the slurry to impart desired properties.

After the medium pour point fraction is congealed or during the congealing and/or comminution thereof, the particles can be coated with a solid material. This inhibits agglomeration of the particles and may permit higher slurry temperatures during transportation. Examples of coatings include those disclosed in U.S. Pat. No. 3,468,986 to Watanabe. Where the high pour point fraction is prilled, the coating can be applied as a spray, either hydrous or anhydrous, or as an aqueous bath containing the solid material. Examples of useful coating materials include inorganic and organic salts of the metals of Group II, III, IV, A, V, VI, VII, and VIII of the Periodic Table; synthetic resins such as cellulose acetate, polystyrene, polyethylene, polyvinyl acetate, and like resins; and other materials such as clay (e.g., bentonite), kaolin, Fuller’s earth and other aluminum silicates, limestone, etc. Calcium carbonate is a preferred coating material.

At least a portion and preferably all of the congealed particles are slurred in the low pour point fraction. The low pour point fraction contains about 1 to about 20 and preferably about 2 to about 15 and more preferably about 5 to about 10 percent of the high pour point fraction. By adding the high pour point fraction to the low pour point fraction, “fine” crystals which do not have a strong matrix-forming tendency are obtained. As an unusual correlation, if the medium pour point fraction were added to an equivalent amount of low pour point fraction without the high pour point fraction, larger crystals having a strong matrix-forming tendency would be obtained. However, by combining the high pour point fraction with the low pour point fraction, a more fluid slurry is obtained than if the low pour point fraction were combined with a portion of the medium pour point fraction or if both the medium pour point fraction and the high pour point fraction were congealed and thereafter slurred in the low pour point fraction. Based on the volume amount of the low pour point fraction, preferably about 5 to about 15 percent of the high pour point fraction is admixed with the low pour point fraction. Also, “whole” crude oil can be added to the low pour point to obtain the same results; based on the volume of the low pour point fraction and the medium pour point fraction, about 10 to about 30 percent of the “whole” crude oil can be admixed to obtain the smaller wax crystals.

Concentration of the congealed fraction in the slurry is about 1 to about 80 percent and more preferably about 5 to about 55 percent and most preferably about 10 to about 50 percent by weight. Water may be en-
trapped within the congealed fraction or water may be sorbed into the wax particles. In addition, water may "slop" over from the congealing process. As a result, the slurry may contain up to about 20 percent and preferably less than about 10 and more preferably less than about 2 percent by weight of water within the slurry.

During the slurring operation, temperature of the low pour point fraction is preferably about 30° below to about 30° above and more preferably about 20° below to about 20° above the minimum seasonally ambient temperature of the transportation system. Also, the temperature of the low pour point fraction during slurring should be below, and preferably at least about 5°F and more preferably at least about 15°F and most preferably at least about 30°F below the solution temperature of the congealed medium pour point fraction.

A liquid diluent, such as crude oil and preferably a non "waxy" crude, straight-run gasoline, reservoir condensate, crude oil fraction(s), or like hydrocarbon can be admixed with the low pour point fraction either before or after the slurring operation. Generally speaking, any diluent which is miscible or substantially miscible with the low pour point fraction and which preferably has a pour point below the minimum ambient average temperature of the transportation system at the time of transporting the hydrocarbon mixture is useful with this invention.

A gas miscible with the low pour point fraction but preferably immiscible with the congealed fraction can be admixed with the slurry to reduce the viscosity thereof. The gas can be liquid at the temperature and pressure conditions of the transportation system. Examples of such gases include carbon dioxide, lower hydrocarbons containing less than 4 carbon atoms, etc. The gas can be injected into the slurry under conditions such that the gas is present in concentrations greater than that present at atmospheric conditions.

The slurry can be subjected to shearing action before it is actually transported. For example, it can be sheared in a centrifugal pump or like mechanical means before it is injected in a pipeline for transportation therein. Transportation of the slurry can be in bulk, e.g., tank car, tank truck, tank trailer, tank barge, tanker or like means but it is preferably transported in a conduit such as pipeline. Of course, the conduit system may have tank batteries, i.e., collection or holding tanks associated with it.

The slurry is preferably transported in a pipeline at a temperature which is not below the average pour point of the low pour point fraction of the slurry and preferably is at least about 1°F and more preferably at least about 5°F and most preferably at least about 10°F above the pour point of the low pour point fraction.

WORKING EXAMPLES

EXAMPLE I

A "waxy" crude having an average pour point of 110°F and an average API gravity of about 50°, is fractionated by distillation into a low pour point fraction (average pour point about 130°F), a medium pour point fraction (average pour point about 125°F) and a high pour point fraction (average pour point about 15°F). The average hydrocarbon molecule of the low pour point fraction contains up to about 20 to 22 carbon atoms, the average molecule of the medium pour point fraction contains 18 to about 28 carbon atoms and the average molecule of the high pour point fraction contains more than about 28 carbon atoms. To show the effect of combining the low pour point fraction with the high pour point fraction and the effect of obtaining finer crystals and the reduction in the wax matrix-forming tendency, the following series of mixing experiments were conducted:

1. 85 ml of the low pour point fraction are mixed with 15 of the medium pour point fraction and the resulting mixture agitated and observed after standing for 24 hours-the crystals formed were rather large in diameter and exhibited a very strong wax matrix-forming tendency. 1. 85 ml of the low pour point fraction are admixed with 15 ml of the high pour point fraction and the resulting mixture let stand for 24 hours. A finer wax crystal than the mixture of 1 is observed and it has less tendency to form a strong wax matrix as compared to 1. 3. The mixture of 1 is duplicated except 20 ml of the high pour point fraction is admixed and the resulting mixture let stand for 24 hours. Upon observation, it was determined that the wax crystals were smaller in size than the crystals of 1 and also the resulting mixture had less tendency to form a strong wax matrix.

EXAMPLE II

A given waxy crude oil is distilled in one distillation to give 40 wt. percent low pour point fraction, 15% medium pour point fraction and 45 percent high pour point fraction. A second distillation on the same crude is performed to give 50 percent low pour point fraction and 50 percent high pour point fraction. Enough of the high pour point fraction from the first distillation is dissolved in the 40 percent low pour point fraction to give a mixture comprising 50 percent of the whole crude. The medium pour point fraction is then combined with the remaining high pour point fraction and this mixture congealed to obtain substantially spherical prills. The congealed prills are then added to the 50 percent low pour point mixture to give a 30 percent slurry. This slurry is then pumped through a 3/8 inch pipeline at 40°F. The high pour point fraction from the 2nd distillation is then congealed into prills and the prills are added to the 50 percent overhead fraction from that distillation to give a 30 percent slurry. This slurry is then pumped through the same 3/8 inch pipeline at 40°F. Comparison of the two runs shows that the 30 percent slurry made up with the 50 percent mixture from the first distillation gives lower pressure drops than did the slurry made from the products of the 2nd distillation.

The above examples are not intended to limit the invention. All equivalents obvious to those skilled in the art are intended to be incorporated within the scope of the invention as defined within the specification and appended claims.

What is claimed is:

1. An improved process of transporting a hydrocarbon mixture that contains at least about 25 percent wax (this wax is defined as the precipitate which forms after 1 part of the hydrocarbon mixture is dissolved in 10 parts of methylketone at 80°C. and the mixture chilled to -25°C.), the improved process comprising fractionating the hydrocarbon mixture into at least a low pour point fraction, a medium pour point fraction, and a high pour point fraction, substantially congealing at least a portion of the medium pour point fraction and
optionally a portion of the high pour point fraction, admixing at least a portion of the high pour point fraction with the low pour point fraction and thereafter slurring the congealed particles with the low pour point fraction to obtain a hydrocarbon slurry suitable for transport at predetermined temperatures.

2. The process of claim 1 wherein the hydrocarbon mixture has an average pour point above the average seasonably minimum temperature of the transportation system.

3. The process of claim 1 wherein the slurry is transported in a pipeline.

4. The process of claim 1 wherein the concentration of the congealed fraction in the slurry is about 1 to about 80% by weight.

5. The process of claim 1 wherein the concentration of the congealed fraction in the slurry is about 5 to about 55 percent by weight.

6. The process of claim 1 wherein slurring is effected at a temperature at least about 5° below the average solution temperature of the congealed fraction within the slurry.

7. The process of claim 1 wherein the medium pour point fraction is congealed at a temperature at least about 5° below its pour point.

8. The process of claim 1 wherein the congelation is effected by prilling.

9. The process of claim 1 wherein the average diameter of the congealed fraction is about 0.05 to about 20 mm.

10. The process of claim 1 wherein the slurry contains up to about 10 percent by weight water.

11. The process of claim 1 wherein a hydrocarbon diluent is admixed with the hydrocarbon slurry to improve the pumpability thereof.

12. A process for preparing a hydrocarbon slurry from a "waxy" crude oil containing at least 25 percent wax (wax is defined as the precipitate which forms after 1 part of hydrocarbon mixture is dissolved in 10 parts of methylethyl ketone at about 80°C. and the mixture chilled to −25°C.) that can be effectively transported in a conduit, the process comprising fractionating the crude oil into at least a low pour point fraction, a medium pour point fraction and a high pour point fraction, substantially congealing at least a portion of the medium pour point fraction which can optionally contain at least a portion of the high pour point fraction, thereafter slurring at least a portion of the congealed particles in the low pour point fraction which contains at least a portion of the high pour fraction to obtain a hydrocarbon slurry containing about 5 to about 55 percent by weight of the congealed particles and transporting the slurry in a conduit at a temperature below about the average pour point of the low pour point fraction.

13. The process of claim 12 wherein the concentration of the congealed fraction in the slurry is about 5 to about 55 percent by weight.

14. The process of claim 12 wherein a hydrocarbon diluent is admixed with the slurry to improve the pumpability thereof.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION


Inventor(s) LaVaun S. Merrill, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 11, after "15" insert -- ml --.
Column 6, line 15, after "dency," delete "1." and insert -- 2. --.
Column 6, line 20, "mixture" should read -- mixture --.
Column 8, line 22, following "temperature" insert -- not --.

This certificate supersedes Certificate of Correction issued March 4, 1975.

Signed and Sealed this

Second Day of May 1978

[SEAL]

Attest:

RUTH C. MASON LUTRELL F. PARKER
Attesting Officer Acting Commissioner of Patents and Trademarks
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION


Inventor(s) L. S. Merrill, Jr.

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Col. 6, line 15: After density, delete "1." and insert --2.--.

Col. 6, line 20: Delete "mixture" and insert --mixture--.

Signed and sealed this 4th day of March 1975.

(SEAL)
Attest:
RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks