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TRANSPORTATION OF WAXY OILS

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This invention relates to the transportation of waxy oils through pipe-lines, and more particularly pertains to a method for increasing the throughput capacity of pipe-lines used for transporting crude oils having high wax contents. The invention also provides an improved process whereby the energy required to transport a very waxy crude oil through a pipe-line may be materially reduced.

The transportation of high pour point oils containing relatively high concentrations of waxes, e.g. waxy crude oils and products derived from fractionation thereof, through pipe-lines presents difficulties. Even when pressures near the maximum permissible for standard pipe and pumping equipment are employed, such oils, due to their relatively high wax content, require the utilization of special procedures to make pipe-line transportation thereof practical.

It has been customary to facilitate the flow of waxy, high pour point crude petroleum and the like by reducing its viscosity through the installation of heating equipment at suitably spaced stations along the pipe-line. This expedient is costly, inconvenient, and also frequently causes the loss, through volatilization, of valuable low-boiling constituents or fractions of the petroleum oil being transported. This is particularly true in the case of the transportation of crude oils which, while containing high concentrations of waxy constituents, are in themselves relatively light oils, having relatively low specific gravities, and containing substantial amounts of low-boiling constituents which are capable of being vaporized and thus lost when the crude oil is heated repeatedly to sufficiently high temperatures to effect the liquefaction of all of the wax contained therein.

It is known that substantial amounts of water may be introduced into a pipe-line containing a stream of petroleum flowing therethrough to reduce the drag on the stream, and thus facilitate the flow through the pipe-line. Although viscous petroleum oils and the like have been and still are transported through pipe-lines in the form of relatively unstable oil-in-water emulsions, this technique, when applied to the transportation of highly waxy, high pour-point petroleum oils, is generally too costly, uneconomical and technically impractical, if not wholly undesirable. In the first place, most if not all known waxy, high pour-point, low specific gravity petroleum crude oils do not contain any naturally occurring emulsifier; nor do these have any acids which could be neutralized (saponified) to produce emulsifiers in situ. Since emulsification involves stabilization of the particles at the water-oil interface by means of some surface-active material, transportation of the aforesaid waxy, high pour-point crude oils (as well as fractions thereof) in the form of oil-in-water emulsions requires the addition of an emulsifier, which would materially increase the cost of such transportation. Also, it was found that it is frequently very difficult to recover the emulsifier from the oil after it has reached the refinery or other point to which it has been transported as an emulsion. Additionally, considerable experimentation is necessary, when using these waxy crudes, to find suitable emulsifier; even then, the resulting emulsions are frequently of a nature or character such that they either break up too readily or become permanently inverted to the undesirable water-in-oil type, the transportation of which through a pipe-line is usually more difficult than that of the oil itself.

It is an object of the present invention to obviate and avoid the above and other defects and objects of the prior art methods of transporting waxy, high pour-point petroleum oils and similar highly waxy water-insoluble liquid products. It is another object of this invention to improve the transportation of the above class of liquids. Still another object is to facilitate the movement of waxy, high pour-point petroleum and fractions thereof through pipe-lines. It is a further object of this invention to provide a method for moving the above class of liquids through pipe-lines at a high rate of speed while at the same time utilizing considerably lower amounts of energy than heretofore found essential for the transport of the same liquids.

In accordance with the present invention, it has now been found that the above and other objects may be attained by transporting waxy, high pour-point petroleum oils, as well as their fractions, through pipe-lines while maintaining said oils in a state of suspension in water, said suspension being formed and maintained, during its transport, within a certain critical temperature range. It has been also found that suspensions having relatively very low viscosities, e.g. less than 50 centipoises, may be obtained by commingling waxy, high pour-point petroleum oils with water at such temperatures and under such conditions that the equilibrium temperature of the resulting oil-water suspension is below that defined by the following formula:

$$T_e = 0.6T_p + 30$$

where: T_e is the equilibrium temperature in degrees Fahrenheit, and T_p is the pour point of the waxy oil, also in degrees Fahrenheit, said resulting equilibrium temperature being however, above the freezing point of the water. It has been still further found that by operating in the general manner defined above oil-water suspensions containing high concentrations of oil, e.g. up to about 75% by volume of the aforementioned petroleum oils having a high wax content and a high pour point, may be transported through a pipe-line at relatively high throughput rates, while utilizing minimum or close to minimum amounts of energy, if the said oil is suspended in water under conditions such that the resulting suspension is at an equilibrium temperature within the above defined range, and if the suspension is maintained in said range during the time that it is being conveyed through the pipe-line.

The reason for forming the suspension (as well as maintaining it during transport) under conditions of oil and water temperatures and their proportions in the final suspension such that the equilibrium temperature of this resulting suspension is below that defined by the aforementioned formula is that it has been found that if the equilibrium temperature of the suspension is at or above that defined by this formula $T_e = 0.6T_p + 30$, then the suspension becomes inverted to the undesirable water-in-oil variety with the result that all of the advantages obtainable from transporting the waxy crude as a suspension in water are lost, the transportation problem becoming frequently even more aggravated than when attempting to pump the petroleum per se. This is due to the finding that the effective viscosity of the water-in-oil inversion is even higher than the already excessively high viscosity of the waxy, high pour-point petroleum which one is trying to transport. The inversion temperature being still below the pour point of the waxy oil, the latter is partially solid (due to the crystalline particles in the oil), these solid particles being the cause, at least in part, of the high viscosity of the inverted emulsion and of the resultant high energy output necessary for its pumping. Also, when inversion occurs, capacity is lost because, in addition to the oil, it is necessary to transport the water which latter is of no assistance in this case since its presence in this inverted emulsion or suspension only increases the resultant viscosity, thus increasing unnecessarily the total energy required to pump a given volume of the high pour point oil through a pipe-line at a given throughput rate.

The reason for having the equilibrium temperature above the freezing point of the water is considered to be fairly obvious: In the case of oil-in-water suspensions in which the oil contains a relatively high concentration of wax, the oil is congealed into solid or substantially solid particles which are in the form of a discontinuous phase in the continuous water phase, the relative amounts or proportions of oil and of water (as more particularly explained hereinbelow) being such that the oil particles are permitted to and do move in the water phase. Obviously, if the latter becomes frozen this latter would be impossible and all of the benefits and advantages outlined and described above would disappear.

It has been pointed out that effective and efficient transportation of waxy, high pour-point petroleum oils, and the like, is effected if and when they are made into and maintained in the state of an oil-in-water suspension, the equilibrium temperature of which is below a temperature depending on the pour point of the oil, more specifically below a temperature defined by the above formula $T_e=0.6T_p+30$, but above the freezing point of water. Nevertheless, at least in some cases, e.g., where the pipeline, for one reason or another, suddenly has a smaller diameter, it is advantageous or preferable to avoid equilibrium temperatures which are too close to the freezing temperature of water because otherwise excessive pressure pulses occur probably due to the impact of the relatively large slugs of oil (in the suspension) suddenly hitting the orifice of the narrowed section. Such pulsation is not really dangerous, and can be avoided by either raising the equilibrium temperature or having nipples of gradually decreasing diameter, e.g., reducing swedges, disposed between the pipes of different diameter.

In considering the profitability and other advantages of a given process of transporting a given petroleum oil or the like through a pipe-line, the two most important aspects which have to be considered are the maximum throughput of oil possible and the amount of energy necessary for pushing said throughput through a given length of pipe-line. One of the main advantages of the present invention is that, when applied to waxy, high pour-point oils, there is no inversion of the oil-in-water suspension as long as the equilibrium temperature thereof is maintain within the above-defined range, which, as stated, depends on the pour point of the waxy oil to be transported, this noninversion persisting even when the throughput of the suspension is increased to the economic maximum for the given pipe-line and/or pumping equipment employed.

The suspensions produced and transported by the process of the present invention can vary within a wide range insofar as their oil concentration is concerned. Thus, it has been actually applied to the pumping of suspensions containing as low as about 10% by volume of oil and as high as about 70 to 75% by volume of oil, the transport of highly waxy, high pour-point crude petroleum oils over this entire range of oil content having been proved to be feasible when effected as an oil-in-water suspension in accordance with the process of the present invention. In fact, the criticality of the oil-to-water ratio may be considered one of economics. Thus, the pumping of suspensions containing very low oil concentrations, e.g., 10% by volume or less, may be considered to be uneconomical

(at least in some cases) since one is required to expend considerable energy for the transport of large amounts of water for each unit of oil thus conveyed. When on the other hand, the oil concentration in the suspension is too high, the transportation of such suspension might likewise be uneconomical because of the excessive viscosities of the suspension, which would require expenditure of excessive and possibly impractical amounts of energy to transport such suspension through a given pipeline. Generally speaking, the practical maximum oil concentration in the suspension is in the neighborhood of 75% by volume. It has been also found that the optimum oil content in the suspension (at least from energy requirement point of view) is generally close to the above practical maximum, i.e. about 65–70% by volume. Above this one does not generally have a proper suspension because there is not enough water to permit free movement of the oil particles in the suspension.

The process of the present invention is applicable to the transportation of petroleum oils, and like water-insoluble liquids, which have high wax contents and high pour points. These petroleum oils may have wax contents as low as about 5% by wt. (as measured by mixing the oil with about ten volumes of methyl isobutyl ketone, chilling the solution, with Dry Ice, to −10° C. and filtering). Although actual field transports through pipe-lines have been effected according to the present process using oils having wax contents as high as 36 wt. percent, crude oils having even higher wax concentrations may be thus transported.

The term "high pour point oils" is intended to refer primarily to those oils which have pour points above about 75° F., the pour points of the oils which may be transported in accordance with the process of the present invention varying from about 75° F. (preferably above about 80° F.) to as high as 110° F. and even higher.

It is to be noted that when waxy oils have pour points below 75° F., their equilibrium temperature (when using the formula $T_e=0.6T_p+30$) is above the pour point temperature. It was pointed out that it is generally desired, and, in the case of the transportation of high pour point waxy oils, it is essential that the equilibrium temperature be below the pour point temperature. Therefore, the above formula is applicable (insofar as the full range is concerned) to oils of pour points above 75° F.; in the case of oils having lower pour points (if it is desired to transport them as a solid suspension in water) it is necessary to go to a somewhat lower temperature than that defined by the above formula and operate under conditions such that at least the waxy constituents are in the solid state.

Petroleum oils, or fractions thereof, which may be transported according to the present process may vary within wide limits insofar as their specific gravities is concerned. The high pour point of the oils depends on the wax content. Thus, some crude oils with high pour points, e.g., as high as from 100° F. to 110° F., and even higher, were found to have relatively low specific gravities, e.g., in the order of 0.82 and 0.83.

It was stated above that the desired oil-in-water suspensions, which may be transported through pipe-lines economically, effectively and efficiently are obtainable when the waxy petroleum hydrocarbons are mixed with water under conditions that the equilibrium temperature, while being above 32° F. is below that defined by the equation $T_e=0.6T_p+30$. This equilibrium temperature, or the temperature after mixing, must always be below the pour point of the oil, this in order that a suspension is obtained in which the oil is in the form of solid particles, or contains substantial portions in such solid form. Sometimes, in order to obtain this, it is necessary to pre-cool either the water or the oil, or both. Thus, the temperature of a highly waxy oil in Indonesia ranges from about 104° F. to about 108° F., while the pour points of these oils are from about 100° F. to about 110° F., or even higher. At the same time, the temperature of the water available for the preparation of the suspensions necessary for the transport of said oils, after passing through a water-treatment plant for coagulation and separation of solids, is about 85° F. In order to obtain suspension temperatures which are reasonably near ground temperatures (80–85° F.), and to prevent excessive loss of the continuous water phase into the oil phase during combination of the oil and water streams, it was found desirable to lower the oil temperature before intermixing. Alternatively, the same result was attained by continuously mixing the waxy oil with a large excess of water in a pressure vessel at slightly above 85° F., draining away excess water, and directing the desired amount of congealed oil and water into the pipe-line.

The intermixing of the oil and water to produce the desired suspension may be effected by the use of various techniques and injection devices. Thus, one may employ ordinary T arrangements as well as those involving perforated plates in either the oil or water inlet sides, or in both. Very satisfactory results have been obtained by the use of concentric injection devices, preferably those in which the oil is introduced through the inner pipe, while the water is conveyed through the annulus between the pipes.

The pumping may be effected by using any types of pumps, e.g., reciprocating or centrifugal pumps, which may be installed at the head of the line, or disposed at a number of points along the pipe-line. In the latter case it may be advisable to inject additional water into the system at the intermediate or booster stations to replace that part of the external water phase which becomes dispersed as droplets in the oil phase by the shearing action of the pumps.

When utilizing the process of the present invention, it has been found that separation of the suspensions can be readily effected by elevating their temperature sufficiently to effect the complete liquefaction of the oil. At this temperature, the suspension breaks and stratifies, the upper layer of which is the oil phase containing substantially no water. Sometimes, demulsifying agents may have to be used to resolve any emulsion which may have been formed during the pumping of the suspension through a long line which may have intermediate booster pumping stations.

The following non-limiting examples are presented to illustrate the claimed invention and to point out some of the advantages gained by the use of the present invention.

Example I

A waxy crude oil from Indonesia having a pour point of about 105° F. and a wax content of about 36% wt. (as measured at −10° C. by the above-described process which involves dilution with methyl isobutyl ketone), was mixed with water under the following conditions:

Oil temperature	° F.	110
Water temperature	° F.	70
Volumetric ratio of oil to water		65:35

This mixture had an equilibrium temperature of about 93° F. It was found to consist of an oil-in-water suspension having a viscosity of 60 centipoises when transported at a velocity of 3 ft./sec. through ½" pipe. This suspension was readily transported through both large and small diameter pipes (ranging from ½ inch up to 18 inches in diameter) without the necessity of using excessive power and without the suspension becoming inverted.

Example II

When the above Indonesian crude oil was mixed with water in the same volumetric ratio, but under temperature conditions such that the equilibrium temperature of the mixture was about 95° F., the mixture was found to be a viscous water-in-oil emulsion, which had a viscosity of about 650 cps. and could be pumped through a ½ inch pipe-line only when very large amounts of energy was applied. Also, the oil proceeded to stick to the sides of the pipe-line.

Example III

A waxy petroleum oil having a pour point of 95° F. and a wax content of about 27½% wt. (as measured by the above-outlined process), was mixed at 93° F. with water at 76° F. in a volumetric ratio of 60 parts of oil to 40 parts of water. The resulting mixture had an equilibrium temperature of 85° F. The mixture was an oil-in-water suspension, which was readily and smoothly transported even through a small pipe of ½ inch internal diameter without any inversion, and without the necessity of using high power input. It had a viscosity of 45 centistokes when pumped at rate of 5.6 ft./sec. through the above pipe.

At the same time when this same oil was mixed with the same amount of water under such conditions that the equilibrium temperature was above about 88° F., the result was a very viscous water-in-oil emulsion which could not be transported through a pipe line without it sticking to the sides and without the utilization of very large amounts of power.

Example IV

A Texas crude oil having a pour point of 85° F. and a wax content of about 17% wt., was mixed at 86° F. with water at 63° F. in a volumetric oil-to-water ratio of 70:30. The mixture had an equilibrium temperature of 75° F., was an oil-in-water suspension readily transported through a pipe-line.

When the same crude oil was mixed with water in the same proportions but under such conditions that the equilibrium temperature was 82° F. or higher, a highly viscous water-in-oil emulsion was obtained.

Other water-in-oil suspensions in which high pour point oils (having pour points of between about 80° F. and about 115° F.) were prepared using oil-to-water ratios of from 10:90 to 70:30, and higher. As long as they were prepared under the conditions defined in the appended claims, they were all oil-in-water suspensions which had low viscosities and which were readily transported through pipe-lines of varying internal diameters without use of excessive power.

We claim as our invention:

1. In a process for transporting waxy oils through pipe-lines, the steps of mixing a waxy oil having a pour point above about 75° F. with water to form an oil-in-water suspension, and effecting said mixing under conditions whereby the equilibrium temperature of the resulting oil-in-water suspension is above the freezing point of water but below that defined by the general formula

$$T_e = 0.6T_p + 30$$

wherein T_e is the equilibrium temperature in degrees Fahrenheit, and T_p is the pour point of the waxy oil, also in degrees Fahrenheit.

2. In the transportation of waxy liquid petroleum by pipe-line, the improvement which comprises mixing a waxy liquid petroleum oil having a pour point above about 75° F. with water to form a petroleum-in-water suspension, effecting said mixing under conditions whereby the equilibrium temperature of the resulting petroleum-in-water suspension is above the freezing point of the water used but below that defined by the general formula

$$T_e = 0.6T_p + 30$$

wherein T_e is the equilibrium temperature in degrees Fahrenheit, and T_p is the pour point of the waxy petroleum, also in degrees Fahrenheit, and passing it through the pipe-line.

3. The process according to claim 2, wherein the suspension is conveyed through the pipe-line under high-speed turbulent flow conditions.

4. In the transportation of waxy liquid petroleum oil by pipe-line, the improvement comprising mixing a waxy liquid petroleum oil having a pour point above about 75° F. with water to form a petroleum-in-water suspension, effecting said mixing under conditions whereby the resulting petroleum-in-water suspension contains between about 10% and about 75% by volume of the oil and an equilibrium temperature above the freezing temperature of the water used, but below that defined by the general formula

$$T_e=0.6T_p+30$$

wherein T_e is the equilibrium temperature in degrees Fahrenheit, and T_p is the pour point of the waxy petroleum oil, also in degrees Fahrenheit, and passing said oil-in-water suspension through the pipe-line.

5. The process according to claim 4, wherein the waxy petroleum oil has a pour point of between about 75° F. and about 110° F.

6. The process according to claim 4, wherein the waxy oil has a pour point of between about 80° F. and about 110° F.

7. The process according to claim 4, wherein the suspension is resolved, after passage through the pipe-line, by raising its temperature to effect the substantially complete liquefaction of the oil.

8. The process according to claim 4, wherein the

equilibrium temperature is above that at which the suspension pulsates in the pipe-line during the transport of the suspension therethrough.

9. The process of transporting waxy crude oil through a pipe-line which comprises mixing a waxy oil having a pour point of between about 80° F. and about 110° F. with water to form an oil-in-water suspension, said water being used in such an amount that the resulting suspension contains between about 10% and about 75% by volume of oil, effecting said mixing so that the equilibrium temperature of the suspension is above the freezing point of the water used but below that defined by the general formula

$$T_e=0.6T_p+30$$

wherein T_e is the equilibrium temperature in degrees Fahrenheit, and T_p is the pour point of the waxy oil in degrees Fahrenheit, passing said oil-in-water suspension through the pipe-line, raising the temperature of said suspension to effect the substantially complete liquefaction of the oil at the end of its transport, thereby resolving the suspension, and separately recovering the substantially water-free oil.

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