(57) **Abstract:**
A hydrocarbon based fluid additive which reciprocally can be added to either condensate diluent or heavy oil, such as in situ, mined oils sands or crude oils, to form a less viscous whole fluid.
ABSTRACT

A hydrocarbon based fluid additive which reciprocally can be added to either condensate diluent or heavy oil, such as in situ, mined oils sands or crude oils, to form a less viscous whole fluid.
HEAVY OIL MODIFICATION AND PRODUCTIVITY RESTORERS

Field of the Invention

[0001] This invention relates to compositions for enabling heavy crude oil to flow in pipelines. The compositions can also be used to rehabilitate or open up pipeline systems with restricted flow.

Background

[0002] In North America today pipeline construction is not keeping up with expansion of oils sands mining, SAGD projects and other heavy oil extraction techniques. Currently producers use condensate and light oils (diluent) gathered from western Alberta oil fields to dilute the heavy crude oil so that is will meet pipeline specifications and ultimately flow as freely in the pipelines as Western Canadian Select. Sources of the diluents include the Beaver Hill Lakes, Bigstone, Devon, Unicol, Gold Creek, Pass Creek, Tony Creek, Snipe Lake, Obed and plays such as the Montney plays, Duvernay plays and other fields. One clear reaction of increased heavy oil prices is that the “light” condensate oil supply is becoming gradually heavier due to the economic advantages drillers are experiencing from producing heavy oils. This western Alberta industry swing from production of 680 kg per m³ oil to heavier 800 plus kg per m³ specific gravity ultimately means less effective diluent which industry wide translates into greater dilution at a greater cost.

[0003] The diluents currently used are from routine bulk production facilities and its composition, although monitored and regulated, is not specifically designed to reduce viscosity in specific oils. Chemicals, polymers and DRAs are used in pipelines to try and get oil to flow but generally they cause fouling of upstream processes, process equipment and vessels, specifically where heat or pressure is used to refine or separate product. Many polymers and chemicals are used to clean vessels but many are water based and cause emulsion problems in pipelines and process vessels.
[0004] Heavy oil producers are currently using approximately one barrel of condensate for the transportation and upgrading of two barrels of heavy or very heavy oil. With the oil sands production projected to climb from the current 1.8 million barrels of oil in 2013 to an estimated 5.3 million barrels by 2020, this would mean an increased usage of 1.2 million barrels of condensate diluent. This predicted steep increase in demand for light oils has and will continue to make diluents a sought after commodity. Although industry groups have developed elaborate extraction processes, mechanical processes and transportation systems focused on the recycling of these diluent hydrocarbons, the oil industry as a whole has not yet escaped the high cost of recycled transportation or the inevitable high percentage losses that happen during the refining process. The amount of diluent present and the corresponding costs depress oil pricing incrementally.

[0005] Often consumers and financial marketers think of crude oil as a single element, like that of gold, or as separate brands, but in fact oil is a collection or spectrum of different molecules. Oil removed from oil sands and other bitumen operations contain several components including carbon, sulfur, oxygen, hydrogen, water, acids, bases, olefins, cycloaromatics, and salts. Carbon chains can range in length from single carbons to long chain hydrocarbons in excess of 150 carbons. Oil is a dynamic fluid which is constantly evolving in reservoir. Crude oils in separate reservoirs are as unique as fingerprints and are in unique stages of decomposition, more specifically understood as slow thermal maturation. The very elements and paramagnetic species that make up the oil also act as catalysts and radicals to decompose it into a simpler shorter chains, which creates a more volatile product. The most dense and viscous oils contain asphaltenes that form highly stable nanoparticles within oil due to the types of bonding (acid base interactions, hydrogen bonding, coordination complexes, associated molecular groups and aromatic stacking) that they undergo. These large highly stable molecules ultimately can seal up reservoir seams, impede pipes and facilities and ultimately impede flow in the large continental pipelines.

[0006] Once the nature of the specific heavy oil is understood it can be considered in mathematical context with its condensate diluents.
Formulations that meet specified pipeline specifications and ultimately yield highly effective formulas or safer benzene free alternatives are most advantageous.

[0007] Diluent is added to the heavy oils to reduce viscosity but there has also been industrial usage of polymers or other elemental or surfactant based compounds to achieve viscosity benefits. Generally these compounds are known as drag reducing agents (DRA’s). This general technique of adding non-like compounds, however, is best described as “chemical warfare”. These chemical cocktails can interact in pipes and processing facilities, corroding pipelines, vessels sometimes destroying compressors, fouling process towers, pumps and large scale production equipment. This warfare leads to pipeline integrity and corrosion issues which are ultimately precursors to pipeline failures and environmental damage.

[0008] Using “like” chemicals in pipelines ultimately means less chemical interactions in pipelines and less chemical precipitation in process equipment down line. These products may also be useful in the preparation of pipelines for smart pigging or for re-establishing flow in lines restricted by heavy oil. Ultimately reduced corrosion and better more effective preventative maintenance monitoring information means less down time for the pipeline, upgrading and refining systems and in turn most certainly equates to more oil shipped to be made into more final product with less environmental impact.

[0009] Currently producers in Alberta are adding between 6% and 33% diluent to their heavy production oils in order to get them to flow and meet pipeline specifications. This means that these pipelines have 6- 33% less oil in them than they could otherwise. When oil isn’t being shipped through the pipeline it is being hauled in trucks or shipped in overland train cars. Shipping such as this is less cost effective than pipelines and also has more environmental risk, which translates into greater risk to the public. The public is showing increased concern regarding transportation of heavy oil through populated areas and environmentally sensitive areas. Recent oil platform failures, train derailments and pipeline corrosion failures have been gaining media attention. As oil production in northern Alberta ramps up to meet continental needs, proposals to simultaneously increase the size
of pipeline transportation systems have been slowed. This means that with every month there are more trains and more trucks transporting crude oil across and through our public infrastructure. The use of excessive amounts of diluent is wasteful, uneconomical, produces excess environmental footprint and ultimately wastes a non-renewable resource.

[0010] Intercontinental transport of heavy oil as undiluted bitumen is also gaining favor as it has proven to have increased cost benefits to some producers. Although this has an economic benefit in that 30% condensate diluent is not added, it does not have the volume of impact that would be intuitively believed. Tank cars are loaded with heated heavy oil and then pulled by diesel train engine to the southern or central US where they are unloaded. When they are unloaded by refineries they are drained to the extent possible. However, oil that cooled on the walls of the tank cars or was in contact with the bottom of the car becomes so viscous that it cannot be removed. Few southern refineries have heated unloading facilities to remove this viscous oil. Thus one third full tank cars are returned north to refill. This wasteful cycle is repeated until the cars are finally purged of their solidified oil. This is a very inefficient use of transportation having a high environmental toll. Using a viscosity reducer that fluidizes the oil during rail transport to refineries in the south would allow full extraction of the oil from the tank cars and thereby reduce the number of cars required, effectively reducing cost and environmental and public impact.

[0011] Developing a diluent that can be used at lower volumes and with the same flow characteristics within a pipe means one can greatly increase efficiency of existing transportation systems. This would mean more room in the pipeline, fewer trucks on public roads, less environmental impact, and fewer train cars to ship the same volume of oil. Ultimately it could cause a dynamic shift in the way oil is priced.

Summary of the Invention

[0012] The present inventors have found a hydrocarbon based fluid additive
which reciprocally can be added to either condensate diluent or heavy oil, such as in situ or crude oils, to form a less viscous whole fluid. Reducing viscosity and reducing the amount of diluent used can enable greater transportation volumes within existing pipelines at specification, and can allow blocked pipeline lengths to be freed.

[0013] The additive makeup is a calculated ratio of short chain alkanes and volatile aromatic organic compounds formulated specifically to manipulate the alkane and aromatic compounds intermolecular interactions already present in the parent diluents and/or oil. A process of profiling the total alkane make up of both the heavy oil and the diluent condensate oil including density, viscosity, inorganic percentages and desired pipeline specification and/or viscosities are typically an integral experimental and mathematical part of implementing additives final formulation.

[0014] The present inventors have found specific formulations and corresponding stabilized blends have resulted from this evolution of understanding. These products are effective across a wide range of oil types. Formulations which are particularly useful do not contain benzene.

[0015] By utilizing a predictive viscosity calculation that takes into effect the densities of the parent heavy oil and specific light oil condensate diluent to be used the present inventors were able to predict and thereby experimentally determine an ideal alkane to volatile aromatic ratio necessary to maximize viscosity, while minimizing diluent use for heavy and condensate diluent oils. The present inventors were able to develop an active viscosity reducing benzene-free product.

[0016] Thus in preferred embodiments, the invention teaches a composition comprising pentane and hexane in a ratio of about 8:11, pentane:hexane.

[0017] The composition may further comprise xylene and/or toluene. It may be in a ratio of about 27-37:39-49:1-9, pentane:hexane:aromatics, or in a ratio of


[0019] The invention further teaches the use of these compositions as one or more of an oil additive, an oil diluent, to enhance oil viscosity, to decrease oil pipeline transport, as an oil vessel cleaner, to remove oil well plugs. It may be particularly useful with heavy oil. It may be particularly stable with a light oil condensate diluent.

Detailed Description of the Invention

[0020] This invention relates to enabling maximum amounts of heavy crude oil meeting pipeline specification to flow in pipelines from upstream production wells and facilities and intermediate processing facilities down to final refining facilities in all climatic temperatures with significantly less diluent. Alternatively or simultaneously the formulation could be used to prevent or open up pipeline systems with restricted flow due to oil viscosity caused by paraffins or asphaltene complexes.

[0021] The solution is to decrease the viscosity of crude and heavy oil so that it will flow in the pipe but not have to dramatically increase the volume of the oil. Light oils allow the crude to flow but they have changed in character over the past 15 years. By producing an additive that corrects diluent composition to the most advantageous composition for the current heavy oil it is possible to dramatically reduce the amount of diluent that is needed. The present inventors developed the best “additive” for diluents (condensate) that would reduce viscosity in crude oils. The idea was based in part on “like dissolves like”, and give the viscous oils the
same characteristics of the less viscous oils; long-term occupational study and analysis of field condensate light oils with like densities but differing viscosities; long term occupational studying of oils with like viscosities and differing densities and their effect on process equipment fouling. This led to the understanding of a pattern. Once this was determined, a group of ideal compounds could be identified. Viscosity and density calculations were thereby used in conjunction with this knowledge to reduce the necessity of large scale testing and predict possible formulation ratios. What the present inventors found was dramatic. There is a "perfect" ratio that makes a step change in the viscosity effect. With only a small addition of the right hydrocarbons the effectiveness of diluents can be improved. It was important that the additive be "natural" and contain compounds that would not harm or upset process equipment upstream, midstream or downstream. By using compounds the oils already contain the present inventors were able to preserve the natural state and bond interactions of the oil.

[0022] The chemical formulations were made by a combination of mathematical predictions of viscosity and density of a target blend and then by experimentally making several blends within that range, and finally by testing. As it happens, many of the heaviest oils have similar properties therefore the blend for oils with a density over 1010 have less variation than blends for lighter oils.

Example 1

[0023] Product A was formulated from typical grade chemical in an effort to make large scale manufacturing as cost effective and similar to experimental conditions as possible. It was specifically formulated to provide a safer less carcinogenic formula.

[0024] The following were used in the process of formulation:

Toluene: 99.9% Pure, Fisher Scientific
Xylene: Certified ACS 99.9% Pure, Fisher Scientific
Pentane: 98% Pure, Acros Organics
Hexane: 99.9% Honeywell B& J
The TX was made by 75 Toluene and 25 Xylene by volume in an ultra cold environment.

Pentane: 98% Pure, Acros Organics Density @ 15C: 630.5 kg/m3 / 630.6 kg/m3
Viscosity @ 7.5C: 0.43185 cST

Hexane: 99.9% Honeywell B& J Density @ 15C: 673.5 kg/m3 /
674.0 kg/m3 Viscosity @ 7.5C: 0.56474 cST

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**Comments:** nC5 40.35g + nC6 56.10g + (75 Toluene/25 Xylene% by volume) 5.05g

**Methods:**
- Density (AP)  
  ASTM D4052-11
- Viscosity @ 7.5 deg C  
  ASTM D445
Example 2

[0025] **Description:** Peace River Heavy Oil with Product A

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**Comments:** PROS 39.7080g + Product A 10.27g

**Methods:**
- Density (AP) ASTM D4052-11
- Viscosity @ 7.5 deg C ASTM D445

Example 3

[0026] **Description:** MO10

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**Comments:** MO10-2: CRW 35.6139g (lean oil condensate) + diluent 33.1946g = 68.8085g

**Methods:**
- Density ASTM D1298-99(2005)
- Density (AP) ASTM D4052-11
- Viscosity @ 7.5 deg C ASTM D445

[0027] This formulation reduced the use of diluent by between 8 and 18%. By adding the active ratio to the condensate it was meant to enhance we created a stable safe product. Considerations in this final preparation may include vapor pressure, flash point, shipping temperature, safety issues or any environmental concerns specific to the implementation.

[0028] The product reduces the 1015 kg/m³ Peace River heavy oil (16557
cSt at 25 deg C) to 930 kg/mg with a viscosity of 355 cSt (at 15 deg C) with a 24 percent addition of typical condensates containing the diluent. The diluent can reduce the viscosity by 70% with an addition of less than 12% product to the whole mixture. This means a pipeline could carry between 8-18% more oil and still have the same flow characteristics.

[0029] Benefits of the formulations include:

a. Decreases Viscosity of Heavy Oils
b. Decreases Density of Heavy Oils
c. Does not cause emulsions
d. Does not become inactive or molecularly breakup in the presence of heat or pressure.
e. Does not change the pH of the native Oil
f. Similarly noncorrosive as typical condensate(diluents)

[0030] When the diluent is added to oil “plugs” containing asphaltenes, paraffins and silicon, it breaks them apart (at ambient temperatures) turning them into a light oil that is easy to manipulate. By adding the diluent to specific condensates (lean oils) it is makes it into a universal oil solvent. In the gas and oil field it could be used to:

a. Free pipe structure in which oil has stopped flowing due to high density

b. Clean heavy oil (paraffins, asphaltenes, sulfur compounds, nitrogen compounds, chloride deposits) deposits from light oil systems for example stabilizer or facing towers and process vessels; universal vessel cleaner.

c. Can be utilized “down hole” to help free wells that have stopped flowing due to plugging in their upper structure due to hardening
of paraffins and asphaltenes.

d. Can be used as a “wash” to accelerate the removal of heavy oils from sand laden bitumens or as a agent to assist in the removal of waters from SAGD oils.

e. Can be used to fluidize or reduce the viscosity of raw heavy oils or semi processed heavy oils being transported by truck or rail tanker.

The diluent and MO10 can be used in concentrate to enable better smart pigging of heavy oil pipelines.

[0031] The additive accentuates the C4 to C10 behavior and character of condensate diluents and makes them more effective. By doing this, less diluent can be used and more oil can travel in a pipeline within the specific pipeline specification. The formulations alter the viscosity of heavy oils, bitumen and sludge oils such that they will flow. Accordingly, the formulations provide:

1. Increased oil in pipelines, which results in:
   a. Decreased carbon footprint in shipping oil in pipeline rather than rail or tuck.
      i. Cost benefit in that less diluents will need to be shipped to upstream terminals.
      ii. Cost benefit in that the efficiency of shipping has been increased.
   b. Decrease plugging or unplug lines in upstream, downstream and midstream. Saves money in downtime and makes money in increased production.
   c. Cost benefit in reduced diluents used
2. Cost benefit in reduced fouling due to “non-like” chemistry use
3. Public and company safety benefit in that there will be fewer trucks on populated highways and locations.
4. Public safety and company liability benefit as less oil is shipped overland by rail.
5. Reduced environmental risk due to less oil is shipped overland by rail.
6. Reduced cost as pipeline systems will hold more and not need additional pipelines and use of more compatible chemistries will extend pipeline life.
7. Reduced pipeline and process downtime due to more favorable and effective risk based assessment (less chemical warfare).
8. Improve pipeline safety by increasing effectiveness of smart pigging (reduced risk of pipeline failure due to better prevention).

[0032] The formulations also provide the following benefits:

1. They may be sold in MO10 form to increase stability.
2. Do not contain alcohols
3. Do not contain carbon disulfide, sulfurs or mercaptan
4. Do not contain ethers.
5. Do not contain polymers or DRAs
6. Do not contain phosphorus or volatile phosphorus
7. Do not need to adjust the pH or affect the corrosion properties of diluents (not an acid or a base)
8. Is not an emulsifier or does not by itself cause emulsions with pure hydrocarbon oil.
WE CLAIM:

1. A composition comprising pentane and hexane in a ratio of about 8:11, pentane:hexane.

2. The composition of claim 1, further comprising xylene.

3. The composition of claim 1 or 2, further comprising toluene.


5. The composition of claim 2 or 3, in a ratio of about 8:11:1, pentane:hexane:aromatics.


8. The composition of claims 1-3, further comprising an aromatic.


10. The composition of claim 8, in a ratio of about 8:11:1, pentane:hexane:aromatics.


13. The composition of claims 1 to 12 further comprising a light oil condensate diluent.
14. The composition of claims 1 to 13 for use as an oil additive.
15. The composition of claims 1 to 13 for use as an oil diluent.
13. The composition of claims 1 to 13 for use to decrease oil viscosity.
17. The composition of claims 1 to 13 for use to enhance oil pipeline transport.
18. The composition of claims 1 to 13 for use as an oil vessel cleaner.
19. The composition of claims 1 to 13 for use to remove oil well plugs.
20. The composition of claims 1 to 13 for use to decrease oil density.
21. The composition of claims 1 to 13 for use to accelerate the removal of oil from sand laden bitumens.
22. The composition of claims 1 to 13 for use to assist in the removal of water from oil.
23. The use of a composition of claims 1 to 13 as an oil additive.
24. The use of a composition of claims 1 to 13 as an oil diluent.
25. The use of a composition of claims 1 to 13 to decrease oil viscosity.
26. The use of a composition of claims 1 to 13 to enhance oil pipeline transport.
27. The use of a composition of claims 1 to 13 as an oil vessel cleaner.
28. The use of a composition of claims 1 to 13 to remove oil well plugs.
29. The use of a composition of claims 1 to 13 to decrease oil density.
30. The use of a composition of claims 1 to 13 to accelerate the removal of oil from sand laden bitumens.
31. The use of a composition of claims 1 to 13 to assist in the removal of water from oil.

32. The use of claims 13 to 21 wherein said oil is a heavy oil.