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SULFUR-HYDROCARBON SLURRY PIPELINE TRANSPORTATION CONTAINING CORROSION AND PLUGGING INHIBITORS

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ABSTRACT OF THE DISCLOSURE

An improved method of transporting sulfur-liquid hydrocarbon slurries through pipelines without causing plugging or corrosion of the pipelines.

The invention relates to an improved and novel process of preventing plugging and corrosion of pipelines transporting sulfur in the form of a sulfur-liquid hydrocarbon slurry.

BACKGROUND OF THE INVENTION

The transportation of sulfur neat or as a water or oil slurry in pipelines is well known in the art as noted by reference to U.S. Pats. 2,798,772; 2,917,345 or 2,947,578 or as described in Pipeline Industry, June 1967, pages 58–60. In making the sulfur into a sulfur-hydrocarbon slurry, the sulfur is generally sprayed in molten form into either water or a hydrocarbon to form a slurry suitable for transportation through a pipeline. Formation of a stable slurry wherein the sulfur does not undergo any undesirable change or the slurry does not exhibit a tendency to wide variation in viscosity is essential to the process in addition to other problems which may be encountered during and after transportation of the slurry through a pipeline. Thus, separation of the sulfur from the carrier fluid, plating or coating of the sulfur on pipeline walls causing plugging of the pipeline, corrosion, viscosity changes due to pressure and temperature variations encountered requiring increases in pumping power which increases operation costs, etc., are only a few of the problems normally encountered in transporting sulfur-liquid hydrocarbon slurries through pipelines.

Although the above are serious problems for consideration in transporting sulfur through pipelines, nevertheless the transportation of sulfur in slurry form through pipelines can be made to be an effective, attractive and economic means of transportation, particularly since sulfur is recovered or obtained from isolated, remote and inaccessible areas, and must be transported to desired accessible areas. As noted above, a number of methods have been proposed for pipeline transportation of sulfur slurries such as injecting molten sulfur into water or a liquid hydrocarbon thereby forming a sulfur slurry for pipeline transportation. Such means for transporting sulfur generally do not overcome corrosion, coating and/or plugging problems described above.

An object of the present invention is to transport sulfur as a sulfur-liquid hydrocarbon slurry through pipelines which is stable and flowable.

Another object of the present invention is to transport through a pipeline sulfur-liquid hydrocarbon slurries without causing sulfur coating, deposition or plugging or corrosion of the pipeline.

Still another object of this invention is to form a slurry of sulfur in a liquid hydrocarbon medium, which when formed is stable, non-corrosive, does not tend to cause pipeline plugging when said slurry is transported through a pipeline and from which the sulfur can be readily recovered as essentially pure sulfur.

Other objects will be apparent from the following description.

SUMMARY OF THE INVENTION

The present invention is directed to an improved, novel and new technique for transporting a sulfur-liquid hydrocarbon slurry through pipelines over great distances without causing corrosion, coating, deposition or plugging of the pipeline due to the tendency of sulfur under such conditions to adhere to the pipeline walls because of temperature, pressure, and other variable conditions which tend to cause corrosion and plugging of said lines; by admixing or adding or injecting prior to or after injection of a sulfur-liquid hydrocarbon slurry into the pipeline, a small amount of from 0.1% by weight to 10% by weight, preferably between about 0.5% by weight to about 5% by weight basis total slurry, of an aqueous solution and from about 0.01% by weight to about 50% by weight of a polar-containing organic solvent basis oil phase preferably selected from the group consisting of mutual soluble alcohol, ketone and/or aldehyde. The aqueous liquid in an amount preferably not exceeding 5% by weight basis total slurry and the polar-containing organic mutual liquid solvent can be preferably present in an amount not exceeding 50% by weight basis oil phase and each liquid can be injected alternately or simultaneously when necessary in various places along the pipeline where indications are that corrosion or plugging of the line might take place. Any corrosion and plugging detection means known in the art can be used for this purpose. It has been noted that by injection of 1–5% by weight basis total slurry of an aqueous solution and 0.01–50% by weight of a polar-containing organic solvent basis oil phase such as an alkanol, e.g., methanol or propanol, into a pipeline transporting a sulfur-liquid hydrocarbon slurry in which the sulfur content of the slurry can vary from about 10% by weight to about 75% by weight or higher, preferably between 40 and 70% by weight sulfur, not only inhibits corrosion but prevents plugging of the line due to sulfur agglomeration and deposition on the walls of the pipeline resulting in improved flow of the slurry at reduced pumping cost. A preferred plugging and corrosion preventing composition for sulfur-liquid hydrocarbon slurries being pipeline transported is the addition to such slurries of from 1 to 5% by weight water basis total slurry and from 0.01 to 25% by weight methanol basis oil phase.

The sulfur-liquid hydrocarbon slurry can be made by any suitable means such as described in U.S. Pat. 2,798,772 or by the method described in copending patent application Serial No. 663,755, filed August 28, 1967 which matured as U.S. Pat. 3,443,827. It is preferred that methods for making the sulfur-liquid hydrocarbon slurry be used in which the sulfur is produced in spherical form since this facilitates the stable dispersion and suspension of the sulfur in the liquid hydrocarbon carrier and inhibits attrition. The phase transfer method for making the sulfur slurry as described in the above copending application comprises first forming a sulfur-aqueous liquid (water) slurry and thereafter phase transferring the sulfur particles

from the aqueous liquid into a liquid hydrocarbon. In this process the phase transformation to form the sulfur-hydrocarbon slurry can be so controlled that a small amount (1–5% by weight) water basis total slurry is transferred with the sulfur-water phase into the hydrocarbon phase and thereafter water-alcohol can be added to accomplish the desired ends of the present invention.

The hydrocarbon carrier for the sulfur can be any liquid hydrocarbon ranging from a light petroleum fraction such as liquefied petroleum gas (LPG), fuel oil, gasoline, kerosene, petroleum distillates, condensates, crude oil and mixtures thereof. Preferred are liquid hydrocarbons containing at least 10% by weight or higher of aromatics, preferably about 15–50% by weight aromatic enriched kerosene or crude oil or crude oil condensate fractions containing 15–20% by weight aromatics which include mono- and polyaromatic hydrocarbons.

At the terminal end of the line the aqueous solution can be readily separated from the sulfur-hydrocarbon system by suitable phase separation, distillation or the like.

PREFERRED EMBODIMENT OF THE INVENTION

A 40–60% by weight sulfur-crude oil slurry was prepared by phase transfer by first injecting molten sulfur into an aqueous liquid such as water and thereafter contacting the slurry thus formed with the aromatic enriched kerosene to effect phase transfer of the sulfur particles into the aromatic enriched kerosene, and injecting this slurry into a pipeline followed by injection of 1–5% by weight water basis total slurry and 0.01–25% by weight methanol basis oil phase. Sulfur-hydrocarbon slurries thus formed in the presence of the water-alcohol mixture do not corrode or plug the pipeline. Instead of using the phase transfer technique for making the slurry, the molten sulfur can be injected in an oil, e.g., crude oil, directly and thereafter admixed with the water-alcohol mixture.

An advantage of the present process for transporting through pipelines sulfur-liquid hydrocarbon slurries is that the slurry can be also prepared by directed injection of molten sulfur into a suitable liquid hydrocarbon as described in U.S. Pat. 2,798,772 and injecting therein a small amount of water-alcohol mixture so as to prevent corrosion and plugging of the line. Either process as well as other processes can be used to make the sulfur-liquid hydrocarbon slurry depending on the availability of the liquid carriers. Thus, where water is available the first process can be used and if not the second one can be used.

The corrosive effect of added or adventitious water on sufur-liquid hydrocarbon slurries is evident from the data presented in Table 1 and the selectiveness of water-alcohol mixture as a corrosion preventive agent is shown in Table 2.

The slurry tested comprised 40% by weight sulfur and 60% hydrocarbon. The conditions for the corrosion test were as follows:

Corrosion by sulfur slurries

Conditions:

150 ml. magnesia bottles rotated at 10 r.p.m. in EPR bottle rotator.
120 grams of slurry added to each bottle.
Slurry concentration=40% by weight sulfur.
Sulfur particle size: Waterton sulfur 82% greater than 45 microns.
Jumping Pound sulfur 81% greater than 45 microns.
Oil phase: Aromatic hydrocarbon, kerosene with 17% w. aromatics.
Water additions are percent by weight of the oil fraction.
½ x 6⅛-inch specimens of 20-gauge mild steel sheet with sandblasted surface.
Specimens wedged into bottles to reduce mechanical damage.
Room temperature (72°), atmospheric pressure, 48 hours exposure.

TABLE 1

Sulfur slurry corrosion as a function of water concentration

[Conditions: As above. 40% w. Waterton sulfur/kerosene with 17% w. aromatics]

Water concentration, percent w.[a]	Corrosion rate, mils/yr.[b]
0	1
0.28	50
1.12	120
2.2	230
4.4	250
5.0	280

[a] Concentration of added water, basis oil.
[b] From weight loss and exposure time. Corrosion rate has not been corrected for weight loss due to cleaning.

TABLE 2

Sulfur slurry corrosion

[Conditions: As above. 40% Jumping Pound sulfur/liquid phase as given]

Liquid phase,[a] percent methanol in aromatic hydrocarbon oil:	Corrosion rate (m.p.y.) [b]
2	15
5	10
10	6

[a] Liquid phase as indicated plus 2% by weight H_2O basis liquid phase.
[b] From weight loss and exposure time. Corrosion rate has not been corrected for weight loss due to cleaning.

At the terminal end of the line the water-polar-containing organic compound mixture can be readily removed by phase separation and the sulfur can be removed from the liquid hydrocarbon by suitable means such as described in U.S. Pat. 2,798,772 and the sulfur purified by methods as described in U.S. Pat. 2,809,885 or as described in the copending patent application Ser. No. 684,507, filed Nov. 20, 1967, which matured as U.S. Pat. 3,489,677 which comprises treating oil contaminated sulfur with an aqueous solution containing a mixture of alkali hydrosulfide and corresponding hydroxide, e.g., ammonium hydrosulfide and ammonium hydroxide, or by other suitable means such as sulfur can be recovered from the oil slurry by filtration of molten sulfur and liquid-liquid extraction with a hydrocarbon solvent containing 10–50% by weight aromatic. Thus, at the receiving terminal the sulfur slurry can be filtered and washed. The recovered sulfur is then melted and purified by liquid-liquid extraction with an aromatic hydrocarbon such as cumene. Also, if desired, the filtered sulfur can be steam stripped to recover bright yellow sulfur.

The foregoing description of the invention is merely intended to be explanatory thereof. Various changes in the details of the described method may be made within the scope of the appended claims without departing from the spirit of the invention.

I claim as my invention:

1. A method of transporting sulfur through a pipeline to a terminal preventing corrosion and without plugging the line comprising:
   (a) injecting from 10% to 75% of molten sulfur into a liquid hydrocarbon to form a sulfur-liquid hydrocarbon slurry;
   (b) mixing with the slurry (a) from 0.1% to about 10% basis total slurry of an aqueous solution containing from about 0.01% to about 25% of a polar-containing organic compound basis oil phase;
   (c) injecting the slurry of (a) and solution (b) into a pipeline; and,
   (d) transporting the slurry containing the slurry (a) and mixture (b) through a pipeline to a terminal station.

2. The method of claim 1 wherein the liquid hydrocarbon of (a) is a petroleum oil.

3. The method of claim 1 wherein solution (b) is injected into the slurry (a) after the slurry (a) has been injected into a pipeline.

4. The method of claim 1 wherein the slurry (a) contains 10%–75% by weight sulfur and the balance being a liquid hydrocarbon containing aromatic components and the solution (b) added to slurry (a) comprises of a mixture of water and an alkanol.

5. The method of claim 4 wherein mixture (b) comprises 1–5% by weight water basis oil slurry and the alcohol is methanol present in an amount of from 0.01 to 25% by weight basis oil phase in a liquid aromatic hydrocarbon.

6. The method of claim 1 wherein the liquid carrier is a crude oil.

7. The method of claim 1 wherein the sulfur-liquid hydrocarbon slurry is separated into its component parts at the terminal end of the pipeline.

References Cited

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