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SLURRYING OF SULFUR IN LIQUID CARRIER

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ABSTRACT OF THE DISCLOSURE

An improved method of transporting sulfur-liquid hydrocarbon slurries through pipelines without causing sulfur agglomeration, sticking, deposition or plugging of the pipeline.

The invention relates to an improved and novel process of preventing sulfur agglomeration, sticking, deposition and plugging 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, pp. 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, agglomeration and separation of the sulfur from the carrier fluid, plating, depositing or coating of the sulfur on pipeline walls causing plugging of the pipeline, corrosion, viscosity changes due to pressure and temperature variations requiring great 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 from through pipelines can be made to be effective, attractive and economic means of sulfur transportation, particularly since sulfur is recovered or obtained from isolated, remote and inaccessible areas, and must be transportated to desired accessible areas. As note 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. These methods for making sulfur slurries suitable for transporting through pipelines generally do not overcome the agglomeration, deposition, sticking, 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.

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

Still another object of this invention is to form a slurry of sulfur in a liquid hydrocarbon medium, which does not tend to cause sticking, agglomeration or pipeline plugging or cause any difficulty in circulation of the slurry when said slurry is pumped and transported through a pipeline and from which the sulfur can be readily recovered at the terminal end of the pipeline as essentially pure sulfur.

Another object is to transport sulfur as a liquid hydrocarbon slurry by pipeline over great distances under conditions of reduced pumping and handling costs.

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 slurry of a sulfur-liquid hydrocarbon through pipelines over great distances without causing sulfur agglomeration or sticking or sulfur deposition on the walls of the pipelines due to the tendency of sulfur under such conditions to adhere to the pipeline walls because of temperature, pressure and other variable conditions so as to plug said lines; by forming a non-agglomerating sulfur-liquid hydrocarbon for transportation by injecting liquid sulfur into a liquid hydrocarbon containing a sulfur anti-agglomerating agent, preferably one capable of forming free radicals and optionally having also an effect of lowering the freezing point of sulfur so that major portions of the sulfur particles are in essentially S_8 ring form and the liquid hydrocarbon into which the liquid sulfur is sprayed is kept relatively cold. The liquid hydrocarbon can range in viscosity from a gasoline to a heavy lube oil fraction such as gasoline, kerosene, fuel oil, lubricating oil or crude oil, and fractions and mixtures thereof. The anti-agglomerating agents can be also added to the sulfur or to both sulfur and the liquid carrier in amounts ranging from 0.1% to over 50% and in the case of gaseous material until saturation of the liquid hydrocarbon is achieved and includes such materials as halogens e.g. chlorine gas, iodine, hydrogen sulfide, hydrogen persulfides and polysulfides, ammonia and other materials which react to form free radicals. The anti-agglomerants can be injected or admixed with the liquid hydrocarbon or with the liquid sulfur used to make the slurry. The anti-agglomerants agent can be added to the liquid or molten sulfur or to the liquid petroleum as described or it can be injected when necessary in various places along the pipeline carrying the slurry where indications are that sulfur agglomeration, deposition, sticking or plugging of the line is taking place. Any plugging detection means known in the art can be used for this purpose. Thus it has been found that by adding or injecting into a slurry of sulfur and liquid an anti-agglomerant e.g. NH_3 or H_2S or H_2Sx where $x=3–6$, in which the sulfur content of the slurry can vary from about 10% to about 75% by weight or higher, preferably between 30 and 60% by weight sulfur, that not only does the presence of these materials prevent plugging, agglomeration, sticking and deposition of pipelines transporting said slurry of sulfur on the walls of the pipelines but also improves the flow of the slurry and reduces pumping costs.

During the preparation of the sulfur-oil slurry improvement additives other than the anti-agglomerants described above can be introduced in amounts from 0.1% to 10% in order to aid in formation of spherical sulfur particles generally within the range of 1 to 800 and preferably between 20 and 300 microns and which impart to the slurry other additional benefits. The additives best suited for this purpose include asphaltenic additives which can be obtained from unrefined or refined crude oil and fractions thereof. By unrefined crude oil is meant any crude oil which has not been processed in a refinery. Thus, a crude oil may be used as it is removed from the ground, or it may be first processed in field units such as oil-water separators, degasers, etc. Although just how the asphaltenes function in the slurry mixture is not understood, it has been found that the asphaltenes prevent sulfur agglom-

eration, sticking and aid in the formation of spherical sulfur particles having dimensions of from 1 to 800 microns and preferably between 20 and 350 microns.

The asphaltenes can be recovered from petroleum stocks by any suitable means such as described in the Journal of the Institute of Petroleum, February 1968, pages 50–53 and April 1968, pages 107–117 or as described in U.S. Pats. 3,206,388; 3,228,870; 3,153,623; 2,729,589; 3,368,-876; 3,364,138; 3,206,388 and 3,275,076. The latter two base materials can be used per se as the asphaltene additive and carrier for the slurry. In other words, high aslphaltenic crudes or fractions thereof containing at least 1% asphaltenes can be used both as the carrier and additive for the sulfur slurry. The asphaltenes, asphaltogenic acids and carboids and their method of recovery and separation from crudes and fractions thereof is also fully described in Chapter 9 of Sachanen's book on "The Chemical Constituents of Petroleum" and includes petroleum resin, aslphaltenes, asphaltogenic acids and their derivatives. Also, the asphaltenic materials described in U.S. Pats. 2,274,076; 3,284,340 or 3,336,146 can be used and they can be separated from petroleum by methods described in U.S. Pats. 3,364,138 and 3,368,876.

Instead of asphaltenes, natural surfactant components present in crude oil can be used. The natural surfactants present in crude oil include the natural polar-containing constituents present in crude oil such as the nitrogen-, oxygen- and sulfur-containing materials can be added to the slurry of sulfur and liquid petroleum as described prior to or during the making of the slurry or these active surfactant materials can be injected when necessary in various places along the pipeline.

The sulfur-liquid hydrocarbon slurry can be made by any suitable means. It is preferred that in the making of the sulfur-liquid hydrocarbon slurry that the conditions of preparation be controlled so that the sulfur in the slurry is present in particle size 340–350 microns and is in spherical form since sulfur in this form in the slurry is more resistant to agglomeration, attrition and frictional forces.

A method for making the sulfur slurry is described in copending application, Ser. No. 663,755, filed Aug. 8, 1967 which matured as U.S. Pat. No. 3,443,837 namely forming a sulfur-aqueous liquid (water) slurry and thereafter phase transferring the sulfur particles from the aqueous liquid into a liquid hydrocarbon containing the anti-agglomerants e.g. NH_3 or H_2S. The sulfur may be phase transferred directly into a liquid hydrocarbon such as crude oil. Thereafter, the anti-agglomerant can be added as desired.

PREFERRED EMBODIMENT OF THE INVENTION

(I) A 40–60% by weight sulfur-aromatic (17%) enriched kerosene 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 saturated with H_2S to effect phase transfer of the sulfur particles into the aromatic enriched kerosene. To the sulfur H_2S saturated kerosene slurry was added from about 1% to about 2% of asphaltenes and thereafter this slurry was injected into a pipeline for transportation to a terminal station. Sulfur-H_2S saturated kerosene slurries containing optionally a small amount of asphaltenes do not form agglomerates or cause plugging of the pipeline.

(II) An advantage of the present process for transporting through pipelines sulfur-liquid petroleum slurries as defined is that the slurry can be also prepared by direct injection of molten sulfur into a suitable petroleum fraction such as kerosene, fuel oil, oil condensate or distillate and mixtures thereof which contains H_2S or NH_3 and to which has been added a small amount of asphaltenes so as to aid in making spherical sulfur particles and prevent sulfur agglomeration, deposition and plugging of pipelines. Either process as well as other processes can be used to make the sulfur-liquid petroleum fraction slurry depending on the availability of the carrier. Thus, where water is available the first process can be used and if not the second one can be used.

The presence of the anti-agglomerants during the preparation of the final slurry by method (I) or (II) has an additional advantage in that the crude oil aids in the formation of spherical sulfur particles which are most desirable since spherical sulfur particles in slurries as defined provide optimum pipeline performance such as low pressure drops during its transportation and ease of recovery and purification at the terminal end of the pipeline.

The following examples illustrate the essence of the present invention.

(A) Molten sulfur at 120–160° C. was sprayed into aromatic (17%) enriched kerosene through a spray nozzle at about 200 p.s.i. pressure drop to give a homogeneous slurry with sulfur solids content of about 16% by volume in which the sulfur particles were essentially large angular-crystalline particles which began to stick together and agglomerate into a sticky mass within about 10–15 minutes.

(B) The method of (A) was repeated except that H_2S was added to the kerosene carrier. The particles formed were microspherical (20–450 microns) in shape and no tendency of the particles to stick or agglomerate were noted.

In another test different petroleum fractions were used to form sulfur slurries wherein a 90-ml. portion of molten sulfur at 140° C. was injected as a continuous stream for 0.5 minute into a well-stirred 500 ml. charge of a petroleum carrier. As shown in the table some of the carriers were used neat and to some were added H_2S or NH_3. For comparison various surfactants were added to sulfur-oil slurries and the results are shown in Table 1.

TABLE.—EFFECT OF ADDITIVES ON SULFUR DISPERSION

Conditions: 500 ml. carrier in 1 liter Morton flask; 90 ml. sulfur at approximately 140° C. added 0.5 minute; 1,200 r.p.m. with crescent blade stirrer

Run	Carrier	Initial temp., ° C.	Level, percent w.	Type	Coagulum (+12 mesh), percent w. basis S fed	Major Fractions, percent w. basis slurry			d_{50}, μ	Particle shape [a]
						−16, +30,	−30, +50			
1	Petroleum fraction (Waterton condensate).[c]	22		None	19.1	57.7	19.3		680	A
2	do.[c]	22	1	Bryton 430 (62% allylaryl sulfonate)	20.4	60.0	21.0		710	A
3	do.[c]	24	1	Oleic acid	>30	72.0	13.7		770	A
4[b]	do.[c]	23	1	Naphthenic acid bottoms	>30					A
5[b]	do.[c]	23	1	Dehydroabietic acid	>30					A
6	do.[c]	21	1	50% dodecyltrimethylammonium chloride	13.8	62.6	20.8		700	A
7	35% kerosene/white oil (Waterton condensate).	23	Saturated.	NH_3	7.0	64.6	24.0		690	S
8	Crude oil	23	Saturated.	H_2S	5	60.5	20.5		500	S

[a] S=spherical; A=agglomerated, in estimated order of abundance in +30 mesh fractions.
[b] 600 r.p.m. in early scouting runs and in all 60° C. runs.
[c] Derived from Canadian oil field. API Gravity=54.9; Viscosity, CS 59° F.=0.953 and 77° F. 2 0.805; Flash point, Tag Open Cup, ° F=7; Pour Point, ° F=80; Sulfur, % w. Total=1.14; FIA, % w. Saturates=82 and Aromatics=18.

Sulfur slurries of the present invention containing anti-agglomerants, e.g. H_2S or NH_3 can be transported through pipelines over great distances without the danger of sulfur deposition, agglomeration, sticking or plugging of the pipelines.

At the terminal end of the line 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 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% 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.

We claim as our invention:

1. A method of transporting sulfur through a pipeline in slurry form without causing sulfur sticking, agglomerating and plugging of the line comprising injecting from 10% to 75% of sulfur having essentially spherical shape and dimensions of from 1 to 800 microns into a crude oil saturated with an anti-agglomerate selected from the group consisting of NH_3 and H_2S and injecting said sulfur slurry into a pipeline and transporting said slurry via said pipeline to a terminal station.

2. The method of claim 1 wherein to the crude oil is added from 0.1% to 10% asphaltenes.

3. The method of claim 1 wherein the sulfur injected into the oil is in molten form.

4. A method of transporting sulfur through a pipeline in slurry form without causing sulfur sticking, agglomerating and plugging of the line comprising injecting from 10% to 75% of sulfur particles having essentially spherical shapes and dimension of from 1 to 800 microns into a crude oil to which has been added from 0.1% to 10% asphaltenes and from 0.1% to 50% of NH_3, to form a sulfur-crude oil slurry composition and transporting said slurry composition through a pipeline to a terminal station.

5. The method of claim 4 wherein the sulfur injected into the oil is in molten form.

6. A method of transporting sulfur through a pipeline in slurry form without causing sulfur sticking, agglomerating and plugging of the line comprising injecting from 10% to 75% of sulfur particles having essentially spherical shapes and dimensions of from 1 to 800 microns into a crude oil saturated with NH_3 to form a slurry composition and transporting said slurry composition through a pipeline to a terminal station.

7. The method of claim 6 wherein the sulfur injected into the oil is in molten form.

References Cited

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