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[54] **SULFUR-OIL SLURRY PIPELINE TRANSPORTATION UNDER INERT GASEOUS CONDITIONS**
10 Claims, No Drawings

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[56] **References Cited**

UNITED STATES PATENTS

3,438,680	4/1969	Scheueman et al.	302/14
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ABSTRACT: An improved method of transporting sulfur-liquid hydrocarbon slurries through pipelines without causing plugging or corrosion of the pipelines by maintaining an inert atmosphere therein.

SULFUR-OIL SLURRY PIPELINE TRANSPORTATION UNDER INERT GASEOUS CONDITIONS

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 by maintaining an inert atmosphere in the pipeline and optionally if desired adding to or injecting into the sulfur-liquid hydrocarbon slurry a small amount of an aqueous solution containing optionally a selected class of corrosion inhibitors.

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. Pat. Nos. 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 the 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, noncorrosive, 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.

Another object is to transfer sulfur as a liquid hydrocarbon slurry by pipeline over great distances reducing 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 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 in said lines; by maintaining the slurry in the pipeline under inert conditions and optionally, if desired, by admixing or adding or injecting prior to or after injection or addition of a sulfur-liquid hydrocarbon slurry into a pipeline, a small amount of from 0.01 percent to 10 percent by weight, preferably between about 0.1 percent to about 5 percent by weight, of an aqueous solution basis total slurry containing optionally a small amount of a selected class of corrosion inhibitors. The slurry in the pipeline can be maintained in an inert atmosphere by deaeration of the line or injecting therein an inert gas such as nitrogen or a lower hydrocarbon of not more than three carbon atoms in an amount sufficient to prevent oxidation.

The aqueous solution can be neat water or water containing corrosion inhibitors selected from the group consisting of (a) alkali metal chromate, (b) an oil-soluble nitrogen-containing organic compound having in the molecule at least one amino or amino-amide or imidazole group in the molecule and optionally possessing a slight degree of water solubility, (c) a polar-containing organic solvent selected from the group consisting of a lower molecular weight alcohol, ketone and/or aldehyde, (d) an organic sulfonate and (e) an asphaltenic material.

The corrosion inhibitor of group (a) includes the alkali metal chromates such as sodium or potassium chromates or mixtures of said chromates and the corresponding hydroxides such as mixtures of sodium chromate and sodium hydroxide. The amount of additive in the aqueous solution can vary from about 0.1 percent by weight to about 5 percent by weight basis aqueous solution and it is preferred that the solution have a pH greater than 7.

The corrosion inhibitor of group (b) namely the nitrogen-containing organic compound can be present in the aqueous solution in amounts of from about 5 to about 5000 p.p.m. based on the oil phase and can be selected from the group consisting of oil-soluble amino-, amino-amide-imidazole-containing compounds and mixtures thereof as well as quaternary ammonium salts, salts and quaternary derivatives of amino amides, salts and quaternary derivatives of imidazolines, salts and quaternary derivatives of amino esters, diamine naphthenates, hydrolyzed acid amines and oxyethylated amines and amides. The oil-soluble amino compound includes salts and esters of long chain fatty polyamine such as tallow diamine hydrolyzed acid available under the trade name of Wellaid 630, 651 and 652 (Amoco Chemical Company); or tallow diamine napthernate available under the trade name of Wellaid 601 and 602 (Amoco Chemical Company); and amino-amide compounds such as are available under the trade name of Visco 928, or the quaternary amine compounds, *e.g.*, Visco 937 (Nalco Chemical Company) and the imidazoline compounds available under the trade name of Kontol 148 or 175 (Tretolite Corporation) or Magna 63, 66-A, 828 or 829 (Magna Chemical Company) and 1-ethylhydroxyl-2-tallowimidazole, available under the trade name Hodag C-100-T from the Hodag Chemical Corporation.

The corrosion inhibitor of group (c) includes polar-containing organic solvents selected from the group consisting of mutual soluble alcohol, ketone and/or aldehyde, and preferably includes lower alcohols such as methanol or propanol.

The corrosion inhibitor of group (d) includes organic sulfonates such as ammonium, amine, monovalent and polyvalent organic sulfonates of which preferred are the alkali metal petroleum sulfonates such as sodium petroleum sulfonate, sodium alkyl naphthalene sulfonate, sodium alkyl benzene sulfonate and mixtures thereof.

The corrosion inhibitor of group (e) is an asphaltenic material derived from any suitable petroleum product such as described in U.S. Pat. Nos. 3,364,134; 3,336,146 or 3,275,076 or in the Journal of the Institute of Petroleum, Feb., 1968, pages 50—53, and April, 1968, pages 107—114.

The sulfur-liquid hydrocarbon slurry can be made by any suitable means such as described in U.S. Pat. No. 2,798,772 or by the method described in copending U.S. Pat. application Ser. No. 663,755, filed Aug. 28, 1967 which issued as U.S. Pat. No. 3,344,383 on May 13, 1969. 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 and reduces friction. 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 percent by weight) water basis total slurry is transferred with the sulfur-water phase into the hydrocarbon phase, if desired, and thereafter a small amount of a selected class of corrosion inhibitors can optionally 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 percent by weight or higher of aromatics, preferably about 15—30 percent by weight aromatic enriched kerosene or crude oil or crude oil condensate fractions containing 15—20 percent by weight aromatics which include monoaromatic 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.

Once the sulfur-liquid hydrocarbon slurry optionally containing water or water solutions containing a corrosion inhibitor is injected into the pipeline for transportation to a terminal station, the pipeline should be maintained under inert conditions which can be accomplished by deaerating the pipeline by removing air or oxygen therefrom by any suitable means or by injecting into the pipeline an inert gas such as nitrogen, gaseous hydrocarbons having less than three carbon atoms, such as natural gas, flue gases or mixtures thereof. The amount of inert gas injected and maintained in the pipeline containing the sulfur-liquid hydrocarbon slurry should be sufficient to maintain an inert atmosphere therein.

PREFERRED EMBODIMENT OF THE INVENTION

40—60 percent by weight sulfur in (a) aromatic (17 percent by weight) enriched kerosene or (b) a petroleum condensate or (c) a blend of (b) and crude oil slurries, were prepared by phase transfer by first injecting molten sulfur into an aqueous liquid such as water and thereafter contacting the slurry thus formed with hydrocarbons (a), (b) or (c) to effect phase transfer of the sulfur particles into the hydrocarbon, and injecting this slurry into a pipeline followed by deaeration and, if desired, injection of 2 percent by weight water basis oil phase or water-containing additives shown in table 2. Sulfur-hydrocarbon slurries thus formed and deaerated and, if desired, containing water and an additive of the present invention, do not corrode or plug pipelines. Instead of using the phase transfer technique for making the slurry, the molten sulfur can be injected in the hydrocarbons (a), (b) or (c) directly and thereafter deaerated and, if desired, admixed with the aqueous solution and an additive of the present invention.

An advantage of the present process for transporting through pipelines deaerated 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. No. 2,798,772 and injecting therein if desired a small amount of water containing optionally an additive of the present invention 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 sulfur-liquid hydrocarbon slurries is evident from the data presented in table 1 and the selectiveness and unexpected effect of deaeration or deaeration plus chemical inhibition as corrosion-preventive agents is shown in table 2 and table 3.

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

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% w. sulfur.
- Sulfur particle size: Waterton sulfur 82% greater than 45 microns. Jumping Pound sulfur 81% greater than 45 microns.
- Oil phase: Kerosene with 17% w. aromatics.
  - Canadian Oil Products:
    - 8–6: 8 parts Medicine River crude; 6 parts Innisfail crude.
    - 10–8–6: 10 parts Waterton condensate; 8 parts Medicine River crude; 6 parts Innisfail crude.
    - Waterton condensate.
    - Innisfail crude.
    - Medicine River crude.
- 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.
- Deaerated by bubbling N_2 through slurry ½-one hour at 1 c.f.m.

TABLE 1.—SULFUR SLURRY CORROSION AS A FUNCTION OF WATER CONCENTRATION

Conditions: As given 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 rates have not been corrected for weight loss due to cleaning.

TABLE 2.—DEAERATION AND CORROSION RATE

Conditions: As given above. 40% w. Jumping. Pound sulfur/oil phase as indicated.

Oil Phase	Corrosion rate, m.p.y.[a] Aerated	Deaerated
Waterton condensate	45	30
Do	30	15
Plus 1% w. 8–6: [b]		
10–8–6 [b]	10	6
8–6 [b]	11	5

[a] From weight loss and exposure time. Corrosion rate has not been corrected for weight loss due to cleaning.
[b] Note conditions.

Table 3.—Effect of Deaeration and Chemical Inhibition on Sulfur Slurry Corrosion

Conditions:
As given above. 40% w. sulfur/oil; oil phase as noted; 2% w. water added (basis oil); deaerated.

Additive [a]	Corrosion rate, m.p.y.[b]
Oil phase, kerosene with 17% w. aromatics:	
2.0% NaOH	3
1.0% Na_2CrO_4	2
2.0% Na_2CrO_4	2
0.5% Na_2CrO_4+0.5% NaOH	3
1.0% Na_2CrO_4+1.0% NaOH	2
Oil phase, Waterton condensate:	
Hodag C-100-T:	
170 p.p.m.	6
85 p.p.m.	5
40 p.p.m.	6
Oil phase, Waterton condensate plus 1% w. 8-6:	
1.0% Na_2CrO_4	4
2.0% Na_2CrO_4	4

[a] Na_2CrO_4 and NaOH were added percent by weight basis water. Hodag C-100-T was added volume fraction basis oil.
[b] From weight loss and exposure times. Corrosion rate has not been corrected for weight loss due to cleaning.

At the terminal end of the line the water phase 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. No. 2,798,772 and the sulfur purified by methods as described in U.S. Pat. No. 2,809,885 or as described in the copending U.S. Pat. application Ser. No. 684,507, filed Nov. 20, 1967, now U.S. Pat. No. 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 percent 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:

1. A method of transporting sulfur through a pipeline to a terminal station preventing corrosion of the pipeline and without plugging the pipeline comprising injecting molten sulfur into a liquid hydrocarbon to form a sulfur-liquid hydrocarbon slurry, injecting the slurry into the pipeline and deaerating the pipeline and maintaining the slurry therein under an inert atmospheric condition until the slurry reaches the terminal station of the pipeline.

2. The method of claim 1 wherein deaeration is accomplished by removing air and oxygen from the pipeline.

3. The method of claim 1 wherein deaeration is accomplished by injecting an inert gas into the pipeline.

4. The method of claim 3 wherein the inert gas is selected from the group consisting of nitrogen and a hydrocarbon gas having less than three carbon atoms.

5. The method of claims 1—4 wherein a small amount of water is added to the sulfur-liquid hydrocarbon slurry.

6. The method of claim 5 wherein the water contains a corrosion inhibitor selected from the group consisting of an alkali metal chromate, an organic-nitrogen containing compound, an organic sulfonate, a lower alcohol and an asphaltene.

7. The method of claim 6 wherein the corrosion inhibitor is sodium chromate.

8. The method of claim 6 wherein the corrosion inhibitor is sodium petroleum sulfonate.

9. The method of claim 6 wherein the corrosion inhibitor is 1-ethylhydroxy-2-tallowimidazole.

10. The method of claim 6 wherein the corrosion inhibitor is asphaltene.