July 9, 1957 A. K. REDCAY 2,798,772

TRANSPORTATION OF SULFUR

Filed Jan. 22, 1953 3 Sheets-Sheet 1

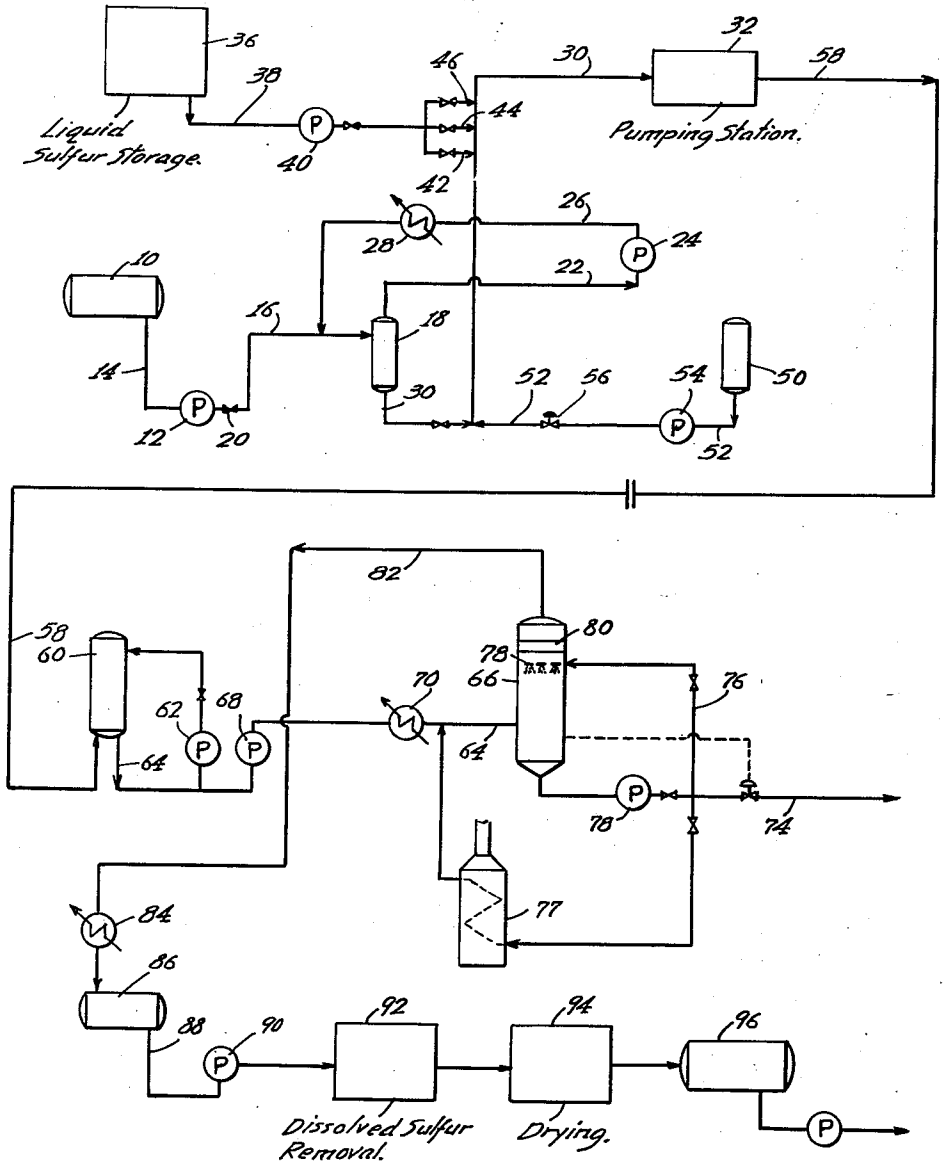


Fig. 1.

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Filed Jan. 22, 1953 3 Sheets-Sheet 2

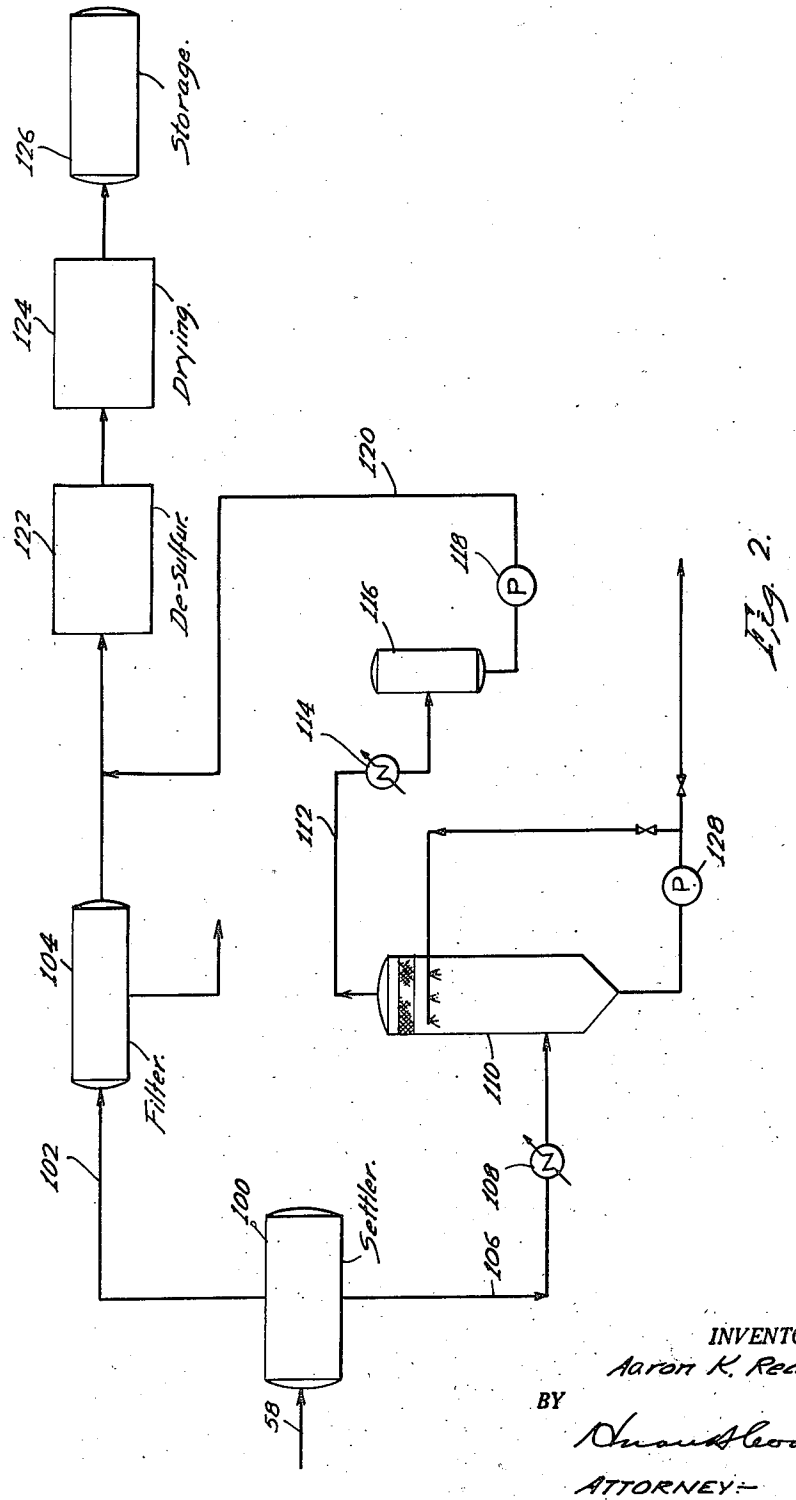


Fig. 2.

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TRANSPORTATION OF SULFUR

Filed Jan. 22, 1953 3 Sheets-Sheet 3

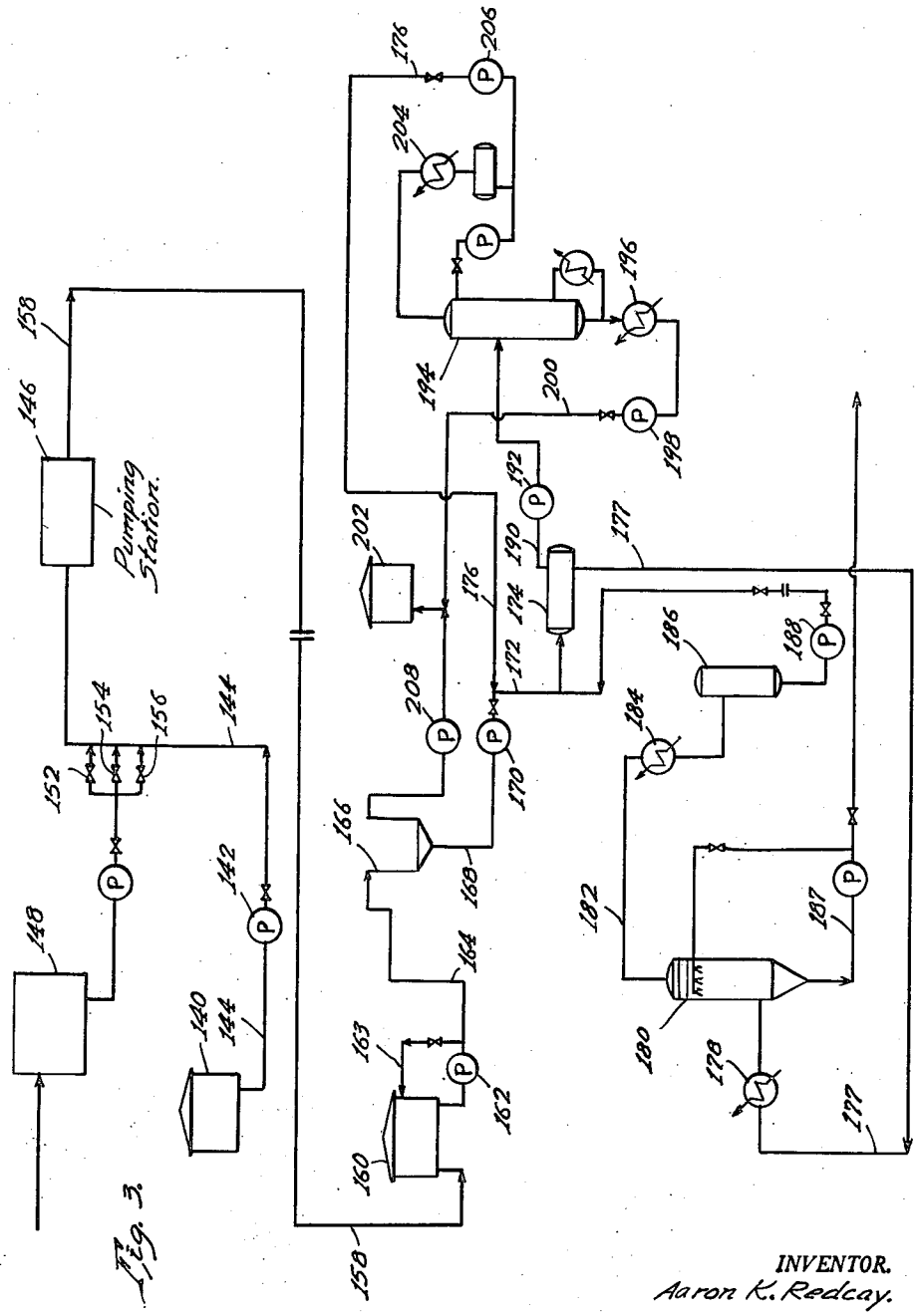


Fig. 3.

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TRANSPORTATION OF SULFUR

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Application January 22, 1953, Serial No. 332,716

6 Claims. (Cl. 302—14)

This invention relates to a process and apparatus for the transportation of sulfur and more particularly to a method of transporting sulfur through pipe lines to a terminal station.

The most important source of sulfur in this country is in the salt domes near the coast of the Gulf of Mexico. While this source is extremely large, it has not, in recent years, been sufficient to supply the tremendous demands, and a shortage of sulfur has existed. Additionally, transportation charges from the gulf coast to other parts of the country, and particularly the Pacific coast area, add seriously to the cost of sulfur in those sections.

A large potential source of sulfur is in the crude petroleum and natural gas produced in some fields. For example, natural gas from the Pincher Creek field of Canada may contain as much as 8% sulfur, present principally as hydrogen sulfide. Usually it is desirable to remove the sulfur from the natural gas near the field in order to reduce corrosion of the pipe lines for the gas and to permit a sulfur-free gas to be tapped from the pipe line along its length. Since many of the gas and oil fields are in remote, inaccessible locations at some distance from consumers of sulfur, the transportation of the sulfur recovered offers a real problem.

This invention provides a method for transporting sulfur through readily available equipment at a low cost and which greatly reduces corrosion of the equipment. According to this invention, molten sulfur is mixed with a liquid hydrocarbon to form a suspension of finely divided solid sulfur in the hydrocarbon, which suspension is pumped through pipe lines to the point of use of the sulfur. The suspension of sulfur and liquid hydrocarbons is separated and hydrocarbon present on the sulfur is flashed therefrom.

In the drawings:

Figure 1 is a diagrammatic illustration of a flow sheet for the preferred form of this invention in which the sulfur is transported in a volatile liquid hydrocarbon, such as LPG.

Figure 2 is a diagrammatic flow sheet of the terminal end of a modified embodiment of this invention in which the sulfur is transported in a volatile liquid hydrocarbon.

Figure 3 is a diagrammatic illustration of the flow sheet of a process embodying this invention and employing a relatively non-volatile hydrocarbon liquid for the transportation of the sulfur.

In the preferred form of this invention, the sulfur is transported through pipe lines in the form of a suspension of solid particles in a volatile hydrocarbon. Throughout the description of the preferred form of the invention, the volatile liquid hydrocarbon will be designated as LPG (liquefied petroleum gas) for convenience. LPG is ordinarily largely propane, but may contain appreciable quantities of butane. Any volatile liquid hydrocarbon which may be vaporized at the melting temperature of sulfur, or higher temperatures at which the vapor pressure of sulfur is low, is suitable. For example, natural

gasoline may be used for the transporting of the sulfur according to this invention. Thus, in this invention, a single pipe line may be employed to transport a valuable hydrocarbon product and the sulfur simultaneously. In this preferred form of the invention, the liquid employed to transport the sulfur may be easily and completely separated from the sulfur at the terminal end of the pipe line, and recovered in a condition suitable for immediate use.

Referring to Figure 1 of the drawings, the LPG used to transport the sulfur is stored in a conventional pressure tank **10** to prevent loss by evaporation. A pump **12** connected to the outlet of the storage tank **10** by a line **14** is provided for delivering the LPG through a line **16** to a separator **18** in which the LPG is flashed in an auto-refrigeration process. A valve **20** at the outlet of the pump **12** allows control of the rate of flow to the separator **18** and the amount of vaporization therein. Vapors liberated in separator **18** are passed through an overhead line **22** to a compressor **24** from which they are returned to separator **18** through a line **26** and line **16**. A heat exchanger **28** in line **26** condenses the vapors before they are returned to the separator **18**. LPG is withdrawn from the bottom of the separator **18** through a line **30** connecting the separator **18** with a pumping station **32**.

Sulfur, which may have been derived from any source, for example, by separation from crude petroleum or from natural gas by any of the well-known processes, is stored in the molten state in a sulfur storage tank **36**. Any suitable means, such as steam coils or a steam jacket (not shown), may be provided to maintain the sulfur in the molten state. The molten sulfur is withdrawn from the storage tank through a line **38** by means of a pump **40** and is discharged to a plurality of mixing orifices or nozzles, indicated by reference numerals **42**, **44**, and **46**. The mixing nozzles **42**, **44**, and **46** intimately mix the molten sulfur with the LPG in line **30** to form a suspension of very finely divided sulfur in the LPG. The refrigeration provided by separator **18**, compressor **24**, and heat exchanger **28** will preferably cool the LPG to a temperature sufficiently low that the resultant suspension of finely divided sulfur particles in LPG will be at a temperature of about 75 to 125° F., but any temperature below the melting point of sulfur will be operative as long as the LPG remains a liquid.

In general, the sulfur will constitute as high as about 50% to 60% of the suspension which still may be readily pumped through the pipe line without difficulty caused by the sulfur settling from the liquid. It will be appreciated that the maximum sulfur concentration will depend, at least in part, on such variables as the particular liquid employed to transport the sulfur and especially the rate at which the suspension is pumped through the pipe line. In some instances, it may be desirable to increase the stability of the suspension, and, for this purpose, a dispersant storage tank **50** is provided from which the dispersant is withdrawn through a line **52** by means of a pump **54** and delivered into line **30**. A valve **56** is provided for control of the rate of addition of the dispersant.

The pumping station **32** may be equipped with any conventional equipment for the pumping of suspensions. The suspension is easily pumped and is of neither an erosive nor corrosive nature; hence, unless very heavy suspensions are formed, the equipment ordinarily used to pump hydrocarbon liquids through pipe lines is satisfactory. It will be appreciated, of course, that where suspensions containing high concentrations of sulfur are transported, suitable provisions for the increased load on the pumping equipment must be made.

The suspension is delivered from the pumping station **32** through a line **58** to the terminal of the line. Any number of intermediate pumping stations between station

32 and the terminal may be employed as required. Since the sulfur is present in the suspension in the solid state and the melting point of the LPG is far below any temperature likely to be encountered, no danger of freezing of the line 58 is experienced.

At the terminal end of the line, the suspension is delivered into a suspension storage tank 60 in which the sulfur is maintained in suspension in the LPG by means of a circulating pump 62. In the embodiment of the invention illustrated in Figure 1, the suspension is pumped from the suspension storage tank 60 through line 64 to a flash chamber 66 by means of a pump 68. Between the flash chamber 66 and the storage tank 60 is a heat exchanger 70 in which the suspension is heated to a temperature sufficiently above the melting point of the sulfur to permit flash vaporization of the LPG from the sulfur in the flash chamber. In general, the minimum temperature which may be present within the flash chamber 66 is approximately 260° F., and in most instances, the flash chamber will be operated at a temperature of approximately 300° F. Liquid sulfur is withdrawn from the bottom of flash chamber 66 by a pump 72 and delivered through line 74 to a storage bin. In the embodiment of the invention illustrated, a portion of the sulfur is recirculated to the flash chamber through line 76 and sprays 78 to knock out any sulfur which may be entrained in the LPG vapors rising within the flash chamber 66. A mist eliminator 80 is provided in the flash chamber for further removal of sulfur from the LPG vapors discharged overhead. Another portion of the sulfur may be circulated through a heater 77 and returned to the line 64 entering the flash chamber 66, if necessary to supply additional heat for the complete vaporization of the LPG from the sulfur.

The LPG vapors are taken overhead from the flash chamber 66 through line 82 and passed to a condenser 84 before delivery to intermediate storage tank 86. From storage tank 86, the LPG is delivered through line 88 by a pump 90 to treatment for removal of dissolved sulfur. Any of the well-known processes for the removal of dissolved sulfur from hydrocarbons, such as the "Doctor" treatment with sodium plumbite, may be employed. The sulfur removal treatment is indicated diagrammatically at 92 in Figure 1 of the drawings. From the sulfur removal treatment, the LPG is dried at 94, and then delivered to an LPG storage tank 96.

A second embodiment of this invention for the separation of the sulfur from the LPG in the suspension is illustrated in Figure 2 of the drawings. The apparatus at the supply of sulfur or pumping end of the process, is similar to that illustrated in Figure 1, and is not shown in Figure 2. The LPG-sulfur suspension is delivered through line 58 to a settler 100 in which the sulfur in the suspension is allowed to settle from the LPG, and relatively sulfur-free LPG is removed overhead through a line 102. The LPG is delivered through line 102 to a filter 104 in which sulfur remaining in the LPG after the settler 100 is removed. The sulfur from filter 104 may be delivered to a storage bin or may be mixed with the sulfur separated from the LPG in settler 100 for flashing of the LPG from its surface in the manner to be described.

The sulfur is settled in settler 100 to form a sludge of maximum sulfur concentration consistent with ready movement of the sludge through a line 106 and heat exchanger 108 to a flash chamber 110. Flash chamber 110 is similar to flash chamber 66, illustrated in Figure 1 of the drawings, with the exception that the ratio of sulfur to LPG present within the flash chamber 110 is considerably higher. LPG vapors are taken overhead from flash chamber 110 through line 112 and passed through a condenser 114 into a receiving tank 116. A pump 118 delivers the LPG through a line 120 for admixture with the LPG discharged from filter 104. The LPG is then passed through conventional desulfurization and drying steps indicated by reference numerals 122 and 124, respectively, prior to passing to a storage tank 126. The molten sulfur from the bottom of the flash chamber 110 is delivered by a pump 128 to storage. A portion of the molten sulfur is recirculated through the flash chamber 110 to strip entrained sulfur from the LPG.

In the embodiment of this invention illustrated in Figure 3 of the drawings, the sulfur is transported in a non-volatile hydrocarbon oil such as crude oil or a gas oil which may be stored in a suitable storage tank 140. The crude oil is delivered by a pump 142 through a line 144 to a pumping station 146. Molten sulfur is stored in a suitable storage vessel 148 and delivered therefrom by means of a pump 150 to any desired number of mixing nozzles 152, 154, and 156 for intimate mixing with the crude oil in line 144 to form a suspension of solid, finely divided particles of sulfur in the crude oil. The crude oil and sulfur suspension is pumped from pumping station 146 through a pipe line 158 to a crude oil-sulfur suspension storage tank 160. As in the preferred form of the invention, intermediate pumping stations will be employed as required. The sulfur is preferably maintained in suspension in the crude oil in storage tank 160 by means of a pump 162 and circulating line 163.

The crude oil-sulfur suspension is delivered from storage tank 160 through line 164 to a thickener 166 of any conventional type, as for example, the Dorr thickener, by means of a pump 168. Thickener 166 separates the suspension into a heavy sludge of sulfur which is discharged from the bottom of the thickener through a line 168, a pump 170, and a line 172 to a wash tank 174. Wash tank 174 is provided with any suitable equipment for bringing the suspension into intimate contact with the wash oil and means for separating the sulfur from the bulk of the wash oil to form a thick sludge of sulfur, wet with sufficient wash oil to permit movement through pipe lines. Between the discharge of pump 170 and wash tank 174, a stream of wash oil is introduced into line 172 through a line 176 and thoroughly mixed with the sulfur sludge. The wash oil preferably consists of a volatile hydrocarbon such as LPG. In the wash tank 174, the heavy non-volatile crude oil is washed from the surface of the sulfur, leaving a sludge of sulfur and wash oil. The sulfur sludge is then delivered through line 177 to a heat exchanger 178 and a flash chamber 180, similar to those described in connection with the transportation of sulfur in LPG. The volatile wash oil is taken overhead from the flash chamber 180 through a line 182, condensed in condenser 184 and delivered to a receiving tank 186. A pump 188 is provided to return wash oil from the receiving tank 186 to line 172 for reuse in washing the sulfur. Sulfur is discharged from the bottom of the separator 180 through line 187 and delivered to storage.

The wash oil, contaminated with crude oil, is withdrawn from wash tank 172 through line 190 by means of a pump 192 and delivered to a fractionating tower 194. The heavy, non-volatile crude oil is taken from the bottom of tower 194, cooled in a heat exchanger 196 and delivered by pump 198 through line 200 to a crude oil storage tank 202. The LPG taken overhead from the fractionator 194 is condensed in the condenser 204 and pumped by pump 206 through line 176 for admixture with additional sulfur. The overflow from the thickener 166 is delivered by pump 208 to the crude oil storage tank 202.

The process herein described permits the transportation of sulfur for long distances at low cost and with practically no loss. The sulfur is transported in a form that is non-corrosive. Moreover, the method permits the simultaneous transportation of sulfur and other valuable products from remote sources to marketing areas through lines which generally are already available for the hydrocarbon products.

I claim:

1. A method for the transportation of sulfur through a pipe line to a terminal, comprising intimately mixing molten sulfur with a non-volatile liquid hydrocarbon to form a suspension of finely divided solid sulfur particles in the non-volatile liquid hydrocarbon, pumping the suspension through a pipe line to the terminal, separating a major portion of the non-volatile liquid hydrocarbon from the sulfur to form a sludge of sulfur particles, washing the sludge with a volatile liquid hydrocarbon to remove the non-volatile liquid hydrocarbon from the sulfur particles, and flashing the volatile liquid hydrocarbon from the sulfur.

2. A method for the transportation of sulfur through a pipe line to a terminal, comprising mixing molten sulfur with a petroleum crude oil to form a suspension of finely divided solid sulfur particles in the crude oil, pumping the suspension through a pipe line to the terminal, thickening the suspension to form a sludge of sulfur contaminated with the crude oil, washing the sludge with a volatile liquid hydrocarbon to remove the crude oil from the sulfur, heating the sulfur to a temperature above its melting point, and flashing the volatile liquid hydrocarbon from the thus liquidized sulfur.

3. A method for the transportation of sulfur through a pipe line to a terminal, comprising intimately mixing liquid sulfur with a petroleum crude oil to form a suspension of finely divided solid sulfur particles in the crude oil, pumping the suspension through a pipe line to the terminal, thickening the suspension to separate it into a sludge of sulfur and a substantially sulfur-free crude oil, washing the sludge with a volatile liquid hydrocarbon to replace the crude petroleum with a volatile hydrocarbon, separating the thus washed sulfur from the washing liquids, fractionating the washing liquids to form an overhead product of the volatile liquid hydrocarbon and bottoms of the crude petroleum, heating the washed sulfur, and flashing the volatile liquid hydrocarbon from the sulfur.

4. Apparatus for the transportation of sulfur to a terminal, comprising means for mixing molten sulfur with a non-volatile hydrocarbon to form a suspension of finely divided sulfur particles in the non-volatile liquid hydrocarbons, a pipe line extending to the terminal, means for pumping the suspension from the pipe line to the terminals, a separator at the terminal positioned to receive the suspension pumped through the pipe line and adapted to separate the suspension into a substantially sulfur-free liquid and a sludge of sulfur, a washer adapted to receive the sludge from the settler, means for introducing a volatile hydrocarbon liquid into the washer whereby the non-volatile liquid is washed from the sulfur, means for separating the washed sulfur from the major portion of the liquid hydrocarbons in the washer, a heat exchanger, a flash chamber, and means for directing the washed sulfur through the heat exchanger to the flash chamber for vaporization of the hydrocarbons from the sulfur.

5. A process for the recovery of sulfur from a suspension of solid sulfur particles in a non-volatile hydrocarbon liquid, comprising settling the suspension to separate a sludge of sulfur and non-volatile hydrocarbon liquid and a stream of substantially sulfur-free non-volatile hydrocarbon liquid, mixing the sludge with a volatile hydrocarbon to wash non-volatile hydrocarbons from the sulfur and form a sludge of sulfur in a volatile hydrocarbon, heating the sludge of sulfur and volatile hydrocarbon to a temperature above the melting point of sulfur to melt the sulfur and flashing the volatile hydrocarbon from the molten sulfur.

6. A process for delivery of sulfur at a remote terminal comprising mixing molten sulfur with volatile liquid hydrocarbons having a boiling point below the melting point of the sulfur in proportions and at a temperature to form a suspension of finely divided solid sulfur particles in the volatile liquid hydrocarbons, pumping the suspension through a pipeline to the terminal, withdrawing a stream of the liquid hydrocarbons from the suspension to remove a major portion of the liquid hydrocarbons in the suspension from the sulfur particles and form a thickened sludge of sulfur particles, heating the sludge to a temperature above the melting point of sulfur, then injecting the mixture of molten sulfur and volatile liquid hydrocarbons into a flash chamber and flashing volatile liquid hydrocarbons from the molten sulfur, and withdrawing a stream of molten sulfur.

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