

Jan. 15, 1974

A. B. WELTY

3,785,965

PROCESS FOR THE DESULFURIZATION OF PETROLEUM OIL FRACTIONS

Filed Oct. 28, 1971

3 Sheets-Sheet 1

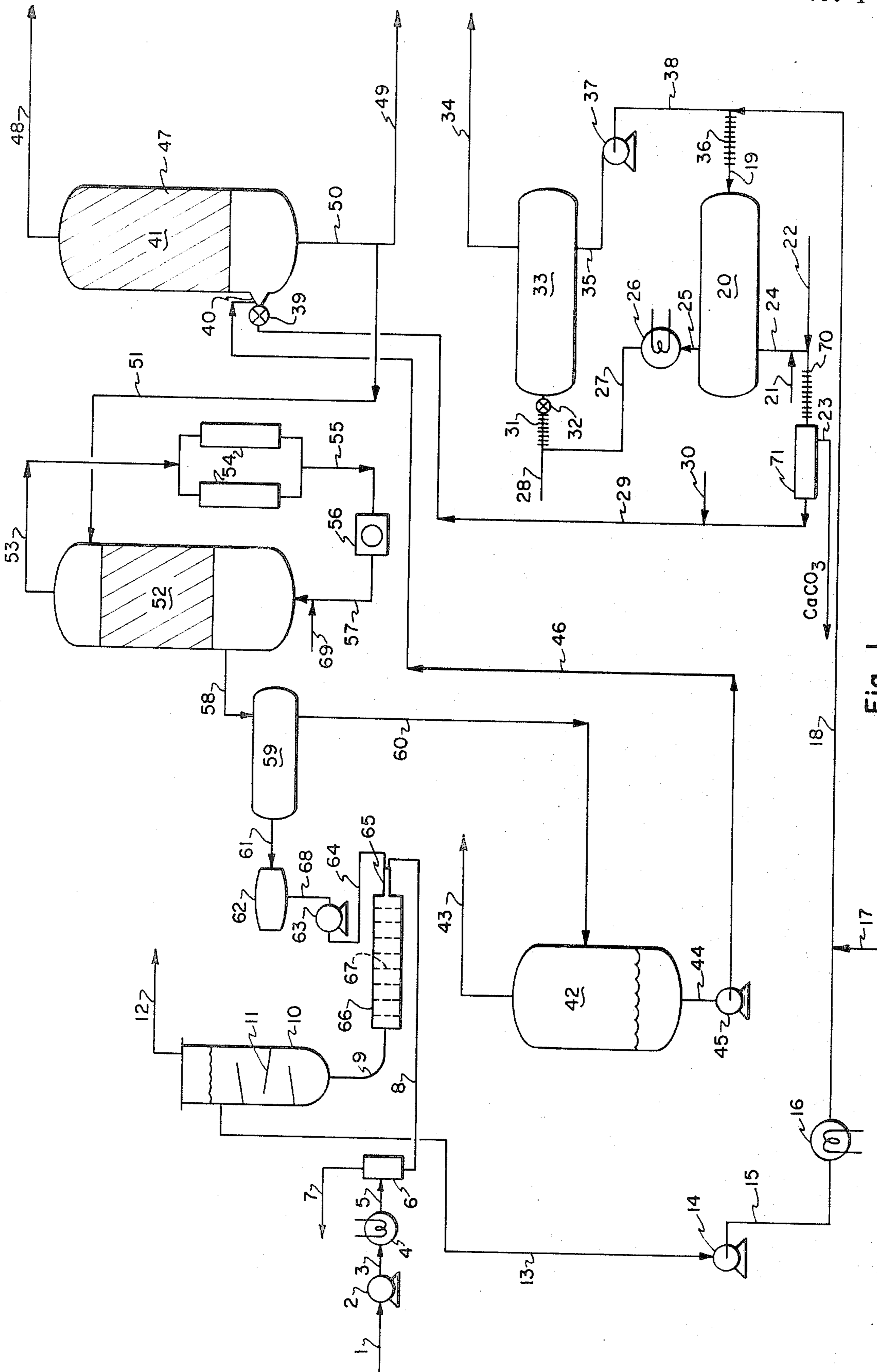


Fig. 1

Jan. 15, 1974

A. B. WELTY

3,785,965

PROCESS FOR THE DESULFURIZATION OF PETROLEUM OIL FRACTIONS

Filed Oct. 28, 1971

3 Sheets-Sheet 2

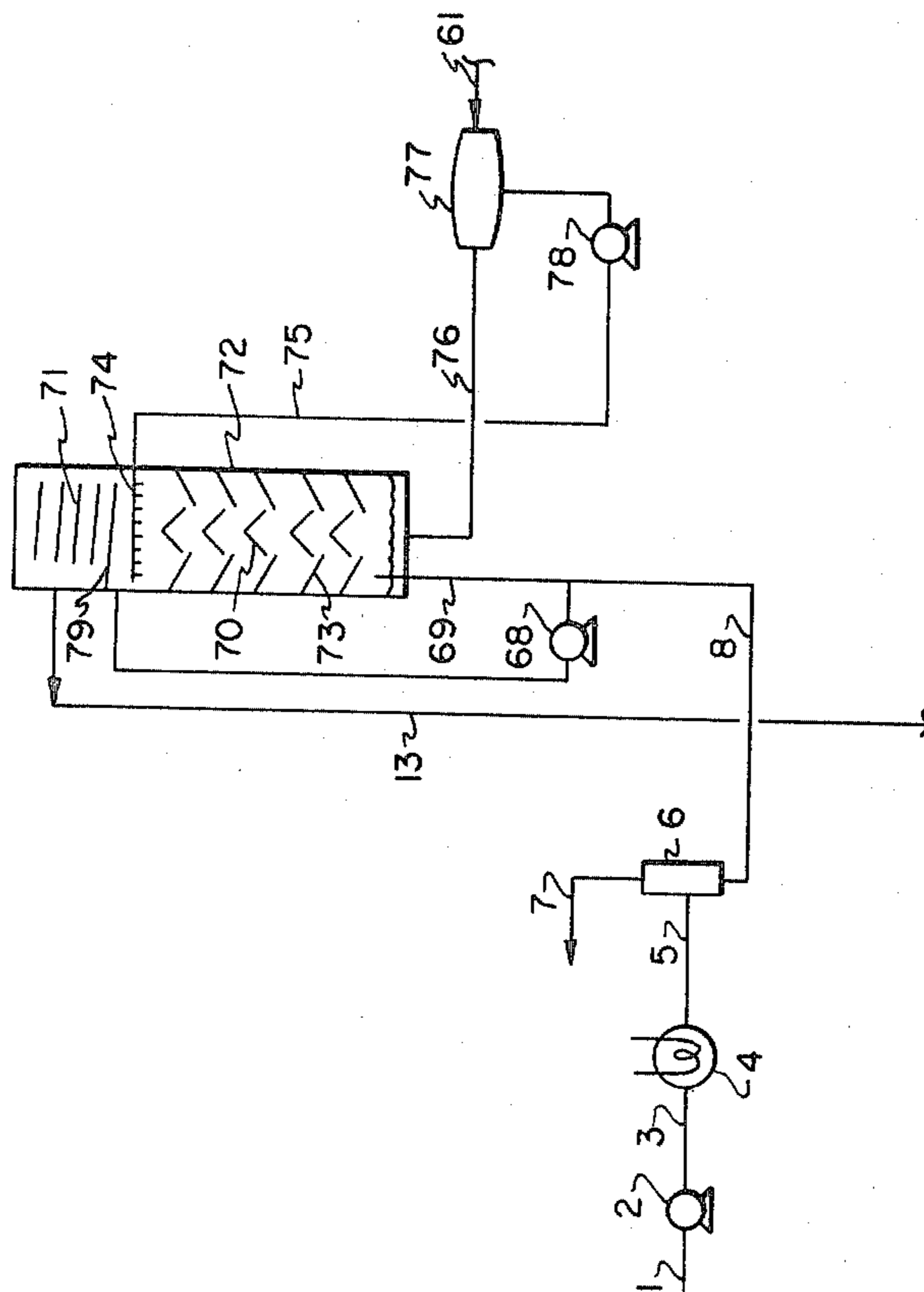


Fig. 2

Jan. 15, 1974

A. B. WELTY

3,785,965

PROCESS FOR THE DESULFURIZATION OF PETROLEUM OIL FRACTIONS

Filed Oct. 28, 1971

3 Sheets-Sheet 3

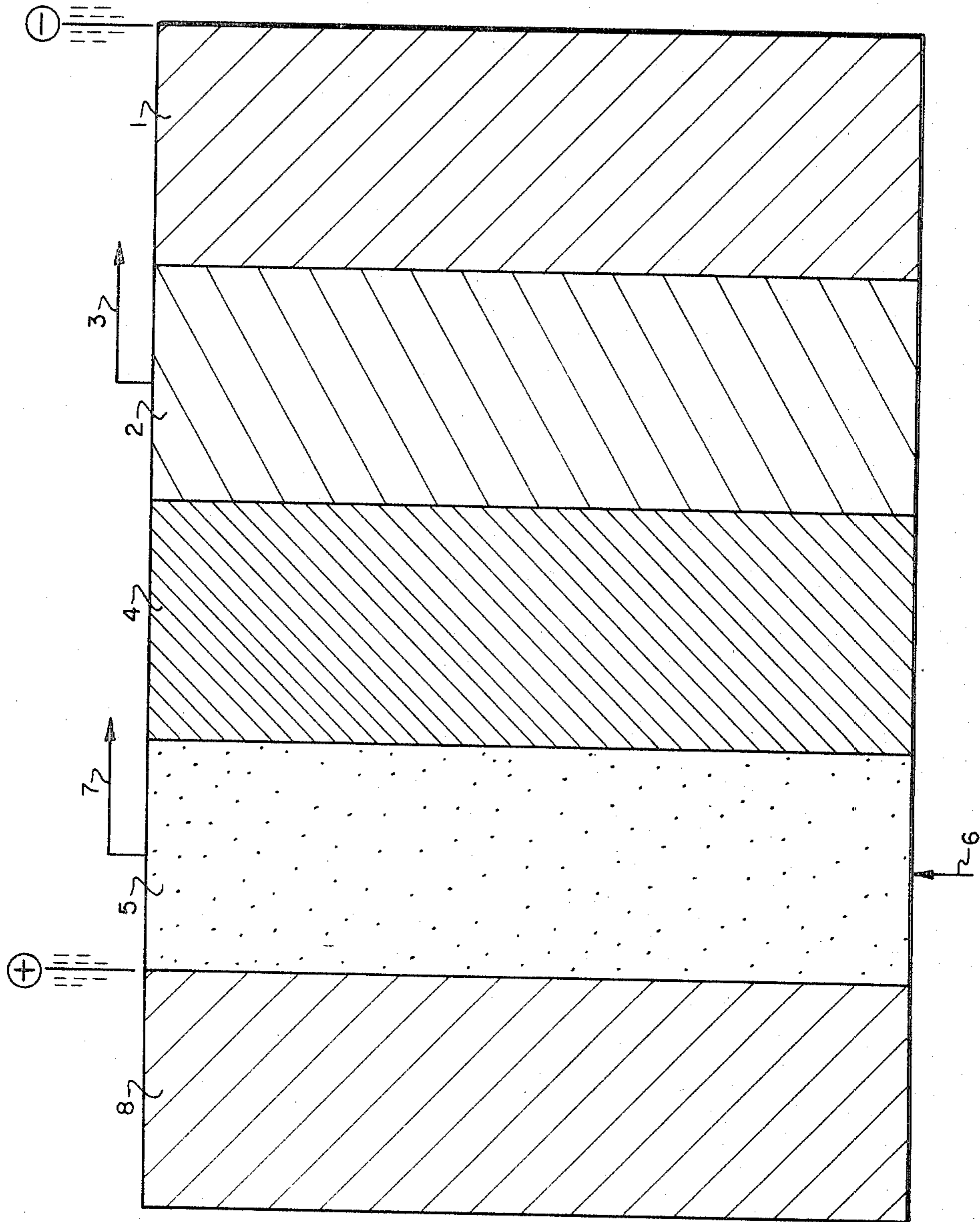


Fig. 3

1

3,785,965

**PROCESS FOR THE DESULFURIZATION OF  
PETROLEUM OIL FRACTIONS**

Albert B. Welty, Jr., Westfield, N.J., assignor to Esso  
Research and Engineering Company  
Filed Oct. 28, 1971, Ser. No. 193,527  
Int. Cl. C10g 17/00, 19/00

U.S. Cl. 208—208 M

15 Claims

**ABSTRACT OF THE DISCLOSURE**

Low sulfur-content petroleum oil stocks are prepared by contacting a sulfur-containing oil stock with an alkali metal, preferably sodium, or an alkali metal alloy, preferably sodium/lead, to produce an alkali sulfide-oil dispersion. The alkali sulfide is removed from the oil by means of a two-stage washing treatment. The recovered sulfide, after additional treatment, is then electrolytically decomposed thereby reforming alkali metal for reuse in the desulfurization process.

**BACKGROUND OF THE INVENTION**

**Field of the invention**

The present invention relates to a process for the desulfurization of a sulfur-containing petroleum oil stock. More particularly, the process comprises contacting an oil stock with an alkali metal or an alkali metal alloy to form an alkali sulfide-oil dispersion that is subsequently water-washed under predetermined conditions of temperature and pressure to produce an essentially alkali metal sulfide-free oil. Still more particularly, the process comprises contacting the separated alkali metal sulfide with alkali metal polysulfide to yield an anhydrous sulfur-lean alkali metal polysulfide. The latter is decomposed electrolytically to produce alkali metal which is then used in the initial contacting step.

**Description of the prior art**

In the last several years there has been an ever increasing concern about air pollution. One of the objects of this concern is the discharge of sulfur oxides to the atmosphere when burning sulfur-containing fuels. Over a period of many years several studies have been conducted with the object of developing efficient and economical means of reducing the sulfur content of crude petroleum oils and other virgin hydrocarbon fractions.

To the present, the most practical desulfurization process has been hydrogenation of sulfur-containing oils at elevated pressure and temperature in the presence of an appropriate catalyst. The process requires the use of hydrogen pressures ranging from about 500 to about 2500 p.s.i.g. and temperatures ranging from about 650 to about 800° F., depending on the nature of the oil to be desulfurized and the amount of sulfur required to be removed.

The process is efficient in the case of distillate oil feedstocks but is less efficient when used with feeds containing undistilled oil such as whole crudes or residua. This is due to several factors. First, most of the sulfur in the oils is contained in high molecular weight molecules, and it is difficult for them to diffuse through the catalyst pores to the catalyst surface. Furthermore, once at the surface, it is difficult for the sulfur atoms contained in the molecules to "see" the catalyst surface. Additionally, the feedstocks may contain large amounts of asphalt-

2

tenes which tend to form coke deposits, under the process conditions, on the catalyst surface, thereby deactivating the catalyst. Moreover, high-boiling organometallic compounds present in such stocks decompose and deposit metals on the catalyst surface thereby diminishing the catalyst lifetime.

The severe operating conditions employed in the process cause appreciable cracking of high-boiling oils thereby producing olefinic fragments which, themselves, consume hydrogen, thereby lowering the process efficiency and increasing costs.

Alternate desulfurization processes that have been employed in the past used alkali metal dispersions, such as sodium, as desulfurization agents. Basically the process involved contacting a hydrocarbon fraction with a sodium dispersion, the sodium reacting with the sulfur to form dispersed sodium sulfide (Na<sub>2</sub>S). However, such a process has not proven to be economically advantageous, particularly for treatment of high-boiling, high-sulfur content feedstocks due to (a) the high cost of sodium, (b) the impracticability heretofore of regeneration of the sodium sulfide formed in the process, and (c) problems related to removal of the sodium sulfide from the oil.

The cost of sodium as a reagent, if used on a once-through basis, is prohibitively high, and it is therefore clear that one must be able to recover the sodium from the sodium sulfide in order to provide an economically viable process. Much thought has been given to this problem, but until now no economical process has been developed.

For example, it is impractical to electrolyze molten sodium sulfide to sodium and sulfur because of the sulfide's high melting point, i.e. 1740° F. and the large amount of electrical energy required at that temperature to dissociate the sodium sulfide. In addition, the sodium and sulfur are both produced as vapors at 1740° F. and special precautions would have to be taken in order to keep them apart in the electrolytic cell. The capital and operating cost of such a cell would probably be prohibitive.

It is much more convenient to form the products in the liquid phase. An alternate process would involve converting the sodium sulfide to sodium chloride by chemical means and then electrolyzing the sodium chloride. Electrolysis of sodium chloride is well known in the art. By dissolving the sodium chloride in a mixture of potassium and calcium chlorides the compound can be electrolytically dissociated at temperatures of about 1100° F. However, although liquid sodium is produced, the process is still economically impractical due to the large amount of electrical energy required to decompose the relatively stable sodium chloride, and because of the problem of handling the chlorine produced.

In theory, the best approach would be to electrolyze an alkali metal salt that melts at about the same temperature as used for the desulfurization process and which can be electrolyzed with minimum consumption of electrical energy.

The alkali polysulfides, preferably sodium polysulfides, meet the above enumerated requirements. There are three sodium polysulfides with melting points as follows: Na<sub>2</sub>S<sub>2</sub> (885° F.), Na<sub>2</sub>S<sub>4</sub> (545° F.), and Na<sub>2</sub>S<sub>5</sub> (485° F.). These polysulfides are mutually soluble and intermediate compositions, having intermediate properties, can form. A eutectic occurs at about Na<sub>2</sub>S<sub>3.1</sub> with a melting point of 450° F. Moreover, the electrolysis of molten sodium poly-

sulfide consumes less electrical energy than electrolyzing either molten sodium monosulfide or molten sodium chloride. Finally, due to the low melting points of the polysulfides, the desulfurization process can be carried out with less heating and cooling load and at about the same temperature as the desulfurization reaction, and hence with less heat exchange equipment and at lower cost.

#### SUMMARY OF THE INVENTION

In accordance with the invention, it has now been discovered that an economically feasible desulfurization process vis-a-vis hydrosulfurization of whole crude or residual oils can be achieved and that outstanding sulfur removal can be realized. Specifically, the process involves contacting a sulfur-containing petroleum oil stock with a desulfurization agent comprising an alkali metal, such as lithium, sodium, potassium, rubidium and the like, preferably sodium, or an alkali metal alloy, preferably sodium-lead, thereby forming an alkali metal sulfide-oil mixture. (Hereinafter the invention will be described with respect to sodium although it is understood that other alkali metals can be used.) At least a portion of the mixture (in the form of a dispersion of the sulfide in the oil) is subsequently contacted with water in a two-stage contacting operation wherein the dispersion is first treated with water under high pressure and temperature conditions followed by water treatment under low temperature and pressure conditions, the water being used preferably concurrently with respect to the flow of the oil. This insures virtually complete removal of the sodium sulfide therefrom, while simultaneously producing a highly concentrated aqueous sodium sulfide solution.

The aqueous solution may also contain other sodium compounds such as hydroxide, sulfite, thiosulfate and carbonate which may be removed by standard techniques as described in more detail hereinbelow. The alkali metal sulfide solution is then contacted with at least a portion of sodium polysulfide to vaporize the water and to yield an essentially anhydrous sulfur-lean sodium polysulfide. The latter is subsequently dried and at least a portion thereof electrolytically dissociated to reform sodium metal and to produce a sulfur-rich sodium polysulfide from which sulfur, corresponding to the amount removed from the sulfur-containing oil, is recovered.

Any feedstock from which sulfur is desired to be removed may in theory be used in the instant process. Thus, suitable feedstocks include whole crudes such as Safaniyah crude (Middle East), Lagunillas crude (Venezuela), or U.S. crudes, residual fractions or any distillate fraction. The subject process is particularly adapted to the desulfurization of whole crude or residua that are difficult to treat by other methods such as hydrosulfurization.

While the feedstock may be fed directly to the initial contacting or desulfurization zone without pretreatment, it is desirable to desalt the feed in order to prevent contamination of the molten polysulfide contained in the electrolytic cell. Desalting is a well established process in the industry. A particularly preferred desalting process involves the addition of a small amount of water to the oil in order to dissolve the salt contained therein followed by electrical coalescers. The oil is then dehydrated by conventional methods known in the industry.

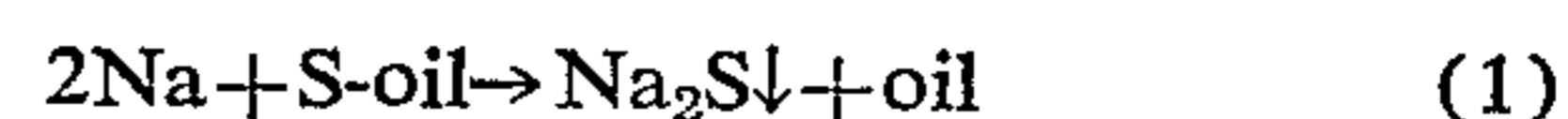
The sodium may be used as a dispersion of the pure metal or in the form of a molten alloy such as sodium/lead or sodium/tin. When sodium/lead is the alloy, suitable atom proportions desirably comprise about 0.3-0.5 sodium/0.7-0.5 lead, and when using sodium/tin, about 0.2-0.3 sodium/0.8-0.7 tin.

While the molten alloy form of the metal facilitates dispersion of the metal in the oil, nevertheless, it suffers from several disadvantages. First, the reaction temperature must be kept above the melting point of the alloy since sodium will not diffuse through solid lead. The melting point of the sodium/lead alloy, for example, is about 620° F. depending upon the proportion of sodium used in

the alloy. Since it is desirable to absorb the exothermic heat of reaction by using feed substantially below reaction temperature, this presents an additional engineering complication. On the other hand, pure sodium metal, for example, has a melting point of about 208° F. and imposes no such limitation to the process. Additionally, when employing the alloy, the spent lead or tin must be separated and recycled. On the other hand, the quantity of pure sodium metal added to the oil can be controlled so that the metal is completely consumed.

The contacting of the sodium metal or sodium metal alloy with the sulfur-containing oil is preferably carried out at temperatures and pressures sufficient to maintain the bulk of the reactants within the reaction zone in the liquid phase. However, conditions may be varied to provide vapor phase contact. Thus, the reaction temperature will generally be maintained between about 450 and 750° F., preferably 600 to 700° F. The reaction pressure will depend on the feed and temperature employed. For reduced crude fractions the pressure will range between 10 and 100 p.s.i.g., preferably 40 to 60 p.s.i.g. For whole or topped crude pressures may be raised to as high as about 500-600 p.s.i.g. in order to maintain all or most of the oil in the liquid phase. Lower pressures can be used where extensive desulfurization of the lower-boiling (vapor phase) fractions is not necessary.

The sodium metal reacts with the sulfur-containing oil stock, as shown in Equation 1, to yield sodium sulfide which precipitates from the oil, forming a dispersion therein.



In addition, organo-oxygen contained in the feedstock is removed therefrom by reacting with the sodium metal. Furthermore, depending on the amount of water present in the feed and the reaction conditions, varying amounts of sodium sulfite, thiosulfate and hydroxide in addition to salts of organic acids may be formed. (Typical crudes contain between about 0.1 and 0.2% organic oxygen.) Additionally, some organo-nitrogen and organo-metals are also removed from the oil.

The desulfurization step is conducted as a batch or continuous type operation, but is preferably continuous. In general, the various means customarily employed in extraction processes to increase the contact area between the oil stock and the sodium metal or sodium metal alloy can be employed. The apparatus used in the desulfurization step is of a conventional nature and can comprise a single reactor or multiple reactors equipped with (a) shed rows or other stationary devices to encourage contacting; (b) orifice mixers; (c) efficient stirring devices such as mechanical agitators, jets of restricted internal diameter, turbo mixers and the like. The petroleum oil stock and the sodium metal or sodium metal alloy can be passed through one or more reactors in concurrent, cross-current or countercurrent flow, etc. It is preferable that oxygen and water be excluded from the reaction zone; therefore, the reaction system is thoroughly purged with dry nitrogen and the feedstock dried prior to introduction into the reactor. It is understood that trace amounts of water, i.e. less than about 0.5 wt. percent, preferably less than about 0.1 wt. percent based on total feed, can be present in the reactor without affecting the process efficiency.

The resulting oil dispersion is subsequently removed from the desulfurization zone and washed with water in order to remove the sodium sulfide and the relatively smaller amounts of sodium hydroxide, sodium sulfite, sodium thiosulfate, sodium carbonate and the salts of organic acids dispersed therein. It is preferable to carry out the water-wash treatment in a plurality of stages, preferably two stages, at different conditions of temperature in each stage. Additionally, the operating pressure in each stage must be maintained at a sufficient level to maintain the water in substantially the liquid phase.

The water-wash operation accomplishes several objectives:

- (1) removal of substantially all of the sodium sulfide and other sodium compounds dispersed in the oil;
- (2) reduction of the heat load and cost of subsequent separation of the water from the sodium sulfide by minimizing the amount of water required to effectuate sodium sulfide removal;
- (3) employment of operating conditions sufficient to preclude emulsion formation.

As will be evident in the further description of the process and in view of the above-mentioned process objectives, it is essential to minimize the amount of water used in the water treatment step in order to minimize the heat requirement for its subsequent removal via contact with hot sodium polysulfide. Thus, the water washing is conducted in the first stage at elevated temperatures and pressures where the solubility of the sodium sulfide is high, thereby requiring only a minimum amount of water. Temperatures in the range of about 400–500° F., preferably 425–475° F., are used for this first stage. The solubility of the sodium sulfide in the water will be in excess of about 70 wt. percent (based on total aqueous solution) at this temperature. The pressure in the first stage is kept at a level sufficient to maintain the water substantially in the liquid phase. Thus, a pressure ranging from about 250–700 p.s.i.g., preferably 330–540 p.s.i.g., is employed. An important feature of the high temperature washing operation is the minimization of emulsion formation, particularly with the more viscous feedstocks, due to the removal therefrom of certain emulsifying agents such as the sodium salts of organic acids.

At these high temperature and pressure water-treating conditions, too much sodium sulfide-containing water solution, about 0.8 to 1.9 wt. percent based on the oil present, remains dissolved in the oil. To reduce the remaining sodium sulfide content to an acceptable level, the oil is introduced into a second washing stage, which is operated at relatively low temperature and pressure conditions in order to minimize aqueous solution solubility in the oil. Organic emulsifying agents having now been largely removed, emulsion formation is no longer a problem at the low temperature. Temperatures in the range of about 150 to 300° F., preferably 195 to 205° F., are suitable. Higher temperatures within the broad range may be necessary for more viscous oils in order to maintain their fluidity. The pressure need be only high enough to maintain the water substantially in the liquid phase. Thus, a pressure in the range of atmospheric to about 75 p.s.i.g., preferably 5–10 p.s.i.g. is employed. By use of this dual temperature water-wash treatment, the sodium metal content of the recovered desulfurized oil is reduced to trace levels.

The physical nature of the washing and separation system is not critical and may be of a conventional design. While cocurrent, cross-current or countercurrent contacting within a given stage may be employed, cocurrent contacting is preferred. In general, a system similar to that which is sometimes used in crude de-salting is preferred. In such a system, the oil and water or water solution are vigorously mixed, typically in an orifice line, or other mixer. Subsequently the water droplets are coalesced and settled in an electric field, and then separated from the oil. Contact times in each of the water-treatment stages varies from about 5 to 30 minutes and preferably 10 to 25 minutes.

The hot concentrated sodium sulfide solution is subsequently removed from the wash system. As indicated above, the solution may contain other sodium compounds such as hydroxide, sulfite, thiosulfate and carbonate. These compounds can be removed by standard techniques. Thus, the carbonate can be continuously removed as calcium carbonate by the addition of calcium hydroxide. Other means may also be used for removing the carbonate. For example, other compounds whose carbonates

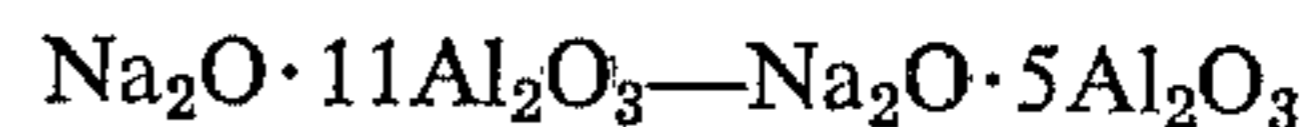
are insoluble may be added. Or the carbonate concentration in the circulating molten salt can be allowed to increase to a level such that the incremental alkali metal added with each cycle causes precipitation of solid sodium carbonate which is separated from the molten salt. The remaining compounds are converted to sodium sulfide by adding hydrogen sulfide.

Subsequently, the hot aqueous sodium sulfide solution is contacted directly with hot sodium polysulfide, i.e.  $\text{Na}_2\text{S}_x$  where  $x$  varies from about 4.4 to 4.9, preferably from about 4.5 to 4.8, most preferably from about 4.5 to 4.6. The polysulfide is added to the sulfide at a temperature ranging from about 700–820° F., preferably 725 to 765° F. Simultaneously the pressure on the sodium sulfide solution is released. The relative rates and compositions of the sulfide and polysulfide are controlled in such a way that (1) all of the water is vaporized as steam, (2) sodium polysulfide, i.e.  $\text{Na}_2\text{S}_y$  where  $y$  ranges from about 3.5 to 4.3, preferably from about 3.8 to 4.1, most preferably from about 3.9 to 4.0, is formed, and (3) the temperature of the resulting sodium polysulfide is above its melting point, i.e. a polysulfide melt. Polysulfide with less sulfur holds water too tenaciously for it to be removed readily. Polysulfide with more sulfur tends to be hydrolyzed by water, forming  $\text{H}_2\text{S}$ . A suitable final temperature for the polysulfide melt is about 525 to 600° F., preferably 550 to 570° F.

The reaction of the sodium sulfide solution and the hot sodium polysulfide is rapid and much steam is evolved as pressure is released. Several systems are available to effect reactions having these characteristics. A preferred system comprises two concentric nozzles arranged in such a manner that the sodium polysulfide contacts the sodium sulfide solution simultaneously with the pressure release, followed by a separator that allows the steam to be taken overhead alone, while the liquid sodium polysulfide so produced collects and is withdrawn.

The sodium polysulfide melt is dried and subsequently cycled to electrolytic cells wherein it is dissociated to form molten sodium and a sulfur-rich sodium polysulfide, i.e.  $\text{Na}_2\text{S}_z$  where  $z$  ranges from about 4.5 to 5.0, preferably from about 4.6 to 4.9, most preferably from about 4.7 to 4.8. The sodium is then withdrawn and either alloyed with a molten metal such as lead or tin or introduced directly into the desulfurization zone in undiluted form as hereinabove described.

The electrolytic cell unit will preferably comprise a sodium ion-conducting physical and electronic barrier or membrane that separates alkali metal on the one side from alkali metal polysulfide on the other side. Generally, the membrane may be composed of any material that can function as a sodium ion-conducting separator; however, beta-alumina containing sodium oxide is preferred. Such beta-alumina will contain sodium oxide in the general range of about

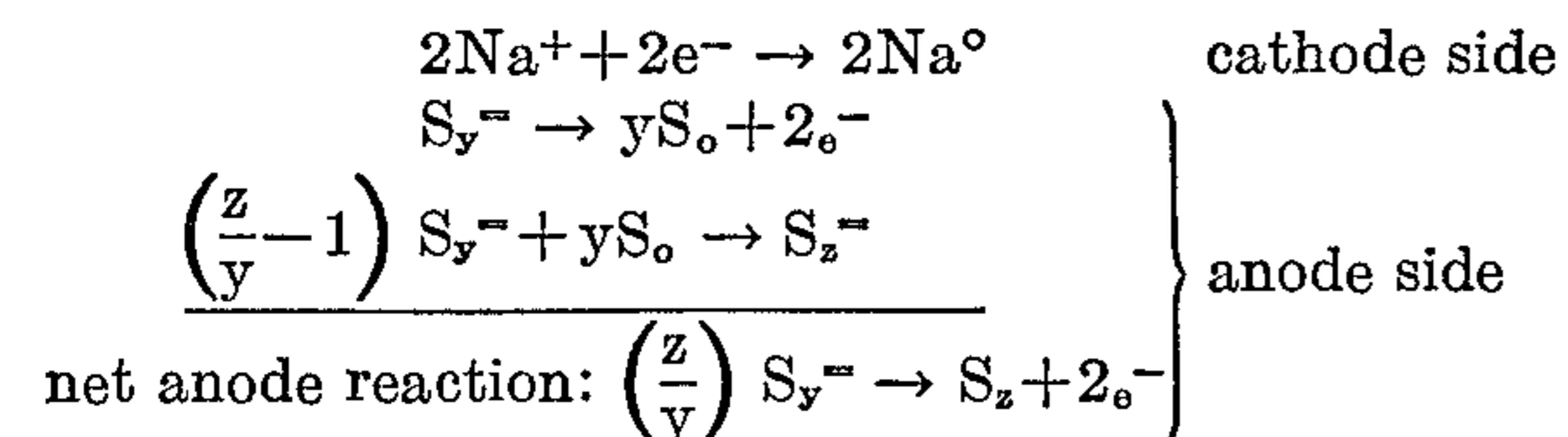


It is noted that when an alkali metal other than sodium is employed in the instant process, the oxide of the alkali metal will be admixed with beta-alumina in lieu of  $\text{Na}_2\text{O}$ .

The beta-alumina may be used in the pure form or doped with a small amount of metal oxide such as  $\text{MgO}$ ,  $\text{Li}_2\text{O}$  and the like. A detailed discussion of doped beta-alumina is provided in an article appearing in the Electrochemical Society Extended Abstracts—Los Angeles Meeting—May 10–15, 1970, entitled "Ionic Conduction in Impurity Doped  $\beta$ -alumina," by Atsuo Imai et al., the disclosure of which is incorporated herein by reference. Reference is also made to U.S. Pats. 3,488,271 to J. T. Kummer et al. and 3,475,225 to G. T. Tennenhouse. During cell operation, sodium ions migrate from the sodium polysulfide side, i.e. the anode side, through the barrier to the sodium metal side, i.e. the cathode side, where they are neutralized by electrons. At the same time polysulfide ions give up their electrons at the electron-con-

ducting anode to form elemental sulfur that then reacts with additional polysulfide anions to form new polysulfide ions, i.e.  $S_z^-$ , of greater sulfur content.

As indicated above,  $z$  will take values in the range of about 4.5 to 5.0. The  $S_z^-$  anions are continually removed from the cell in combined form with sodium, i.e.  $Na_2S_z$ . The anode may comprise any suitable electron conducting-current collector such as graphite, molybdenum, titanium, chromium or aluminum that can withstand corrosive attack of the sodium polysulfide. The cells are arranged preferably in series electrically, so that the anode for one cell is the cathode for the one adjacent to it. The overall reaction is shown below:



In other embodiments elemental sulfur is allowed to build up in the cell and the operating temperature therein is maintained high enough so that the sulfur is continuously removed therefrom as vapor. Additionally, the sodium/lead alloy may be formed internally, i.e. in situ, before the molten sodium metal is withdrawn from the electrolytic cell by continuously feeding lead or spent sodium/lead alloy to the cathode side of the cell.

While a beta-alumina type cell has been described, any other cell that is capable of economically decomposing sodium polysulfide into molten sodium is sufficient for the present purposes. A particular beta-alumina electrolytic cell and methods for the preparation of beta-alumina are described in such patents as U.S. 3,488,271 and 3,404,036 to J. T. Kummer et al., U.S. 3,368,709 to J. T. Kummer and U.S. 3,446,677 and U.S. 3,475,225 to G. J. Tennenhouse, the disclosures of which are incorporated herein by reference.

#### BRIEF DESCRIPTION OF THE DRAWING

A preferred embodiment of the present invention is shown in the accompanying drawings:

FIG. 1 is a flow diagram of the overall desulfurization process using sodium metal in the pure form.

FIG. 2 is a flow diagram of the overall desulfurization process utilizing an alloy of sodium, i.e. sodium/lead.

FIG. 3 is a simplified scheme showing the formation of the molten sodium within the electrolytic cell.

The desulfurization reactor systems used in the instant process vary depending on whether sodium or sodium alloy is used as the reactant. The system using sodium will be described first, then the system using sodium alloy.

Turning now to FIG. 1, a sulfur-containing feedstock is fed by means of line 1 to charge pump 2 where the pressure is raised to about 500 p.s.i.g. for whole crudes and distillates and 50 p.s.i.g. for residual stocks. The feed is preliminarily desalted by conventional means (not shown), prior to introduction into line 1. The feedstock will ordinarily be a whole crude of one to three percent sulfur or a residual stock of two to seven percent sulfur, although distillate stocks can be used.

The oil enters heat exchanger 4 via line 3, where the temperature is raised to approximately 450° F. The oil flows via line 5 to separator 6 where the hydrocarbon vapors are taken overhead through line 7. Water present in the feedstock is also taken overhead as steam. To facilitate drying, a stream of dry gas can be introduced to the bottom of separator 6 (not shown). The oil enters first reactor vessel 66 via line 8.

Sodium is pumped by pump 63 from sodium storage vessel 62 via lines 68 and 64 through dispersing nozzle 65 into first reactor vessel 66. Nozzle 65 consists of a multiplicity of nozzles (not shown) which are so arranged as to give thorough dispersion of sodium in the flowing oil. Reactor 66 contains orifice baffles 67 to promote

movement of the sodium particles throughout the oil. The holding time in first reactor 66 is about 5 to 30 minutes. Temperature in this first reactor rises to about 625° F., depending on the amount of sulfur to be removed.

The oil stream flows via line 9 to second reactor 10 where the remaining sodium is reacted. Second reactor 10 contains baffles 11 to promote continuing contact between the sodium and oil and to prevent by-passing from the inlet to the outlet. The temperature at the top of second reactor 10 is about 650° F. Gas that is formed due to the increase in temperature is taken overhead through line 12 and is condensed and depressured by conventional means (not shown). The desulfurized oil containing dispersed sodium sulfide mixed with lesser amounts of other sodium compounds such as sodium oxide and hydroxide, sulfite, thiosulfate and carbonate, leaves the top of second reactor 10 via line 12.

The remainder of FIG. 1 will be explained below after describing the alternate reactor system for sodium alloy shown in FIG. 2.

FIG. 2 shows the reactor system for the case where sodium alloy is used. It differs from the case where sodium alone is used primarily in that oil is recycled to the reactor in order to prevent cooling of the alloy below its melting point and in order to recover and recycle the spent alloy. Feed is charged through line 1, line 3, heat exchanger 4, line 5, separator 6 and line 8, analogously and at the same conditions as described for the sodium case in FIG. 1. Water vapor and hydrocarbon vapors are withdrawn via line 7. The preheated, dehydrated oil in line 8 is mixed with recycled desulfurized oil from pump 68. The relative feed rates are maintained so as to keep the oil at a temperature above about 620° F.

The mixed oil stream enters reactor vessel 72 via line 69 and flows in an upward direction therethrough. The vessel is of such a size that the oil remains in the reaction portion below the sodium alloy distributor for ten minutes to one hour. The sodium alloy, preferably sodium/lead or sodium/tin or a mixture of the two enters reactor 72 via disperser 74. Atom compositions of about 0.3-0.5 Na/0.7-0.5 Pb or 0.2-0.3 Na/0.8-0.7 Sn are suitable.

The alloy droplets commingle with the rising oil stream, and being heavier than the oil and of large enough size, fall downwardly through the rising oil stream. Baffles 73 promote contact. The spent alloy collects in the bottom of reactor 72 and passes via line 76 to the alloy storage vessel 77. The alloy is fortified by contact with freshly regenerated sodium entering vessel 77 via line 61. Pump 78 feeds the fortified alloy via line 75 to disperser 74.

The desulfurized oil passes into a settler zone located in the top of reactor 72 where any small, entrained alloy particles are allowed to settle. Baffles 71 and 79 act as collecting plates for the alloy particles and are placed at a slight angle so that the coalesced alloy can run off the ends. The desulfurized oil/sodium sulfide dispersion leaves reactor 72 via line 13.

One particular reactor system has been described. However, the alloy and oil can flow concurrently, and any one of several well-known types of mixers such as pump mixers, high shear mixers or paddle blade mixers can be employed. Other settling means, in particular external, long, horizontal flow vessels or liquid cyclones can be also used.

The sodium sulfide-oil dispersion in line 13 is pumped up to a pressure of about 475-525 p.s.i.g. by pump 14, through line 15 and through cooler 16 where the temperature is reduced to about 430-500° F., preferably 450-480° F. If residuum is being processed and distillate flux stock needs to be added in order to make a burning fuel of suitable viscosity, this flux stock is added through line 17.

Dilute aqueous sodium sulfide solution from settler 33 is discharged, through line 35 and pump 37, through line 38 where it joins the sodium sulfide-oil dispersion in

line 18. The two streams flow cocurrently through orifice mixer 36 and thence via line 19 into coalescing and separation vessel 20. The temperature therein is about 400–500° F., preferably 425–475° F. and the pressure is about 250–700 p.s.i.g., preferably 330–540 p.s.i.g. In this vessel, approximately 70 to 90 weight percent of the sodium sulfide and of the other sodium compounds present originally dispersed in the oil is removed in the aqueous phase. Here organo-sodium compounds are hydrolyzed and the resulting sodium hydroxide is likewise removed in the water phase. Vessel 20 provides a holding time for the oil of about 10 to 25 minutes.

The aqueous sodium sulfide layer is withdrawn from vessel 20 by way of line 24. The oil phase, containing a reduced amount of sodium sulfide, is removed from chamber 20 by means of line 25 and subsequently passed through cooler 26 and line 27 where it is joined by fresh water entering through line 28. The amount of water used is the amount which when added to the sodium present in the oil gives a highly concentrated solution in the range of about 60–80 weight percent, preferably 65–75 weight percent as sodium sulfide.

The combined water-oil stream passes through orifice mixer 31 and through pressure reducing valve 32 to coalescing and separating vessel 33. The temperature in this vessel ranges from about 150–300° F., preferably 195–205° F. and the pressure ranges from atmospheric to about 75 p.s.i.g., preferably 5–10 p.s.i.g. The desulfurized feedstock has a maximum sulfur content of about 75 to 98 weight percent of that present in the original feed, and a maximum sodium content of about 0.05–0.5 weight percent. It is removed from vessel 33 via line 34. The dilute aqueous sodium sulfide solution is withdrawn via line 35 through pump 37 and recycled via line 38 to orifice mixer 36 and the first stage coalescer settling vessel 20.

The concentrated aqueous sodium sulfide solution is withdrawn from vessel 20, via line 24. A calcium hydroxide slurry is added via line 21 to react with the sodium carbonate present. Hydrogen sulfide is added through line 22 to convert the sodium hydroxide, sulfite and thiosulfate present to sodium sulfide. The aqueous solution is introduced into separation vessel 71 through orifice mixer 70. Solid calcium carbonate is separated from the solution by centrifuging, filtering, settling, etc., by known means in vessel 71 and withdrawn through line 23. A concentrated solution of sodium sulfide is added through line 30 in order to replace sodium subsequently lost in the purge stream taken through line 49. The solution is then passed via line 29 to pressure release valve 39 and subsequently injected into separating zone 41.

Molten sodium polysulfide ( $\text{Na}_2\text{S}_x$  where  $x$  varies from about 4.4 to 4.9) at a temperature of about 700–820° F., preferably 725–765° F., is withdrawn from sulfur vapor-release vessel 42 via line 44 through pump 45 and transferred via line 46 to the outlet of pressure reducing valve 39 where it is mixed with the aqueous sodium sulfide solution. The mixing must occur rapidly and completely at the point where the pressure is reduced so that solid sodium sulfide which would plug the line will not form when the steam evaporates.

The hot sodium polysulfide supplies the heat required for dissolution of water and its vaporization and in addition supplies the sensible heat to bring the sodium polysulfide to a temperature above its melting point. The combined stream enters vessel 41 via expanded section 40. The steam goes overhead through line 48 and the collected sodium polysulfide is removed via line 50. The sodium sulfide from the water solution and the molten sodium polysulfide react to form  $\text{Na}_2\text{S}_y$  where  $y$  varies from about 3.5 to 4.3. The temperature in vessel 41 is 525–600° F., preferably 550–570° F. Vessel 41 contains de-entrainment packing 47 of a conventional type to avoid entrainment of sodium polysulfide overhead with the steam.

Line 49 is used to purge a small stream of sodium polysulfide from the system in order to prevent build-up of impurities to an inoperable level. These dissolved impurities arise from the feed and from equipment corrosion as well as from the organometallic compositions removed from the feed by the action of the sodium. Specifically, compounds containing combined iron, vanadium, silica, nickel, chromium, lead and tin may form and are removed from the system via line 49.

The molten sodium polysulfide ( $\text{Na}_2\text{S}_y$ ), thus formed, is withdrawn from vessel 41 and passed via line 51 to nitrogen stripping vessel 52. Nitrogen that has been previously dried is introduced into vessel 52 by means not shown and is continuously recycled via line 53 through drier 54, line 55, compressor 56 and again into vessel 52. The purpose of the nitrogen stripper is to remove as much water as possible from the molten sodium polysulfide ( $\text{Na}_2\text{S}_y$ ) from vessel 41. Generally,  $\text{H}_2\text{S}$  is added to the nitrogen via line 69 or substituted for the nitrogen in order to react with any hydroxide or any thiosulfate or other oxygen-containing compounds still present, the water thus formed being continuously removed by the driers.

The dried molten sodium polysulfide is subsequently removed from vessel 52 via line 58 and is passed directly to electrolytic cells 59. The electrolytic cells are of a conventional design and may comprise any cell capable of converting the sodium polysulfide to sodium metal. Preferably, the individual cell unit comprises a molten sodium-containing cavity and a molten sodium polysulfide-containing cavity separated from each other by a sodium ion-permeable membrane comprising preferably, crystalline beta-alumina, as already described.

A schematic representation of a cell unit is shown in FIG. 3. In operation, electrons flow through the metal separator sheet 1 entering the molten sodium-containing cavity 2, wherein sodium cations combine with the electrons and are reduced to elemental sodium that is withdrawn from the cavity via line 3. The beta-alumina membrane 4 acts both as a mechanical separator and an electron separator of the two cavities and at the same time as a sodium ion-permeable membrane. Sodium polysulfide is introduced into cavity 5 via line 6; it is, by its nature, highly ionized into sodium cations and polysulfide anions. The latter are oxidized to elemental sulfur that reacts further to yield sulfur-enriched polysulfide anions. The anions along with the requisite sodium cations are subsequently removed via line 7 from cavity 5 as sulfur-enriched sodium polysulfide ( $\text{Na}_2\text{S}_z$  where  $z$  varies from about 4.5 to 5.0). Electrons which are given up by the polysulfide anions flow through the metal separating sheet 8 to form a complete circuit. Thus the anode for one cell becomes the cathode for the next. The cell anode will comprise a solid, electron-conducting current collector such as graphite, molybdenum, titanium, chromium, aluminum, nickel-iron alloys and other alloys and the like.

As noted above, although beta-alumina is shown as the preferred separator, any other separator that is sufficient for the purposes may be employed. Additionally, an alternate embodiment comprises forming and continually removing elemental sulfur from the cell. In practice, the electrolytic cell 48 comprises a plurality of individual cell units in order to provide a sufficient output of sodium. The cells, although operated in parallel relative to sodium polysulfide flow are operated in series from an electrical point of view.

About 100–200 cells are operated in series in order to build up the overall voltage to about 300–600 volts. The total amount of cell area required depends on the amount of sodium required, and is in the range of 10 to 50 square feet per pound per minute of sodium. The temperature in the cell rises to about 700–820° F., depending on the amount of cell area, current density used, the resistance of the cell elements and their condition. Cell pressure is atmospheric or slightly above.



The composition of the sodium polysulfide leaving the electrolytic cell can be controlled by the flow rate and the current. The greater the flow rate the less is the increase in sulfur content; the greater the current the greater is the increase in sulfur content. The composition is controlled such that by applying a reasonable vacuum (and/or heat if desired), sulfur corresponding to that which was removed from the oil can be taken overhead.

Accordingly, the sodium polysulfide formed in the electrolytic cell is passed via line 60 (FIG. 1) to sulfur-reducing vessel 42 which is partially evacuated, e.g. to an absolute pressure of 10 to 300 mm. Hg, preferably 50–100 mm. Hg, to vaporize some of the sulfur and reduce the sulfur content of the polysulfide so that the final polysulfide composition is  $\text{Na}_2\text{S}_x$  wherein  $x$  takes values from about 4.4 to 4.9, preferably 4.5 to 4.8. At one-tenth atmosphere sulfur vapor pressure, for example, the composition in equilibrium therewith is approximately  $\text{Na}_2\text{S}_{4.75}$  at 700° F.,  $\text{Na}_2\text{S}_{4.62}$  at 750° F. and  $\text{Na}_2\text{S}_{4.53}$  at 800° F.

The sulfur vapor is taken overhead through line 43 and condensed by conventional means (not shown). As indicated supra the resulting polysulfide is then recycled to contacting zone 41. The molten sodium is subsequently removed from cell 59 and passed via line 61 to the reaction system which has already been described.

#### DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention will be more clearly understood by reference to the following hypothetical example (refer to FIG. 1).

Crude petroleum from the Safaniyah field in Saudi Arabia is used as the process feedstock. Its properties are as follows:

Sulfur content, weight percent	3.04
Oxygen content, weight percent	0.14
Vanadium, p.p.m.	55
Nickel, p.p.m.	18
Iron, p.p.m.	8
Density, ° API	27.1
Pour point, ° F.	–11
Viscosity, SSU at 100° F.	105
% Distilled at 375° F.	21.6
% Distilled at 650° F.	45.2
% Distilled at 1050° F.	76.6
NaCl—#/1000 bbls.	310

The crude containing 0.20 weight percent water is desalted by conventional means thereby reducing the salt content to 1.5 pounds per 1000 barrels of crude. The desalted oil is subsequently dehydrated at a pressure of 550 p.s.i.g. and a temperature of 450° F., thereby producing an oil containing less than about 0.1 weight percent water.

The oil is then passed to reactor 66. Sodium, after passing through a dispersion device 65 comprising uniformly spaced holes, is introduced into reactor 66 as fine droplets and at a rate of 330 pounds per minute. The reactor has ten equally-spaced baffles perpendicular to the line of flow, each with 354  $\frac{3}{8}$ " diameter holes equally spaced. At the outlet of this vessel the temperature is 623° F. and the pressure is 480 p.s.i.g. Oil from reactor 66 flows to reactor 10 where sodium reaction is completed. Reactor 10 contains eight equally-spaced partial baffles sloped as shown in FIG. 1. At the top of the reactor the temperature is 650° F. and the pressure is 465 p.s.i.g. About 9.2 weight percent of the oil is taken overhead from the reactor as vapor for further processing or to disposition to final product.

The desulfurized oil containing the sodium sulfide and other sodium compounds formed is pumped up to 600 p.s.i.g. and passed through a cooler where the temperature is reduced to 465° F. and thence to a conventional line orifice mixer 36.

Also entering the mixer is 196 pounds per minute of water solution from the second stage water wash vessel

33. This solution contains 13.5 weight percent of sodium sulfide and other sodium salts and 86.5 weight percent water. The thoroughly mixed oil-water solution enters electrical coalescer and settling vessel 20 where the pressure is 430 p.s.i.g. and the temperature is 450° F. The electrical coalescing vessel is 8 feet in diameter and 23 feet long.

The oil from vessel 20 passes through cooler 26 where the temperature is reduced to 200° F. This cooled oil stream joins a 170 pound per minute stream of water and together pass through a conventional line orifice mixer 31. The mixed stream passes through a pressure reducing valve into coalescer-separator 33 identical in shape to vessel 20. The pressure is 20 p.s.i.g. and the temperature 197° F.

The desulfurized oil leaving this separator is bright and contains 0.14 weight percent sulfur and 40, 15, and 5 p.p.m. (weight) of vanadium, nickel and iron respectively. The API density is 26.2° and the viscosity is 72 SSU at 100° F. The desulfurized oil is sent to further processing or to final product.

The aqueous solution from vessel 20 contains 55.5 weight percent of sodium sulfide, 15.0 weight percent NaOH, 4.8 weight percent  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.4 weight percent  $\text{Na}_2\text{SO}_3$ , 1.8 weight percent  $\text{Na}_2\text{CO}_3$  and 22.5 weight percent water. Thirty-one pounds per minute of calcium hydroxide slurry containing 30% calcium hydroxide is added to the aqueous solution to react with the sodium carbonate. One hundred and twenty-six pounds per minute of hydrogen sulfide is added to the solution to neutralize the sodium hydroxide, thiosulfate and sulfite and convert them to sodium sulfide and sodium polysulfide. The calcium carbonate precipitate is separated from the aqueous solution by conventional means such as by liquid cyclones, settling and filtration.

The concentrated sodium sulfide solution at 450° F. and 430 p.s.i.g. is then fortified with 65 weight percent sodium sulfide solution and then passes to pressure reducing valve 39. The aqueous solution passes from the valve throat immediately into a funnel-shaped section which expands into a three foot diameter section, which in turn empties into separator vessel 41. Sodium polysulfide having an average composition of  $\text{Na}_2\text{S}_{4.54}$  at 750° F. is injected at the narrow end of the funnel immediately beyond the point of concentrated solution pressure release. This incorporates the sodium mono-sulfide into the sodium polysulfide and supplies the heat required for steam dissolution and vaporization. The steam and newly constituted sodium polysulfide enter separator 41. Two hundred and forty-three pounds per minute of steam are taken overhead. The newly constituted sodium polysulfide has a composition  $\text{Na}_2\text{S}_{4.0}$  and amounts to 7750 pounds per minute. This sodium polysulfide is withdrawn from the bottom of the separator and passes to the top of drying tower 52.

Dry nitrogen at a rate of 460 cubic feet per second passes up through the tower and removes traces of moisture. The moisture-containing nitrogen passes overhead through line 53, through conventional molecular sieve dryers 54, and is recirculated to the bottom of the dryer vessel 52 by compressor 56. Hydrogen sulfide is continuously bled into the system through line 69 in order to maintain a fifty percent by volume  $\text{H}_2\text{S}$  concentration in the circulating nitrogen. The dry molten  $\text{Na}_2\text{S}_{4.0}$  accumulates in the bottom of dryer vessel 52 and passes to electrolytic cells 59.

The electrolytic cells are arranged in packs of 200 cells each, arranged in series electrically and serviced by a direct current voltage of 520 volts. Each cell is 10 inches square. Each pack consumes 1050 amperes and produces 13.2 pounds of sodium per minute. Twenty-five cell packs arranged in series electrically are used and produce 330 pounds per minute of sodium and 7410 pounds per minute of sodium polysulfide of composition  $\text{Na}_2\text{S}_{4.76}$ . Heat is generated by the cell and the temperature rises therein to 762° F.

## 13

Each cell consists of a 30-mil thick sheet of beta-alumina, having a composition 9.0 weight percent  $\text{Na}_2\text{O}$ —8.5 weight percent  $\text{MgO}$ —82.5 percent  $\text{Al}_2\text{O}_3$ , with a 40-mil thick sodium metal compartment formed by a parallel 20-mil molybdenum sheet on one side and a 40-mil thick sodium polysulfide compartment formed by a similar molybdenum sheet on the other side. The cells are packed together back-to-back like a multi-layered sandwich. Provision is made to interrupt the electrical circuit at the exit of each cell where the sodium leaves. The sodium is collected and passes through line 61 to sodium storage vessel 62. The sodium polysulfide passes through all of the cells in parallel.

The sodium polysulfide at  $762^\circ\text{F}$ . passes from the electrolytic cells through line 60 to sulfur release vessel 42. A vacuum is applied to reduce pressure to 55 mm. Hg absolute and 260 pounds per minute of sulfur vapor is taken overhead, condensed and recovered in accordance with standard practice. The sodium polysulfide remaining has a composition  $\text{NaS}_{4.54}$  and amounts to 7150 pounds per minute. Its temperature is  $750^\circ\text{F}$ . This hot  $\text{Na}_2\text{S}_{4.54}$  is conveyed to pump 45 and line 46 to pressure reducing valve 39, the operation of which has been described previously.

What is claimed is:

1. A process for the desulfurization of a sulfur-containing petroleum oil stock comprising introducing said oil stock into a desulfurization zone, contacting said oil stock therein, at desulfurization conditions, with a desulfurization agent selected from the group consisting of the alkali metals and alloys thereof, thereby precipitating at least a portion of the sulfur contained in said oil stock as alkali metal sulfide and forming an oil/alkali metal sulfide mixture, contacting at least a portion of said mixture with water at a pressure ranging from about 250 to 700 p.s.i.g. and at a temperature ranging from about  $400$  to  $500^\circ\text{F}$ . thereby forming an aqueous alkali metal sulfide solution and an oil of reduced sulfur content, contacting said aqueous alkali metal sulfide solution with hot alkali metal polysulfide thereby vaporizing at least a portion of the water from said aqueous solution and forming an alkali metal polysulfide of reduced sulfur content, contacting at least a portion of said oil of reduced sulfur content with additional water at a pressure ranging from about 0 to 70 p.s.i.g. and at a temperature ranging from about  $150$  to  $300^\circ\text{F}$ ., to remove additional metal sulfides from said oil and recovering a desulfurized oil.

2. The process of claim 1 wherein said petroleum oil stock is selected from the group consisting of whole crude and residua.

3. The process of claim 1 wherein said desulfurization agent is sodium.

4. The process of claim 1 wherein said oil/alkali metal mixture is contacted with water at a pressure ranging from about 330 to 540 p.s.i.g. and at a temperature ranging from about  $425$  to  $475^\circ\text{F}$ . thereby forming an aqueous alkali metal sulfide solution and an oil of reduced sulfur content.

5. The process of claim 4 wherein said oil of reduced sulfur content is contacted with water at a pressure ranging from about 5 to 10 p.s.i.g. and at a temperature ranging from about  $195$  to  $205^\circ\text{F}$ .

6. A process for the desulfurization of a sulfur-containing petroleum oil stock comprising contacting said oil stock, at desulfurization conditions, with a desulfurization agent selected from the group consisting of sodium and alloys thereof, thereby precipitating at least a portion of the sulfur contained in said oil as sodium sulfide and forming an oil/sodium sulfide mixture, contacting at least a portion of said mixture with water at a temperature ranging from about  $400$  to  $500^\circ\text{F}$ . and at a pressure ranging from about 250 to 700 p.s.i.g. thereby forming an aqueous sodium sulfide solution and an oil of reduced sulfur content, contacting at least a portion of said oil of reduced sulfur content with additional water at a tempera-

## 14

ture ranging from about  $150$  to  $300^\circ\text{F}$ . and at a pressure ranging from about 0 to 75 p.s.i.g. and recovering a desulfurized oil, contacting at least a portion of said aqueous sodium sulfide solution with hot sodium polysulfide thereby vaporizing at least a portion of the water from said aqueous sodium sulfide solution and forming sulfur reduced sodium polysulfide, employing at least a portion of said sulfur reduced sodium polysulfide as an electrolyte in an electrolytic cell for the production of sodium metal, and, thereafter, contacting at least a portion of said sodium metal with sulfur-containing petroleum oil stock.

7. The process of claim 6 wherein said oil stock is selected from the group consisting of whole crude and residua.

8. The process of claim 6 wherein said oil/sodium sulfide mixture is contacted with water at a pressure ranging from about 330 to 540 p.s.i.g. and at a temperature ranging from about  $425$  to  $475^\circ\text{F}$ . thereby forming an aqueous sodium sulfide solution and an oil of reduced sulfur content.

9. The process of claim 8 wherein said oil of reduced sulfur content is further contacted with water at a temperature ranging from about  $195$  to  $205^\circ\text{F}$ . and at a pressure ranging from about 5 to 10 p.s.i.g.

10. The process of claim 6 wherein said sodium polysulfide is represented by the formula  $\text{Na}_2\text{S}_x$  where  $x$  takes values from about 4.4 to 4.9, and said sulfur reduced sodium polysulfide is represented by the formula  $\text{Na}_2\text{S}_y$  where  $y$  takes values ranging from about 3.5 to 4.3.

11. The process of claim 6 wherein said electrolytic cell comprises an anodic cavity containing polysulfide anions and a cathodic cavity containing sodium cations, said anodic and cathodic cavities separated by a sodium ion-conducting membrane.

12. The process of claim 11 wherein said membrane comprises beta-alumina.

13. The process of claim 6 wherein said aqueous sodium sulfide solution is contacted with calcium hydroxide and hydrogen sulfide prior to contact with said sodium polysulfide.

14. In a process for the desulfurization of a sulfur-containing petroleum oil stock comprising contacting said oil stock in a desulfurization zone with a desulfurization agent selected from the group consisting of sodium and alloys thereof, thereby precipitating at least a portion of the sulfur contained in said oil stock as sodium sulfide and forming an oil/sodium sulfide mixture, the improvement comprising contacting said mixture with water at a pressure ranging from about 250 to 700 p.s.i.g. and at a temperature ranging from about  $400$  to  $500^\circ\text{F}$ ., thereby forming an aqueous sodium sulfide solution and an oil of reduced sulfur content, contacting said oil of reduced sulfur content with additional water at a temperature ranging from about  $150$  to  $300^\circ\text{F}$ . and at a pressure ranging from about 0 to 75 p.s.i.g., and recovering a desulfurized petroleum oil stock.

15. A process for the desulfurization of a sulfur-containing petroleum oil stock comprising introducing said oil stock into a desulfurization zone, contacting said oil stock therein, at desulfurization conditions, with a desulfurization agent selected from the group consisting of the alkali metals and alloys thereof, thereby precipitating at least a portion of the sulfur contained in said oil stock as alkali metal sulfide and forming an oil/alkali metal sulfide mixture, contacting at least a portion of said mixture with water at a pressure ranging from about 250 to 700 p.s.i.g. and at a temperature ranging from about  $400$  to  $500^\circ\text{F}$ . thereby forming an aqueous alkali metal sulfide solution and an oil of reduced sulfur content, contacting said oil of reduced sulfur content with additional water at a pressure ranging from about 0 to 70 p.s.i.g. and at a temperature ranging from about  $150$  to  $300^\circ\text{F}$ ., thereby removing residual alkali metal sulfide from said oil, and recovering a desulfurized oil.

(References on following page)

15

References Cited

UNITED STATES PATENTS

1,300,816	4/1919	Cobb	208—229	
1,413,005	4/1922	Cobb	208—230	
3,004,912	4/1964	Kaneko	208—208	5
3,093,575	6/1963	Kimberlin, Jr. et al.		
			208—208	M
3,565,792	2/1971	Haskett	208—208	M
3,004,912	10/1961	Kaneko et al.	208—208	
2,020,661	11/1935	Schulze et al.	208—230	10
3,164,545	1/1965	Mattox	208—230	

16

3,488,271	5/1968	Kummer	204—180
3,404,036	5/1968	Kummer	136—6
3,468,709	5/1968	Kummer	136—6
3,446,677	5/1968	Tennenhouse	136—6
3,475,225	5/1968	Tennenhouse	136—6

DELBERT E. GANTZ, Primary Examiner

J. M. NELSON, Assistant Examiner

U.S. Cl. X.R.

208—226, 227, 229, 230