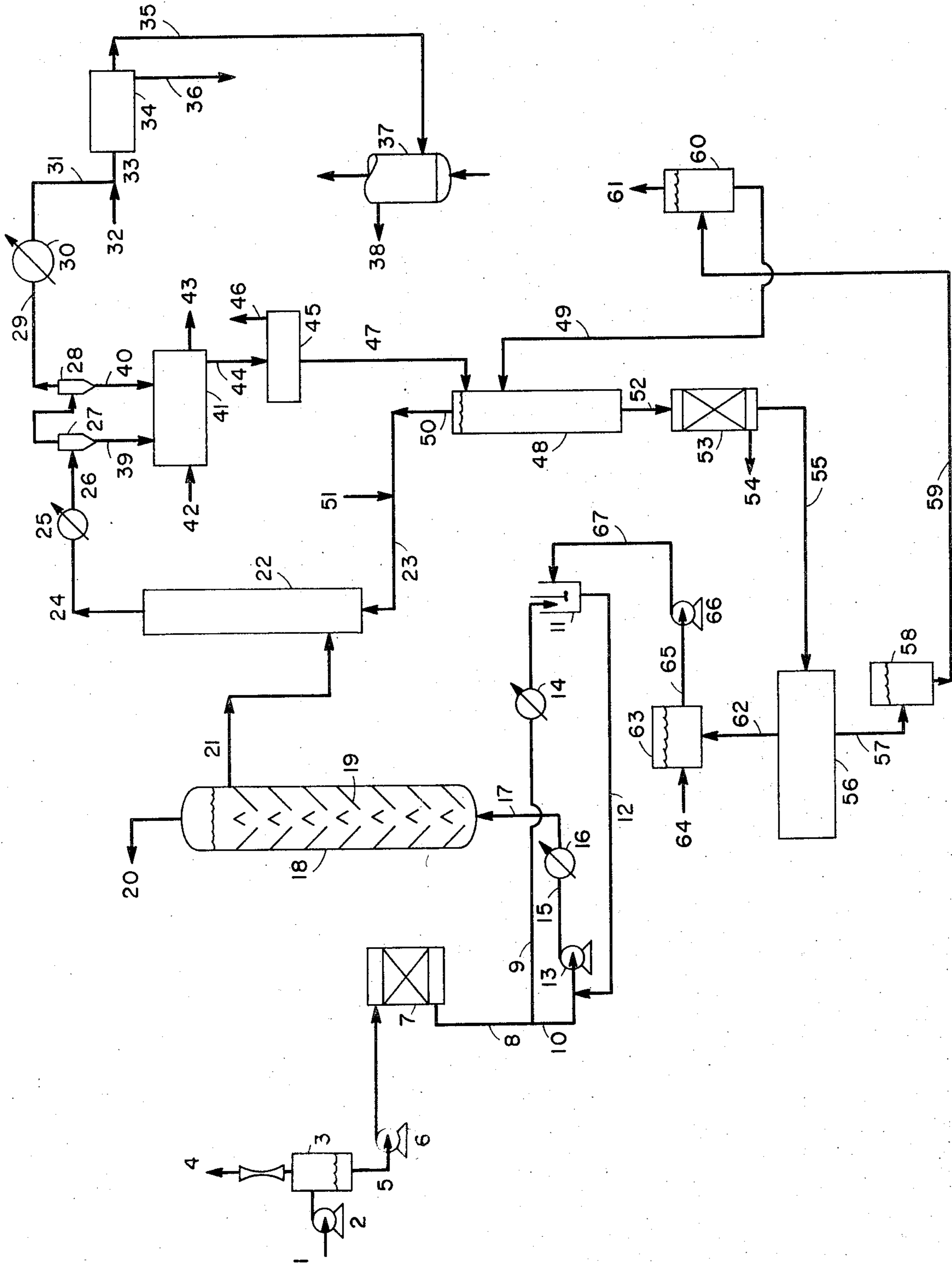


FIGURE 1



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FIGURE 2

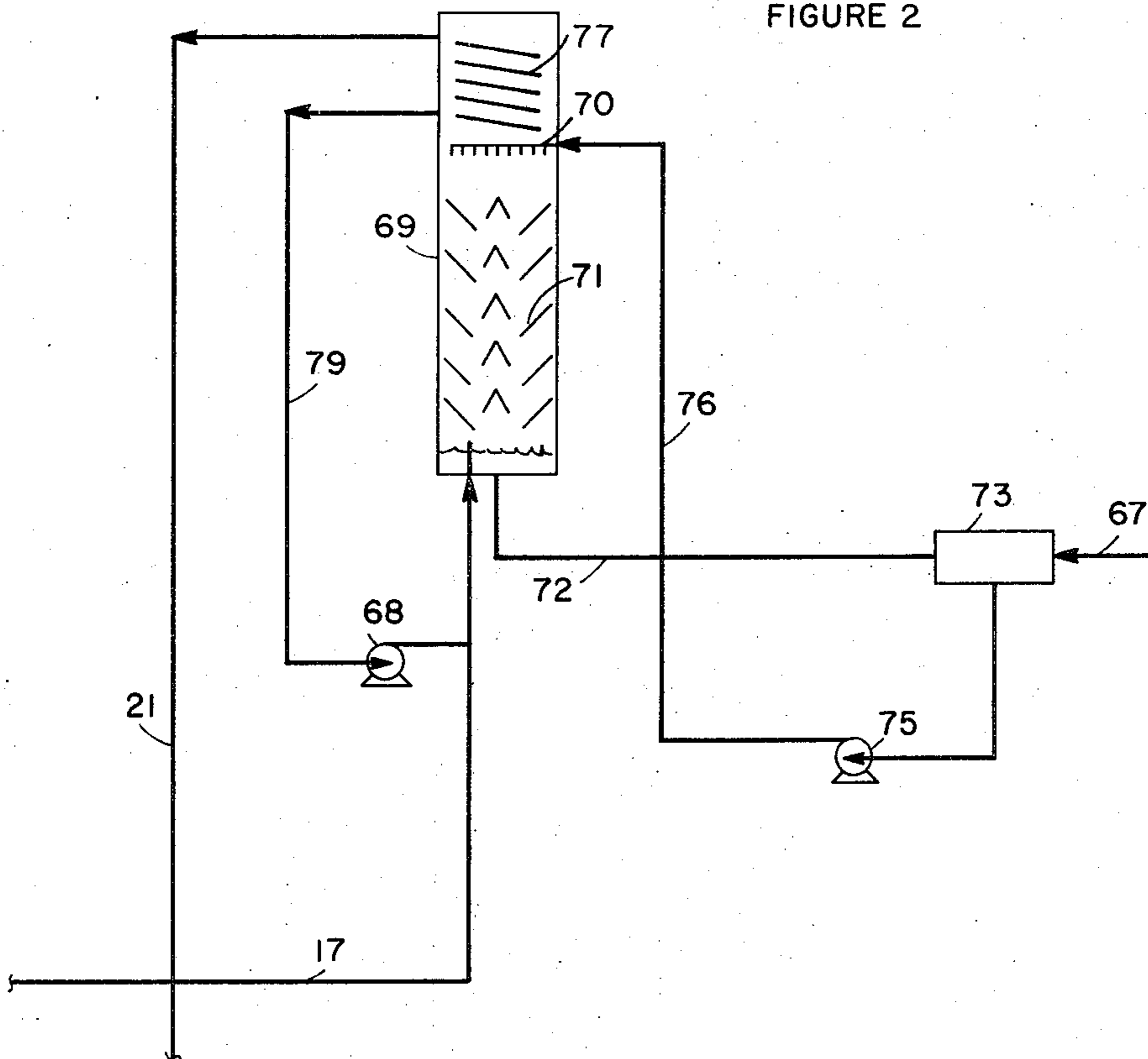
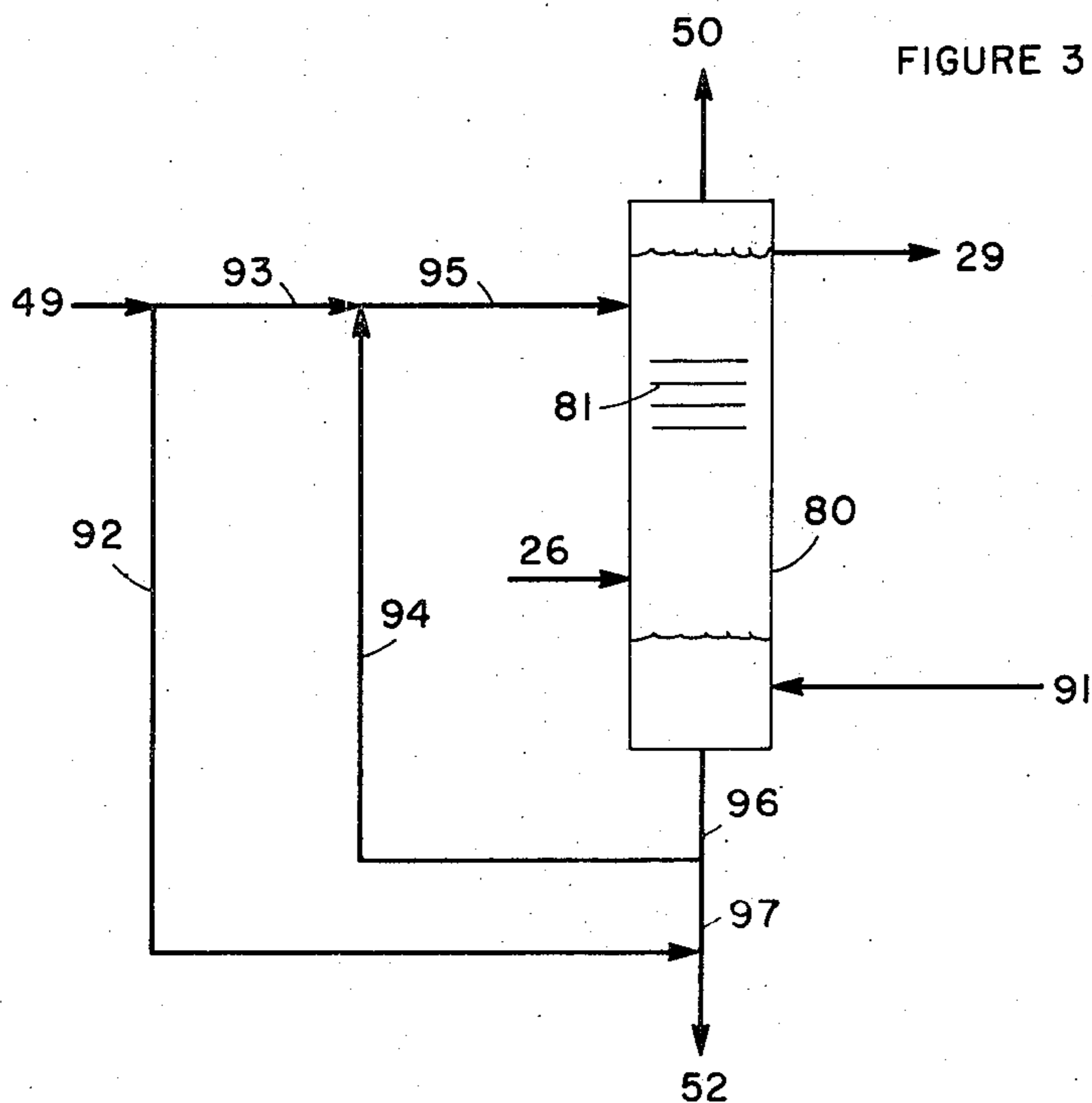


FIGURE 3



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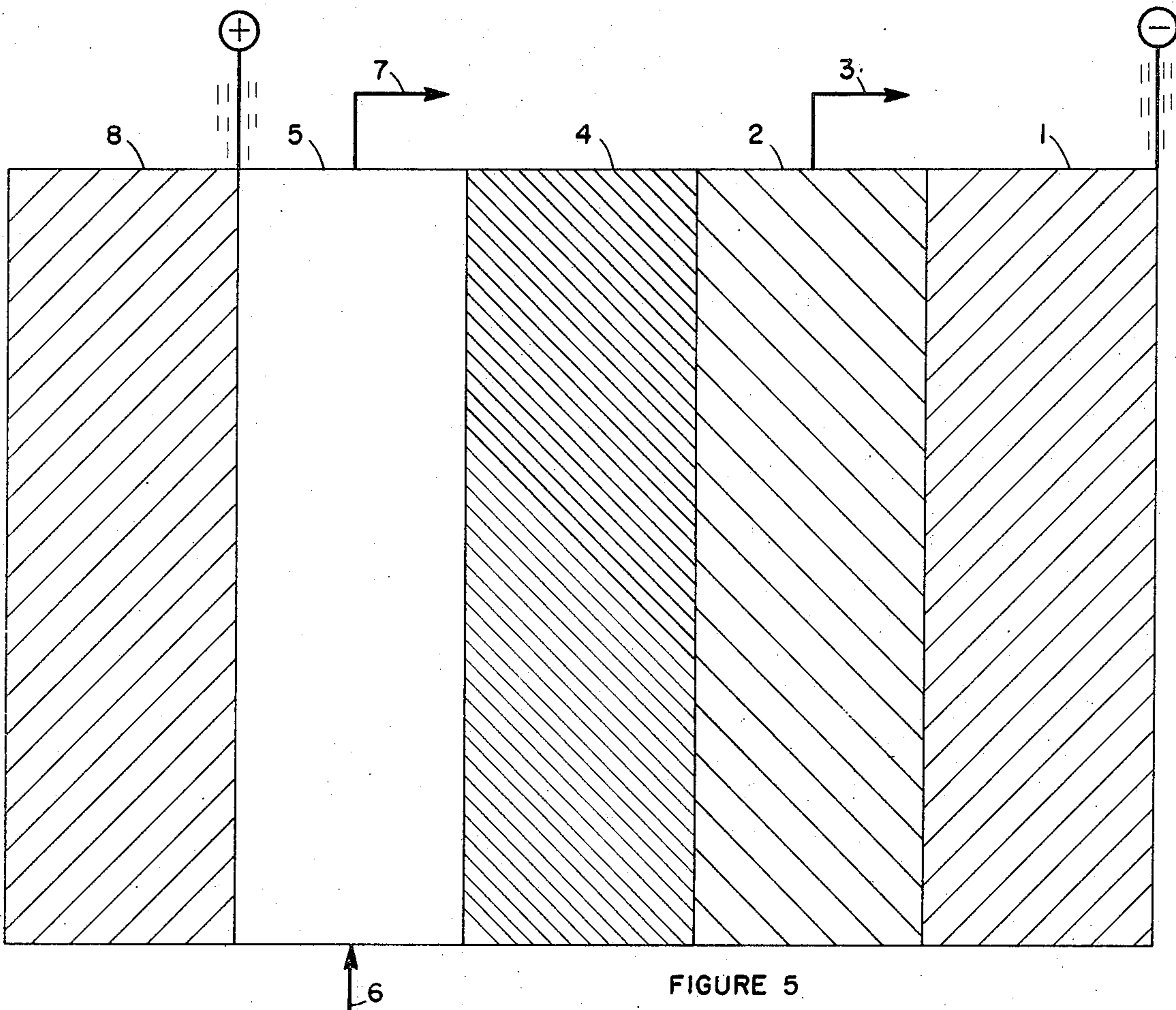
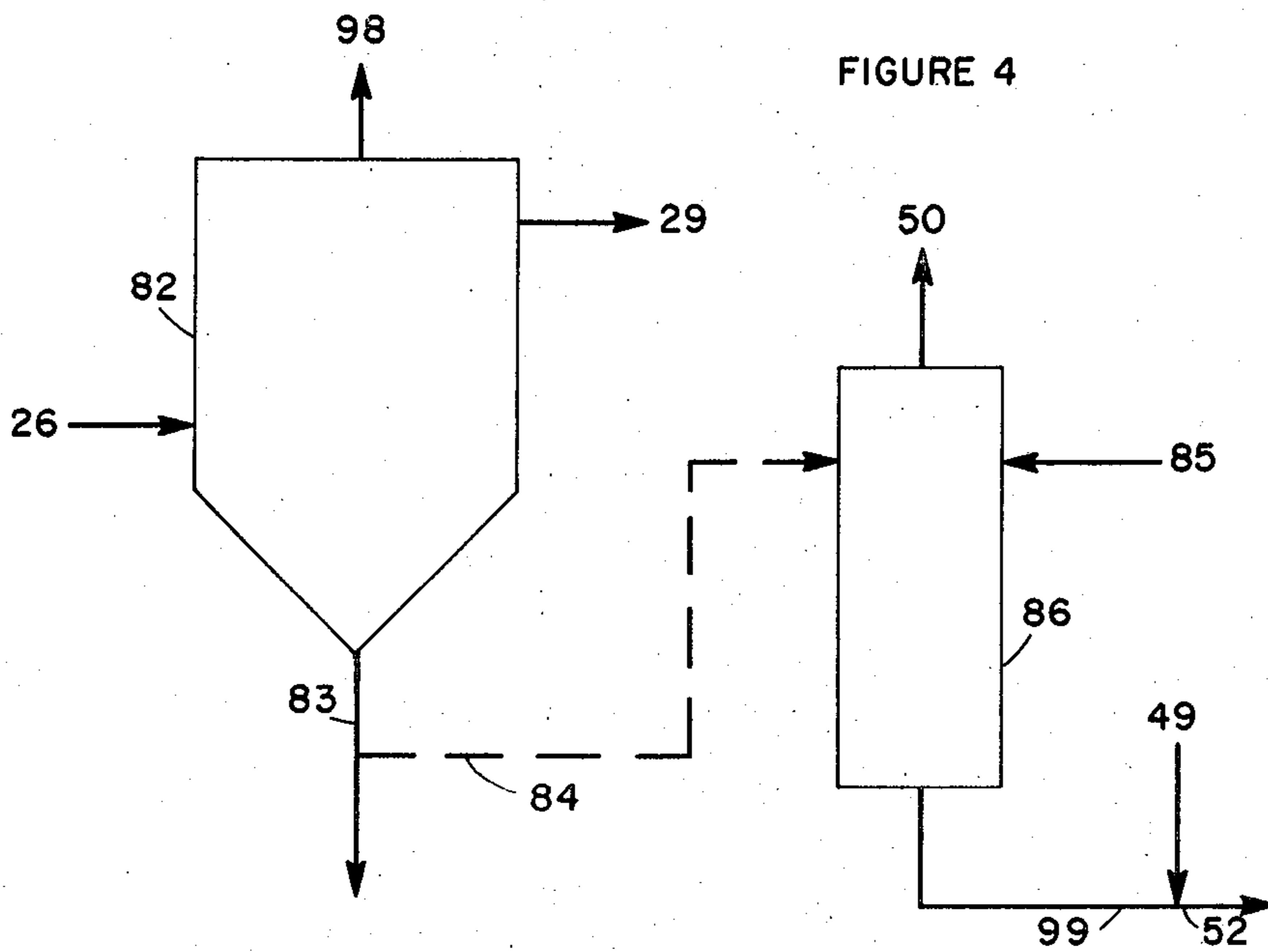
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3,788,978

## PROCESS FOR THE DESULFURIZATION OF PETROLEUM OIL STOCKS

Roby Bearden, Jr., Baton Rouge, La., Robert B. MacMullin, Lewiston, N.Y., William E. Lewis, Baton Rouge, La., and Albert B. Welty, Jr., Westfield, N.J., assignors to Esso Research and Engineering Company  
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Int. Cl. C10g 17/00, 19/00

U.S. Cl. 208—208 M

23 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 a mixture comprising a low sulfur oil and a mixture of alkali metal salts dispersed therein. The mixture of salts in oil is resolved by contacting the same with, preferably, 30–160 mole percent hydrogen sulfide based on total moles of salt in the oil, at a temperature of about 670° F. or above whereupon a salt phase separates from the oil. Thus separated the salt is blended with a molten sulfur-rich alkali metal polysulfide thereby forming a sulfur-depleted alkali metal polysulfide and liberating hydrogen sulfide. In another embodiment of the invention, molten sulfur may be used in place of the polysulfide. The sulfur-depleted polysulfide is then decomposed electrolytically to reform alkali metal and a sulfur-rich polysulfide, from which elemental sulfur is recovered.

### BACKGROUND OF THE INVENTION

#### Field of the invention

The present invention relates to a process for the desulfurization of sulfur-containing petroleum oil stock. More particularly, the process comprises contacting a sulfur-containing oil stock with an alkali metal or alkali metal alloy.

#### Description of the prior art

In the last several years there has been an ever-increasing concern about air pollution. Some of the objects of this concern have been the discharge of sulfur oxides to the atmosphere upon burning sulfur-containing fuels. Over a period of many years several studies have been conducted with the object of developing efficient and economical means for 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 pressures and temperatures in the presence of an appropriate catalyst. The process requires the use of hydrogen pressures ranging from about 200 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 and less efficient when used with those 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 asphaltenes which tend to form coke deposits under the process conditions on the catalyst surface thereby deactivating the catalyst. Moreover, high boiling organometallic compounds pres-

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ent in such stocks decompose and deposit metals on the catalyst surface thereby diminishing the catalyst life time. 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 the sodium dispersion, the sodium reacting with the sulfur to form dispersed sodium sulfide ( $\text{Na}_2\text{S}$ ). However, such a process was 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) problems related to removal of sodium sulfide formed in the process from the oil and (c) the impracticability heretofore of regenerating sodium from the sodium sulfide.

In theory, it has been determined that the best approach to this problem of sodium regeneration 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 the sodium polysulfides meet this requirement. There are three sodium polysulfides with melting points as follows:  $\text{Na}_2\text{S}_2$  (885° F.),  $\text{Na}_2\text{S}_4$  (545° F.) and  $\text{Na}_2\text{S}_5$  (485° F.). These polysulfides are mutually soluble and intermediate compositions, having intermediate properties, can form. The eutectic is at about  $\text{Na}_2\text{S}_{3.1}$  with a melting point of about 450° F. Moreover, the electrolysis of molten sodium polysulfide consumes less electrical energy than electrolyzing molten sodium chloride, the traditional electrolysis salt.

The cost of sodium as a reagent 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 in the past, but until now no economical process has been developed. One of the major difficulties has been the separation of the sodium sulfide from the oil.

### SUMMARY OF THE INVENTION

In accordance with this invention, it has now been discovered that an economically feasible desulfurization process vis-a-vis hydrodesulfurization 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, and the like, preferably sodium, or an alkali metal alloy, preferably sodium/lead, at desulfurization conditions, thereby forming a mixture comprising an oil of diminished sulfur content containing alkali metal salts and contacting at least a portion of said mixture with  $\text{H}_2\text{S}$ .

The alkali metal salts comprise in addition to alkali metal sulfide, by-product alkali metal salts such as organo metal salts, metal oxides, mercaptides, amides and the like. Hereinafter the invention will be described with respect to sodium although it is understood that other alkali metals as hereinbefore disclosed may be used.

In a preconditioning step for salt recovery at least a portion of the oil-salt mixture (generally in the form of a dispersion of submicron sodium salts in oil) is contacted with  $\text{H}_2\text{S}$  in amounts ranging from about 10 to about 100 mole percent, based on the total number of moles of salt present in the mixture, preferably 30 to 60

mole percent. The net consequence of the H<sub>2</sub>S treatment is twofold: (1) at least a portion of the by-product sodium salts such as sodium oxide, sodium hydroxide and the like are converted to sodium hydrosulfide, and (2) submicron salts are agglomerated to yield a macrocrystalline salt phase (preferably having a particle size between about 150 and 200 microns) which readily disengages from the oil phase. The salt phase is separated from the oil phase and recovered employing one of several well known commercial techniques, notably filtration or centrifugation. The H<sub>2</sub>S-treated mixture of salts is then contacted with a sulfur-rich sodium polysulfide, desirably in the molten state and preferably represented by the formula, Na<sub>2</sub>S<sub>x</sub> (where *x* varies from about 4.0 to 4.9, preferably from about 4.4 to 4.8, most preferably from about 4.5 to 4.7). The contacting results in the formation of a sulfur-depleted sodium polysulfide, i.e., Na<sub>2</sub>S<sub>y</sub> (where *y* ranges from about 2.8 to 4.5, preferably from about 3.5 to 4.3, most preferably from about 4.0 to 4.2), desirably at a temperature above the melting point of the resulting polysulfide. This recovery and conversion method will be hereinafter referred to as Scheme A.

Alternatively, the H<sub>2</sub>S-treated mixture of salts in oil i.e., without salt separation from the oil, can be contacted directly with the molten polysulfide (Na<sub>2</sub>S<sub>x</sub>) thereby converting at least a portion of the salts in situ to a sulfur-depleted polysulfide, Na<sub>2</sub>S<sub>y</sub>, which is preferably in a molten state (Scheme B). It is preferable that the value of *y* in the sulfur-depleted polysulfide Na<sub>2</sub>S<sub>y</sub> be in the range of about 2.8 to 3.5 in order to avoid back-sulfiding of the oil phase by the polysulfide.

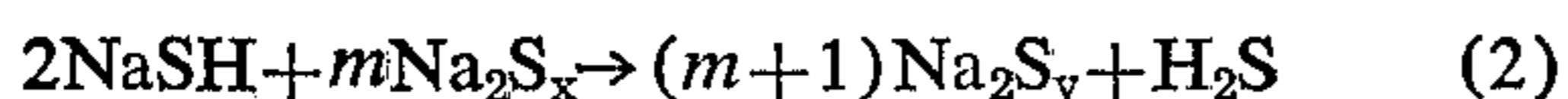
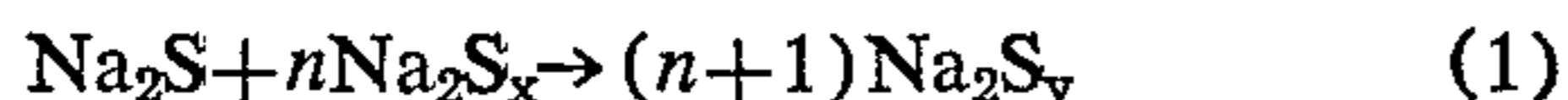
The Na<sub>2</sub>S<sub>y</sub> is subsequently electrolyzed in an electrolytic cell as more fully described below, and sodium is withdrawn therefrom and either alloyed with a molten metal such as lead or tin or introduced directly into the desulfurization zone in undiluted form.

In a second embodiment of the invention (Scheme C) an excess amount of H<sub>2</sub>S is added to the sodium sulfide/oil mixture thereby converting the sodium sulfide (and other sodium salts present therein) to sodium hydrosulfide (NaSH). The amount of hydrogen sulfide added can range from about 110 mole percent based on the total number of moles of salt present in the oil up to about 400 mole percent, but is preferably used in amounts ranging from about 120 to 160 mole percent. At the contacting temperature employed, the NaSH is substantially molten and is readily separable from the oil. Thereafter, the NaSH is contacted with either Na<sub>2</sub>S<sub>x</sub> or sulfur to form Na<sub>2</sub>S<sub>y</sub> which is electrolyzed to form sodium.

It is also possible, and, perhaps desirable, to convert NaSH to Na<sub>2</sub>S<sub>y</sub> by contact with molten sulfur rather than the molten polysulfide Na<sub>2</sub>S<sub>x</sub>. According to this procedure, (Scheme D), molten sulfur obtained from pyrolysis of the electrolysis product, Na<sub>2</sub>S<sub>z</sub>, is added to the oil-free, molten NaSH stream. Normally, sufficient sulfur is added to give the desired electrolysis feed, i.e., Na<sub>2</sub>S<sub>y</sub>, where *y* ranges from about 3.5 to 4.3.

It should be noted that in each of the foregoing schemes for the recovery and conversion of desulfurization salts, that hydrogen sulfide is liberated when the H<sub>2</sub>S-treated salts are contacted with sulfur-rich sodium polysulfide or elemental sulfur. The hydrogen sulfide is recovered, purified to remove traces of water and recycled in the process.

The amount of Na<sub>2</sub>S<sub>x</sub> that is required to react with the H<sub>2</sub>S-treated salt mixture varies and is dependent on the compositions of both the sulfur-rich polysulfide and the sulfur-depleted polysulfide. The reaction of Na<sub>2</sub>S<sub>x</sub> with either Na<sub>2</sub>S or NaSH is thought to proceed as follows:



From the above stoichiometry, it is seen that the same amount of Na<sub>2</sub>S<sub>x</sub> is required to react with 2 moles NaSH

as with 1 mole Na<sub>2</sub>S to yield the same quantity of Na<sub>2</sub>S<sub>y</sub>. The values of *n* and *m* in the above equations will depend on the values chosen for *x* and *y*. Using the equations, the amount of Na<sub>2</sub>S<sub>x</sub> required to react with a salt mixture comprising 1 mole of Na<sub>2</sub>S, i.e., *n* and 1 mole of NaSH, i.e., *m* is:

$$\begin{array}{l} \text{Moles Na}_2\text{S}_x \text{ to react with} \\ \text{1 mole of Na}_2\text{S (n)} \end{array} = \frac{y-1}{x-y} \quad (3)$$

$$\begin{array}{l} \text{Moles Na}_2\text{S}_x \text{ to react with} \\ \text{1 mole of NaSH (m)} \end{array} = \frac{1}{2} \left( \frac{y-1}{x-y} \right) \quad (4)$$

where:

*y* = the number of sulfur atoms in Na<sub>2</sub>S<sub>y</sub>  
*x* = the number of sulfur atoms in Na<sub>2</sub>S<sub>x</sub>

Knowing the number of moles of Na<sub>2</sub>S and NaSH present in the salt mixture and the values for *x* and *y*, the required amount of Na<sub>2</sub>S<sub>x</sub> can be determined. It is noted that the calculated amounts of Na<sub>2</sub>S<sub>x</sub> are minimum values and that larger quantities may be required depending on the amount of other salts that may be present in the salt mixture which also react with the Na<sub>2</sub>S<sub>x</sub>.

Any feedstock from which sulfur is desired to be removed may in theory be used in the instant process. Thus, for example, suitable feedstocks include whole crude such as Safaniya crude (Middle East), Lagunillas crude (Venezuelan), 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 hydrodesulfurization. While the feedstock may be fed directly to the initial contacting zone for desulfurization without pretreatment, it is desirable to desalt the feed in order to prevent NaCl contamination of the molten polysulfide feed to the electrolysis 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 means 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, desirable proportions comprise about 0.3 to about 0.5 g.-atom sodium/0.7 to about 0.5 g.-atom lead, and when using sodium/tin, about 0.2 to 0.3 g.-atom sodium/0.8 to 0.7 g.-atom tin.

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. 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 about 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 to 600 p.s.i.g. in order to maintain all or most of the oil in the liquid phase.

The sodium metal reacts with the sulfur-containing oil stock as shown in Equation 5 below to yield sodium sulfide which generally forms as a microcrystalline dispersion in the oil.



In addition, organo-oxygen contained in the feedstock is removed therefrom by reacting with the sodium metal. Furthermore, depending on the amount of trace water present in the feed and the reaction conditions, varying amounts of thiosulfate, hydroxide and 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 by reaction with the sodium.

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 alloy thereof 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, turbomixers and the like, or (d) a packed bed. The petroleum oil stock and the sodium metal or sodium metal alloy can be passed through one or more reactors in concurrent, crosscurrent, or countercurrent flow, etc. It is preferable that oxygen and water be excluded from the reaction zones; therefore, the reaction system is thoroughly purged with dry nitrogen and the feedstock dried prior to introduction into the reaction. It is understood that trace amounts of water, i.e., less than about 0.5 weight percent, preferably less than about 0.1 weight percent based on total feed, can be present in the reactor. Where there are larger amounts of water, process efficiency will be lowered somewhat as a consequence of sodium reacting with the water.

The resulting oil dispersion is subsequently removed from the desulfurization zone and contacted with H<sub>2</sub>S as described supra. Treatment of the H<sub>2</sub>S-treated salt mixture according to any of Schemes A-D, results in the formation of a sulfur-depleted sodium polysulfide, i.e., Na<sub>2</sub>S<sub>y</sub>.

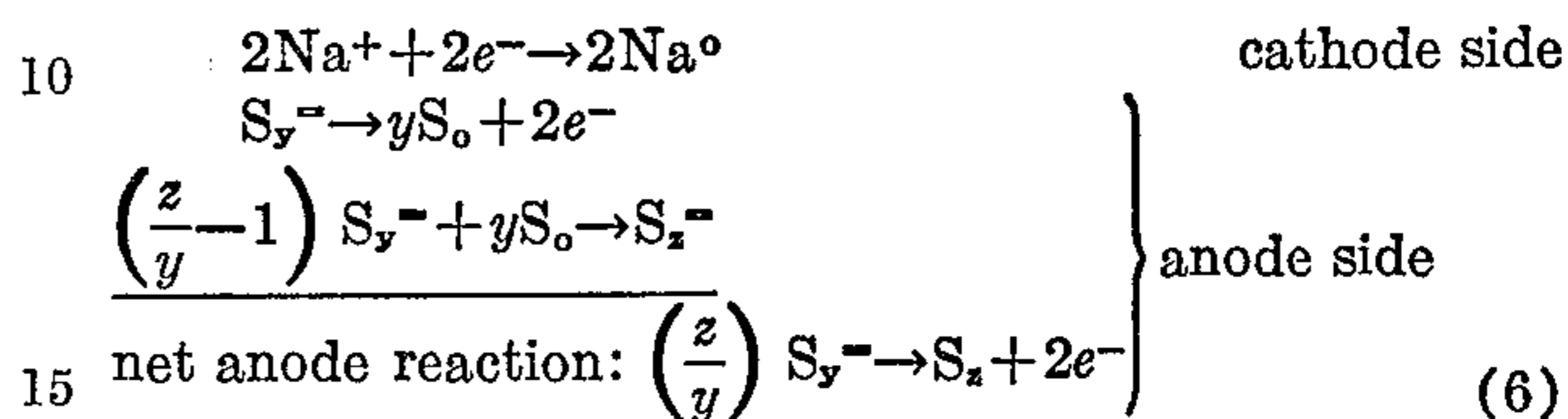
After further treatment of the Na<sub>2</sub>S<sub>y</sub> to remove various impurities present therein, the Na<sub>2</sub>S<sub>y</sub> is cycled to electrolytic cells wherein it is dissociated to form molten sodium and a sulfur-rich sodium polysulfide, i.e., Na<sub>2</sub>S<sub>z</sub> wherein z ranges from about 4.5 to 5.0, preferably from about 4.6 to 4.9, most preferably from about 4.7 to 4.9. The sodium thereby formed 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 Na<sub>2</sub>O·11Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O·5Al<sub>2</sub>O<sub>3</sub>. 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 the beta-alumina in lieu of Na<sub>2</sub>O.

The beta-alumina may be used in the pure form of doped with a small amount of metal oxide such as MgO, Li<sub>2</sub>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 β-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-conducting anode to form elemental sulfur that then reacts with additional polysulfide anions to form new polysulfide ions, i.e., S<sub>z</sub><sup>-</sup>, of greater sulfur content.

As indicated above, z will take values in the range of about 4.5 to 5.0. The S<sub>z</sub><sup>-</sup> anions are continually removed

from the cell in combined form with sodium, i.e., Na<sub>2</sub>S<sub>z</sub>. The anode may comprise any suitable electron conducting-current collector such as graphite, molybdenum, titanium, chromium, stainless steel, 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:



The recovered Na<sub>2</sub>S<sub>z</sub> can be reduced in sulfur content to Na<sub>2</sub>S<sub>x</sub> (the latter being contacted with the H<sub>2</sub>S-treated salt mixture as described supra) by application of a vacuum and/or heat thereby liberating sulfur corresponding to that which was removed from the oil. Alternatively, at least a portion of the Na<sub>2</sub>S<sub>z</sub> may be contacted directly with the H<sub>2</sub>S-treated salt mixture.

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. In another embodiment liquid sulfur forms in the cell and is separated from the polysulfide outside the cell. In yet another embodiment liquid sulfur forms in the cells and is separated from 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. 3,468,709 to J. T. Kummer and U.S. 3,446,677 and U.S. 3,755,225 to G. T. Tennenhouse, the disclosures of which are incorporated herein by reference.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow diagram of the overall desulfurization process using sodium metal in pure form. Desulfurization salts are recovered from the oil according to Scheme A.

FIG. 2 shows the reactor system for desulfurization with an alloy of sodium, i.e., sodium/lead.

FIG. 3 shows the changes required to operate the process using salt recovery Scheme B.

FIG. 4 shows the steps used in salt recovery Schemes C and D.

FIG. 5 is a simplified scheme showing the formation of the molten sodium within the electrolyte cell.

Referring to the drawings in detail, 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 and the description of Scheme A, a sulfur-containing feedstock, preheated to 450-500° F., is fed by means of line 1 and pump 2 to separator vessel 3 where trace amounts of water and light hydrocarbon fractions are removed through line 4. The feed is then discharged through line 5 by pump 6 to filter vessel 7 wherein particulate matter, i.e., coke, scale, etc., is removed.

The feed is preliminarily desalted by conventional means (not shown). Feed exiting the filter via line 8 is split into two streams. A small portion is fed through line 9 and heat exchanger 14 to dispersator vessel 11 where a dispersion is formed with sodium entering through

line 67. The dispersator vessel is of a conventional design and is operated at 250–300° F. at atmospheric pressure. The vessel is blanketed with nitrogen. The resultant dispersion, drawn through line 12, blends with the balance of the feed in line 10 and enters the charging pump 13, where the pressure is raised to about 500 p.s.i.g., for whole crudes and distillates and about 50 p.s.i.g. for residual fuels. The feedstock will ordinarily be a whole crude of about 1 to about 3 weight percent sulfur based on total feed or a residual stock of about 2 to about 7 weight percent sulfur based on total feed, although distillate stocks can be used.

The oil enters heat exchanger 16 via line 15 where the temperature is raised to about 500 to 550° F. and is then fed through line 17 to reactor vessel 18. The reactor contains baffles 19 to promote continuing contact between sodium and the oil and to prevent bypassing from the inlet to the outlet. Holding time in the reactor is about 15 to 60 minutes and is preferably 30 minutes. The temperature at the top of reactor 18 is about 680° F. Gas that is formed due to the increase in temperature is taken overhead through line 20 and is condensed and depressurized by conventional means (not shown). The desulfurized oil containing dispersed sodium sulfide and other salts leaves the top of reactor 18 via line 21.

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. The feedstock which has been preliminarily preheated, dehydrated and de salted as per FIG. 1 is premixed in line 17 with desulfurized recycled oil from pump 68. The mixed oil stream enters reactor vessel 69 via line 17 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 disperser 70 for about 10 minutes to about 1 hour. The sodium alloy, preferably sodium/lead or sodium/tin or a mixture of the two, enters reactor 69 via disperser 70. Atom compositions of about 0.3 to 0.5 Na/0.7 to 0.5 Pb or 0.2 to 0.3 Na/0.8 to 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 71 promote contact. The spent alloy collects in the bottom of reactor 69 and passes via line 72 to the alloy storage vessel 73. The alloy is fortified by contact with freshly regenerated sodium entering vessel 73 via line 67. Pump 75 feeds the fortified alloy via line 76 to disperser 70.

The dispersed oil passes into a settler zone located in the top of reactor 69 where any small, entrained alloy particles are allowed to settle. Baffles 77 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 69 via line 21.

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 and the like can be employed. Other settling means, in particular external, long, horizontal flow vessels or liquid cyclones and the like can be also used.

Sodium sulfide-oil dispersion in line 21 is introduced into contacting vessel 22 wherein the said dispersion is contacted with 30–80 mole percent hydrogen sulfide based on the total moles of salts contained in the oil, at a temperature between about 600–800° F., preferably 625–750° F., e.g., 700° F., and most preferably at the temperature of the desulfurization step. The pressure is main-

tained between about 25–50 p.s.i.g. Hydrogen sulfide is introduced into said contactor via line 23. Residence time in the contactor vessel is on the order of about 10 minutes, although longer or shorter times may be used if desired.

The H<sub>2</sub>S-treated dispersion exits through line 24 at about 700° F., and 25–100 p.s.i.g. and is then cooled to about 450° F. in heat exchanger 25. The mixture is then fed through line 26 to hydroclone vessels 27 and 28 in series. Desulfurized oil is withdrawn via line 29 to heat exchanger 30 and exits at 250–300° F. through line 31. An acid, such as dilute sulfuric acid or acetic acid, may be injected into line 31 through line 32 to react with oil soluble sodium salts, e.g., sodium mercaptides and the like and the resultant mixture enters the electrostatic precipitator 34 via line 33. The acidic aqueous phase from vessel 34 is withdrawn through line 36 and discarded. Desulfurized oil is fed through line 35 to steam stripper 37 and subsequently to storage via line 38.

Oil-salt slurry drawn from the hydroclone vessels through lines 39 and 40 is fed to wash vessel 41 where a light hydrocarbon wash, entering through line 42, is used to remove heavy adhering oil. The wash effluent is drawn off through line 43 and is eventually fractionated to recover the desulfurized oil content and the light hydrocarbon. The wash vessel operates at 25–100 p.s.i.g. at temperatures of 150–300° F. A slurry of washed solids is fed through line 44 to drier 45 to remove light hydrocarbon, which is taken off through line 46.

Dry solids are fed to blending vessel 48 via line 47, wherein contact is made with sulfur rich polysulfide (Na<sub>2</sub>S<sub>x</sub> as hereinabove described) that enters the vessel through line 49. The contacting is conducted at a temperature of about 500 to 820° F., preferably 600–800° F., most preferably from about 650–750° F., e.g., 700° F., and at a pressure between about atmospheric pressure and 100 p.s.i.g., preferably between atmospheric pressure and 50 p.s.i.g. Hydrogen sulfide released in the blending reaction along with some small amount of light hydrocarbon is removed through line 50, blended with makeup hydrogen sulfide entering from line 51 and is recycled to vessel 22 by way of line 23.

The molten sulfur depleted polysulfide (Na<sub>2</sub>S<sub>y</sub> as hereinabove defined) formed by the reaction of H<sub>2</sub>S-treated salts with sulfur-rich polysulfide is removed from blending vessel 48 through line 52 and fed to filter vessel 53 to remove particulate matter such as coke and melt insoluble salts. Line 54 is used to purge a small stream of sodium polysulfide from the system in order to prevent buildup 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 sodium. Specifically, compounds containing combined iron, vanadium, silica, nickel, chromium, lead and tin may form and are removed from the system via line 54.

In addition to the above-mentioned impurities, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>3</sub> and the like may also be present in the polysulfide. With the exception of Na<sub>2</sub>CO<sub>3</sub> (which can be removed by Ca(OH)<sub>2</sub> treatment), these impurities can be removed by treatment with H<sub>2</sub>S, thereby converting at least a portion of the impurities to polysulfide. Treated Na<sub>2</sub>S<sub>y</sub> is introduced into cell 56 via line 55.

The process incorporating salt recovery Scheme B is illustrated by reference to FIG. 3. The hydrogen sulfide-treated oil-salt dispersion removed from contactor vessel 22 is fed through line 26 to scrubbing tower 80 wherein it is contacted countercurrently with molten sodium polysulfide (Na<sub>2</sub>S<sub>x</sub>) that is introduced via line 95.

The tower is divided into a series of stages by foraminous plates 81 and is maintained at a temperature ranging from about 500 to 800° F., preferably 650 to 700° F., and a pressure ranging from about 50 to 500 p.s.i.g., preferably about 50 to about 100 p.s.i.g. The

sodium sulfide dispersed in the oil reacts with the sodium polysulfide to yield a molten sulfur-depleted polysulfide ( $\text{Na}_2\text{S}_y$  wherein  $y$  varies from 2.8 to 3.5), which drops from the oil and collects at the tower bottom. If necessary, additional hydrogen sulfide can be added to the melt through line 91 to effect conversion of by-product salts to the sodium polysulfide.

While the polysulfide contacting step has been shown here to be continuous, it may also be conducted as a batch operation. In general, the various means customarily employed in extraction processes to increase the contact area between the various materials can be employed. The apparatus is of a conventional nature and can comprise a single reactor or multiple reactors equipped with efficient stirring devices such as mechanical agitators, jet of restricted internal diameter, turbomixers and the like. The sodium polysulfide, i.e.,  $\text{Na}_2\text{S}_x$  and the oil/sodium sulfide mixture can be passed through one or more reactors in concurrent, crosscurrent or counter-current flow.

Excess hydrogen sulfide, hydrogen sulfide liberated in the  $\text{Na}_2\text{S}_x$ — $\text{NaSH}$  reaction and liberated water are removed from the reaction through line 50. After suitable drying (not shown) the hydrogen sulfide stream is recycled to the contactor vessel 22. As in the preceding case, desulfurized oil exits via line 29 for further processing and storage.

The molten sulfur-depleted polysulfide ( $\text{Na}_2\text{S}_y$  where  $y$  varies from 2.8 to 3.5) removed from the tower via line 96 is split into two parts. One portion is fed through line 94 to blend with a portion of the sulfur-rich polysulfide product entering from line 93. The ratio of sulfur-rich and sulfur-depleted polysulfide will be regulated by the value of  $x$  in the desired scrubbing agent,  $\text{Na}_2\text{S}_x$ . The remaining sulfur-depleted polysulfide in line 97 is blended with the remaining sulfur-rich polysulfide entering from line 92 and the resultant mixture is fed via line 52 to the electrolytic cells.

The process incorporating salt recovery Scheme C is illustrated by reference to FIG. 4. According to this scheme an excess amount (110–160 mole percent based on total salts contained in the oil) of hydrogen sulfide is added to the oil-salt dispersion in vessel 22 at a temperature of about 670°–800° F., preferably 680°–750° F. and at a pressure of about 50–500 p.s.i.g., preferably 100–200 p.s.i.g. The resultant mixture is then fed via line 26 to the settler vessel 82 which operates at conditions similar to those used in vessel 22. Residence time is on the order of 5 to 30 minutes, preferably about 15 minutes. Molten sodium hydrosulfide separates from the oil, collects at the bottom of the settler and is drawn off through line 83 which feeds directly to the polysulfide blending vessel 48 as noted in FIG. 1. Subsequent steps are identical to those described in FIG. 1. The product oil is withdrawn through line 29 and is processed according to Scheme A of FIG. 1.

The process variation noted as Scheme D is illustrated in FIG. 4. Molten sodium hydrosulfide is withdrawn from settler vessel 82 and fed via lines 83 and 84 to blending vessel 86, where it is contacted with molten sulfur (line 85) at a temperature between about 500°–800° F., preferably between 600° and 700° F. and at a pressure between atmospheric pressure and 100 p.s.i.g., preferably between atmospheric pressure and 50 p.s.i.g., rather than molten sodium polysulfide,  $\text{Na}_2\text{S}_x$ . The mole ratio of sulfur to  $\text{NaSH}$  is maintained in the range of 1:1 up to 3:1 but preferably at 1.5 to 2.0.

The sodium polysulfide product, i.e.,  $\text{Na}_2\text{S}_y$  withdrawn through line 99, is blended with pyrolyzer polysulfide product ( $\text{Na}_2\text{S}_x$ ) and fed via line 52 to the electrolytic cells. Liberated hydrogen sulfide is taken overhead through line 50 and is ultimately recycled to contacting vessel 22. The pyrolyzer vessel 60 is operated at conditions rela-

tively more severe than those used in Scheme A in order to furnish the volume of sulfur required.

A dry nitrogen stream (not shown) blankets the electrolytic cells. The electrolytic cells may comprise any cell capable of converting the 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 one embodiment of a cell unit is shown in FIG. 5. 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 physical separator and alkali ion conductor between the two cavities. 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 (current collector) 8, which also serves as the anode to form a complete circuit. Thus the anode for one cell becomes the cathode for the next. The cell cavity 5 may be partially or fully filled with a porous or non-porous electron-conducting material 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 56 comprises a plurality of individual cell units in order to provide a sufficient output of sodium.

A plurality of cells, e.g., about 100–200 cells may be operated in series in order to build up the overall voltage to about 280–700 volts. The total amount of cell area required depends on the amount of sodium required, and is in the range of about 20 to 70 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.

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 57 to surge vessel 58 and then to stripping vessel 60 which is partially evacuated, e.g., to an absolute pressure of about 10 to about 300 mm. Hg, preferably about 50 to 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 ranging from about 4.0 to about 4.9, preferably about 4.4 to about 4.8. At one-tenth atmosphere sulfur vapor pressure, for example, the composition in equilibrium therewith is approximately  $\text{Na}_2\text{S}_{4.82}$  at 700° F.,  $\text{Na}_2\text{S}_{4.73}$  at 750° F., and  $\text{Na}_2\text{S}_{4.64}$  at 800° F. The sulfur vapor is taken overhead through line 61 and condensed by conventional means (not shown). As indicated supra the resulting polysulfide is then recycled via line 49 to scrubbing tower 48. Alternatively, at least a



portion of the sodium polysulfide stream exiting from the cell can be contacted directly with the H<sub>2</sub>S-treated salt mixture, thereby by-passing the evacuating operation in vessel 60. Thus, for example, Na<sub>2</sub>S<sub>5</sub> exiting from the cell can be contacted directly with the H<sub>2</sub>S-treated salt mixture. The molten sodium is subsequently removed from the electrolytic cell through a current breaker (not shown) and passed via line 62 to surge vessel 63 where it is blended with makeup sodium entering at line 64 and then fed via line 65, pump 66 and line 67 to vessel 11.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will be more clearly understood by reference to the following examples:

##### Description of apparatus and procedures

(A) Sodium treatment reaction: The reactor consisted of a standard, one liter Paar autoclave, which was constructed of Monel steel. Two modifications were made, however. An oversized turbine blade stirrer head was substituted for the standard item to aid in lifting and dispersing sodium and its alloys, particularly the alloy with lead. Also, the dipleg was fitted with a 50 micron metallic filter element to aid in sampling the oil phase when mixtures of salts and oil were present. The reactor head contained the usual openings and fittings for measurement of pressure and temperature and for the addition of gases.

In the typical run the reactor was charged at room temperature with the desired quantity of sulfur-containing oil and freshly cut sodium. Alternatively, in some runs, sodium was added as an alloy with lead. The reactor was sealed and thoroughly flushed with nitrogen. About 50 p.s.i.g. of the flush gas was present when heatup was begun. The reactor temperature was brought to approximately 450° F. prior to beginning stirred contact, thereby minimizing the reaction time below the normal run temperature range of 600–700° F.

The yield of gaseous products, comprising materials lighter than or the same weight as pentane was determined by cooling the reactor to room temperature, venting the gases through a wet test flow meter to determine volume and then submitting a representative sample for component analysis by mass spectrometry.

Coke formed in the desulfurization reaction was most often recovered with the sodium salts and is reported as the water insoluble fraction of the salt.

Without exception, the combined coke and C<sub>5</sub><sup>-</sup> gas yield never amounted to more than 1.0 wt. percent of the feed and usually was less than 0.5 wt. percent on feed. Therefore, coke and gas yields are not reported in the examples which follow. Also, desulfurized oil recoveries were essentially quantitative in all examples.

(B) Hydrogen sulfide treatment preparatory to salt recovery: Hydrogen sulfide, was added directly to the reactor mixture contained in the sodium-treating reactor. Normally, the addition was made immediately at the end of the sodium treating step and at the same temperature employed in that step. A weighed amount of reagent was loaded into a 200 ml. stainless steel bomb which was then fitted to a reactor inlet valve. Hydrogen sulfide was injected under its own vapor pressure. The bomb, previously tared, was always reweighed after addition to determine the amount of reagent retained.

(C) Separation of the oil and salt phases: Again, the sodium-treating reactor was used. After injection of hydrogen sulfide, stirring was ceased for a time sufficient to allow the salt phase, either macrocrystalline solids or molten salts, to settle (the salts exhibit a density roughly twice that of oil). If desired, oil samples could then be withdrawn through the filter-modified dipleg while still at the approximate temperature of the sodium treating reaction. Ultimately, however, the reactor was cooled to about 200° F., opened and the bulk of the oil phase

decanted. Precipitated salts were slurry washed with toluene to remove adhering oil and then dried.

If the preparatory treatment was designed for generation of molten salts then the reactor was cooled to 200° F. without agitation. In this case the salts formed a solid layer on the reactor bottom and were removed with hammer and chisel. The solidified molten layer was subsequently crushed, washed with hydrocarbon and dried.

Salt recovery via blending with molten sodium polysulfide (Na<sub>2</sub>S<sub>x</sub>) required cooling the reactor to 200° F., adding the polysulfide as a powder and heating again to the melting point of the polysulfide end product. The molten salt recovery procedure was then used.

##### (D) Conversion of salts to sodium tetrasulfide

###### (Na<sub>2</sub>S<sub>y</sub>)

The reactor for this step consisted of a three neck, 500 ml. roundbottom flask made of Pyrex glass. The reactor was fitted with a stirrer, a temperature indicator probe, a gas inlet tube and a screw feeder for adding powdered solids.

Conversion of H<sub>2</sub>S-treated salts to sodium tetrasulfide was accomplished by melting the required amount of sodium pentasulfide (M.P. ~485° F.) in the reactor under an atmosphere of dry nitrogen. With the temperature adjusted to 600° F. (above the melting point of end-product salt), powdered H<sub>2</sub>S-treated salt was fed in by means of the screw feeder. Hydrogen sulfide evolution was instantaneous. Gentle stirring was used to break up solid crusts that formed on the surface from time to time. Upon completing the salt addition, the resultant melt was held for 15 minutes at 600° F. to insure complete reaction. A continuous nitrogen sweep was employed to carry the evolved H<sub>2</sub>S to a sodium hydroxide scrubber. Upon completion of the heating period, the melt was cooled to room temperature, pulverized and stored under nitrogen.

When small samples of the H<sub>2</sub>S-treated salts were converted (10 g. or less), the salts were simply premixed with polysulfide and heated to 600° F.

Sulfur can be substituted for the sodium pentasulfide reactant, in which case the powdered sulfur and H<sub>2</sub>S-treated salts are premixed and then heated to 600° F. Hydrogen sulfide evolution is rapid beginning at about 400° F. and is complete by the time a homogeneous melt is obtained at 600° F.

(E) Electrolysis of sodium tetrasulfide (Na<sub>2</sub>S<sub>y</sub>) (sodium regeneration—proposed technique): The laboratory electrolytic cell consists of a beta-alumina tube sealed into a Pyrex glass reservoir for sodium metal and surrounded by graphite felt packing. The outer shell of stainless steel serves as the anode current collector. The cell has a bottom inlet line and a top outlet line. Molten sodium acts as the cathode current contact. Molten sodium tetrasulfide is fed through the bottom inlet line and sodium pentasulfide product is withdrawn through the top outlet line just below the sodium reservoir. Since molten sodium acts as the cathode surface, it is necessary to load sodium in the beta-alumina tube prior to startup.

(F) Pyrolysis of sodium pentasulfide (Na<sub>2</sub>S<sub>5</sub>) (sulfur recovery): The apparatus for this step consists of a roundbottom Pyrex flask fitted with a nitrogen inlet tube, temperature indicator probe and an outlet line connected to a chilled receiver and vacuum pump.

In a proposed run, sodium pentasulfide is charged to the flask and brought to the desired temperature and pressure. A slow nitrogen bleed into the melt is used to regulate the vacuum and to provide stirring. Sulfur vapor swept from the flask is collected in the chilled receiver. The pyrolysis rate and depth of pyrolysis, i.e., approach to Na<sub>2</sub>S<sub>4</sub>, can be increased by raising the temperature and/or lowering the pressure.

(G) Salt analyses: The total analysis of sodium sulfide mixtures was based on the procedure outlined in Scott's Standard Methods of Chemical Analysis, 5th edition (1939), vol. 2, pp. 2181–2187. The procedure does not differentiate between the various polysulfides; therefore,

polysulfide samples were always analyzed for total sodium and total sulfur content to establish the probable molecular formula.

(H) Oil product analyses: Sodium-treated oil products were analyzed not only for sulfur content, but also for changes in metals content and general physical properties such as API gravity, viscosity and asphaltene content. The oil product obtained from each recovery scheme was filtered hot through a number 2 grade Whatman paper prior to analysis. Also a sample of the filtered oil was always refluxed in toluene with a small amount of acetic acid to decompose any salts that escaped filtration and particularly oil soluble salts such as the sodium mercaptides.

Hydrogen sulfide was liberated from any  $\text{Na}_2\text{S}$  or  $\text{NaSH}$  that escaped filtration. The salt product from this step was sodium acetate which was filtered from solution. Finally, desulfurized oil was recovered by distillation. The acetic acid-treated sample was used as a control to establish the effectiveness of the salt recovery procedure being evaluated, i.e., to determine how much sodium (in the form of the salt) was left in the oil after extraction. Also, it was the practice to sample the sodium-treated oil prior to testing a salt recovery scheme and removing the salts by decomposing with acetic acid. This allowed a comparison of the properties of desulfurized oil both before and after the particular salt recovery procedure being evaluated.

(I) Sulfur-containing feedstocks: This invention has been demonstrated with several different sulfur-containing feedstocks. These include both the  $650+^\circ\text{F}$ . and  $1030+^\circ\text{F}$ . fractions of the Bachequero and Tia Juana crudes from South America and also the Kuwait and Safaniya crudes from the Middle East. Examples hereinbelow however, are all based on the  $650+^\circ\text{F}$ . Safaniya fraction, which is considered to be typical of the residuum feeds to be encountered commercially. The properties of this feed are noted below.

#### INSPECTIONS OF SAFANIYA ATMOSPHERIC RESIDUUM

API gravity	14.4
Sulfur, wt. percent	4.1
Nitrogen, wt. percent	0.26
Oxygen, wt. percent	0.27
Metals, p.p.m. (w.):	
Ni	20
V	77
Fe	4
Viscosity, VSF at $122^\circ\text{F}$ .	235
Pour point, $^\circ\text{F}$ .	33
Percent boiling below $1030^\circ\text{F}$ .	59.2
Percent boiling above $1030^\circ\text{F}$ .	40.8

#### EXAMPLE 1

The data below relate to Recovery Scheme A of the specification in which hydrogen sulfide is used to induce agglomeration of the microcrystalline salts.

To the product mixture obtained from contacting 391 g. (contains 0.476 g.-atom sulfur) Safaniya Atmospheric Residuum with 24.8 g. (1.07 g.-atom) sodium at  $650^\circ\text{F}$ . under 150 p.s.i.g. hydrogen, there was added 7.7 g. (0.23 mole) of hydrogen sulfide. The addition was made at  $650^\circ\text{F}$ . with stirring. The  $\text{H}_2\text{S}$  reacted instantly and no measurable increase in reactor pressure was noted. The amount of  $\text{H}_2\text{S}$  added constituted approximately 35 mole percent based on the total moles of salts present in the oil. The reactor temperature was raised to  $685^\circ\text{F}$ . for a 5 minute stirred contact time to insure that  $\text{NaSH}$  produced by  $\text{H}_2\text{S}$  treating would melt. The temperature was then dropped back to room temperature.

Desulfurized oil was decanted from the bomb, leaving a slurry of precipitated salts. The salts were subsequently washed with toluene to remove adhering oil and then dried under vacuum. There was recovered 40.5 g.

of a tan colored salt which had a particle size in the 150–200 micron range, a material suitable for recovery by filtration or centrifuged action such as provided by liquid cyclones.

Salt analysis, Table 1, revealed (1) that  $\text{H}_2\text{S}$  treatment converted substantially all of the by-product salts with the exception of  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{S}$  to  $\text{NaSH}$  and (2) that the salt mixture now contained 98.7 mole percent of desirable components, i.e., components that could be converted to the electrolysis feed,  $\text{Na}_2\text{S}_4$ .

TABLE 1

Component:	Mole percent
$\text{Na}_2\text{CO}_3$	1.26
$\text{Na}_2\text{S}_2$	0.99
$\text{Na}_2\text{S}$	60.80
$\text{NaSH}$	36.90
$\text{NaOH}$	0.00
$\text{Na}_2\text{SO}_3$	0.00
$\text{Na}_2\text{S}_2\text{O}_3$	0.00
$\text{Na}_2\text{SO}_4$	0.00

Conversion to the  $\text{Na}_2\text{S}_4$  compound was accomplished by blending 20 g. of the salt with 176 g. (0.855 mole) of sodium pentasulfide and heating the mixture in a stirred flask at  $600^\circ\text{F}$ . for 30 minutes. Hydrogen sulfide evolution began when the first signs of melting were noted at above  $500^\circ\text{F}$ . and was complete when the sample became a homogeneous melt at  $600^\circ\text{F}$ . The hydrogen sulfide evolved was collected in dilute sodium hydroxide solution which subsequently was analyzed for sulfide content. The value determined was equivalent to 0.05 mole of  $\text{H}_2\text{S}$  or about 92% of the theoretical amount expected.

Analysis of salt product, Table 2, showed a residual  $\text{NaSH}$  content of less than 2 mole percent and a reduction of sodium carbonate to less than 0.5 mole percent. The analytical procedure does not differentiate between the various polysulfides, hence the notation  $\text{Na}_2\text{S}_R$ . Sodium and sulfur analysis, however, closely checked the theoretical values for the desired  $\text{Na}_2\text{S}_4$  product.

TABLE 2

Component:	Mole percent
$\text{Na}_2\text{CO}_3$	0.42
$\text{NaSH}$	1.81
$\text{Na}_2\text{S}_R$	97.77

<sup>1</sup> Sample analyzed for 27.1 wt. percent Na and 73.1% sulfur. Theoretical for  $\text{Na}_2\text{S}_4$  is 26.4 wt. percent Na, and 73.6 wt. percent sulfur.

It is assumed that a somewhat more stringent treat with  $\text{Na}_2\text{S}_5$  will entirely eliminate residual  $\text{NaSH}$ , thereby providing an exceptionally pure  $\text{Na}_2\text{S}_4$  melt for the electrolytic regeneration of sodium. The carbonate impurity is deemed to be at sufficiently low concentration not to cause trouble with electrolysis. The carbonate concentration would be controlled by taking a purge stream from the molten salt feed to electrolysis.

Desulfurized oil decanted from the salt slurry was combined with oil recovered from the toluene wash used in salt purification and was filtered hot ( $160^\circ\text{F}$ .) through number 2 grade Whatman paper to remove suspended salts. The sample was then split into two parts, one for direct analysis and the other for treatment with acetic acid, to decompose any submicron sodium salts or oil soluble sodium salts such as might be contained as sodium mercaptides ( $\text{NaSR}$ ). Upon filtration of the acid-treated sample, there was obtained a small amount of sodium acetate which corresponded roughly to the difference in oil sodium contents of the untreated and acid treated samples (Table 3).

The data indicate that about 650 p.p.m. sodium remains in the oil after sodium salt recovery via Scheme A, but that it can be reduced to a level of  $<50$  p.p.m. by treat-

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ment with acid. Also the increase in API gravity and drop in asphaltene content shows that the reaction has actually improved the quality of the oil.

TABLE 3.—DESULFURIZED SALT ANALYSES

Sample	(Feed)	Desulfurized oil	
		Filtered	Acid treated
Sulfur, weight percent.....	3.9	0.532	0.529
Asphaltenes, weight percent.....	14.9	7.8	.....
Vanadium, p.p.m.....	77	29	26
Sodium, p.p.m.....	<5	650	43
API gravity.....	14.4	19.4	.....

## EXAMPLE 2

This example relates to Recovery Scheme C of the specification in which the desulfurization salts are removed from the oil as a molten phase of sodium hydrosulfide. In this example the desulfurization reaction was carried out with sodium alone.

In the desulfurization reaction 403.5 g. (contains 0.492 g.-atom sulfur) of Safaniya Atmospheric Residuum was contacted with 28.1 g. (1.22 g.-atom) sodium under an atmosphere of nitrogen for one hour at 650° F. Approximately 34 g. (1.0 mole) of hydrogen sulfide, about 20 mole percent in excess, was injected into the reactor, thereby increasing the reactor pressure from 80 to 220 p.s.i.g. The reactor temperature was raised to 685° F., held there for 15 minutes with stirring and then dropped to room temperature without stirring. Excess hydrogen sulfide was flushed from the reactor prior to opening.

Upon decanting the oil phase, the salts were observed to be plated out on the reactor internal surfaces, particularly on the bottom of the reactor, thus indicating that a molten salt phase had formed at 685° F. In commercial operation the molten layer would be withdrawn continuously from an appropriately designed settling vessel. The solid salts were removed from the reactor, washed with toluene to remove oil and then dried under vacuum. There was recovered 48.5 g. of salt (no attempt at quantitative recovery) which gave the analysis shown below in Table 4.

TABLE 4.—ANALYSIS OF HYDROGEN SULFIDE PRECIPITATED SALT

Component	Weight percent	Mole percent (normalized)
Water insoluble.....	2.6	.....
Na <sub>2</sub> SO <sub>3</sub> .....	0.0	.....
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .....	0.0	.....
Na <sub>2</sub> SO <sub>4</sub> .....	0.8	0.3
NaOH.....	0.0	.....
Na <sub>2</sub> CO <sub>3</sub> .....	1.6	3.4
Na <sub>2</sub> S <sub>2</sub> .....	2.4	1.2
Na <sub>2</sub> S.....	0.0	.....
NaSH.....	94.3	95.1

As noted, the treat with excess H<sub>2</sub>S has eliminated all undesirable by-product salts, with the exception of sodium sulfate and carbonate. The water insoluble fraction is coke, which undoubtedly would slag on the surface of the NaSH melt in commercial operation.

Conversion to sodium tetrasulfide was accomplished by blending 20 g. of the salt with 117 g. (0.568 mole) of sodium pentasulfide and heating at 600° F. for 30 minutes. Evolution of hydrogen sulfide began as soon as melting was observed, at about 500° F., and was complete when a homogeneous melt was obtained at 600° F.

The H<sub>2</sub>S collected (5.75 g.) amounted to about 101% of the theoretical amount expected. Analysis of the melt, Table 5, shows that a remarkably pure polysulfide product was formed with the only significant contaminate being sodium sulfate. Elemental analysis supports the proposed Na<sub>2</sub>S<sub>4</sub> formula of the polysulfide product.

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TABLE 5

Analysis of the polysulfide melt <sup>1</sup>

Component:	Mole percent (normalized)
Na <sub>2</sub> S <sub>R</sub> .....	99.5
Na <sub>2</sub> CO <sub>3</sub> .....	0.3
Na <sub>2</sub> SO <sub>4</sub> .....	0.2

<sup>1</sup> Melt analyzed for 26.8% Na, 72.2% S; calculated value for Na<sub>2</sub>S<sub>4</sub> is 26.4% Na, 73.6% S.

Inspections made on the recovered oil product are shown in Table 6. The sodium content of the oil is substantially lower than that of the oil obtained in Example 2. The data suggest that salt recovery by generating molten NaSH with excess amounts of H<sub>2</sub>S is an effective recovery procedure. It is noted further that sodium treating is very effective for reducing the sulfur content of the oil without degrading the oil properties. In this case some improvement in oil properties is noted as manifested in the higher API gravity value and lower viscosity value.

TABLE 6.—INSPECTIONS ON DESULFURIZED OIL

Sample	Feed	Na-treated
Inspection:		
Sulfur, weight percent.....	3.9	0.41
Asphaltenes, weight percent.....	14.9	13.4
Vanadium, p.p.m.....	77	64.8
Sodium, p.p.m.....	<5	150
API gravity.....	14.4	17.3
Viscosity, VSF <sup>1</sup> at 122° F.....	235	200

<sup>1</sup> Viscosity Sabolt Furol.

## EXAMPLE 3

The data below illustrate the results obtained using Recovery Scheme D, which is essentially the same as Scheme C, except that sulfur is substituted for sodium pentasulfide in the NaSH conversion step.

To demonstrate this step, 20 g. of a H<sub>2</sub>S-treated salt mixture containing 96.0 wt. percent (98.30 mole percent-normalized) NaSH was blended with 16.9 g. (0.529 g.-atom) of elemental sulfur and then heated at 600° F. for 30 minutes. Hydrogen sulfide evolution began at about 300° F. and was complete when a homogeneous melt was obtained at 600° F. There was recovered 31 g. of melt which exhibited the analysis given in Table 7 below. The elemental analysis on the melt (Footnote 1) shows that the desired salt, Na<sub>2</sub>S<sub>4</sub> was obtained.

TABLE 7

Analysis of polysulfide melt <sup>1</sup>

Component:	Mole percent
Na <sub>2</sub> S <sub>R</sub> .....	98.8
Na <sub>2</sub> SO <sub>4</sub> .....	1.2

<sup>1</sup> Melt analyzed for sodium 27.0%, S, 72.8%; calculated for Na<sub>2</sub>S<sub>4</sub> is Na, 26.4%, S, 73.6%.

It is noted that low pressure hydrogen, e.g., less than about 500 p.s.i.g., for example 200 p.s.i.g., may be admitted to the desulfurization zone, if desired, in order to suppress organo metallic salt formation during the sodium-contacting step; this desulfurization embodiment may be used in conjunction with any of Schemes A to D.

What is claimed is:

1. A process for the desulfurization of a sulfur-containing petroleum oil stock comprising contacting said oil stock with a desulfurization agent comprising an alkali metal or an alloy thereof, at desulfurization conditions, thereby forming a mixture comprising oil of reduced sulfur content containing alkali metal salts dispersed therein and contacting said mixture with H<sub>2</sub>S, thereby disengaging a substantial portion of said alkali metal salts from said oil.

2. The process of claim 1 wherein said mixture is contacted with about 10 to about 400 mole percent H<sub>2</sub>S, based on total moles of salt present in said mixture.

3. The process of claim 1 wherein said mixture is contacted with  $H_2S$  at a temperature ranging between about 600 and 800° F. and at a pressure ranging between about 25 and 50 p.s.i.g.

4. The process of claim 1 wherein said alkali metal is sodium.

5. The process of claim 2 wherein the desulfurization is conducted at a temperature ranging between about 450 and 750° F. and at a pressure ranging between about 10 and 600 p.s.i.g.

6. A process for the desulfurization of a sulfur-containing petroleum oil stock comprising contacting said oil stock with a desulfurization agent selected from the group consisting of sodium and alloys thereof, at desulfurization conditions, thereby forming a mixture comprising oil containing alkali metal salts, contacting at least a portion of said mixture with  $H_2S$  thereby forming a mixture comprising an oil phase of reduced sulfur content and a salt phase, contacting the  $H_2S$ -treated mixture with a sulfur-rich sodium polysulfide thereby forming a sulfur-depleted sodium polysulfide, and, thereafter using at least a portion of said sulfur-depleted sodium polysulfide as an electrolyte in an electrolytic cell for the production of sodium.

7. The process of claim 6 wherein said sulfur-rich sodium polysulfide is  $Na_2S_5$ .

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

9. The process of claim 6 wherein the amount of  $H_2S$  added to the sodium-treated mixture ranges between about 10 and 80 mole percent based on total moles of salt present in the mixture.

10. The process of claim 6 wherein said sulfur-rich sodium polysulfide is represented by the formula  $Na_2S_x$  where  $x$  takes values ranging from about 4.0 to 4.9 and said sulfur-depleted sodium polysulfide is represented by the formula  $Na_2S_y$  where  $y$  takes values ranging from about 2.8 to 4.5.

11. The process of claim 10 wherein  $y$  varies from about 2.8 to 3.5.

12. A process for the desulfurization of a sulfur-containing petroleum oil stock comprising contacting said oil stock with a desulfurization agent selected from the group consisting of sodium and alloys thereof, at desulfurization conditions, thereby forming a mixture comprising oil containing alkali metal salts, contacting at least a portion of said mixture with  $H_2S$  thereby forming a mixture comprising an oil phase of reduced sulfur content and a salt phase, then separating said salt phase from said oil phase and contacting at least a portion of said salt phase with a sulfur-rich sodium polysulfide thereby forming a sulfur-depleted sodium polysulfide, and thereafter using at least a portion of said sulfur-depleted sodium polysulfide as an electrolyte in an electrolytic cell for the production of sodium metal.

13. The process of claim 12 wherein the amount of  $H_2S$  added to the sodium-treated mixture ranges between about 10 and 400 mole percent, based on total moles of salt present in said mixture.

14. The process of claim 12 wherein said sulfur-rich sodium polysulfide is represented by the formula  $Na_2S_x$  where  $x$  takes values ranging from about 4.0 to 4.9 and

said sulfur-depleted sodium polysulfide is represented by the formula  $Na_2S_y$  where  $y$  takes values ranging from about 2.8 to 4.5.

15. The process of claim 12 wherein said electrolytic cell comprises an anodic cavity containing polysulfide anions and a cathodic cavity containing sodium metal, said anodic and cathodic cavities separated by a sodium ion-conducting membrane comprising beta-alumina.

16. A process for the desulfurization of a sulfur-containing petroleum oil stock comprising contacting said oil stock with a desulfurization agent selected from the group consisting of sodium and alloys thereof, at desulfurization conditions, thereby forming a mixture comprising oil containing alkali metal salts, contacting at least a portion of said mixture with  $H_2S$  thereby forming a mixture comprising an oil phase of reduced sulfur content and a salt phase, then separating said salt phase from said oil phase and contacting at least a portion of said salt phase with sulfur thereby forming sodium polysulfide, and thereafter using at least a portion of said sodium polysulfide as an electrolyte in an electrolytic cell for the production of sodium metal.

17. The process of claim 16 wherein said electrolytic cell comprises an anodic cavity containing polysulfide anions and a cathodic cavity containing sodium metal, said anodic and cathodic cavities separated by a sodium ion-conducting membrane comprising beta-alumina.

18. The process of claim 16 wherein the amount of  $H_2S$  added to the sodium-treated mixture ranges between about 110 and 400 mole percent, based on total moles of salt present in said mixture.

19. The process of claim 16 wherein said sodium polysulfide is represented by the formula  $Na_2S_y$  where  $y$  takes values ranging between about 2.8 and 4.5.

20. The process of claim 16 wherein said oil phase is separated from said salt phase and contacted with an acid comprising dilute sulfuric acid or acetic acid.

21. The process of claim 16 wherein the sodium alloy is sodium-lead.

22. The process of claim 6 wherein said oil phase is separated from said salt phase and contacted with an acid comprising dilute sulfuric acid or acetic acid.

23. The process of claim 12 wherein said oil phase is separated from said salt phase and contacted with an acid comprising dilute sulfuric acid or acetic acid.

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DELBERT E. GANTZ, Primary Examiner

J. M. NELSON, Assistant Examiner

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