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CYCLIC PROCESS FOR DESULFURIZING CRUDE PETROLEUM
FRACTIONS WITH SODIUM

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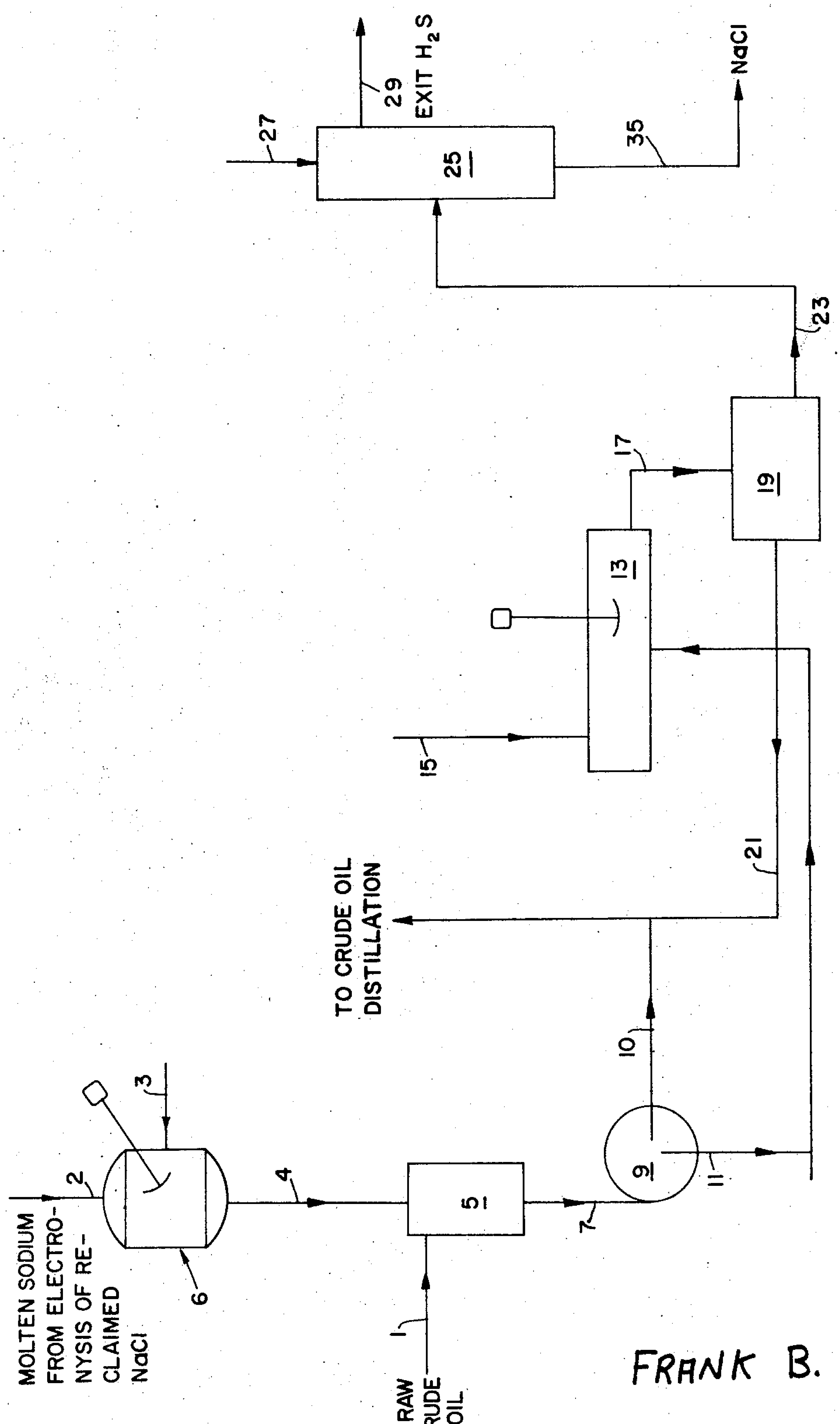

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CYCLIC PROCESS FOR DESULFURIZING CRUDE PETROLEUM FRACTIONS WITH SODIUM

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ABSTRACT OF THE DISCLOSURE

An integrated process for the desulfurization of crude oil or similar virgin hydrocarbon fractions wherein a dispersion of metallic sodium is employed to react with the sulfur contaminants present within such crude oil to form a sodium sulfide precipitate eliminated from the treated crude through centrifugation. The integrated system is provided by reacting the sodium sulfide precipitate with hydrochloric acid to produce sodium chloride which after reclamation can be employed through electrolysis to provide the necessary sodium for desulfurization of the crude oil.

The present invention relates to a process for the desulfurization of crude oils or similar virgin hydrocarbon fractions and, more particularly, to an integrated process of desulfurizing such crude oils wherein metallic sodium is employed.

Due to the ever-increasing concern about air pollution, a great deal of study has been conducted in recent years to develop efficient and economical means of reducing the sulfur content present in crude petroleum oils and other virgin hydrocarbon fractions. In this respect, tolerances are now being set which limit the maximum sulfur content permissible in various types of refined petroleum products. Thus, for example, heating oils, gasolines, etc., will be limited to strict tolerances in the maximum amount of sulfur content present therein so as to effect a reduction of the air pollution associated with the burning of such petroleum products having high sulfur contents.

While various and sundry process and techniques for reducing the sulfur content of hydrocarbon fractions have been developed in the past, most of such processes have involved complicated and expensive catalytic reactions, which reactions cannot be economically, justifiably employed to reduce the sulfur content of the hydrocarbon material below those limits which are now being set. Accordingly, there has been a great deal of concern and investigation relative to the production of a simple and efficient method of reducing the sulfur content of hydrocarbon fractions, particularly crude oil and similar virgin hydrocarbon materials.

While the use of alkali metals in the refining of hydrocarbon oils has been previously proposed, such use of alkali metals has been generally limited to the treatment of refined petroleum fractions, the treatment being conducted at elevated temperatures for the purpose of removing an insoluble "polymer" from the refined hydrocarbon fraction. In this respect, U.S. Patent 1,952,616 is exemplary of those patents dealing with the refining of hydrocarbon materials, e.g. fractionated lubricating oils with a molten alkali metal at an elevated temperature so as to produce and agglomerate a "polymer" byproduct and separate such insoluble material from the refined oil. Similarly, where it has been proposed to employ alkali metals for the desulfurization of hydrocarbon oils, such desulfurization has generally been conducted by heating a refined petroleum distillate or fraction with a molten alkali metal at a suitable temperature so as to cause the necessary reaction between the alkali metal, e.g. sodium, and sulfur content of the refined hydrocarbon fraction.

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The process of the present invention is clearly distinguished from any of these prior art processes by providing a simple, efficient unitary process for the desulfurization of crude oils and other virgin petroleum fractions by the utilization of sodium metal. Thus, in accordance with the present invention, the sulfur content and metallic content of crude petroleum fractions are reduced below acceptable maximum limits by reacting the crude petroleum fraction with a dispersion of sodium metal at ambient temperatures, a solution of sodium chloride suitable for replenishing the supply of sodium metal through electrolysis being produced by a reaction of the sodium sulfide dispersion, obtained by reacting the crude petroleum fraction with the dispersion of sodium, with hydrochloric acid. Accordingly, a unitary, cyclic process is provided wherein the desulfurization of crude petroleum oils and other virgin petroleum fractions is provided in a simple and efficient manner.

Accordingly, it is a principal object of the process of the present invention to provide a method for the desulfurization of crude petroleum fractions, e.g. crude oil, in a manner which eliminates the inherent disadvantages and deficiencies of prior art processes.

It is yet a further object of the process of the present invention to provide such a process for the desulfurization of crude oil and other virgin petroleum fractions wherein a dispersion of sodium metal is employed to react with the crude oil at ambient temperature so as to remove sulfur and metal contaminants.

A further object of the present invention is to provide a simple and efficient cyclic process for the desulfurization of crude petroleum fractions so as to reduce the sulfur content thereof below maximum acceptable limits, such desulfurization being conducted by reacting the crude petroleum oil with a dispersion of sodium metal with subsequent replenishing of the sodium metal employed.

A still further object of the process of the present invention comprises a desulfurization of crude petroleum oils wherein the sodium sulfide precipitate formed by the reaction of sodium metal with the crude oil is further reacted with hydrochloric acid so as to produce a solution of sodium chloride useful in the production and replenishing of sodium metal by electrolysis.

Still further objects and advantages of the novel process of the present invention will become more apparent from the following more detailed description thereof and the descritpion of the accompanying drawings wherein the figure is a diagrammatic representation of the process of the present invention.

As described previously, the process of the present invention is applicable to the desulfurization of crude or virgin petroleum oils. Thus, in accordance with the process of the present invention, a cold crude oil or other virgin hydrocarbon fraction is desulfurized and the metal contaminants removed therefrom by contacting such cold crude oil or other virgin hydrocarbon fraction with a dispersion of sodium metal. In this respect, the reaction between the sodium metal and the sulfur contaminants present in the cold crude oil or other virgin hydrocarbon fraction can be simply represented as follows:

$$2Na + S \rightarrow Na_2S$$

As can be seen from the above, the desulfurization of the cold crude oil or other virgin hydrocarbon fraction in accordance with the process of the present invention is accomplished by the formation of sodium sulfide formed as a precipitate by the reaction of sodium metal with the sulfur contaminants. In addition, metal contaminants present in the cold crude oil or other virgin hydrocarbon fraction will be displaced in a similar manner by the sodium metal and, accordingly, will appear either as a sulfide of the displaced metal or as a pure metal itself in precipitated and agglomerated form. The basic metal contaminants found in crude oil include, for example, nickel, molybedenum, vanadium and cobalt. Since all of these metals are heavier than sodium, and more electro-negative than sodium, they will be displaced by the addition of the sodium dispersion to the cold crude oil or other virgin hydrocarbon fraction.

It can therefore be seen that the contacting of the crude oil with a dispersion of sodium metal acts in a two-fold manner, i.e., to reduce the sulfur content of the crude oil or other virgin hydrocarbon fraction by the formation of a precipitate, i.e., sodium sulfide, and to remove metal contaminants generally present in the crude petroleum fraction by a displacement of the same with the sodium metal. Most important, however, is the reduction of the sulfur content by the utilization of the dispersion of sodium metal since, as noted previously, there has been a great deal of concern recently relative to air pollution, etc., relating to the high sulfur content of fuels and similar petroleum products utilized.

In addition to providing for desulfurization and demetallization of the cold crude oil or other virgin hydrocarbon fraction, the process of the present invention further includes a method of replenishing the sodium metal employed in the sodium dispersion utilized in the desulfurization and demetallization of the present invention. This is accomplished by reacting the precipitated sodium sulfide with hydrochloric acid so as to produce a solution of sodium chloride which can be employed to provide replenished sodium metal through electrolysis.

The process of the present invention, including the cyclic nature thereof, can best be described by reference to the accompanying drawings.

As shown in the figure, a raw crude oil or similar virgin petroleum fraction enters through line **1** into a contactor **5** where it is combined with a dispersion of sodium metal entering the contactor **5** through line **4**.

The dispersion of sodium metal entering contactor **5** through line **4** is produced by mixing a molten sodium such as produced from the electrolysis of sodium chloride in a dispersion vessel **6**, the molten sodium entering such vessel through line **2**. The dispersion is produced by mixing the molten sodium with a normally liquid hydrocarbon entering the dispersion vessel **6** through line **3**. Suitable hydrocarbons used for producing the dispersion of sodium metal employed in accordance with the present invention include, for example, n-butane, isobutane, n-hexane, n-heptane, n-octane, etc.

In the contactor **5**, which need not be operated at elevated temperatures and which preferably operates at ambient temperatures the sulfur contaminants present in the cold crude oil or other virgin hydrocarbon fraction combine with the sodium metal of the sodium dispersion to produce a precipitate of sodium sulfide. This reaction can be simply represented as:

$$2Na+S\rightarrow Na_2S$$

In addition, the metal contaminants present in the crude oil or other virgin hydrocarbon fraction, e.g., primarily nickel, molybdenum, vanadium and cobalt will be displaced by the sodium metal of the dispersion, and will appear precipitated either as metallic sulfides or the pure metal.

The desulfurized crude oil along with precipitated sodium sulfide and other procipitated metals or metallic sulfides leave the contactor **5** through line **7**, and enters a centrifuge or similar apparatus **9** wherein the precipitated sodium sulfide and other precipitated metals, etc., are removed by centrifugal force. The precipitate, containing the sodium sulfide contaminant and metal contaminants leaves the centrifuge **9** through line **11** and subsequently charged to a repulper **13**. In the repulper **13**, a slurry is produced by contacting the precipitate from centrifuge **9** with a light hydrocarbon fraction, e.g., butane, hexane, heptane, etc., entering the repulper **13** through line **15**. While not shown in the figure, such light hydrocarbon fraction can result from the further distillation and fractionation of the disulfurized crude oil produced in accordance with the present invention, the light hydrocarbon fraction being only one fraction produced from the fractional distillation of the crude oil.

The slurry produced in repulper **13** exits through line **17** and enters a filter **19**, preferably operated continuously. The filter employed can be any conventional filter press or similar apparatus generally employed to separate liquid and solid portions from slurrys, dispersions and similar systems. From filter **19** the filter liquor consisting of the desulfurized petroleum fraction containing some light hydrocarbon leaves through line **21** and combines with the liquor leaving centrifuge **9** through line **10**. The combined filter liquor from centrifuge **9** and filter **19** is now ready for further crude oil distillation and fractionation in order to provide the desired petroleum products. Such petroleum products will now have a sulfur content below acceptable maximum limits since the sulfur contaminants present in the crude oil or other virgin hydrocarbon fraction have been removed pursuant to the reaction of the virgin hydrocarbon fraction with the dispersion of sodium metal. The crude oil distillation or similar fractionation is not illustrated in the figure, and any conventional workup of the desulfurized crude oil can be utilized. Again, as indicated previously, such distillation and fractionation of the desulfurized crude oil or other virgin hydrocarbon fraction can provide the light hydrocarbon fractoin employed in repulper **13** to wash the precipitate from centrifuge **9**.

The washed sodium sulfide exits the filter **19** through line **23** from which it enters a reaction vessel **25** wherein it is combined with hydrochloric acid entering reaction vessel **25** through line **27**. The reaction of the washed sodium sulfide precipitate with hydrochloric acid produces hydrogen sulfide which exits reactor **25** through line **29** and sodium chloride leaving through line **35**. The reaction which takes place in reactor **25** can be exemplified as follows:

$$Na_2S+2HCl\rightarrow H_2S+2NaCl$$

The liquid product of reactor **25** exiting through line **35** and containing sodium chloride can be sent to any conventional sodium chloride and other metalic chloride reclaiming system. After providing the required sodium chloride through conventional reclamation, such sodium chloride can be employed in an electrolytic cell to produce the sodium metal initially utilized in the desulfurization of the crude oil or other virgin hydrocarbon fraction. The electrolytic cell (not shown) can comprise any conventional electrolytic cell which is uitlized to produce sodium metal and chlorine by the electrolysis of sodium chloride. In this respect, suitable electrolytic cells include, for example, a conventional Downs or Chlorometal cell employing molten sodium chloride as an electrolyte. The molten sodium which is produced from such electrolysis of molten sodium chloride can be used directly in dispersion vessel **6** to produce the sodium dispersion vessel **6** to produce the sodium dispersion utilized in the desulfurization process. Here again, the light hydrocarbon fraction entering through line **3** into dispersion vessel **6** can be separately supplied or can be a portion of the light hydrocarbon fraction produced from the further distillation and fractionation of the desulfurized crude oil.

The hydrogen sulfide which leaves reactor **25** through line **29** can be utilized in any convenient manner. Thus, for example, it is possible to react the hydrogen sulfide in a Claus reactor (not shown) with air so as to provide molten elemental sulfur as a byproduct of the integrated process of the present invention.

As seen from the above description of the process in conjunction with the figure, the process of the present invention comprises an easy and efficient way of reducing the sulfur content of crude oils and other virgin petroleum fractions below acceptable maximum limits while providing sodium chloride as a byproduct of the integrated process. This sodium chloride produced as a primary byproduct of the desulfurization reaction in accordance with the process of the present invention can be used as a source of the sodium metal employed as a sodium dispersion in the desulfurization reaction. Thus, by employing the sodium chloride as the electrolyte in a contentional electrolytic cell, it is possible to produce sodium metal which when dispersed in a light hydrocarbon fraction can be suitably employed as the desulfurization medium.

While the amounts of the various components employed in the desulfurization process are in no way critical to the sucessful desulfurization of the crude oil or other virgin hydrocarbon fraction, generally, the light hydrocarbon fraction dispersion of sodium metal is employed in an amount so that the same corresponds to about .001% to about 10% by weight of the crude oil contacted therewith. Of course, the amount of sodium dispersion necessary for the desulfurization of the crude oil or other virgin hydrocarbon fraction will depend on the total sulfur contaminants present in the crude oil and in the degree of desulfurization desired. The above amounts, however, are generally those suitable for providing a desulfurized crude oil or other virgin hydrocarbon fraction within maximum specified limits of sulfur content.

Similarly, the dispersion of sodium metal in the light hydrocarbon fraction can vary considerably with respect to sulfur content; here again, the sulfur content of such varying depending on the amount of sulfur contaminants present in the crude oil and in the degree of desulfurization desired. Also, however, the nature of the sodium dispersion is dependent to a minor extent on the stability of the sodium metal dispersed in the light hydrocarbon fraction. Generally, sodium metal dispersions containing from about 10% to about 80% solid content are utilized. Of course, lesser or greater amounts of the dispersed sodium metal can be employed where desired for particular purposes.

The present invention will now be described by reference to following specific example. It is to be understood, however, that such example is presented for purposes of illustration only, and the present invention is in no way to be deemed as limited thereto.

EXAMPLE

In accordance with the present invention, a crude Pennsylvania oil which has not been previously refined for the elimination of any containants or the removal of any undesirable constituents is contacted for a period of one minute at ambient temperatures with a dispersion of sodium metal in butane, the sodium content of such dispersion being approximately 30% by weight. The dispersion of sodium metal and raw crude oil are introduced continuously into a contractor with agitation so that the dispersion at all times corresponds to approximately 5% by weight of the contents of the contractor. The contents of the contractor are continuously withdrawn and delivered to a centrifuge which provides a desulfurized liquor for further crude oil distillation and fractionation and a precipitate containing sodium sulfide in a minor amount of precipitated metals. The precipitate from the centrifuge is fed to a repulper wherein the precipitate is washed with a stream of butane in a sufficient amount to rid the precipitate from unwanted contaminants and provide a slurry of sodium sulfide which is subsequently

filtered and reacted with hydrochloric acid to provide sodium chloride and hydrogen sulfide byproducts. After removal of residual light hydrocarbon from the sodium chloride byproduct, the sodium chloride is melted and used as the molten electrolyte in a Chlorometal electrolytic cell employing a molten lead cathode. The electrolysis of the molten sodium chloride in the electrolytic cell provides a stream of molten sodium as a primary product with gaseous chlorine being evolved. The molten sodium is then ready for reuse as a dispersion for the desulfurization of further crude oil by admixing the same with a further light hydrocarbon fraction. By such a process, the sulfur content of the crude oil is reduced from an initial content of 1.2% by weight to a content of less than 0.008% by weight. This is well below acceptable maximum limits.

As used throughout the instant specification, the term "cold crude oil" is meant to embrace those virgin petroleum products which are not preheated prior to the desurfurization reaction.

While the present invention has been described primarily with respect to the drawings and the foregoing specific example, it is to be understood that the present invention is in no way to be deemed as limited thereto but must be construed as broadly as all or any equivalents thereof.

It is claimed:

1. A cyclic process for desulfurizing crude petroleum fractions and providing sodium metal by electrolysis which comprises (a) contacting a cold crude petroleum fraction with a dispersion of sodium metal in a light hydrocarbon fraction under ambient temperature conditions; (b) separating the product of step (a) into a desulfurized crude petroleum fraction and a sodium sulfide precipitate; (a) reacting said precipitate from step (a) with HCl to obtain hydrogen sulfide and by-product sodium chloride; (d) employing said sodium chloride obtained in step (c) as an electrolyte in an electrolytic cell for the production of molten sodium metal; and (e) forming a dispersion of the sodium metal recovered in step (d) in a light hydrocarbon fraction for use in step (a).

2. The process of claim 1 wherein prior to step (c) said precipitate of step (b) is washed with a light hydrocarbon fraction.

3. The process of claim 2 wherein said dispersion of sodium metal comprises a dispersion of about 10% to 80% by weight based on said light hydrocarbon fraction.

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U.S. Cl. X.R.

23—181

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,565,792 Dated February 23, 1971

Inventor(s) Frank B. HASKETT

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claim 1, line 35 of column 6, delete "(a)" and insert -- (c)

Signed and Sealed this

Twenty-first Day of September 1

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks