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(71) Applicant: **Taiyo Oil Co., Ltd.**
Chiyoda-ku, Tokyo 100 (JP)

(72) Inventors:
- **Morita, Fumiyasu**
  Ochi-gun, Ehime-ken (JP)
- **Murakami, Tadahiko**
  Ochi-gun, Ehime-ken (JP)
- **Fukuda, Kazuyuki**
  Matsuyama-shi, Ehime-ken (JP)
- **Nagai, Akihisa**
  Imabari-shi, Ehime-ken (JP)
- **Ono, Yasumasa**
  Ochi-gun, Ehime-ken (JP)
- **Miyauchi, Akira**
  Hojo-shi, Ehime-ken (JP)
- **Ikushima, Kenji**
  Yachiyo-City, Chiba-Ken (JP)

(74) Representative: **Müller-Boré & Partner**
Patentanwälte
Grafinger Strasse 2
81671 München (DE)

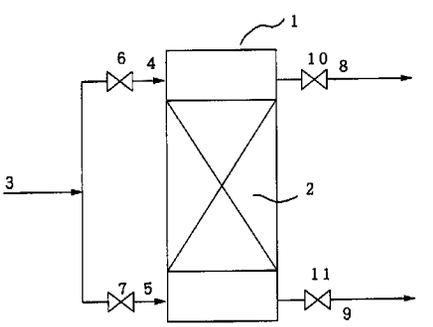
(54) Process for eliminating mercury form liquid hydrocarbons

(57) The present invention provides a process for eliminating mercury and mercury compounds from liquid hydrocarbons in a naphthametal elimination process having an adsorption treatment zone provided with a packed layer of mercury adsorbent, comprising the steps of:

(a) introducing the mercury-containing liquid hydrocarbon into the adsorption treatment zone;
(b) contacting the mercury-containing liquid hydrocarbon with the packed layer of mercury adsorbent in the adsorption treatment zone at a temperature of 10°C to 200°C and a LV value of 1 cm/min to 100 cm/min; and
(c) removing treated liquid hydrocarbon from the adsorption treatment zone.

According to this mercury elimination process, the mercury present in liquid hydrocarbons can be almost completely, efficiently and continuously removed through adsorption treatment regardless of the amount of mercury present and regardless of the presence of any sulfur compounds.

FIGURE 1



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Description

The present invention relates to a process for eliminating mercury and mercury compounds from liquid hydrocarbons, and more particularly to a process for eliminating mercury and mercury compounds from liquid hydrocarbons, wherein a liquid hydrocarbon which constitutes a blending stock for petroleum products, or liquid hydrocarbons such as intermediate products or raw materials for petrochemical product etc. are loaded into a NAPHTHAMETAL ELIMINATION PROCESS having an adsorption treatment zone provided with a packed layer of mercury adsorbent, and wherein the mercury present in said liquid hydrocarbons can be almost completely, efficiently and continuously removed through adsorption treatment regardless of the amount of mercury present and regardless of the presence of any sulfur compounds.

Conventionally, the process of petroleum refining includes a step of hydrogenating the liquid hydrocarbons such as distillate oil and residue oil which are used as the blending stock for petroleum products. If mercury is included in such liquid hydrocarbons, they poison in particular the hydrogenation catalysts made up of noble metal systems, thereby hindering the activity thereof. In addition, even in the case that hydrocarbon gases such as ethylene or propylene, or liquid hydrocarbons such as naphtha are used as the chemical raw materials, the presence of any mercury causes the catalyst to become poisoned with a consequent reduction in its activity. Furthermore, one property of mercury is that it forms amalgams with many metals, and when the equipment is made from, in particular, an aluminum based alloy, there is the problem of amalgam corrosion.

Accordingly, various methods for eliminating mercury have been studied, and adsorption-elimination methods using all kinds of mercury adsorbents have been reported. For example, porous materials such as alumina, silica, silica-alumina, zeolites, activated clays etc. have been the subject of focus as mercury adsorbents, and in addition, a mercury adsorbent using these as carriers, and having sulfides of heavy metals such as molybdenum, tungsten, vanadium etc. carried thereon have been proposed for example in Japanese Patent Publication No. Hei 6-24623(24623/1994). Mercury adsorbents having sulfur carried on a porous carrier have also been proposed. As an example thereof, sulfur-carrying activated carbon obtained by mixing activated carbon and fine particles of sulfur and then heating the resulting mixture (see Japanese Patent Application Laid-open No. Sho 59-7891(7891/1984)), and activated carbons incorporating organic sulfur compounds (see Japanese Patent Application Laid-open No. Sho 62-114632(114632/1987)) have been disclosed. When these type of adsorbents are used, it is presumed that the mercury reacts with the above-mentioned sulfide or sulfur compounds, and is eliminated from the liquid hydrocarbon as mercury sulfide.

However, although as mentioned above, various kinds of mercury adsorbents have been developed, a device for the adsorption-elimination of mercury composed of a single adsorption treatment zone including the above adsorbents which is capable of continuous operation and is industrially useful has not yet been developed. In other words, in the prior art, it had not yet been grasped under which adsorption conditions the adsorption treatment of mercury in a single adsorption zone could be conducted smoothly regardless of the type of mercury contained in liquid hydrocarbons. Furthermore, when mercury containing liquid hydrocarbon is supplied to the packed layer of mercury adsorbent, and adsorption treatment is effected, an area saturated with mercury is formed and grows. If the growth of such a mercury saturated area to an excessive level is not detected, a so-called breakthrough concentration is exceeded, and the amount of mercury remaining in the liquid hydrocarbon after adsorption treatment rapidly increases meaning that the adsorption treatment up to that point has effectively come to nothing.

In order to address such problems, 5% to 10% of the concentration at the inlet of the adsorption zone has been taken as the break-point concentration. However, since this standard cannot be applied to the elimination of the mercury, it is necessary to replace the mercury adsorbent for a new one ahead of time. Replacement of the mercury adsorbent ahead of time leaves problems such as loss due to wasteful disposal of the unused part of the adsorbent, reduction of the efficiency of the adsorption operation due to the complicated task of changing the adsorbent and consequent loss of time etc. which in actual practice makes it problematic to effect stable continuous operation of such a process for the elimination of mercury from liquid hydrocarbons.

In addition, it is often the case that sulfur compounds are included in the liquid hydrocarbon, and it has been pointed out that when such sulfur compounds such as mercaptans are present together with mercury, there occurs the phenomenon that mercury becomes separated from the adsorbent through redissolution in the liquid hydrocarbon. From this background, there has been a demand for a process for eliminating mercury and mercury compounds from liquid hydrocarbons with which continuous adsorption treatment can be effected smoothly even with a single adsorption zone, which is favourable from the view point of operation and device construction, and with which continuous operation with high elimination efficiency is possible even if sulfur compounds are present.

The main objective of the present invention is to provide a process for eliminating mercury and mercury compounds from liquid hydrocarbons in which mercury present in liquid hydrocarbons can be almost completely, efficiently and continuously eliminated even in a single adsorption treatment zone having provided a packed layer of mercury adsorbent, regardless of the size of the amount of mercury present.

Another objective of the present invention is to provide a process for eliminating mercury and mercury compounds from liquid hydrocarbons according to a continuous process in which elimination using a mercury adsorbent can be

effected almost completely, efficiently and continuously over a long period of time.

Another objective of the present invention is to provide a process wherein when carrying out adsorption-elimination of mercury and mercury compounds present in liquid hydrocarbons containing sulfur compounds through the use of a mercury adsorbent made from porous material such as activated carbon, the redissolution of mercury can be controlled and the mercury and mercury compounds present in the liquid hydrocarbon efficiently eliminated.

The inventors of the present invention, having conducted extensive research to realise the above-mentioned objectives, found that by adopting specific adsorption conditions when contacting the liquid hydrocarbon with the solid adsorbent, it is possible to achieve efficient and continuous elimination of mercury and mercury compounds even in a single adsorption treatment zone. They also found that by providing at least two adsorption treatment zones in parallel, feeding the mercury-containing liquid hydrocarbon into one of the adsorption zones, effecting adsorption of the included mercury, and then switching from the adsorption zone of said mercury-containing liquid hydrocarbon to another adsorption zone when the amount of mercury in the liquid hydrocarbon after adsorption treatment approaches a specific concentration level, it is possible to achieve efficient and continuous elimination of mercury.

Furthermore, they also found that by subjecting liquid hydrocarbons containing sulfur compounds such as mercaptan to hydrogenation treatment before effecting adsorption treatment using a solid mercury adsorbent, to thereby eliminate sulfur compounds, it is possible to control the redissolution of mercury from the mercury adsorbent, and thereby effect efficient and stable elimination of mercury and mercury compounds over a long period of time. The present invention was realised on the basis of these findings.

According to the present invention, there is provided a process for eliminating mercury and mercury compounds from liquid hydrocarbons in a napthametal elimination process having a single adsorption treatment zone provided with a packed layer of mercury adsorbent, comprising the steps of:

(1) introducing a mercury-containing liquid hydrocarbon into the adsorption treatment zone;
(2) contacting the mercury-containing liquid hydrocarbon with the packed layer of mercury adsorbent in the adsorption treatment zone at a temperature of 10°C to 200°C and a LV value of between 1cm/min to 100cm/min; and
(3) removing adsorption-treated liquid hydrocarbon from said adsorption treatment zone.

Furthermore, according to the present invention, there is provided a continuous process for eliminating mercury and mercury compounds from liquid hydrocarbons in a napthametal elimination process having at least two adsorption treatment zones, each provided with a packed layer of mercury adsorbent, arranged parallel to each other, comprising the steps of:

(1) introducing the mercury-containing liquid hydrocarbon into one of the adsorption treatment zones;
(2) contacting the liquid hydrocarbon with the packed layer of mercury adsorbent in said adsorption treatment zone;
(3) removing an adsorption-treated liquid hydrocarbon from the adsorption treatment zone;
(4) measuring the concentration of mercury in the adsorption-treated liquid hydrocarbon; and
(5) switching from the adsorption treatment zone of the mercury-containing liquid hydrocarbon to another adsorption treatment zone under the condition that the concentration of mercury remaining in the treated liquid hydrocarbon has reached a value in the range from about 1 ppb to about 5ppb.

The uniqueness of the present invention is based on the finding that it is possible to efficiently and continuously eliminate mercury from liquid hydrocarbons even using a single adsorber regardless of the type of liquid hydrocarbon and form of mercury, by setting the temperature to between 10°C and 200°C and setting the LV value to between 1cm/min and 100cm/min when contacting the mercury-containing liquid hydrocarbon with the mercury adsorbent. Through studies by the inventors, the conditions for adsorption treatment in the adsorption treatment zone have been optimized, and it has been grasped that this is characteristic to mercury.

Furthermore, the present invention is also based on the finding that when mercury-containing liquid hydrocarbon is contacted with mercury adsorbent, a saturation zone is formed in the packed layer of adsorbent wherein the amount of mercury adsorbed has reached an equilibrium with the concentration of the mercury in the mercury-containing liquid hydrocarbon; that when the concentration of mercury in the liquid hydrocarbon exceeds a certain level it increases rapidly even if the above mentioned saturation zone does not occupy the whole of the packed layer. Studies by the inventors of the present invention have led to the finding that the critical concentration at which the concentration of mercury in the liquid hydrocarbon after adsorption treatment suddenly increases is between about 1ppb and about 5ppb; and that this is a peculiar characteristic of mercury.

There are no particular restrictions concerning the type of mercury-containing liquid hydrocarbon that can be used in the present invention other than it be a mercury-containing hydrocarbon which is liquid under normal conditions. Specific examples include natural gas condensate, naphtha as a chemical raw material, and the blending stocks of all kinds of petroleum products such as naphtha, etc. Furthermore, even hydrocarbons which are gases under normal temperatures and conditions can be subjected to the adsorption treatment of the present invention by first liquefying them

through the application of pressure. Also, the process of the present invention can also be applied to hydrocarbon compounds which are solid at normal temperatures but form liquids upon the application of heat, by first liquefying them. For example, liquefied natural gas (LNG), liquefied petroleum gas (LPG), liquid olefins such as liquid ethylene, liquid propylene etc. and naphtha are all liquids and can be subjected as they are to the adsorption treatment of the present invention. Further, the liquid hydrocarbon which is subjected to the adsorption treatment of the present invention may consist of a single component or may be a mixture containing several components. It may also include large quantities of sulfur compounds, and also other compounds such as nitrogen compounds. Specific examples include mercaptan, aliphatic disulfides in addition to all other types of sulfides. The mercury in the liquid hydrocarbon may be present as elemental mercury, inorganic mercury and organic mercury. Any of these forms can be processed by the mercury elimination process of the present invention. There are no limits to the concentrations of mercury in the liquid hydrocarbon to which the process of the present invention can be applied. Treatment can be effected over a wide range, and even large amounts of included mercury can be almost completely eliminated. There may exist around 2ppb to 500ppb of mercury in a liquid hydrocarbon, such as naphtha, which is used as the blending stock for petroleum products. Natural gas condensates produced in south-east asia etc. contain several tens ppb to several thousands ppb of mercury, but according to the present invention these can also be subjected to adsorption treatment in the same way.

One of the characteristics of the present invention lies in the fact that the LV value and the temperature (representing adsorption conditions) are set to within specific ranges. The LV value is set to a value in the range 1cm/min to 100cm/min and more preferably to a value in the range 10cm/min to 50cm/min. If the concentration of mercury in the liquid hydrocarbon is less than or equal to 50 ppb, then it is preferable to have a LV value in the range of 25cm/min to 50cm/min. On the other hand , if the concentration of mercury in the liquid hydrocarbon exceeds 50 ppb, it is necessary to reduce the LV value. For example, the process of the present invention can be applied without difficulty to liquid hydrocarbons in which the concentration of mercury contained therein is extremely high such as natural gas condensates, but in such a case it is preferable to set the LV value to a value equal to or less than 30cm/min, and in particular to a value equal to or less than 20cm/min, in order to maintain the adsorption performance at a high level. However, according to the circulation type process discussed later, it is possible to set the LV value to a value equal to or greater than 50cm/min even if the concentration of mercury in the liquid hydrocarbon exceeds 100ppb. If the LV value is less than 1cm/min, then not only is the fear of elution of the already adsorbed mercury, but the throughput is extremely small rendering the process valueless as a process to be used in actual production. On the other hand, if the LV value is greater than 100cm/min, the degree of adsorption of mercury is insufficient, and the mercury-containing liquid hydrocarbon passes unchanged through the adsorbent packed layer with the problem of an increase in the concentration of mercury in the liquid hydrocarbon after adsorption treatment. The term LV value used here is a value obtained by dividing the throughput of the liquid hydrocarbon by the cross-sectional area of the packed layer of adsorbent. A large value points to a high processing efficiency.

The above-mentioned temperatures are temperatures measured inside the packed layer of mercury adsorbent, and in order to maintain a good adsorption performance, it is preferable to set the temperature to between 10°C and 200°C, more preferably to less than 100°C and even more preferably to less than 50°C. Furthermore, in the case that the temperature inside the packed layer of adsorbent is raised, it is preferable to appropriately adjust the pressure inside the adsorption treatment zone to between 1kg/cm^2 and 10kg/cm^2 and in particular to no more than 3 kg/cm^2. If the temperature is set to be less than 10°C, the adsorption performance deteriorates, but on the other hand if the temperature exceeds 200°C there occurs redissolution of mercury which is not desirable from the view point of maintaining a good adsorption performance.

According to the present invention, the contacting of the liquid hydrocarbon and the mercury adsorbent can be effected by adopting one of the following contacting systems: fixed bed, moving bed, fluidized bed and ebullated bed. However, from the fact that the construction of the adsorption treatment zone is rendered simple and the operation is rendered easy, the fixed bed system is preferred. In this fixed bed system, the liquid hydrocarbon is continuously fed into a packed layer composed of particles of mercury adsorbent packed securely into the adsorption treatment zone, and then adsorption treatment is effected. On the other hand, in the moving bed system, particles of mercury adsorbent are added intermittently or substantially continuously at one end of the adsorption treatment zone, and then removed intermittently or continuously at the other end. In this system, the batches of particles of mercury adsorbent introduced at the top end make continuous contact with the liquid hydrocarbon as they fall in order under the influence of gravity. In the fluidized bed system and the ebullated bed system, the liquid hydrocarbon and particles of mercury adsorbent are brought into contact with each other by causing the particles of mercury adsorbent to float in the flow of liquid hydrocarbon.

The fixed bed of mercury adsorbent can be provided by packing mercury adsorbent in particulate form, in cylindrical form, spherical form, crushed form or honeycomb form into the adsorption treatment zone, and then securing it according to a standard method. To be specific, glass wool is laid on the bottom of the adsorption treatment zone and silica balls are placed thereon to prevent any flow of the adsorbent out of the adsorption treatment zone. The mercury-containing liquid hydrocarbon can be supplied from the top to flow downwards or alternatively from the bottom to flow upwards in order to bring it into contact with the mercury adsorbent inside the fixed bed, but from the point of view of

stabilizing the adsorbent within the adsorption column, it is preferable to supply the liquid hydrocarbon to flow in a downwards direction.

Furthermore, according to the present invention there is also provided a process for eliminating mercury from liquid hydrocarbons in a napthametal elimation process having a single adsorption treatment zone in which a packed layer of mercury adsorbent is provided, comprising the steps of:

(1) introducing a mercury-containing liquid hydrocarbon into the adsorption treatment zone;
(2) contacting the mercury-containing liquid hydrocarbon with the mercury adsorbent in the adsorption zone under adsorption conditions including a temperature of 10°C to 200°C inside the packed layer of mercury adsorbent and an LV value of 1cm/min to 100cm/min;
(3) removing adsorption-treated liquid hydrocarbon from the adsorption treatment zone; and
(4) recirculating liquid hydrocarbon in which an amount of mercury still remains after adsorption treatment back through the adsorption treatment zone.

In other words, adsorption-treated liquid hydrocarbon which has been taken from the exit is recirculated back to the adsorption treatment zone, mixed with fresh liquid hydrocarbon i.e. liquid hydrocarbon which has not yet been subjected to adsorption treatment, and then subjected once again to adsorption treatment. It is preferred that the post adsorption treatment liquid hydrocarbon be mixed with "fresh" liquid hydrocarbon in an amount corresponding to between 10% to 70% by volume, particularly 20% to 30% by volume on the basis of the total volume.

According to this recirculation process, mercury can be eliminated efficiently from the liquid hydrocarbon under relaxed adsorption conditions and irrespective of the size of the amount of mercury contained in the liquid hydrocarbon. In other words, it is possible to adopt a relatively high LV value, and the adsorption treatment can be effected at a high liquid flow rate. Accordingly, the process of the present invention can even be applied to for example liquid hydrocarbons containing a high concentration of mercury such as natural gas condensates.

It is preferred that a porous material be used as the mercury adsorbent in the present invention. For example, as well as carbon materials such as activated carbon, mainly inorganic compounds having a high surface area and whose average pore radius is a suitable size for mercury adsorption such as silica gel, zeolites, alumina, silica-alumina and activated clay can be used. Activated carbon is a particularly preferred porous material, and for example, an activated carbon whose specific surface area is in the range of 100m^2/g to 2,500m^2/g, preferably in the range of 1000m^2/g to 1500m^2/g, whose average pore diameter is in the range of 5Å to 200Å, preferably in the range of 5Å to 100Å, more preferably in the range of 10Å to 50Å, and whose pore volume is in the range of 0.4ml/g to 1.5ml/g, preferably in the range of 0.6ml/g to 1.3ml/g is suitable. In other words, an activated carbon having a high surface area and high porosity and whose micropores are developed can be used as the porous material in the present invention. In consideration of adsorption efficiency and pressure loss in the fixed bed, it is preferred that the particle size of the adsorbent be in the range of 0.05mm to 5mm and in particular between 0.5mm and 2mm. Furthermore, it is also possible to increase the mercury adsorption performance by using an adsorbent which is comprised of a porous material having alkali metal sulfides and/or alkaline earth metal sulfides carried thereupon. There are no particular limitations concerning the alkali metal sulfides or alkaline earth metal sulfides. For example, Li_2S, Na_2S and K_2S can be used as the alkali metal sulfides, and MgS and CaS can be used as the alkaline earth metal sulfides. It is also possible to use a mixture of one or more compounds selected from the above-mentioned compounds. The amount of such sulfides carried on the porous material is arbitrary, but it is preferred that it be in the range of 0.1% to 30% by weight, more particularly in the range of 1 % by weight to 15 % by weight on the basis of the total weight of the mercury adsorbent.

The packed layer of mercury adsorbent of the present invention is constructed by the packing and securing of particulate mercury adsorbent made from the above-mentioned porous material. As the packed layer, it is possible to select one type of mercury adsorbent, but it is also possible to use a mixture of two or more types of particulate adsorbent. In the present invention, it is preferred to use an adsorbent layer constructed by packing and securing towards the inlet of the adsorption treatment zone a mercury adsorbent comprising a porous material, for example, particulate activated carbon having alkali metal sulfides and/or alkaline earth metal sulfides carried thereupon, and packing and securing downstream thereof a mercury adsorbent made of particulate activated carbon. By adopting such a construction, any mercury which might happen to become redissolved after reaction with the sulfides on the porous material, can be caught later in the latter stage of the adsorption treatment zone, therefore making it possible to control the degree of elution of mercury into the liquid hydrocarbon.

There are no limitations concerning the volume ratio between the above-mentioned activated carbon layer and the metal sulfides carrying activated carbon layer, but it is preferred that for every 1 part by weight of the former, there be 1 part to 2 parts by weight of the latter.

In the present invention, it is also possible to have a hydrogenation zone positioned before the adsorption zone. Normally, sulfur compounds are also contained in the mercury-containing liquid hydrocarbon. If such sulfur compounds are present, there appears the phenomenon that mercury which has been adsorbed by the mercury adsorbent in the adsorption treatment zone is eluated, thereby causing the problem that the adsorption efficiency of the mercury adsorb-

ent is reduced.

Accordingly, it is preferred that the mercury-containing liquid hydrocarbon should be subject to hydrogenation treatment when introducing it into the adsorption treatment zone.

There are no particular limitations concerning the type of hydrogenation catalyst used in the hydrogenation zone. For example, one composed of a carrier and a hydrogenation active component, wherein the carrier is a heat resistant inorganic oxide and the hydrogenation active component is a metal component from group VIII and/or a a metal component from group VI of the periodic table can be used. The heat resistant inorganic oxide may be a porous material such as alumina, silica, silica-alumina or zeolite. Furthermore, with a view to improving the heat resistance, any of the above materials having magnesia, zirconia etc. added thereto can also be used.

A particularly preferred carrier for the present invention is alumina or silica-a-lumina preferably having a specific surface area of at least 100m^2/g and an average pore radius between 5Å and 100Å.

With respect to the hydrogenation active component, iron, cobalt, nickel, ruthenium, rhodium, palladium etc. are specific examples of the group VIII metal, and chromium, molybdenum, tungsten etc. are examples of the group VI metal. The following combination of metal components are particularly preferred: cobalt-molybdenum, nickel-molybdenum and cobalt-nickel-molybdenum. Specifically, a product comprising the above-mentioned carrier having the above-mentioned hydrogenation active component carried thereupon is used as the hydrogenation catalyst. With respect to the amount of hydrogenation active component carried upon the carrier, in the case of Group VIII metal component, an amount of the oxide in the range of 1% to 30% by weight, and preferably 5% to 15% by weight, and in the case of the Group VI metal component, an amount of the oxide in the range 1% to 30% by weight and preferably 5% to 20% by weight can be used. Before effecting the hydrogenation of the liquid hydrocarbon, it is preferred that the hydrogenation catalyst having the above-described composition be contacted with for example hydrogen sulfide, carbon disulfide, or a sulfur compound-containing hydrocarbon oil to convert the metal oxides into sulfides, and it is favourable that the resulting sulfides of each metal make up at least 50% of the total metal component.

The following may be adopted as the reaction conditions for the hydrogenation of the mercury-containing liquid hydrocarbon in the hydrogenation zone: reaction temperature: 100°C to 300°C, preferably 150°C to 250°C; reaction pressure: 10kg/cm^2 to 50kg/cm^2, preferably 15kg/cm^2 to 20kg/cm^2.

The above-described hydrogenation treatment of the liquid hydrocarbon containing mercury and sulfides makes it possible to obtain a hydrogenation product in which sulfur compounds, in particular mercaptan is reduced. The use of such a hydrogenation product in the adsorption treatment zone contributes to an improvement in the adsorption efficiency of the adsorbent, thereby, as shown in the examples described later, making it possible to lengthen the period of time over which the adsorption treatment can be continued.

Hereunder, the present invention shall be explained using the attached figures. Pipes, valves, measuring devices etc. which are not necessary to the understanding of the present invention have been omitted from the figures. Figure 1 is a simplified representation of the mercury elimination process according to the present invention using a single adsorption treatment zone. Mercury-containing liquid hydrocarbon is introduced from pipe 3, and by opening valve 6 is supplied into adsorption treatment zone 1 via pipe 4. It flows downwards and makes contact with the packed layer of mercury adsorbent 2. If valve 6 is closed and valve 7 opened, the mercury-containing liquid hydrocarbon flows upwards from pipe 5 into adsorption zone 1 and is subjected to adsorption treatment. Adsorption-treated liquid hydrocarbon is removed via pipe 8 in the case of up-flow adsorption treatment, and via pipe 9 in the case of down-flow adsorption treatment.

Figure 2 shows a recirculation type process which is another embodiment of the present invention. The case when the mercury-containing liquid hydrocarbon flows downwards to make contact with the packed layer of adsorbent 2 is shown as an example. Valve 8 is opened, and a portion of the adsorption-treated liquid hydrocarbon removed via pipe 6 is directed via pipe 7 to be mixed with mercury-containing liquid hydrocarbon from pipe 3 and then this mixture is supplied to the adsorption zone. In the adsorption treating zone, it is subjected to mercury adsorption treatment in the diluted state.

Figures 3 and 4 show cases when two adsorption columns are arranged parallel to each other. In figure 3, 1 and 2 are adsorption columns. Mercury-containing liquid hydrocarbon is introduced from pipe 3. When valve 9 is closed and valve 8 opened, the liquid hydrocarbon is fed into adsorption column 1 via pipe 4. In adsorption column 1, activated carbon particles are packed to form a fixed bed 30. The mercury-containing liquid hydrocarbon is then contacted with fixed bed 30, and adsorption-treated liquid hydrocarbon is removed from pipe 13 by opening valve 17. When the amount of mercury remaining in the liquid hydrocarbon taken from pipe 13 reaches between 1ppb and 5ppb, valve 8 is closed, valve 10 is opened, and the mercury-containing liquid hydrocarbon is introduced from pipe 6 into adsorption column 2. Thereafter, adsorption treatment is effected in adsorption column 2. In the case that the mercury-containing liquid hydrocarbon is to be caused to flow upwards to make contact with the packed layer of adsorbent in adsorption column 1, valve 8 is closed, valve 9 is opened and the mercury-containing liquid hydrocarbon is introduced into adsorption column 1 from pipe 5. Valve 16 is opened and adsorption-treated liquid hydrocarbon is removed via pipe 12. In the case that the mercury containing liquid hydrocarbon is to be caused to flow upwards to make contact with the packed layer of adsorbent in adsorption column 2, valves 10 and 19 are closed, valves 11 and 18 are opened and the mercury-con-

taining liquid hydrocarbon is introduced from pipe 7. Adsorption-treated liquid hydrocarbon is removed via pipes 14 and 22.

Figure 4 is a generalized representation of another embodiment of the present invention, which comprises an adsorption process in which hydrogenation treatment and mercury adsorption treatment are integrally combined. In the figure, 100 is the hydrogenation reaction column, and 200 and 300 are adsorption columns. The mercury-containing liquid hydrocarbon is introduced from pipe 50 and subjected to hydrogenation in hydrogenation reaction column 100. After hydrogenation, the liquid hydrocarbon is fed along pipe 51, and then from pipe 52 into adsorption column 200 through operation of valve 55. Adsorption-treated liquid hydrocarbon is removed via pipe 57. When the concentration of mercury in the treated hydrocarbon reaches between 1ppb and 5ppb, the mercury-containing liquid hydrocarbon is introduced into adsorption column 300 by opening valve 56.

Hereunder, the invention shall be explained in detail using several Examples. However, the scope of the present invention shall not be limited by these Examples.

Example 1

Into an adsorption column of internal diameter 30cm and length 1m is packed and secured particulate activated carbon having a particle size of 0.5mm to 1.7mm, a specific surface area of 1400m^2/g and an average pore diameter of 24Å, to provide a fixed bed of height 0.9m.

Light naphtha (specific gravity of 15/4°C 0.700, initial boiling point 50°C, end point 120°C) containing mercury in a concentration of 28ppb is introduced from the top of the adsorption column to flow downwards, and is contacted with the fixed bed of adsorbent at a temperature inside the packed layer of adsorbent of 25°C and a LV value of 30cm/min.. Adsorption treatment is continued for 3 hours, and then the concentration of the mercury in adsorption-treated light naphtha at the bottom end of the adsorption column was measured and found to be no more than 1ppb showing that almost of the mercury had been eliminated.

Example 2

Adsorption treatment was continued for 3 hours in the same way as in Example 1 except that the LV value was set to be 15cm/min. The concentration of mercury in the adsorption-treated light naphtha taken after 3 hours was measured and found to be no more 1ppb showing that almost all of the mercury had been eliminated. The adsorption treatment was then continued under the same conditions and the concentration of mercury the adsorption-treated light naphtha taken after the elapse of two months was measured and found to be 1ppb.

Example 3

Mercury adsorption treatment was effected under the same conditions as in Example 1 except that the temperature inside the packed layer of adsorbent in the adsorption column was set to 50°C. The concentration of mercury in adsorption-treated light naphtha taken after 3 hours was no more than 1ppb, and the concentration of mercury in adsorption-treated light naphta taken after two months was measured to be 1ppb.

Examples 4 to 6

Light naphtha was subjected to adsorption treatment in the same way as in Example 1 except that the values for the LV value and temperature inside the packed layer of adsorbent shown in Table 1 for each respective example were adopted. The results of adsorption treatment are also shown in Table 1. It is clear from the results shown in Table 1 that the method of the present invention can be applied without difficulty even if the concentration of mercury in the liquid hydrocarbon is as great 100ppb.

Example 7

A light naphtha containing mercury in a concentration of 100ppb was supplied to a packed layer of mercury adsorbent and subjected to adsorption treatment under the conditions shown in Table 1. A portion (amount corresponding to 20% by volume of the total amount of light naphtha supplied to the adsorption column) of adsorption-treated naphtha which contained mercury in a concentration of 4ppb was mixed with untreated light naphtha and re-supplied to the packed layer. Compared to the case when the concentration of mercury is made to be 1ppb without any recirculation of the light naphtha, the adsorption throughput was increased by 20% by volume.

The concentration of mercury in adsorption-treated light naphtha taken after three hours after the start of adsorption treatment was no more than 1ppb, and the concentration of mercury in adsorption-treated light naphtha taken after the elapse of two months was also 1ppb.

Example 8

Adsorption treatment was effected in the exactly the same way as in Example 7, except that light naphtha containing mercury in a concentration of 200ppb was used. The concentration of mercury after adsorption treatment was 1ppb, and the throughput was increased by 20% by volume compared to the case when the concentration is made to be 1ppb without any recirculation of the liquid hydrocarbon.

Example 9

To the inlet side of an adsorption column was packed and secured in an amount corresponding to one third of the total volume of all adsorbent an adsorbent comprising a particulate activated carbon having a particle size of 0.5mm to 1.7mm, a specific surface area of 1400m^2/g and an average pore diameter of 24Å, and also having sodium sulfide (Na_2S) carried thereupon in a sulfur content of 1% by weight. Downstream thereof, the above-mentioned particulate activated carbon is packed and secured in an amount corresponding to two-thirds of the total amount of all adsorbent. Light naphtha containing mercury in a concentration of 100ppb was supplied to the above-described adsorption column under the same adsorption conditions as example 1. The adsorption performance results are shown in Table 1.

Example 10

Mercury adsorption treatment was effected in the same way as in Example 1 except that heavy naphtha (specific gravity of 15/4°C 0.74, initial boiling point of 100°C, end point of 160°C) containing mercury in a concentration of 100ppb was used instead of light naphtha.

Comparative Example 1

The same kind of mercury containing light naphtha as used in Example 1 is supplied to the top of an adsorption column and subjected to adsorption treatment for 3 hours under the same conditions as in Example 1 except that the LV value was set to 150cm/min instead of 30cm/min. The concentration of mercury in treated light naphtha at the exit at the bottom of the adsorption column after three hours is measured to be 10ppb. The concentration of mercury in treated light naphtha taken after the elapse of two months was measured to be 28ppb.

Comparative Example 2

The same kind of mercury-containing light naphtha as in Example 1 is supplied to the top of the adsorption column and subject to adsorption treatment for 3 hours under the same conditions as in Example 1 except that the LV value is set to be 0.3cm/min. The concentration of mercury in treated light naphtha taken after three hours at the exit at the bottom of the reaction column was measured to be 5ppb. The concentration of mercury in treated light naphtha taken after the elapse of two months had increased to 25ppb.

Comparative Example 3

Mercury-containing light naphtha of the same kind as used in Example 1 was supplied to the top end of the adsorption column and subjected to adsorption treatment for 3 hours under the same conditions as in Example 1 except that the temperature inside the packed layer of adsorbent was set to 250°C and the reaction column pressure was set to 10kg/cm^2.

Example 11

Into each of two adsorption columns, which have an internal diameter of 30cm, a length of 1m and are arranged parallel to each other, is packed a mercury adsorbent comprised of a particulate activated carbon having a particle size of 0.5mm to 1.7mm, a specific surface area of 1400m^2/g and an average pore diameter of 24Å, to provide a fixed bed. Light naphtha (specific gravity of 15/4°C;0.70, initial boiling point of 50°C and an end point of 120°C) containing mercury in a concentration of 28ppb is introduced at normal temperature and pressure and a LV value of 30cm/min into the top end of one of the above-described adsorption columns to flow downwards. Adsorption treatment is effected for 1 hour and when the concentration of mercury in the treated light naphtha at the exit at the bottom of the adsorption column was measured, it was found to be under 1ppb. The light naphtha is continuously introduced, and the adsorption treatment is continued under the same conditions as described above. The mercury concentration in treated light naphtha taken after the elapse of two months was found to be in the range of 1ppb to 5 ppb, and so the introduction of the light naphtha was switched to the swing adsorption column. In this way, the fraction of adsorbent not used could be reduced

to 3% by weight, and the mercury adsorption treatment could be carried on continuously without any increase in the concentration of the mercury in the treated liquid hydrocarbon.

During the adsorption treatment, samples were taken from a number of withdrawal points provided in the side wall of the adsorption column, and the mercury concentration was measured for each sample to analyse the nature of the mercury adsorption. As a result, it was ascertained that from the top of the adsorption column, saturation zones, in which the adsorbed mercury had reached an equilibrium with the concentration of mercury in the light naphtha, are formed one after the other, that these saturation zones grow as the adsorption treatment proceeds, and that the mercury concentration reaches a breaking point under the condition that only a slight amount of unused adsorbent remains in the packed layer.

Comparative Example 4

The same kind of adsorption column as used in example 11 was prepared, and 50kg of mercury adsorbent comprised of particulate activated carbon, is packed therein. Starting from a concentration of mercury in the liquid hydrocarbon of 28ppb, the time for switching the adsorption columns was determined according to a theoretical value for the amount of mercury adsorbed. The period over which adsorption treatment was possible was no more than two months. More than 20% by weight of unused adsorbent was left remaining.

Comparative Example 5

The same kind of adsorption column as used in Example 11 was prepared, and the adsorption treatment of light naphtha containing mercury in a concentration of 10ppm under the same adsorption conditions as used in Example 11. A possible adsorption period of 5 months was calculated from theoretical values. In this case, the amount of adsorbent left unused was about 10% by weight of the total amount of adsorbent.

Example 12

Light naphtha containing mercury in a concentration of 10ppb and having a sulfur content of 0.02% by weight is introduced into a hydrogenation column and then contacted with hydrogen at a reaction temperature of 200°C and reaction pressure of 20kg/cm^2 and in the presence of the hydrogenation catalyst described below, to obtain a treated light naphtha having a sulfur content of 1ppm.

Hydrogenation Catalyst

An alumina carrier having a specific surface area of 100m^2/g, and an average pore radius of 50Å, has oxides of cobalt and molybdenum loaded thereupon in amounts of 5% and 14% by weight respectively, and is then subjected to presulfiding treatment by contact with sulfur containing light naphtha under a temperature of 200°C and a pressure of 20kg/cm^2.

The light naphtha after being subjected to the above-described hydrogenation treatment is then subjected to adsorption treatment in the same way as example 11. The concentration of mercury remaining in treated liquid hydrocarbon taken after six months was found to have reached a value between 1ppb and 5ppb, and so the introduction of liquid hydrocarbon was switched to the swing adsorption column. The amount of adsorbent not used as this time was found to be about 3% by weight.

Examples 13 and 14

Samples of light naphtha containing mercury in a concentration of 5ppb and 60ppb were respectively introduced into an adsorption column under the same conditions as in example 11. The concentration of mercury in adsorption treated light naphtha was measured whilst carrying out the adsorption treatment, and it was found that the concentration of mercury in the treated light naphtha reached a value between 1 to 5 ppb after 15 and 2 months respectively. The adsorption treatment periods are shown in Table 2. The amount of unused adsorbent was less than 3%.

Comparative Examples 6

Sample of light naphtha containing mercury in the concentrations shown in Table 2, were respectively subjected to adsorption treatment over a period of time calculated from theoretical values. After the completion of the adsorption treatment, the mercury adsorbent was removed from the adsorption column and it was found that the amount of unused adsorbent was 30% by weight.

It was ascertained that when the concentration of mercury remaining in the treated liquid hydrocarbon exceeds 5ppb as shown in Comparative Example 7, it increases suddenly and easily reaches the same value as that before the adsorption treatment.

Furthermore, it is established that the method of the present invention is in actual practice extremely useful in effectively exploiting the mercury adsorbent in that mercury can be eliminated from liquid hydrocarbons continuously over a long period of time without leaving hardly any unused mercury adsorbent. In Example 11, the introduction of light naphtha is switched to a swing adsorption column when the concentration of mercury remaining reaches between 1ppb and 5ppb, thereby making continuous operation possible without leaving hardly any unused mercury adsorbent. On the other hand, in comparative Example 4, the amount of mercury adsorbed is determined from theoretical values, and in comparison to the inventive examples, the adsorption treatment period is extremely short. Comparative Example 7 shows the case when the adsorption treatment is continued until the concentration of remaining mercury exceeds between 1ppb to 5ppb, and in such a case there occurs the problem that the concentration of remaining mercury quickly increases to 28ppb. In each of the comparative examples, the amount of unused adsorbent was between 10% and 30% by weight. Example 12 shows the possibility of extending the life of the adsorbent by reducing sulphur content in the light naptha by subjecting it to a pretreatment before the mercury adsorption treatment. Also, in the cases when hydrogenation is carried out before mercury adsorption treatment, redissolution of the mercury is kept low.

As explained above, it is possible to almost completely eliminate mercury and mercury compounds over a long period of time and with high efficiency , even when using only a single adsorption treatment zone and irrespective of the type of mercury-containing liquid hydrocarbon and the form of mercury, by contacting the mercury-containing hydrocarbon with a packed layer of mercury adsorbent under the special adsorption conditions that the temperature inside the packed layer of adsorbent be between 10°C and 200°C and the LV value between 1cm/min and 100cm/min.

Furthermore, by using a recirculation process in which liquid hydrocarbon which has already been subjected to adsorption treatment is mixed with liquid hydrocarbon which has not yet been subjected to adsorption treatment and then contacted with the packed layer of mercury adsorbent, an increase in throughput can be realised through a relaxation in the reaction conditions.

In addition, by providing at least two adsorption zones in parallel, introducing the mercury-containing liquid hydrocarbon to one of the adsorption zones, and then switching to the other adsorption zone when the amount of mercury remaining in treated liquid hydrocarbon reaches a value in the range 1ppb to 5ppb, the maximum possible exploitation of the unused portion of the packed layer of adsorbent can be effected, making possible the provision of a process of eliminating mercury and mercury compounds from liquid hydrocarbons which is of high practical value and which can be effected continuously over a long period of time without an increase in the concentration of mercury remaining in the treated liquid hydrocarbon.

In addition, it has also been understood that by subjecting a liquid hydrocarbon containing mercury, mecury compounds and sulfides, in particularly mercaptan, to hydrogenation treatment to eliminate a certain amount of the sulfur compounds, it is possible to reduce the degree of dissolution of mercury during the mercury adsorption treatment and thereby prolong the life of the adsorbent.

TABLE-1

	EXAMPLES										COMP. EXAMPLES		
	1	2	3	4	5	6	7	8	9	10	1	2	3
Liquid Hydrocarbon	Light Naphtha									Heavy Naptha	Light Naphtha		
Mercury Concentration (ppb)	28	28	28	28	100	100	100	200	100	100	28	28	28
Adsorption Treatment Conditions													
Temp. inside packed adsorbent layer (°C)	25	25	50	20	20	20	25	25	20	25	20	20	250
LV value (cm/min)	30	15	30	50	30	20	70	70	30	30	150	0.3	30
Adsorption Performance													
Conc. of mercury in treated liquid hydrocarbon													
After 3 hours	<1	<1	<1	<1	<1	<1	1	1	1	1	10	5	10
After 2 months	1	1	1	1	1	1	1	1	1	1	28	25	28

TABLE 2

	EXAMPLES				COMP.EXAMPLES			
	11	12	13	14	4	5	6	7
Liquid Hydrocarbon Mercury Concentration (ppb)	28	10	5	60	28	10	60	28
Mercury Concentration in Treated Liquid Hydrocarbon (ppb)	1-5	1-5	1-5	1-5	1-5	1-5	1-5	28
Adsorption Treatment Period*[1] (months)	3	6	15	2	2	5	10	2.5
Percentage of Unused Adsorbent (%)	3	3	3	3	20	10	30	20

(*1) For the inventive examples, the adsorption treatment period is the period of time until the point of' time when the concentration of mercury in treated liquid hydrocarbon was actually measured to be between 1ppb and 5ppb (adsorption column switch time). In the case of the compartive examples, it is a period of time calculated from theoretical values.

Claims

1. A process for eliminating mercury and mercury compounds from liquid hydrocarbons in a naphthametal elimination process having an adsorption treatment zone provided with a packed layer of mercury adsorbent, comprising the steps of:

   (a) introducing the mercury-containing liquid hydrocarbon into the adsorption treatment zone;
   (b) contacting the mercury-containing liquid hydrocarbon with the packed layer of mercury adsorbent in the adsorption treatment zone at a temperature of 10°C to 200°C and a LV value of 1cm/min to 100cm/min; and
   (c) removing treated liquid hydrocarbon from the adsorption treatment zone.

2. A process for eliminating mercury and mercury compounds from liquid hydrocarbons according to a continuous process using a naphthametal elimination process having at least two adsorption treatment zones provided in parallel, said adsorption zones provided with a packed layer of mercury adsorbent, comprising the steps of:

   (a) introducing the mercury-containing liquid hydrocarbon into one of the adsorption treatment zones;
   (b) contacting the mercury-containing liquid hydrocarbon with the packed layer of mercury adsorbent in the adsorption treatment zone;
   (c) removing the treated liquid hydrocarbon from the adsorption treatment zone;
   (d) measuring the concentration of mercury in the treated liquid hydrocarbon; and
   (e) switching to another adsorption treatment zone when the concentration of mercury remaining in the treated liquid hydrocarbon reaches a value in the range from about 1ppb to about 5ppb.

3. The process for eliminating mercury and mercury compounds according to claim 2, comprising providing in parallel at least two adsorption treatment zones including a swing adsorption treatment zone provided with a fixed bed of packed and secured particles of mercury adsorbent, introducing the mercury-containing liquid hydrocarbon from the above fixed bed of the adsorption treatment zone to flow downwards and subjecting it to mercury adsorption treatment, and switching to another adsorption treatment zone under the condition that the concentration of mercury in the liquid hydrocarbon does not exceed about 5ppb.

4. The process for eliminating mercury and mercury compounds from liquid hydrocarbons according to claim 1 or 2, wherein the packed layer of mercury adsorbent is a fixed bed made by the packing and securing of particles of mercury adsorbent into the adsorption treatment zone.

5. The process for eliminating mercury and mercury compounds from liquid hydrocarbons according to claim 1, 2 or 4 wherein the mercury-containing liquid hydrocarbon is introduced from the above fixed bed of mercury adsorbent to flow downwards.

6. The process for eliminating mercury and mercury compounds from liquid hydrocarbons according to any one of claims 1 to 5 wherein the mercury adsorbent is an activated carbon.

7. The process for eliminating mercury and mercury compounds from liquid hydrocarbons according to claim 6 wherein the activated carbon is an activated carbon having a specific surface area in the range $100m^2/g$ to $2,500m^2g$, an average pore diameter in the range of 5Å to 200Å, a pore volume in the range of 0.4 ml/g to 1.5 ml/g, and a particle size in the range of 0.05mm to 5mm.

8. The process for eliminating mercury and mercury compounds from liquid hydrocarbons according to any one of claims 1 to 7 wherein the mercury adsorbent is an activated carbon having an alkali metal sulfide and/or alkaline earth metal sulfide carried thereupon.

9. The process for eliminating mercury and mercury compounds from liquid hydrocarbons in a naphthametal elimination process having an adsorption treatment zone provided with a packed layer of mercury adsorbent according to any one of claims 1 to 8, comprising the steps of:

(1) introducing the mercury-containing liquid hydrocarbon into the adsorption treatment zone;
(2) contacting the mercury-containing liquid hydrocarbon with the mercury adsorbent in the adsorption treatment zone under a temperature of 10°C to 200°C and a LV value of 1cm/min to 100cm/min;
(3) removing treated liquid hydrocarbon from the adsorption treatment zone; and
(4) recirculating treated liquid hydrocarbon in which mercury remains back to the adsorption treatment zone.

10. The process for eliminating mercury and mercury compounds from liquid hydrocarbons according to claim 2 wherein the packed layer of mercury adsorbent is a moving bed of mercury adsorbent particles, and the mercury-containing liquid hydrocarbon is introduced in the direction of flow of the mercury adsorbent particles.

11. The process for eliminating mercury and mercury compounds from liquid hydrocarbons according to anyone of claims 1 to 10 which further comprises before the step of introducing the mercury-containing liquid hydrocarbon into the adsorption treatment zone the steps of introducing the mercury-containing liquid hydrocarbon into a hydrogenation zone
and contacting the mercury-containing liquid hydrocarbon with hydrogen in the hydrogenation zone under hydrogenation conditions and in the presence of a hydrogenation catalyst.

FIGURE 1

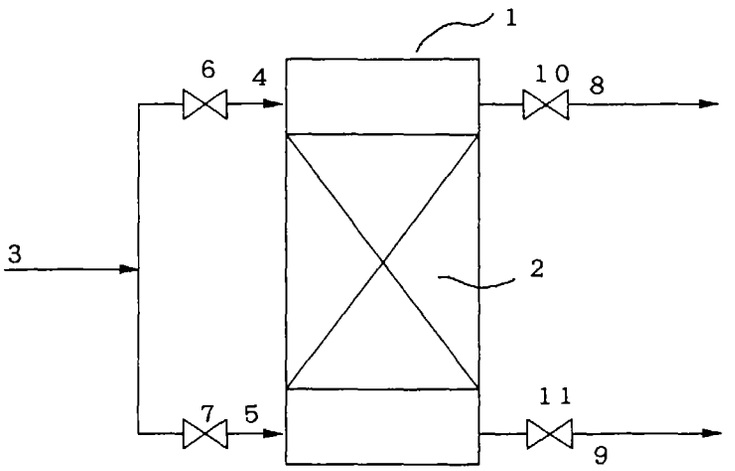

FIGURE 2

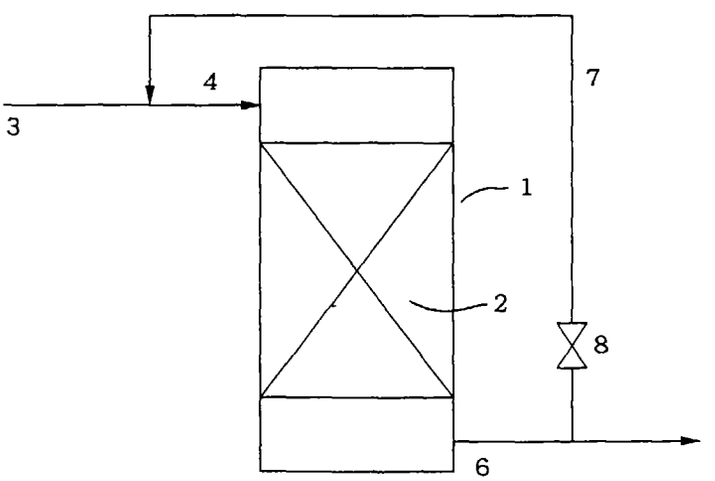

FIGURE 3

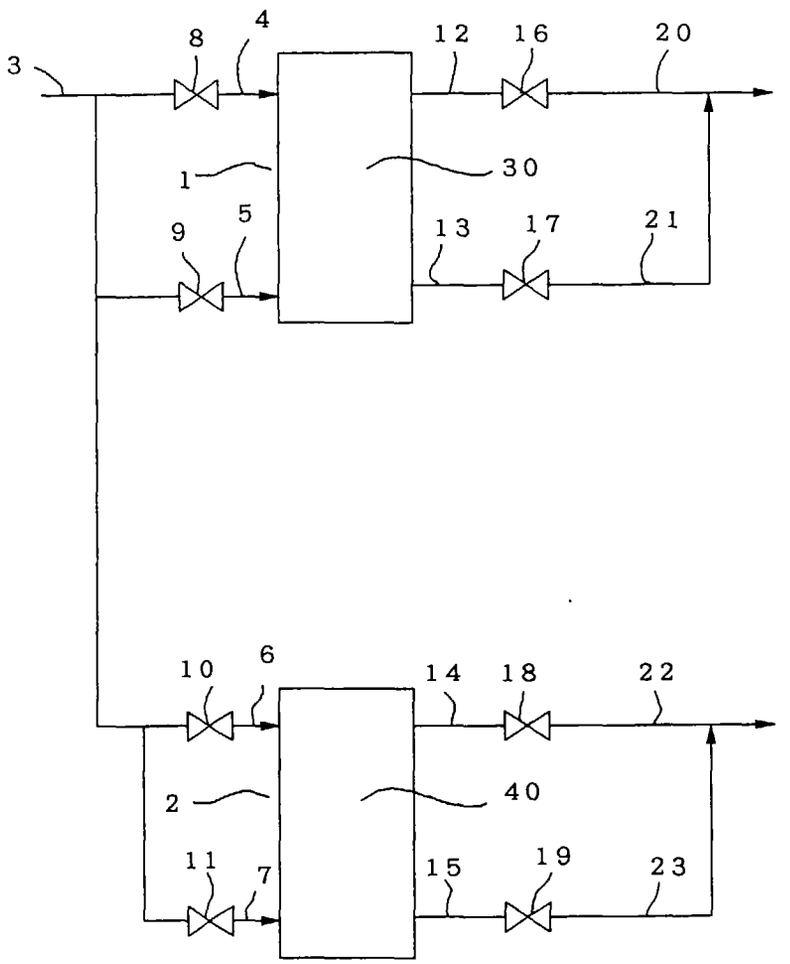

FIGURE 4