

PROCESS FOR REMOVING TRACE QUANTITIES OF METALS FROM HYDROCARBON FRACTIONS BY ADSORPTION

The present invention relates to a process for removing trace quantities of metals from hydrocarbon fractions by adsorption. In more detail, it relates to an effective process of removing trace amounts of metals, in particular mercury, by subjecting a hydrocarbon fraction, such as natural gas condensate or naphtha, which is mainly used as blending stocks for petroleum products, to hydrogenation, and thereafter contacting it with a porous carbon material.

If mercury is present in hydrocarbons such as naphtha, which are used as blending stocks for petroleum products, catalysts, in particular, noble metals such as Pt, Pd etc., used in the refining process become poisoned causing a deterioration in the activity thereof. Also, when hydrocarbon gases such as ethylene, propylene etc. or hydrocarbon fractions such as naphtha are used as chemical raw materials, there is the problem that the mercury can act as a catalyst poisoner and hinder the activity of the catalyst. In addition, mercury has the property that it can form amalgams with many metals, and when apparatus made from, in particular, an aluminum-based alloy is employed, there is the problem of amalgam corrosion. Furthermore, if arsenic is present in the raw material for catalytic reforming, it has a large effect on the operation of the catalytic reforming apparatus in that it hinders the activity of the platinum catalyst with the fear that the catalyst may not

be able to be re-used again as a result.

Accordingly, various kinds of methods for the removal of heavy metals such as mercury and arsenic contained in hydrocarbon fractions have been studied in the prior art, and several methods employing various kinds of adsorbents have been proposed. For example, there have been proposed mercury adsorbents in which sulfur is carried on a porous carrier. In detailed, a sulfur-carrying activated carbon obtained by mixing activated carbon and sulfur particles and then heating the mixture to a specified temperature (Japanese Patent Application Laid-Open No. 78915/1984), and an activated carbon containing organic sulfides (Japanese Patent Application Laid-Open No. 114632/1987) have been disclosed. It has been hypothesized that when these kinds of mercury adsorbents are used, the mercury reacts with the sulfur component and is eliminated from the hydrocarbon fraction as mercury sulfide. Furthermore, as means for removing arsenic, there have been proposed, for example, adsorbents in which sulfur, in the form of a mercapto group etc., is introduced onto a carrier such as activated carbon and organic polymers etc. (Japanese Patent Application Laid-Open No. 250913/1987), and activated carbons which have copper compounds and chromium compounds carried thereupon (Japanese Patent Application Laid-Open No. 238144/1985).

However, when these sulfur-containing adsorbents are used for the removal of trace amounts of metal contained in hydrocarbon fractions, there is the problem

that, although the trace amounts of metal can be removed by adsorption, the sulfur contained in the adsorbent elutes into the hydrocarbon fraction, with the result that the hydrocarbon fraction has to be repeatedly refined. Furthermore, when the mercury is present in the hydrocarbon fraction in the form of organic mercury compounds, the removal by adsorption thereof is extremely difficult; and, in addition, the methods of removing arsenic by adsorption can not be said to have reached a satisfactory level with respect to continuity of processing.

Accordingly, the objective of the present invention is to provide a process for the removal by adsorption of trace amounts of metals, in particular mercury, present in hydrocarbon fractions, with which continuous adsorption over a long period of time is possible, and with which the metals, including organic mercury compounds, can be efficiently removed regardless of the form in which they exist.

In the light of the above-described situation with regard to the development of a process for removing trace amounts of metals from hydrocarbon fractions, the inventors of the present invention have carried out intense research with the aim of attaining the above-described objective. They found as a result thereof that it is possible to remove trace amounts of metals whatever their form (for example, in the case of mercury, elemental mercury, inorganic mercury and even organic mercury), stably over a long period of time, by subjecting the hydrocarbon fraction containing the trace amounts of metal to hydrogenation, and then contacting the

hydrogenated hydrocarbon fraction with a carbonaceous material, thereby realising the present invention.

The first aspect of the present invention thus relates to a process for the removal by adsorption of trace amounts of metal contained in a hydrocarbon fraction using removal apparatus comprising a hydrogenation zone having provided a packed layer of hydrogenation catalyst, and an adsorption zone having provided a packed layer of porous carbon material, said method comprising the steps of:

(A) supplying the hydrocarbon fraction containing the trace amounts of metal to the hydrogenation zone, and contacting it with hydrogen under hydrogenation conditions and in the presence of the hydrogenation catalyst; and

(B) supplying the hydrogenated hydrocarbon fraction to the adsorption zone, and contacting it with the porous carbon material.

Furthermore, the present invention also provides a process for the removal by adsorption of trace amounts of metals contained in a hydrocarbon fraction, wherein a distillation zone is provided after the hydrogenation zone, a light hydrocarbon fraction is distilled off from the hydrogenated hydrocarbon fraction, and the light hydrocarbon fraction is supplied to the adsorption zone.

A second aspect of the present invention thus relates to a process for the removal of trace amounts of metals from a hydrocarbon fraction using removal apparatus comprising a hydrogenation zone provided with a packed layer of

hydrogenation catalyst, a distillation zone, and an adsorption zone provided with a packed layer porous carbon material; said process comprising the steps of:

(A) supplying the hydrocarbon fraction containing metals in a trace amount to the hydrogenation zone, and contacting it with hydrogen under hydrogenation conditions and in the presence of a hydrogenation catalyst;

(B) supplying the hydrogenated hydrocarbon fraction from the hydrogenation zone to the distillation zone, and distilling off a lighter hydrocarbon fraction having a boiling point of 100°C or less; and

(C) supplying the light hydrocarbon fraction to the adsorption zone, and contacting it with the porous carbon material.

The present invention shall be explained in detail hereunder.

There are no particular limitations regarding the hydrocarbon fraction containing trace amounts of metals which is subjected to hydrogenation in the present invention. It may be one having a wide boiling range, for example, a hydrocarbon fraction corresponding to a light naphtha fraction, a heavy naphtha fraction, a kerosene fraction and a gas oil fraction; a crude oil or a heavy oil and a hydrocarbon fraction having a boiling range of 20°C to 300°C is usually employed. This hydrocarbon fraction usually contains 10ppm to 200ppm of sulfur compounds and 2ppm to 20ppm of nitrogen compounds, but a hydrocarbon fraction containing larger amounts of sulfur compounds and nitrogen compounds may also be used.

Specific examples include, naphtha and other blending stocks for various kinds of petroleum products; natural gas condensate; naphtha for use as a chemical raw material; a synthetic hydrocarbon etc.. As for gaseous hydrocarbons at ambient temperature, such hydrocarbons are applied to the process of the present invention after liquefaction by pressure. In particular, liquefied natural gas (LNG), liquefied petroleum gas (LPG), liquefied ethylene and liquefied propylene are handled in liquid state.

Examples of metals contained in trace amounts in hydrocarbon fractions include heavy metals such as mercury, arsenic, vanadium, nickel and lead. Mercury is contained in the hydrocarbon fraction as elemental mercury, inorganic mercury and organic mercury, but each of these forms of mercury can be processed by the process of removal by adsorption of trace amounts of metal according to the present invention. Arsenic is present in hydrocarbon fractions as organic compounds such as alkyl arsines, aryl arsines, dialkylhaloarsines etc.. There is no particular limit to the concentration of mercury in the hydrocarbon fraction to which the process of removal by adsorption of trace amounts of metal from hydrocarbon fractions according to the present invention can be applied. A wide range of concentrations can be processed, and it is possible to almost completely remove even large amounts of mercury. Accordingly, even hydrocarbon fractions such as naphtha, which are usually used as the blending stock

for petroleum products, as well as natural gas condensates originating from south-east Asia and other areas can be processed.

The process of hydrogenating the hydrocarbon fraction in the present invention comprises reacting the hydrocarbon with hydrogen under hydrogenation conditions and in the presence of a hydrogenation catalyst. As a result of the hydrogenation, it is possible to obtain a hydrocarbon fraction having a reduced content of sulfur compounds (in particular, mercaptans), nitrogen compounds and other compounds. At the same time, mercury compounds are reduced.

There are no particular limitations regarding the hydrogenation catalyst used in the hydrogenation process of the present invention, provided it is one used in the hydrofining of hydrocarbon oils. It is preferred, however, to use one comprised of a carrier and an active hydrogenation component. Refractory inorganic oxide compounds may be used as the carrier; and one or more metal components selected from the group of metal components in Group VIII of the Periodic Table, and/or one or more metal components selected from the group of metal components in Group VI of the Periodic Table may be used as the active hydrogenation component. Examples of refractory inorganic oxide compounds include, alumina, silica, silica-alumina, zeolite etc.. It is also possible to use a carrier made by adding magnesia, zirconia etc. to the above-mentioned refractory inorganic oxide compound in order to improve the heat resistance thereof. Preferred carriers for

the hydrogenation catalyst used in the hydrogenation process of the present invention are alumina and silica-alumina. In particular, alumina or silica-alumina whose acid site has been adjusted to control its decomposition activity with respect to the hydrocarbon is particularly suitable. With respect to silica-alumina carriers, the acid site of the silica-alumina can be arbitrarily controlled by adjusting the silica content. For example, one having a silica content in the range of 5% by weight to 50% by weight may be used. Furthermore, alumina and silica-alumina having a specific surface area in the range of 100 m²/g to 1000 m²/g, and an average pore radius in the range of 5Å to 100Å may be used.

Specific examples of Group VIII metal components for use as the active hydrogenation component include iron, cobalt, nickel, ruthenium, rhodium, and palladium. Specific examples of Group VI metal components for use as the active hydrogenation component include chromium, molybdenum and tungsten. A combination of metal components such as cobalt-molybdenum, nickel-molybdenum and cobalt-nickel-molybdenum are particularly preferred. With Group VIII metal components, the amount of metal component carried on the carrier may be 1% by weight—30% by weight in terms of the oxide, preferably 5% by weight—15% by weight in terms of the oxide; and with Group VI metal components, it may be 1% by weight—20% by weight in terms of the oxide, preferably 5% by weight—15% by weight in terms of the oxide. It is preferred that the above-described

hydrogenation catalyst be first treated to presulfiding the metal oxides by contacting it with a hydrocarbon oil containing a sulfur compound, hydrogen sulfide, or carbon disulfide etc. before using it in the hydrogenation of the hydrocarbon fraction. This is preferable, because a catalyst in which active metal sulfides make up at least 50%, in particular at least 70%, of its total metal components brings about a smooth hydrogenation reaction.

It is preferred that the packed layer of hydrogenation catalyst in the hydrogenation zone be used in the form of a fixed bed. The hydrogenation catalyst may be in the pelletized form, spherical form, cylindrical form etc. , or it may have another different shape.

The reaction conditions employed in the hydrogenation zone for hydrogenating the hydrocarbon fraction are as follows: reaction temperature: $100^{\circ}\text{C} - 400^{\circ}\text{C}$, preferably $250^{\circ}\text{C} - 350^{\circ}\text{C}$; reaction pressure: $10\text{kg/cm}^2 - 50\text{kg/cm}^2$, preferably $25\text{kg/cm}^2 - 35\text{kg/cm}^2$; liquid hourly space velocity: $4\text{hr}^{-1} - 10\text{hr}^{-1}$, preferably $6\text{hr}^{-1} - 8\text{hr}^{-1}$; hydrogen gas/hydrocarbon fraction ratio: $400\text{Nm}^3/\text{kl} - 1700\text{Nm}^3/\text{kl}$, preferably $600\text{Nm}^3/\text{kl} - 1500\text{Nm}^3/\text{kl}$.

The above-described hydrogenation removes the sulfur compounds that were contained in the hydrocarbon fraction, and converts the organic mercury compounds to readily adsorbable forms such as elemental mercury. It is preferable

to reduce the total sulfur content to 20ppm or less, more preferably to 10ppm or less.

It is preferable to supply the hydrogenated hydrocarbon fraction to a distillation zone before supplying it to the adsorption zone, to distill off a light hydrocarbon fraction having a boiling point of 100°C or less, and then to supply the light hydrocarbon fraction to the adsorption zone. The light hydrocarbon fraction can be obtained by distilling the hydrogenated hydrocarbon fraction at 100°C or less. A preferable cut temperature is 50°C – 100°C, more preferably 70°C or more. If the cut temperature is lower than 50°C, mercury compounds tend to transfer to the heavy fraction. On the other hand, in the case that the cut temperature exceeds 100°C, the amount of hydrocarbons to be treated in the adsorption zone increase and it becomes a subject of discussion the efficiency on the adsorption declines.

The distillation zone may be comprised of a conventional distillation column. There are no particular limitations with respect thereto, and any type may be used.

The distillation causes most, for example, 90% or more, of the metals, in particular mercury compounds, contained in trace amounts in the hydrogenated hydrocarbon fraction to be concentrated into the light hydrocarbon fraction. Due to this transfer of the mercury compounds to the light hydrocarbon fraction, the heavy hydrocarbon fraction having a boiling point over 100°C, is comprised of heavy naphtha etc. which does not contain trace amounts of mercury and which has good

properties as a feedstock for catalytic reforming, and may thus be supplied as it is to the catalytic reforming.

An activated carbon may be used as the porous carbon material for the adsorption process of the present invention. For example, the specific activated carbons described hereunder may be used.

Namely, the activated carbon has a specific surface area of $100\text{m}^2/\text{g}$ - $2500\text{m}^2/\text{g}$, preferably $500\text{m}^2/\text{g}$ - $1500\text{m}^2/\text{g}$; an average pore radius of $5\text{\AA}$ to $30\text{\AA}$; a volume of pores having a pore radius of $50\text{\AA}$ or less is 0.2ml/g - 1.2ml/g . It is preferable, with a view to increasing the efficiency of mercury removal, that the difference in the pore volumes (a)-(b) between the volume of the pores having a pore radius $35.0\text{\AA}$ to $37.5\text{\AA}$ and the volume of the pores having a pore radius $42.5\text{\AA}$ to $45.0\text{\AA}$ shows zero or a positive value. It is more preferable that the pore volumes (a)-(b) make up less than 5%, specifically 3%, of all the pores having a pore radius of $50\text{\AA}$ or less. An activated carbon having a negative value in the difference between the above-mentioned two pore volumes, hardly adsorb or slightly adsorb mercury compounds contained in liquid hydrocarbons. The reason why the above-mentioned specified pores make a contribution to the mercury adsorption has not been known, but it is presumed that mercury or mercury compounds easily penetrate into micropore structures of activated carbons through the macropores having the above specified

size as means of an entrance.

The present inventors have found based on the result of an extensive study that an activated carbon having such specified pores of specified radius can accomplish remarkable effect in the removal of mercury from liquid hydrocarbon fraction. The specific surface area was measured by the BET nitrogen gas adsorption method, and the pore volume and pore distribution were calculated from the nitrogen adsorption isotherms using, for example, the DH (Dollimore & Heal) method.

The above activated carbons may be prepared by blending commercially available products so as to meet with the required properties mentioned before. Also activated carbons made from raw materials such as coconut shell, coal coke, charcoal etc. are used in the present invention. Activated carbons made from coconut shell are particularly preferred. A wide range of activated carbons may be used, provided it is a porous carbon material having a large specific surface area of at least 100m²/g, and exhibiting high adsorption properties with respect to trace amounts of metals. However, an activated carbon obtained by subjecting a carbonized material, which has been obtained by carbonization of the raw material for the activated carbon, to a steam activation treatment is very effective. Normally, an activation gas having a steam content of between 40% by volume and 60% by volume is employed, but with a view to further increasing the mercury

adsorption capability, it is preferred to subject the carbonized material to activation in an atmosphere having a steam content less than 40% by volume, and preferably less than 30% by volume. In order to realise a further increase in the mercury adsorption performance, an activated carbon which has been activated with an activation gas having a steam content of less than 20% by volume is particularly suitable.

A preferred composition for the activation gas comprises, for example, 50% by volume—75% by volume of nitrogen, 3% by volume—40% by volume of steam, 3% by volume—30% by volume of carbon dioxide, 0% by volume—2% by volume of oxygen, and 0% by volume—2% by volume of hydrogen.

It is preferred to prepare the activated carbon by heating the carbonized material to a temperature between 700°C and 1100°C in the above-described activation gas depending upon other conditions; then, after activation, cooling the activated carbon and then taking the activated carbon out of the system.

There is no particular limitation regarding the form of the porous carbon material. It may be used in anyone of the following forms: powdered form, ground form, cylindrical form, spherical form, fiber form or honeycomb form. Particulate carbon and shaped carbon are produced according to the conventional methods by adding 30 parts to 60 parts of a binder such as petroleum pitch or coal

tar to 100 parts of the carbonized material, followed by mixing and shaping, and finally activation.

In the present invention, the activated carbon, as described above, may be used alone, or it is preferable that a chlorine-containing substance may be combined with the activated carbon, which makes a contribution to the increase of the amount of mercury on the activated carbon. As the concentration of the chlorine-containing substance, more than 0.05 wt.%, as chlorine, is preferable. Even though the concentration is 0.1 wt.% to 1 wt.%, it is satisfactory for enough mercury adsorption. Depending on a kind of hydrocarbon fractions, the concentration may be up to about 5 wt.%.

As a chlorine-containing substance, any chlorine-containing compounds are used. A water-soluble compound, for example, hydrogen chloride is more preferable in connection with mercury adsorption capability and easy handling. The incorporation of hydrogen chloride into an activated carbon is performed by various methods, for example, ① a method of impregnation of the activated carbon with hydrogen chloride aqueous solution, ② a method of adsorption of hydrogen chloride into the activated carbon in vapor phase, and ③ a method of adsorption of hydrogen chloride generated by reacting a material on an activated carbon (see, Japanese Patent Application Laid-Open No.158592/1975). More preferable method is the above ② method. Or, it may be used after being first loaded with alkali metal sulfides and/or alkaline earth metal sulfides. There are no particular limitations regarding the alkali metal sulfides and alkaline earth metal sulfides which may be loaded on the activated carbon. For example, Li_2S , Na_2S and K_2S are examples of alkali metal

sulfides which may be used, and MgS and CaS are examples of alkaline earth metal sulfides which may be used. These alkali metal sulfides and alkaline earth metal sulfides may be used singly or as a mixture of two or more types thereof. Na_2S is the most preferred of the compounds mentioned above.

There are no particular limitations regarding the amount of alkali metal sulfides and alkaline earth metal sulfides carried on the activated carbon, but it is preferred to use an amount in the range from 0.1% by weight to 30% by weight on the basis of the activated carbon. If the amount is less than 0.1% by weight, then there is the tendency for the mercury adsorption performance to be reduced, and if the amount exceeds 30% by weight, then the adsorption performance of the activated carbons is hindered by these metal sulfides with the result that the increase in the mercury adsorption performance tends to be dampened.

The contacting of the hydrocarbon and the porous carbon material in the adsorption zone can be carried out using any one of the following type of contacting systems: fixed bed, moving bed, fluidized bed, ebullated bed. However, from the point of view of simplicity of construction and ease of operation, a fixed bed type is preferred. In the fixed bed system, adsorption is carried out by continuously supplying the hydrocarbon fraction to a packed layer formed by packing and securing particles of the porous carbon material into the adsorption zone. On the other hand, the moving bed system is a contacting method wherein particles of the

porous carbon material are intermittently or substantially continuously added into one end of the adsorption zone, and then intermittently or substantially continuously removed from the other end of the adsorption zone. In the moving bed system, the particles of porous material can be made to continuously contact the hydrocarbon fraction, as the groups of porous particles introduced from the top fall one after the other under the influence of gravity. In the fluidized bed and boiling bed systems, the contacting of the two materials is carried out by floating the particles of porous carbon material in a flow of the hydrocarbon fraction.

The fixed bed of porous carbon material can be provided by securing the particles using a conventional method. The above-described hydrocarbon fraction can be contacted with the porous carbon material inside the fixed bed by flowing it downwards from the top, or flowing it upwards from the bottom. However, with a view to stabilizing the porous carbon material inside the adsorption column, it is preferred to flow the hydrocarbon fraction downwards from the top.

As described above, the mercury contained in hydrocarbon fractions can be efficiently, and almost completely eliminated regardless of the form in which it exists, by subjecting the mercury-containing hydrocarbon fraction, in particular a hydrocarbon fraction having a wide boiling point range, to hydrogenation, and then subjecting the hydrogenated hydrocarbon fraction to mercury adsorption. Furthermore, the efficiency of the adsorption of the mercury may be further

enhanced by distilling off a light fraction having a boiling point of 100°C or less from the hydrogenated hydrocarbon fraction, and then contacting this light naphtha fraction with the activated carbon.

Figure 1 is an explanatory figure showing a typified view of an embodiment of the present invention; and Figure 2 is an explanatory figure showing a typified view of another embodiment of the present invention; wherein reference numerals 1, 20 indicate an hydrogenation column, and reference numerals 2, 22 indicate an adsorption column.

The process of removal by adsorption of mercury according to the present invention shall now be explained with reference to the Figures. In the figures, valves and other components which are not essential to the explanation of the present invention are omitted. Figure 1 shows an embodiment of the present invention in which a hydrogenation zone and an adsorption zone are combined. With reference to Figure 1, the metal-containing hydrocarbon fraction is supplied to hydrogenation column 1 from pipe 3, the hydrogenated hydrocarbon fraction is supplied to flow in a downwards direction to adsorption column 2 via pipe 4, and the hydrocarbon fraction from which a metal, for example, mercury has been removed is taken off via pipe 5. Hydrogenation catalyst is packed into hydrogenation column 1 in the form of a fixed bed 10, and mercury adsorbent is packed into adsorption column 2 in the form of a fixed bed 11. In the adsorption

column 2, the hydrogenated hydrocarbon fraction introduced from pipe 4 is caused to pass, at a normal temperature and at an LV value of 20cm/min, through the fixed bed of granulated activated carbon having an average particle size of 1.1mm (described below), and then the processed liquor whose mercury concentration has been reduced to less than 1ppb is collected via pipe 5.

Figure 2 shows a further preferred embodiment of the present invention.

In figure 2, the mercury-containing hydrocarbon fraction is supplied to hydrogenation column 20 via pipe 23; the hydrogenated hydrocarbon fraction is then supplied to distillation column 21 via pipe 24; a light hydrocarbon fraction having a boiling point of less than 100°C is distilled off, and is supplied via pipe 25 to adsorption column 22 which is provided with a fixed bed of granulated activated carbon having an average particle size of 1.1mm. The hydrogenated light hydrocarbon fraction is flowed downwards from the top of the adsorption column to pass through the fixed bed at a normal temperature and an LV value of 20cm/min, and the light hydrocarbon fraction from which mercury has been removed is collected from pipe 27. Substantially all of the total mercury content in the hydrocarbon fraction at the inlet of the distillation column transfers into the light hydrocarbon fraction distilled off from the distillation column.

Hereunder, the present invention shall be explained in detail using several Examples and Comparative Examples.

Example 1

A naphtha fraction (density at 15°C of 0.720 g/cm³) having a mercury concentration of 10ppb (including 5ppb of organic mercury compound), a sulfur content of 50ppm and a boiling point range of 30°C – 160°C was supplied to a hydrogenation column packed with 30 litres of the hydrogenation catalyst described herebelow, and was reacted with hydrogen under the following conditions:

Reaction conditions:

Reaction Temperature: 315°C

Reaction Pressure: 30kg/cm²

Liquid Hourly Space Velocity: 8hr⁻¹

Hydrogen gas/Liquid hydrocarbon ratio: 1000Nm³/kl

Hydrogenation catalyst

Sulfurized Co-Mo/Al₂O₃ catalyst

Cobalt and molybdenum were loaded onto a shaped alumina carrier having a particle size of 1.5mm. in amounts of 5% by weight and 14 % by weight respectively in terms of the oxide. This was then packed into the hydrogenation column, and then presulfiding was carried out by causing a naphtha fraction having a sulfur content of 100 ppm to pass therethrough at a temperature of 200°C and a pressure of 20kg/cm²

As a result of the above-described hydrogenation treatment, a naphtha fraction having a sulfur content of 1ppm was obtained. There was no change in the mercury concentration.

This hydrogenated naphtha fraction was then supplied to the top of an adsorption column packed with granulated activated carbon, under the following conditions, and was flowed downwards through the packed layer to obtain a naphtha fraction having a mercury concentration of 2ppb. It was shown that almost all the mercury compounds had been adsorbed regardless of their form.

Adsorption column: 0.3m³ of adsorbent packed into an adsorption pipe of internal diameter 30cm and height 4m.

Adsorption conditions: Temperature: 25°C
LV value: 20cm/min

Adsorbent:

Activated carbon A:

Average particle size:	1.1mm
Specific surface area:	1532m ² /g
Average pore radius:	11Å
Pore volume (≤50Å):	0.7959ml/g
Pore volume (a)-(b)*:	0.0048ml/g
Pore distribution** :	0.60%
Chloride content(as cl):	0.026wt. %

*Pore volume (a)-(b)=PV[(35.0Å~37.5Å) - (42.5Å~45Å)]

**Pore distribution=[PV(a)-(b))/PV(≤50Å)]x100

wherein PV is pore volume

The specific surface of the activated carbon was measured by the nitrogen adsorption isotherm BET method.

The total pore volume and pore distribution of the activated carbon were

calculated from measurements of the nitrogen adsorption isotherm made using an Autosorp 1-MP measuring device made by Yuasa Ionics Company.

The particle size of activated carbons was measured by JIS K 1474-1991 method.

The concentration of mercury in the hydrocarbon fraction was measured by using a general automatic mercury analyzer, Mercury/SP-3D made by Nippon Instruments Corporation.

Type of mercury compounds in the hydrocarbon fraction was determined by using a method described in Proceedings of International Trace Analysis Symposium (ITAS) '90 (July 23-27, 1990). Meeting Records 3P-40 (Akio FURUTA, et al.).

The activated carbon A was produced in the following way by utilizing a method.

A carbonized material obtained by the dry distillation of coconut shell was broken down and used as the raw material for the granulated activated carbon. It was then subjected to activation at 800°C using a mixed gas (gas composition: 70% nitrogen gas, 0.1% oxygen gas, 9.9% of carbon dioxide gas, 20% steam), and then cooled. After cooling, the thus obtained activated carbon was crushed and washed with hydrochloric acid aqueous solution in a condition that the hydrochloric acid remains on the activated carbon to obtain a granulated activated carbon.

Example 2

A naphtha fraction (density at 15°C of 0.720 g/cm³) having a mercury concentration of 10ppb, a sulfur content of 50ppm and a boiling point range of

30°C - 160°C was supplied to a hydrogenation column packed with the same kind of hydrogenation catalyst as used in Example 1, and was subjected to hydrogenation under the same hydrogenation conditions as used in Example 1, to thereby obtain a naphtha fraction having a sulfur content of 1ppm.

The hydrogenated naphtha fraction was then supplied to a distillation column, and a light naphtha fraction was distilled off at a cut temperature of 70°C. 30% by volume of the light naphtha fraction was obtained. The concentration of mercury in the light naphtha fraction was 33ppb. The concentration of mercury in the heavy naphtha fraction (having a boiling point greater than 70°C) which was collected from the bottom of the distillation column was less than 1 ppb. It was thus clear that the mercury compounds had been concentrated into light compounds by the distillation after the hydrogenation treatment of the naphtha fraction.

Next, the light naphtha fraction was supplied under the same adsorption conditions as employed in Example 1 to the top of an adsorption column packed with the same activated carbon as used in Example 1, and was passed through the packed layer. A light naphtha fraction having a mercury concentration of less than 1ppb was obtained at the bottom of the adsorption column. It was thus possible to reduce the adsorption time to two thirds of the time required in Example 1, and to completely remove substantially all of the mercury compounds.

Example 3

A naphtha fraction (density at 15°C of 0.720 g/cm³) having a mercury concentration of 10ppb, a sulfur content of 50ppm and a boiling point range of 30°C—160°C was subjected to hydrogenation under the same hydrogenation conditions as used in Example 1 to obtain a hydrogenated naphtha fraction having a sulfur content of 1ppm. The hydrogenated naphtha fraction was then subjected to adsorption using the activated carbon B described below, with the result that an adsorption-treated naphtha fraction having a mercury concentration of 2ppb was obtained.

Adsorbent:

Activated carbon B:

Average particle size:	1.2mm
Specific surface area:	850m ² /g
Average pore radius:	13Å
Pore volume (≤50Å):	0.4391ml/g
Pore volume (a)-(b):	0.0015ml/g
Pore distribution:	0.34%
Chloride content(as cl):	0.078wt. %

The activated carbon B was produced by blending Activated carbon A with commercially available product so as to have the properties shown above.

Example 4

Hydrogenation and adsorption were carried out in the same way as described in Example 3 except that the hydrogenated naphtha fraction was subjected to a

distillation column and distilled at a cut temperature of 70°C. The obtained light naphtha fraction of less than 70°C was subjected to the adsorption column. The result is shown in Table 1. The mercury concentration in the light fraction at the bottom of the adsorption column was less than 1ppb.

Example 5

A natural gas condensate (density at 15°C of 0.739g/cm³ @15°C) having a mercury concentration of 20ppb, a sulfur content of 140ppm and a boiling point range of 27°C to 243°C was subjected to hydrogenation under the same hydrogenation conditions as used in Example 1. A hydrogenated natural gas condensate was then subjected to distillation, and then a light fraction was distilled off at a cut temperature of 70°C. 25% by volume of the light fraction was obtained. The concentration of mercury in the light fraction was 80ppb. A heavy fraction, which has a boiling point of more than 70°C, having a mercury concentration of less than 1ppb was obtained at the bottom of the adsorption column. The light fraction was subjected to adsorption under the same conditions as employed in Example 1. A light fraction having a mercury concentration of less than 1ppb was obtained at the bottom of the adsorption column.

Comparative Example 1

Adsorption was carried out in the same manner and under the same conditions as in Example 1, except that the naphtha fraction was not first subjected to

hydrogenation. The concentration of mercury in the adsorption-treated naphtha fraction, i.e the naphtha fraction which had been passed through the packed layer of activated carbon, was 5ppb.

In other words, the same kind of naphtha fraction as used in Example 1 was subjected directly to adsorption treatment without first subjecting it to any hydrogenation treatment.

Comparative Example 2

The same kind of naphtha fraction as used in Example 1 was supplied to a distillation column without first subjecting it to hydrogenation treatment, and distilled at a cut temperature of 70°C. 30% by volume of the light naphtha fraction having the mercury concentration of 17ppb was obtained. The result was that about 50% of the mercury in the naphtha fraction transferred into the heavy naphtha fraction, making it necessary to subject the mercury in the heavy naphtha fraction to adsorption treatment. The light naphtha fraction was subjected to adsorption under the same conditions in Example 1 and then the mercury concentration was 7ppb. The heavy naphtha fraction was subjected to adsorption under the same conditions employed in the treatment of the light naphtha fraction. The mercury concentration could not be reduced to less than 2ppb. From this result, it is clear that the mercury cannot be completely condensed in the light naphtha fraction if the step of hydrogenating the naphtha fraction is omitted.

The light naphtha fraction was subjected to adsorption treatment under the same conditions as employed in the adsorption treatment of Example 1, with the result that the concentration of mercury remaining in the adsorption-treated naphtha fraction was 7ppb.

Comparative Examples 3 and 4

Hydrogenation, distillation and adsorption were carried out in the same manner as in Example 2 except that an activated clay and a zeolite were used instead of activated carbon A. The result was that the concentration of mercury remaining in the adsorption-treated naphtha fraction was increased to 20ppb in each case.

Comparative Examples 5

Hydrogenation, distillation and adsorption were carried out in the same manner and under the same conditions as in Example 2, except that the commercially available activated carbon C was used instead of the activated carbon A, with the result that the concentration of mercury remaining in the adsorption-treated light naphtha fraction was 5ppb.

Activated carbon C:

Average particle size:	1.2mm
Specific surface area:	639m ² /g
Average pore radius:	20Å
Pore volume ($\leq 50\text{\AA}$):	0.4185ml/g
Pore volume (a)-(b):	-0.0008ml/g
Pore distribution:	-0.19%

Chloride content(as cl): 0.0080wt. %

Comparative Example 6

Hydrogenation, distillation and adsorption were carried out in the same manner and under the same conditions as in Example 2, except that the hydrogenated naphtha fraction was distilled at a cut temperature of 45°C. The result was shown in Table 1. A portion of mercury contained in the naphtha fraction was transferred into the heavy naphtha fraction, making it necessary to subject the heavy naphtha fraction to adsorption treatment.

It is clear from the above Examples 1 to 5, in particular Examples 1 and 2, that the mercury removing effect of the combination of hydrogenation and adsorption using activated carbon is extremely striking; and it is evident from the Comparative Examples that almost no effect can be achieved in the case that any one of the hydrogenation or the distillation is not carried out. Also, a specific activated carbon is useful for the adsorption.

Table I

	Examples				
	1	2	3	4	5
Hydrocarbon fraction					
Boiling range(°C)	30/160	30/160	30/160	30/160	27/243
Mercury concentration (ppb)	10	10	10	10	20
Sulfur content (ppm)	50	50	50	50	140
Hydrogenation conditions					
Temperature(°C)	315	315	315	315	315
Pressure (kg/cm ²)	30	30	30	30	30
Liquid hourly space velocity	8	8	8	8	8
Hydrogenated naphtha fraction					
Mercury concentration (ppb)	10	10	10	10	20
Sulfur content (ppm)	1	1	1	1	
Distillation					
Cut temperature(°C)	-	70	-	70	70
Distillate					
Mercury concentration(ppb)	-	33	-	33	80
Lt. fraction	-	<1	-	<1	<1
Hvy. fraction					
Mercury adsorbent	AC.A	AC.A	AC.B	AC.B	AC.A
Adsorption conditions					
LV value (cm/min)	20	20	20	20	20
Adsorption treated naphtha fraction					
Remaining mercury concentration (ppb)	2	<1*	2	<1*	<1*

*AC is an abbreviation for "activated carbon"

**Concentration of mercury in the light naphtha fraction

Table 2

	Comparative Examples					
	1	2	3	4	5	6
Hydrocarbon fraction Boiling range(°C) Mercury concentration (ppb) Sulfur content (ppm)	30/160 10 50	30/160 10 50	30/160 10 50	30/160 10 50	30/160 10 50	30/160 10 50
Hydrogenation conditions Temperature (°C) Pressure (kg/cm ²) Liquid hourly space velocity	- - -	- - -	315 30 8	315 30 8	315 30 8	315 30 8
Hydrogenated naphtha fraction Mercury concentration (ppb) Sulfur content (ppm)	- -	- -	10 1	10 1	10 1	10 1
Distillation Cut temperature(°C) Distillate Mercury concentration(ppb) Lt.fraction Hvy.fraction	- - - -	70 17 7	70 33 <1	70 33 <1	70 33 <1	45 50 6
Mercury adsorbent	AC.A	AC.A	Act.Clay	Zeolite	AC.C	AC.A
Adsorption conditions LV value (cm/min)	20	20	20	20	20	20
Adsorption treated Light fraction Remaining mercury concentration (ppb)	5	3*	20*	20*	5*	≤1*

•AC is an abbreviation for "activated carbon"

• *Concentration of mercury in the light naphtha fraction



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Claims:

1. A process for the removal of a metal present in trace amounts in hydrocarbon fractions using apparatus comprised of a hydrogenation zone having provided a packed layer of hydrogenation catalyst, and an adsorption zone having provided a packed layer of a porous carbon material; wherein said process comprises the steps of:

(A) supplying the hydrocarbon fraction containing a metal in trace amounts to the hydrogenation zone, and contacting it with hydrogen under hydrogenation conditions and in the presence of the hydrogenation catalyst; and

(B) supplying the hydrogenated hydrocarbon fraction from the hydrogenation zone to the adsorption zone, and contacting it with the porous carbon material.

2. A process for the removal of a metal present in trace amounts in hydrocarbon fractions using apparatus comprised of a hydrogenation zone having provided a packed layer of hydrogenation catalyst, a distillation zone, and an adsorption zone having provided a packed layer of a porous carbon material; wherein said process comprises the steps of:

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(A) supplying the hydrocarbon fraction containing a metal in trace amounts to the hydrogenation zone, and contacting it with hydrogen under hydrogenation conditions and in the presence of the hydrogenation catalyst;

(B) supplying the hydrogenated hydrocarbon fraction from the hydrogenation zone to the distillation zone, and distilling off a light hydrocarbon fraction having a boiling point of 100°C or less;

(C) supplying the light hydrocarbon fraction from the hydrogenation zone to the adsorption zone, and contacting it with the porous carbon material.

3. The process for the removal of a metal present in trace amounts in hydrocarbon fractions according to one of claims 1 or 2, wherein the hydrogenation catalyst is comprised of a refractory inorganic oxide carrier which has been loaded with one or more metal components selected from the group of metal components in Group VIII of the Periodic Table, and/or one or more metal components selected from the group of metals in Group VI of the Periodic Table.

4. The process for the removal of a metal present in trace amounts in

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hydrocarbon fractions according to any one of claims 1 to 3, wherein the hydrogenation conditions comprise a temperature of 100°C - 400°C, a pressure of 10kg/cm² - 50kg/cm², and a liquid hourly space velocity of 4hr⁻¹ - 10hr⁻¹.

5. The process for the removal of a metal present in trace amounts in hydrocarbon fraction according to anyone of claims 2 to 4, wherein the light hydrocarbon fraction is obtained by the distillation of a hydrogenated hydrocarbon fraction at a cut temperature of 50°C or more.

6. The process for the removal of a metal present in trace amounts in hydrocarbon fractions according to any one of claims 1 to 4, wherein the porous carbon material is a granulated activated carbon agglomerate having an average particle size of 0.24mm - 2.4mm.

7. The process for the removal of a metal present in trace amounts in hydrocarbon fractions according to any one of claims 1 to 6, wherein the porous carbon material is an activated carbon having a specific

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surface area of $100\text{m}^2/\text{g}$ — $2500\text{m}^2/\text{g}$, and for which the difference (a)-(b) between (a) a pore volume of pores having a radius of $35.0\text{\AA}$ – $37.5\text{\AA}$ and (b) a pore volume of pores having a radius of $42.5\text{\AA}$ – $45.0\text{\AA}$ is 5% or less of the volume of all pores having a radius of $50\text{\AA}$ or less.

8. The process for the removal of a metal present in trace amounts in hydrocarbon fractions according to anyone of claims 1–7, wherein the porous carbon material contains 0.05% by weight or more, as chlorine, of chlorine-containing substance.