

Description

Naturally occurring crude oils and other fossil fuels may contain a small amount of mercury depending on the location of their production. Mercury as an impurity is a potential cause of such problems as catalyst poisoning and damage to facilities used in refining, reforming or petrochemical processes. Natural gas and the oils that accompany its production often contain mercury and several technologies for removing mercury from hydrocarbon gases have been practiced at many commercial NG plants. US-A-4709118 discloses removing mercury from hydrocarbon liquids using reactive metal particles embedded in a matrix of silica or alumina. However, no commercial method for successfully removing mercury from hydrocarbon oils(hydrocarbon liquids) and other oils that are produced in conjunction with the production of natural gas has yet been developed. The present invention relates to a technology for removing mercury from such hydrocarbon oils, more particularly, to a method for removing mercury selectively and efficiently by utilizing the mechanism of contact with a copper compound and/or a tin compound. Techniques for removing mercury present as a trace impurity in other substances have been described in numerous reports. In one method, mercury in waste water is removed with the aid of a chelating agent, sulfur, activated carbon or an ion-exchange resin ; in another, mercury in waste gases such as combustion gases and air is removed using a molecular sieve, lead sulfide, an alkaline reducing agent, a chelator-supporting activated carbon or an aqueous solution of permanganate. These and other methods known in the art of mercury removal are mostly intended for use in environmental pollution control.

Techniques are also available to remove mercury from natural gas using zeolite or a sulfur-supporting(sulfur-impregnated) activated carbon but their availability is limited to hydrocarbons in gaseous form.

As will be understood from the above, disclosure of prior art methods of removing trace mercury from fluids is very scarce. Methods are known that remove trace mercury from vacuum pump oils using zinc sulfide but the percentage of mercury that can be removed from hydrocarbon oils by adopting these methods is far from being satisfactory for practical purposes. Therefore, a strong need exists for developing a method that is capable of selective and efficient removal of mercury from hydrocarbon oils.

The present invention provides a method by which mercury present in a trace amount in hydrocarbon oils can be removed in a selective and efficient way.

According to the invention there is provided a method of removing mercury from a hydrocarbon oil which comprises contacting said hydrocarbon oil with a cupric compound which is a cupric halide or hydrate thereof and/or a stannous compound which is a stannous halide or hydrate thereof. The cupric compound and/or stannous compound used in this method may be in any suitable form such as a powder, an aqueous solution or an alcoholic solution. If desired, these compounds may be supported on "porous adsorbents" such as activated clay, silica gel, zeolite, molecular sieves, alumina, silica, silica-alumina, and activated carbon. There also is no limitation on the method of contact to be established between mercury-containing hydrocarbon oils and the Cu^{++} and/or Sn^{++} compounds.

In the course of studies that eventually led to the accomplishment of the present invention, we conducted the following experiment: sludge was separated by filtration from heavy natural gas liquid(H-NGL) of the same nature as employed in Example 1 below and 100 ml of the filtrate was treated with various reagents that were believed to react with mercury compounds in view of such factors as electronegativity (see Table A below for the names of these reagents which were used individually in an amount of 1.0 g); after adding these reagents, the mixtures were stirred well and thereafter left to stand for 1 hour; the concentrations of mercury in the treated solutions were compared with those in the untreated filtrates. The results are also shown in Table A.

Table A Removal of Mercury with Various Reagents

	<u>Reagent</u>	<u>Hg concentration (w/v ppb)</u>		<u>Removal%</u>
		<u>Untreated solution</u>	<u>Treated solution</u>	
5	ZnS	103	22	78.6
	ZnO	94	70	25.5
10	ZnCl ₂	94	60	36.2
	FeCl ₂	94	65	30.9
	FeCl ₃	94	26	72.3
15	SnCl ₂	103	13	87.4
	SnI ₂	103	2	98.1
	SnO	86	52	39.5
	SnCl ₄	103	59	42.7
20	SnO ₂	86	87	0
	PbCl ₂	86	86	0
	Cu ₂ Cl ₂	80	53	33.8
25	CuCl ₂	80	6	92.5
	S	103	66	35.9

As shown in Table A, sulfur which previously proved to be effective in the removal of trace mercury from gases was not so effective for the purpose of removing trace mercury from hydrocarbon oils in the liquid state.

On the basis of these experimental results, we found that removal of trace mercury from hydrocarbon oils (liquids) involved a problem that was entirely different from the case of removing mercury from gases. The difference in such factors as the chemical form in which mercury occurred and that the use of specified copper and/or tin compounds was effective for the purpose of removing mercury present in trace amounts in hydrocarbon oils.

The method of the present invention is applicable to all hydrocarbon oils that are liquid at ordinary temperatures. Illustrative hydrocarbon oils include crude oils, straight run naphtha, kerosene, gas oil, vacuum distillates, atmospheric residues, thermal cracked gasoline obtained as a by-product in the thermal cracking unit of an ethylene plant, heat-treated hydrocarbon oils, naphtha fractions produced in a catalytic cracking unit, and recycled oils. The method of the present invention is particularly suitable for the removal of mercury from natural gas liquid (NGL) obtained by stripping natural gas of liquefied petroleum gas (LPG), especially from heavy natural gas liquid which contains high-boiling point components.

The mercury to be removed from hydrocarbon oils by the method of the present invention may be present in any form such as metallic, inorganic or organic. The concentration of mercury in hydrocarbon oils is not limited to any particular value but from the viewpoint of reaction efficiency, the mercury concentration is preferably not more than 400-600 ppb, more preferably up to 100-150 ppb. If necessary, sludge and other solids in the hydrocarbon oil may be removed by passage through a filtration membrane or some other filtration medium before the oil is brought into contact with a cupric compound and/or a stannous compound.

Preferred examples of the cupric and stannous compounds for use in the method of the present invention include CuCl₂, CuI₂ and hydrates thereof and SnCl₂, SnI₂ and hydrates thereof.

The cupric and stannous compounds are preferably contacted by trace Hg containing hydrocarbon oils under the conditions set forth below.

(1) A solution of the cupric or stannous compound is brought into liquid-liquid contact with a hydrocarbon oil. A solution of cupric halide, in particular CuCl₂ in HCl, alcohol or water is added to a hydrocarbon oil. The concentration of a cupric compound is typically at least 10 ppm, say, 10 ppm - 40 wt%, preferably in the range of 0.5-10 wt%. When a stannous halide is to be used, SnCl₂ or some other stannous halide is dissolved in HCl, water or an alcohol in an amount of at least 10 ppm, say 10 ppm-40 wt%, preferably 0.5-10 wt%.

(2) A cupric or stannous compound in powder form is added to a hydrocarbon oil. In case of a cupric compound,

the powder of a cupric halide such as CuCl_2 or a hydrate thereof is brought into contact with a hydrocarbon oil. In case of a stannous compound, the powder of SnCl_2 , SnI_2 or a hydrate of SnX_2 (X is a halogen atom) is preferred.

(3) A carrier supporting a cupric or stannous compound is brought into contact with a hydrocarbon oil. Common granular or powdery activated carbon may be used as a carrier and it is also possible to use steam-activated carbon. Particularly good results are attained with an activated carbon having a pore size of 1 to 50 nm (10-500 Å), preferably 1 to 10 nm (10-100 Å), and a specific surface area of 100-1,500 m^2/g , preferably 800-1,200 m^2/g . Using an activated carbon having these values of pore size and specific surface area will contribute to an improved efficiency of mercury removal.

The amount of cupric or stannous compounds or a mixture thereof to be supported on an activated carbon is preferably in the range of 0.1-30 wt%, more preferably 1-30 wt% of the carrier (activated carbon).

Carriers other than activated carbon that may be used in the method of present invention include commonly employed granular or powdery activated clay, silica gel, zeolite, molecular sieve, alumina, silica and silica-alumina, which may

be used either on their own or as mixtures. Particularly good results are attained with carriers having a specific surface area of at least 100 m^2/g , preferably 100-1,500 m^2/g . Using carriers having these values of a specific surface area will contribute to an improved efficiency of mercury removal. For the purpose of the present invention, it is more preferable to use these carriers after acid treatment. The amount of cupric or stannous compounds or a mixture thereof to be supported on carriers other than activated carbon is preferably in the range of 0.1-30 wt% of the carrier.

To prepare a cupric compound-supporting adsorbent a cupric halide such as CuCl_2 can be dissolved in either water or HCl aqueous solution or a suitable solvent which may be inorganic or organic (e.g. acetone or alcohol); a carrier immersed in the resulting solution and the solvent removed with an evaporator, followed by drying and firing (if required).

To prepare a stannous compound-supporting adsorbent a stannous halide such as SnCl_2 , SnI_2 and hydrates thereof can be dissolved in water, HCl aqueous solution, an inorganic solvent or an organic solvent such as acetone or alcohol, the carrier immersed in the resulting solution and the solvent removed with an evaporator, followed by drying and firing (if required).

Activated carbon and other carriers on which a cupric and/or stannous compound is supported may be brought into contact with a hydrocarbon oil by various methods of establishing solid-liquid contact using, for example, a fixed, moving or fluidized bed system. Non-limiting examples of reaction equipment that are preferably employed in practicing the present invention are described below.

Figs 1 to 4 of the accompanying drawings each illustrate a system for practicing the method of the present invention.

Fig. 1 shows a system employing a reaction vessel 3 furnished with a stirrer 11. The reaction vessel 3 is also furnished with a line for supplying a feed 1 and a line for supplying a Cu^{++} or Sn^{++} compound 2. A fluid can communicate between the vessel 3 and a sedimentation tank 4 which is furnished with outlets that are respectively connected to a product recovery line 9 and a mercury processing line 10. The mercury processing line 10 communicates at one end with a mercury processing apparatus (not shown) through a valve 7 and at the other end with the reaction vessel 3 through a valve 8 and a pump 6.

A feed 1 such as a hydrocarbon oil is supplied to the reaction vessel 3 whereas the Cu^{++} or Sn^{++} compound 2 is separately supplied in solution or powder form into the vessel 3. The supplied hydrocarbon oil and Cu^{++} or Sn^{++} compound are intimately mixed with the stirrer 11 in the reaction vessel 3.

The mixture is transferred to the sedimentation tank 4 where it is left to stand until it separates into a purified solution 13 and a mercury-containing phase 14. The purified solution 13 is recovered from the tank 4 via the product recovery line 9. The mercury-containing phase 14 is discharged to the mercury processing apparatus (not shown) through the valve 7. If necessary, the mercury-free liquid phase is recycled by pump 6 to the reaction vessel 3 through the valve 8.

Fig. 2 shows a system in which a cupric or stannous compound 2 is first mixed with a feed 1 before they are transferred to a subsequent stage by means of a pump 7. Since the feed 1 is further mixed with the Cu^{++} or Sn^{++} compound 2 to have intimate contact with the latter as they are pumped, there is no need to employ a reaction vessel equipped with a stirrer as in the case shown in Fig. 1. If necessary, a plurality of sedimentation tanks 4 and 12 may be adopted as shown in Fig. 2 to separate the mixture into a purified solution 13 and a mercury-containing phase 14 as in the system shown in Fig. 1.

Fig. 3 shows a system that employs adsorption tower 16 and 17 packed with a fixed bed of a Cu^{++} or Sn^{++} supporting adsorbent 15. The first adsorption tower 16 is a cylindrical reactor packed in the middle portion with a fixed bed of a Cu^{++} and/or Sn^{++} supporting adsorbent 15. It has an inlet on its top through which a feed 1 is supplied via a pump 6 and is connected at its bottom to a product recovery line 9. Preferably, more than two

adsorption towers are provided and Fig 3 shows an embodiment using two adsorption towers, the first tower 16 and the second tower 17. The feed 1 such as a hydrocarbon oil is supplied to the first adsorption tower 16 and as it flows down through the fixed bed of Cu^{++} or Sn^{++} supporting adsorbent 15, mercury present in a trace amount in the hydrocarbon oil is removed by being adsorbed on the adsorbent 15. The hydrocarbon oil is transferred to the second adsorption tower 17 via the product recovery line 9 and is stripped of the remaining mercury through adsorption by the fixed bed of adsorbent 15. In a fixed bed system, the adsorption towers are preferably maintained at a temperature of 10-40°C, more preferably 20-30°C. The SV value is preferably in the range of from 0.5-5.0 hr^{-1} , more preferably 0.5-2.0 hr^{-1} .

Fig. 4 shows a system furnished with adsorption vessels 19 and 20 each having a stirrer 18. A feed 1 such as a hydrocarbon oil is supplied to the first adsorption vessel 19 which is also supplied with a Cu^{++} and/or Sn^{++} supporting adsorbent 15. The feed 1 and the Cu^{++} and/or Sn^{++} supporting adsorbent 15 in the vessel 19 make intimate contact with each other as they are agitated with the stirrer 18 and mercury present in a trace amount in the hydrocarbon oil is removed by being adsorbed on the Cu^{++} and/or Sn^{++} supporting adsorbent 15.

If the feed 1 has a high solids content, sludge and other solid matter are preferably removed with a prefilter or some other suitable device to protect the adsorption towers 16 and 17 (Fig. 3) or adsorption vessels 19 and 20 (Fig. 4). Any filtration medium may be employed as long as it is capable of rejecting the solids content of the feed.

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

EXAMPLES 1 AND 2

A hundred milliliters of heavy natural gas liquid was filtered through a Millipore® filter (0.2 μm). The separated sludge had the following composition:

Fe	10.0 wt%
Si	18.3 wt%
Hg	3.1 wt%
S	2.3 wt%

The filtrate had a mercury content of ca. 130 ppb. To the filtrate, stannous compounds (see Table 1 below) were added in the concentrations also shown in Table 1 and the mixtures were stirred well, followed by standing for 1 hour. The concentrations of mercury in the purified solutions were measured and the results are shown in Table 1.

COMPARATIVE EXAMPLES 1-4

Heavy natural gas liquid was filtered to remove sludge as in Examples 1 and 2. To the filtrates, the compounds shown in Table 1 were added and the mixtures were treated as in Examples 1 and 2. The concentrations of mercury in the purified solutions were measured and the results are shown in Table 1.

TABLE 1

	Compound (concentration: 1wt% <u>aqueous solution: 10ml</u>)	Hg concentration of purified <u>solution (ppb)</u>	Hg removal <u>(%)</u>	
5				
	Example 1	SnCl ₂	19	85.4
10	2	SnI ₂	2.7	97.9
	1.0 g (powder)			
	Comparative			
	Example 1	SnCl ₄	79	39.2
15	2	SnO	69	46.9
	1.0 g (powder)			
	3	FeCl ₂	97	25.4
	4	FeCl ₃	103	20.8

EXAMPLES 3 AND 4

25 Filtrates (100 ml) of heavy natural gas liquid were prepared as in Example 1. To the filtrates, cupric chloride (CuCl_2) was added in the amounts shown in Table 2 and the mixtures were stirred well, followed by standing for 1 hour. The concentrations of mercury in the purified solutions were measured and the results are shown in Table 2.

COMPARATIVE EXAMPLES 5-9

30 Filtrates (100 ml) of heavy natural gas liquid were prepared as in Example 1. To the filtrates, the compounds shown in Table 2 were added and the mixtures were treated as in Example 1. The concentrations of mercury in the purified solutions were measured and the results are shown in Table 2.

TABLE 2

5	Compound	Hg concentration in purified Solution (ppb)	Hg removal (%)
10	Example 3 CuCl ₂ 10wt% in 10ml of methanol solution	4.0	96.9
15	Example 4 CuCl ₂ 1.0 g (powder)	8.0	93.8
20	Comparative Example 5 CuCl 10wt% in 10ml of methanol solution	62	52.3
25	6 FeCl ₂ 1wt% in 10ml of aqueous solution	97	25.4
30	7 FeCl ₃ 1wt% in 10ml of aqueous solution	103	20.8
35	8 CuCl 1.0 g (powder)	71	45.4
40	9 PbCl ₂ 1.0 g (powder)	114	12.3

EXAMPLE 5 AND 6

35 Filtrates (100 ml) of heavy natural gas liquid were prepared as in Example 1. To the filtrates, 0.8 g of activated carbon ("CAL" of Toyo Calgon Co., Ltd. having a specific surface area of 1050 m²/g and an average pore size 2 nm (20 Å) which had CuCl₂ supported thereon was added and the mixtures were subjected to an adsorption reaction for 1 hour under stirring. The concentrations of mercury in the purified solutions and the percentages of mercury removal are shown in Table 3.

40 The CuCl₂ supporting activated carbon was prepared by the following procedure: activated carbon was submerged in a CuCl₂ solution, filtered, and dried in a nitrogen gas at 130°C for 3 hours. The contents of CuCl₂ in the so treated activated carbon are shown in Table 3.

COMPARATIVE EXAMPLES 10-17

45 The procedures of Examples 5 and 6 were repeated except that the activated carbon supported the compounds shown in Table 3 (in Comparative Example 17, activated carbon was used on its own). The results are shown in Table 3.

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TABLE 3

	Supported compound*	Content of supported compound (percent by weight of the activated carbon)	Hg concentration of purified solution (ppb)	Hg removal (%)
Example 5	CuCl ₂	10	2.9	97.8
Example 6	CuCl ₂	5	16	87.7
Comparative				
Example 10	CuCl	10	58	55.4
Example 11	PbCl ₂	5	82	36.9
Example 12	FeCl ₂	5	83	36.2
Example 13	FeCl ₃	5	75	42.3
Example 14	LiCl	5	85	34.6
Example 15	NaCl	5	84	35.4
Example 16	ZnCl ₂	5	75	42.3
Example 17	-	-	81	37.7

* Support: activated carbon (CAL) with a specific surface area of 1050 m²/g

EXAMPLES 7 and 8

Filtrates (100 ml) of heavy natural gas liquid were prepared as in Example 1. To the filtrates, 0.8 g of activated carbon ("CAL" of Toyo Calgon Co., Ltd. having a specific surface area of 1050 m²/g and an average pore size of 2 nm (20 Å)) which had SnCl₂ supported thereon was added and the mixtures were subjected to an adsorption reaction for 1 hour under stirring. The concentrations of mercury in the purified solutions and the percentages of mercury removal are shown in Table 4.

The SnCl₂ supporting activated carbon was prepared by the following procedure: activated carbon was submerged in a SnCl₂ solution, filtered, and dried in a nitrogen gas at 130°C for 3 hours. The contents of SnCl₂ in the so treated activated carbon are shown in Table 4.

EXAMPLE 9

Activated carbon of the same type as used in Examples 7 and 8 was treated with a 10 % aqueous solution of SnCl₂ to prepare SnCl₂ supporting activated carbon, which was packed in an adsorption tower of the same type as adsorption tower 16 shown in Fig. 3. Heavy natural gas liquid (H-NGL) of the same composition as employed in Example 1 was passed through this adsorption tower at SV of 1.5 hr⁻¹. The concentration of mercury in the purified solution and the percentage of mercury removal are shown in Table 4.

COMPARATIVE EXAMPLE 18-23

The procedures of Examples 7 and 8 were repeated except that the activated carbon supported the compounds shown in Table 4. The results are shown in Table 4.

TABLE 4

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	Supported compound*	Content of supported compound (percent by weight of the activated carbon)	Hg concentration of purified solution (ppb)	Hg removal (%)
Example 7	SnCl ₂	3	25	80.8
8	SnCl ₂	5	19	85.4
9	SnCl ₂	10	6.7	94.8
Comparative Example 18	PbCl ₂	5	82	36.9
19	FeCl ₂	5	83	36.2
20	FeCl ₃	5	75	42.3
21	LiCl	5	85	34.6
22	NaCl	5	84	35.4
23	ZnCl ₂	5	75	42.3

* Support: activated carbon (CAL) with a specific surface area
of 1050 m²/g

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EXAMPLES 10 AND 11

A hundred milliliters of heavy natural gas liquid (H-NGL) was filtered through a Millipore® filter (0.2 µm).
The separated sludge had the following composition:

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Fe	10.0 wt%
Si	18.3 wt%
Hg	3.1 wt%
S	2.3 wt%

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The filtrate had a mercury content of 128 ppb. To the filtrate, 0.8 g of activated clay ("Nikkanite 36" manufactured by NIPPON KASSEI HAKUDO K.K.) supporting CuCl₂ was added and the mixture was subjected to an adsorption reaction for 1 hour under stirring. The concentrations of mercury in the purified solutions and the percentages of mercury removal are shown in Table 5.

The CuCl₂ supporting activated clay was prepared by the following procedure: activated clay was submerged in a CuCl₂ solution and after the solvent was removed, the residue was dried in a nitrogen gas at 130°C for 3 hours. The contents of CuCl₂ in the so treated activated clay are shown in Table 5.

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EXAMPLE 12

Activated clay of the same type as used in Examples 10 and 11 was treated with a 10% aqueous solution

of CuCl_2 to prepare CuCl_2 supporting activated clay, which was packed in an adsorption tower. Heavy natural gas liquid of the same composition as employed in Example 1 was passed through this adsorption tower at SV of 1.5 hr^{-1} . The concentration of mercury in the purified solution and the percentage of mercury removal are shown in Table 5.

COMPARATIVE EXAMPLE 24

The procedures of Examples 10 and 11 were repeated except that CuCl was supported on activated clay. The results are shown in Table 5.

TABLE 5

Supported compound*	Content of supported compound (percent by weight of the activated clay)	Hg concentration of purified solution (ppb)	Hg removal (%)
Example 10 CuCl_2	10	4.7	96.3
11 CuCl_2	5	13	89.8
12 CuCl_2	10	6.3	95.1
Comparative Example 24 CuCl	10	65	49.2

* Support: activated clay (Nikkanite 36) with a specific surface area of $130 \text{ m}^2/\text{g}$

EXAMPLE 13 and 14

Filtrates (100 ml) of heavy natural gas liquid were prepared as in Example 1. To the filtrates, 0.8 g of activated clay ("Nikkanite 36" manufactured by NIPPON KASSEI HAKUDO K.K.) which had SnCl_2 supported thereon was added and the mixtures were subjected to an adsorption reaction for 1 hour under stirring. The concentrations of mercury in the purified solutions and the percentages of mercury removal are shown in Table 6.

The SnCl_2 supporting activated clay was prepared by the following procedure: activated clay was submerged in a methanol or acetone solution of SnCl_2 and after evaporation the solvent, the residue was dried in a nitrogen gas at 130°C for 3 hours. The contents of SnCl_2 in the so treated activated clay are shown in Table 6.

EXAMPLE 15

Activated clay of the same type as used in Examples 13 and 14 was treated with a 10% methanol solution of SnCl_2 to prepare SnCl_2 supporting activated clay, which was packed in an adsorption tower. Heavy natural gas liquid of the same composition as employed in Example 1 was passed through this adsorption tower at SV of 1.5 hr^{-1} . The concentration of mercury in the purified solution and the percentage of mercury removal are shown in Table 6.

COMPARATIVE EXAMPLES 25-31

The procedures of Examples 13 and 14 were repeated except that the activated clay supported the com-

pounds shown in Table 6 (in Comparative Example 31, activated clay was used on its own). The results are shown in Table 6.

TABLE 6

	Supported compound*	Content of supported compound (percent by weight of the activated clay)	Hg concentration of purified solution (ppb)	Hg removal (%)
Example 13	SnCl ₂	3	24	81.3
14	SnCl ₂	5	16	87.5
15	SnCl ₂	10	7	94.5
Comparative Example 25	PbCl ₂	5	83	35.2
26	FeCl ₂	5	79	38.3
27	FeCl ₃	5	69	46.1
28	LiCl	5	86	32.8
29	NaCl	5	87	32.8
30	ZnCl ₂	5	78	39.1
31	-	-	87	32.0

* Support: activated clay (Nikkanite 36) with a specific surface area of 130 m²/g

EXAMPLE 16 and 17

The procedures of Examples 13 and 14 were repeated except that silica gel G (manufactured by WAKO PURE CHEMICAL K.K.) was used as a support in place of activated clay. The results are shown in Table 7.

COMPARATIVE EXAMPLES 32-38

The procedures of Examples 16 and 17 were repeated except that silica gel G (manufactured by WAKO PURE CHEMICAL K.K.) supported the compounds shown in Table 7 (in Comparative Example 38, silica gel G was used on its own). The results are shown in Table 7.

TABLE 7

	Supported compound*	Content of supported compound (percent by weight of silica gel G)	Hg concentration of purified solution (ppb)	Hg removal (%)
Example 16	SnCl ₂	3	38	70.3
Example 17	SnCl ₂	5	28	78.1
Comparative Example 32	PbCl ₂	5	110	14.1
Example 33	FeCl ₂	5	107	16.4
Example 34	FeCl ₃	5	95	25.8
Example 35	LiCl	5	116	9.4
Example 36	NaCl	5	113	11.7
Example 37	ZnCl ₂	5	108	15.6
Example 38	-		114	10.9

* Support: silica gel G with a specific surface area of 390 m²/g

The method of the present invention has the following advantages. It is capable of selective and efficient removal of mercury from a hydrocarbon oil by bringing a cupric and/or stannous compound into contact with the oil. The purified oil can be readily separated from the reaction system. If desired, a mercury-containing hydrocarbon oil may be brought into solid-liquid contact with an adsorbent supporting a cupric and/or stannous compound. The purified hydrocarbon oil does not contain mercury, therefore, be used extensively in catalytic reactions typified by hydrogenation reaction.

Claims

1. A method of removing mercury from a hydrocarbon oil which comprises contacting said hydrocarbon oil with a cupric compound which is a cupric halide or hydrate thereof and/or a stannous compound which is a stannous halide or hydrate thereof.

2. A method according to claim 1 which comprises liquid-liquid contact.

3. A method according to claim 1 wherein each said compound is supported on activated carbon.

4. A method according to claim 3 wherein said activated carbon has a pore size of 1 to 50 nm (10 to 500Å) and a specific surface area of 100 to 1500 m²/g.

5. A method according to claim 1 wherein each said compound is supported on, as carrier, at least one of activated clay, silica gel, zeolite, molecular sieve, alumina, silica and silica-alumina.

6. A method according to any one of the preceding claims wherein said hydrocarbon oil is a filtrate obtained by removing sludge from a crude hydrocarbon oil.

TABLE 7

	Supported compound*	Content of supported compound (percent by weight of silica gel G)	Hg concentration of purified solution (ppb)	Hg removal (%)
Example 16	SnCl ₂	3	38	70.3
17	SnCl ₂	5	28	78.1
Comparative Example 32	PbCl ₂	5	110	14.1
33	FeCl ₂	5	107	16.4
34	FeCl ₃	5	95	25.8
35	LiCl	5	116	9.4
36	NaCl	5	113	11.7
37	ZnCl ₂	5	108	15.6
38	-		114	10.9

* Support: silica gel G with a specific surface area of 390 m²/g

The method of the present invention has the following advantages. It is capable of selective and efficient removal of mercury from a hydrocarbon oil by bringing a cupric and/or stannous compound into contact with the oil. The purified oil can be readily separated from the reaction system. If desired, a mercury-containing hydrocarbon oil may be brought into solid-liquid contact with an adsorbent supporting a cupric and/or stannous compound. The purified hydrocarbon oil does not contain mercury, therefore, be used extensively in catalytic reactions typified by hydrogenation reaction.

Claims

1. A method of removing mercury from a hydrocarbon oil which comprises contacting said hydrocarbon oil with a cupric compound which is a cupric halide or hydrate thereof and/or a stannous compound which is a stannous halide or hydrate thereof.

2. A method according to claim 1 which comprises liquid-liquid contact.

3. A method according to claim 1 wherein each said compound is supported on activated carbon.

4. A method according to claim 3 wherein said activated carbon has a pore size of 1 to 50 nm (10 to 500Å) and a specific surface area of 100 to 1500 m²/g.

5. A method according to claim 1 wherein each said compound is supported on, as carrier, at least one of activated clay, silica gel, zeolite, molecular sieve, alumina, silica and silica-alumina.

6. A method according to any one of the preceding claims wherein said hydrocarbon oil is a filtrate obtained by removing sludge from a crude hydrocarbon oil.



Patentansprüche

1. Verfahren zur Entfernung von Quecksilber aus einem Kohlenwasserstofföl, umfassend das Zusammenbringen dieses Kohlenwasserstofföls mit einer Kupfer-II-Verbindung, die ein Kupfer-II-halogenid oder ein Hydrat davon ist, und/oder einer Zinn-II-Verbindung, die ein Zinn-II-halogenid oder ein Hydrat davon ist.
2. Verfahren nach Anspruch 1, umfassend einen flüssig/flüssig-Kontakt.
3. Verfahren nach Anspruch 1, wobei jede dieser Komponenten auf Aktivkohle als Träger enthalten ist.
4. Verfahren nach Anspruch 3, wobei die Aktivkohle eine Porengröße von 1 bis 50 nm (50 bis 500 Å) und eine spezifische Oberfläche von 100 bis 1500 m²/g besitzt.
5. Verfahren nach Anspruch 1, wobei jede dieser Komponenten auf aktiviertem Ton, Silicagel, Zeolit, einem Molekularsieb, Tonerde, Kieselerde und/oder Kieselerde/Tonerde als Träger enthalten ist.
6. Verfahren nach einem der vorangehenden Ansprüche, wobei das Kohlenwasserstofföl ein Filtrat ist, das erhalten worden ist durch Entfernen von Schlamm von einem rohen Kohlenwasserstofföl.

Revendications

1. Procédé pour séparer du mercure d'avec une huile hydrocarbonée, qui comprend la mise de ladite huile hydrocarbonée en contact avec un composé cuivrique, qui est un halogénure cuivrique ou un hydrate d'un tel halogénure, et/ou avec un composé stanneux, qui est un halogénure stanneux ou un hydrate d'un tel halogénure.
2. Procédé conforme à la revendication 1, qui comporte une mise en contact liquide-liquide.
3. Procédé conforme à la revendication 1, dans lequel chacun desdits composés est supporté sur du charbon actif.
4. Procédé conforme à la revendication 3, dans lequel ledit charbon actif présente une dimension de pores valant de 1 à 50 nm (10 à 500 Å) et une aire spécifique valant de 100 à 1500 m²/g.
5. Procédé conforme à la revendication 1, dans lequel chacun desdits composés est supporté sur au moins un support choisi parmi une argile activée, un gel de silice, une zéolithe, un tamis moléculaire, une alumine, une silice et une silice-alumine.
6. Procédé conforme à l'une quelconque des revendications précédentes, dans lequel ladite huile hydrocarbonée est un filtrat obtenu par séparation des boues d'avec une huile hydrocarbonée brute.

