

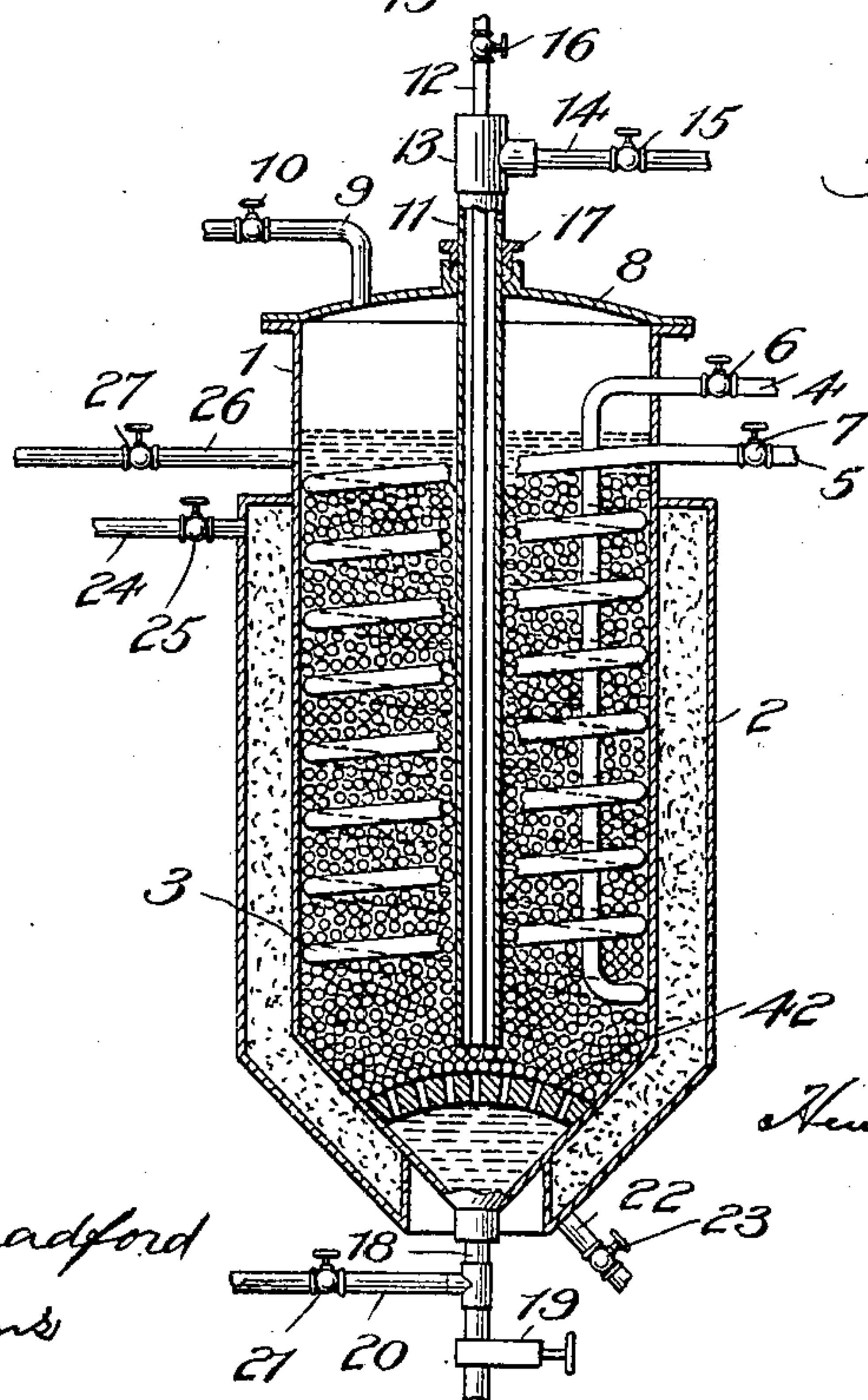
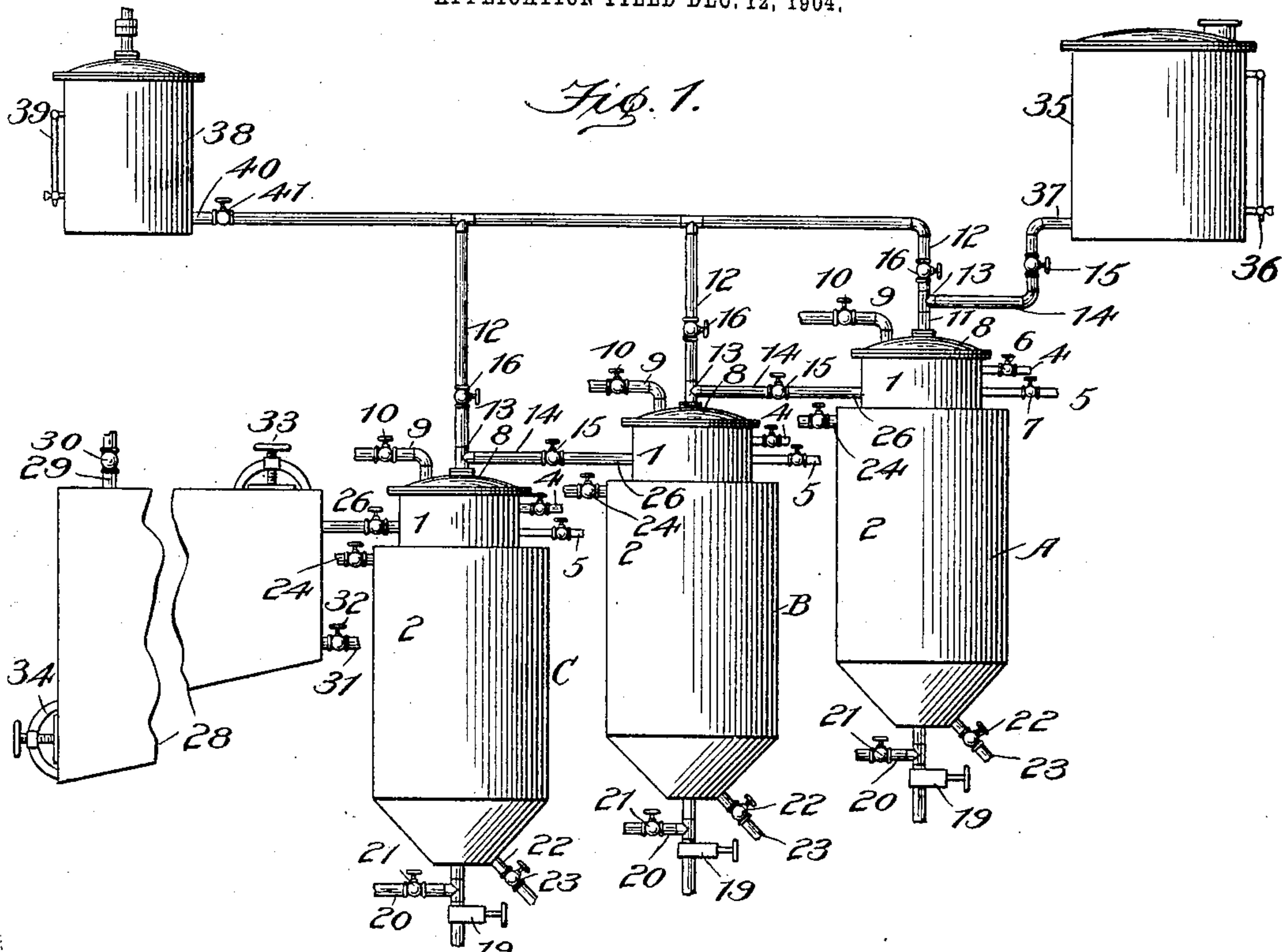
No. 809,087.

PATENTED JAN. 2, 1906.

H. S. BLACKMORE.

PROCESS OF ELIMINATING SULFUR FROM THE SULFUR CONTAINING  
CONSTITUENTS OF PETROLEUM.

APPLICATION FILED DEC. 12, 1904.



Witnesses  
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# UNITED STATES PATENT OFFICE.

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PROCESS OF ELIMINATING SULFUR FROM THE SULFUR-CONTAINING CONSTITUENTS OF PETROLEUM.

No. 809,087.

Specification of Letters Patent.

Patented Jan. 2, 1906.

Application filed December 12, 1904. Serial No. 236,421.

*To all whom it may concern:*

Be it known that I, HENRY SPENCER BLACKMORE, a citizen of the United States, residing at Mount Vernon, in the county of Westchester and State of New York, have invented certain new and useful Improvements in Processes of Eliminating Sulfur from the Sulfur-Containing Constituents of Petroleum, of which the following is a specification.

The object of my invention is to separate sulfur from sulfur-containing petroleums and similar compounds or constituents thereof and produce hydrogen carbide by the direct formation of insoluble sulfur compounds and precipitation thereof from the liquid or fluid oils or substances or other constituents in such a manner as to facilitate the purification and effect a saving in time and labor as compared with processes employed for the direct absorption of sulfur from the liquid or fluid petroleums containing sulfur employed hitherto; and it consists in exposing the sulfur-containing petroleum to the action of a compound of metal with carbonic oxid, such as nickel carbonyl  $\text{Ni}(\text{CO})_4$ , whereby the sulfur of the sulfur-containing petroleum or constituent thereof unites with the nickel content of the nickel carbonyl with the liberation of carbonic oxid with which it is associated, which carbonic oxid is collected and recharged with nickel by passing it over heated nickel in a finely-divided state, which finely-divided nickel may be obtained by burning or oxidizing out the sulfur from the nickel-sulfid precipitate obtained from the oil purified and exposing the resultant oxid to reducing agents in a heated state, such as petroleum-gases.

In carrying out my invention I take a quantity of sulfur-containing petroleum and gradually add thereto nickel carbonyl, which may be in liquid or gaseous form, preferably the latter, care being taken to introduce it below the surface of the oil out of contact with the air by supplying the same from an elevated reservoir or other convenient means and thoroughly agitating the same with the sulfur-containing petroleum, the nickel carbonyl being introduced in about equivalent proportions to precipitate the sulfur content as nickel sulfid. The reaction which takes place may be illustrated by the following chemical formula or equation, which illustrates the action of nickel carbonyl on methyl sulfid, a hydrocar-

bon compound containing sulfur analogous in character to the sulfur-containing petroleum.



When methyl sulfid ( $\text{C}_2\text{H}_6\text{S}$ ) is dissolved in an oil, such as petroleum, and exposed to the action of nickel carbonyl  $\text{Ni}(\text{CO})_4$ , the sulfur of the methyl sulfid combines with nickel and is precipitated as nickel sulfid, while carbonic oxid is liberated.

While the employment of nickel carbonyl as a precipitant of sulfur from sulfur-containing oils would seem to be an expensive operation, it should be noted that the sulfur content of sulfur-containing petroleums rarely exceeds six-tenths of one per cent. and the nickel sulfid produced is readily converted into nickel carbonyl again for reuse.

The manner in which I prefer to carry out my process may be readily understood by referring to the accompanying drawings, in which—

Figure 1 represents a front view or elevation of a series of communicating vessels in which the oil is purified, provided with receptacles for supplying or conveying oil and purifying agent thereto and a precipitating or settling tank for receiving and separating the purified material. Fig. 2 is a transverse vertical section of one of the oil-purifying vessels.

On the drawings the numeral 1 designates a receptacle in which the oil is purified, provided with the jacket 2 for containing a fluid for the purpose of abstracting heat from the reacting ingredients within the apparatus and cooling the same in cases where heat is evolved, and a coil 3, provided with an inlet 4 and outlet 5, controlled by the valves 6 and 7 for the purpose of heating the reacting ingredients by passing steam therethrough in cases where heavier petroleum products are purified or substituting a current of water through the coil in place of steam when heat is spontaneously evolved. The vessel is also provided with a cover 8, having an outlet 9, controlled by the valve 10, and through which cover pass the feeding-pipes 11 and 12, the latter of which is located within the former and both of which terminate within and near the bottom of the vessel. The pipe 12 passes directly through a reducer or stuffing-box (not shown) in the T 13, while the pipe 11 commu-



nicates directly with the T 13 through the inlet-pipe 14, controlled by valve 15, the pipe 12 being also controlled by a valve 16. The pipe 11 passes into the vessel through a stuffing-box 17 in the cover thereof.

The vessel 1 is provided at its lower end with an outlet 18, controlled by a valve 19, for the purpose of discharging any impurities which may separate from the oil and precipitate in the apparatus, and also interiorly with a perforated disk 42 for the purpose of supporting a mass of separators or mixers, such as glass marbles, inert to the reacting ingredients and employed for the purpose of causing the ingredients to become thoroughly mixed in their passage up through the interstices between the same. The mixing of the ingredients supplied to the vessel through the inlet-pipes 11 and 12 is also facilitated by passing an inert gas, such as carbonic-acid gas, into and up through the vessel by means of the pipe 20, controlled by valve 21, which gas may escape through the outlet-pipe 9 upon opening the valve 10. The jacket 2 is provided with an inlet-pipe 22, controlled by valve 23, and outlet-pipe 24, controlled by valve 25. The object of having valves at both inlet and outlet of the various parts of the apparatus is for the purpose of regulating and controlling fluids which may pass therethrough in either direction as the exigency of the case may require, be it either steam for heating or water for cooling. The ingredients conveyed into the vessel through the inlet-pipes 11 and 12 after becoming thoroughly mixed by passing up through the interstices between the small glass marbles contained in the vessels and reacting upon each other overflow through the pipe 26, controlled by the valve 27, carrying with them in suspension any solid precipitate in a finely-divided state which may have been produced, the same being retained in suspended condition by the assistance of the ebullition of the inert gas, such as carbon dioxide, passed through the vessel, the purified ingredients holding in suspension the solid products of the reaction, being conveyed to a precipitating and separating tank 28, Fig. 1, which precipitating-tank is provided with a gas-outlet 29, controlled by an inward check-valve 30, and also an outlet 31, controlled by a valve 32, for drawing off the purified oil after the solid suspended matter has settled to the bottom of the tank. This settling or precipitating tank is also provided with man-holes 33 and 34 for the purpose of removing the precipitate and cleaning the tank.

In carrying on my process for the purification of sulfurous petroleum with the employment of nickel tetracarbonyl (nickel carbonyl) as a precipitant for the sulfur content I place the sulfur-containing petroleum in the reservoir 35, Fig. 1, provided with a liquid-gage 36 and an outlet 37, controlled by the valve 15. I also introduce into the reser-

voir 38, which preferably contains a portion of some light purified petroleum product—such as benzin, nickel tetracarbonyl, (nickel carbonyl)—the said receptacle being provided with the liquid-gage 39 and outlet-pipe 40, controlled by a valve 41. Before introducing the sulfurous petroleum and nickel carbonyl into the purifying apparatus it is advisable to displace all the air from the same by passing into and through the apparatus and communicating pipes an inert gas, such as carbonic-acid gas or carbonic oxid, which is introduced through the pipe 20, controlled by the valve 21.

The air having been discharged from the apparatus, a current of carbon dioxide or carbonic oxid is continuously passed through the vessel 1 and gradually discharged through the pipe 9, controlled by the valve 10. The sulfurous petroleum is then admitted to the vessel by opening valve 15, thereby passing through pipes 14 and 11 into the vessel 1. As soon as vessel 1 is partly filled with sulfurous oil nickel carbonyl is gradually conveyed into the vessel through pipe 12 by opening valves 41 and 16 to vessels A, B, and C, respectively, as the sulfurous petroleum reaches the different vessels through the overflow-pipe 26, the valve 27 being open. As the nickel carbonyl enters the sulfur-containing petroleum it reacts therewith, precipitating the sulfur in the form of nickel sulfid and generating carbonic oxid, in some cases producing complex ketones of petroleum bases which assimilate and mix with the purified petroleum. When carbonic oxid is evolved, it is conveyed into a reservoir from the purifying vessel through the outlet-pipe 9 and valve 10. The nickel sulfid formed is held in suspension in the petroleum by the agitation caused by the passage up through the same of the inert carbon dioxide or carbonic oxid introduced through pipe 20 and passes on through the vessels A, B, and C and into the precipitating-tank 28, where the nickel sulfid is allowed to settle. When the apparatus has become sufficiently filled with petroleum supplied from the reservoir 35, which is kept filled as the oil is gradually discharged therefrom, the nickel carbonyl is carefully fed into the vessels A, B, and C by opening the valves 16, so that by the time the petroleum has passed through the series of vessels and out into the precipitating or settling tank, together with its suspended nickel sulfid, the nickel carbonyl will have been supplied to the sulfurous petroleum in the proportion of approximately five pounds per pound of sulfur contained in the sulfurous petroleum. Any excess of nickel carbonyl retained by the oil after purification may be readily removed by passing a current of air through the same containing sulfur-gases which precipitate the nickel as sulfid. During the passage of the sulfurous petroleum



through the vessel 1, together with the nickel carbonyl, the mixture may be heated by passing steam through the coil 3 to facilitate reaction, or in cases where the lighter sulfur-containing petroleums are employed which react more or less spontaneously the heating may be dispensed with and the substances actually refrigerated in some cases by passing a current of water through the coil instead of steam. The jacket 2 ordinarily used for the purpose of cooling the reacting ingredients may also be employed as a steam-jacket in cases where the heavier sulfur-containing petroleum products are being purified and the application of heat is necessary to facilitate the purifying action.

Any nickel sulfid or other precipitate which may accumulate at the lower part of the apparatus below the perforated disk 42 employed for supporting the marbles or other mixing devices may be removed from time to time by opening the valve 19 and withdrawing a portion of the petroleum, together with the precipitate, and again closing the same as the process proceeds.

The reservoir 38 may be refrigerated in any convenient manner and the nickel carbonyl retained therein under pressure, if desired, in larger operations. The liquefaction of the nickel carbonyl is greatly facilitated by the solvent action of the lighter purified hydrocarbon contained in the reservoir, so that less refrigeration and pressure are required to maintain it in liquid form.

I do not desire to confine myself to the employment of nickel carbonyl, but reserve the right to use other metal carbonyl, such as iron carbonyl, as a precipitant for sulfur from sulfur-containing petroleums without departing from the spirit of my invention, which consists in employing carbonyl in combination with a metal having such superior affinity for sulfur that it will abstract the same from the petroleums with which it is associated.

As the metal carbonyls, such as nickel carbonyl, are quite unstable, it is advisable to retain the same in closed containers and supply the substance to the sulfur-containing oil below the surface thereof, thoroughly agitating the same therewith in order to bring the compound within reacting communication without exposure to the atmosphere.

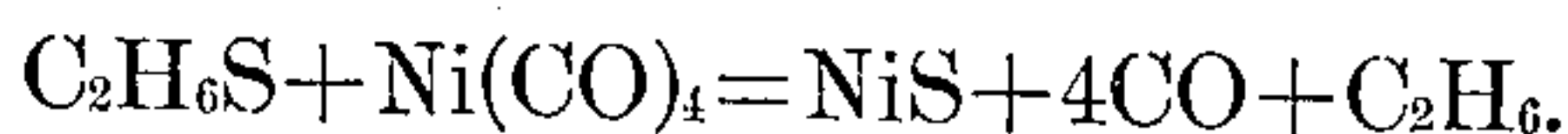
One of the principal objects in employing the metal carbonyls as precipitants for sulfur from sulfur-containing petroleums is that the metal thus combined with the carbonyl readily mixes with or dissolves in the oil, whereby the metal content thereof is brought into close association with the petroleum.

I can use or employ any available sulfur-containing hydrocarbon or sulfurous petroleum, and I can employ, as aforesaid, any metal carbonyl in place of nickel carbonyl so long as the sulfur of the sulfur-containing hydrocarbon or sulfurous petroleum has such superior

affinity for the metal content of the carbonyl that it is withdrawn or separated therefrom when brought in contact therewith, producing an insoluble metal sulfid which may be readily separated from the oil by allowing it to settle or precipitate and removing the petroleum by decantation, filtration, or other convenient means.

The term "metal carbonyl" employed in the specification and claims has reference to compounds consisting of metal with carbonic oxid, such as nickel carbonyl. These compounds readily dissolve in and assimilate with the hydrocarbons, such as petroleum, and are easily decomposed by any sulfurous contamination with the precipitation of the metal from the metal carbonyl as a sulfid.

It can be seen that my process of separating sulfur from the sulfur-containing constituents of petroleum with the use of metal carbonyls, such as nickel carbonyl, can be carried on in a continuous manner by first exposing the sulfurous petroleum to the action of nickel carbonyl whereby nickel sulfid is precipitated and carbonic oxid evolved in accordance with the following chemical formula or equation, which illustrates the action of nickel carbonyl on methyl sulfid, a hydrocarbon compound containing sulfur analogous in character to the sulfur-containing constituents of petroleum, as hereinbefore stated:



The nickel sulfid thus precipitated after the separation of the purified oil therefrom is heated in a proper receptacle and atmospheric air passed over the same, which removes the sulfur by oxidation and leaves nickel oxid as a residue. This nickel oxid is then reduced to metallic state by passing the vapors of hydrocarbon over the same in its heated condition, after which the remaining finely-divided nickel is reconverted into nickel carbonyl for further use by exposing it in a heated condition to the action of the carbonic oxid evolved during the separation of sulfur from petroleum, as illustrated in the above chemical formula, which reaction may be illustrated as follows:



The nickel carbonyl thus produced is then exposed to the action of more sulfur-containing petroleum and the process continued as before. It can be seen, therefore, that the carbonic oxid really acts not only to transform nickel from its solid condition into a form which readily assimilates with the sulfur-containing petroleums, but also acts as a carrier of the nickel from its solid non-assimilating condition to the sulfur-containing constituents of petroleum in a condition to be readily assimilated therewith, whereby reaction is facilitated and rendered feasible, and which carbonic oxid is regenerated during the reaction



with the sulfur content of the petroleum in condition to be again employed to dissolve and transform the solid nickel, as before set forth.

I do not desire to confine myself to the purification of petroleum as a composite composition, but reserve the right to purify any individual product of the sulfur-containing petroleum which may or may not have been separated into its individual products by fractional distillation or otherwise prior to separating the sulfur therefrom, whereby the individual ingredients of the petroleum may be purified separately instead of collectively, as is the case where the petroleum is exposed to the action of a metal carbonyl direct, and purified by the abstraction of the sulfur before separation of the individual ingredients.

Having now described my invention, what I claim as new, and desire to secure by Letters Patent, is—

1. The process of removing sulfur from petroleum containing the same, which consists in exposing sulfur-containing petroleum to the action of a metal carbonyl.

2. The process of removing sulfur from petroleum containing the same, which consists in exposing the sulfur-containing petroleum to the action of nickel carbonyl.

3. The process of removing sulfur from the constituents of petroleum, which consists in exposing the sulfur-containing constituent to the action of a metal carbonyl.

4. The process of removing sulfur from the constituents of petroleum, which consists in exposing the sulfur-containing constituent to the action of a nickel carbonyl.

5. The process of removing sulfur from oil containing the same, which consists in exposing the sulfur-containing oil to the action of a metal carbonyl.

6. The process of removing sulfur from oil

containing the same, which consists in exposing the sulfur-containing oil to the action of nickel carbonyl.

7. The process of purifying petroleum, which consists in exposing petroleum to the action of a metal carbonyl.

8. The continuous process of removing sulfur from sulfur-containing constituents of petroleum, which consists in exposing the sulfur-containing constituent to the action of a metal carbonyl, oxidizing the metal sulfid produced, deoxidizing the resultant metal oxid, exposing the same to the action of carbonic oxid liberated during the precipitation of the metal content of a previous increment of metal carbonyl whereby a new increment of metal carbonyl is produced, and exposing the metal carbonyl thus produced to the action of more sulfur-containing petroleum, substantially as described.

9. The continuous process of removing sulfur from sulfur-containing constituents of petroleum, which consists in exposing the sulfur-containing constituent to the action of a nickel carbonyl, oxidizing the metal sulfid produced, deoxidizing the resultant metal oxid, exposing the same to the action of carbonic oxid liberated during the precipitation of the metal content of a previous increment of nickel carbonyl whereby a new increment of nickel carbonyl is produced, and exposing the nickel carbonyl thus produced to the action of more sulfur-containing petroleum, substantially as described.

In testimony whereof I affix my signature in presence of two witnesses.

HENRY SPENCER BLACKMORE.

Witnesses:

H. N. JENKINS,  
C. C. WRIGHT.