E. B. COBB.

PROCESS OF DESULFURIZING PETROLEUM OILS.

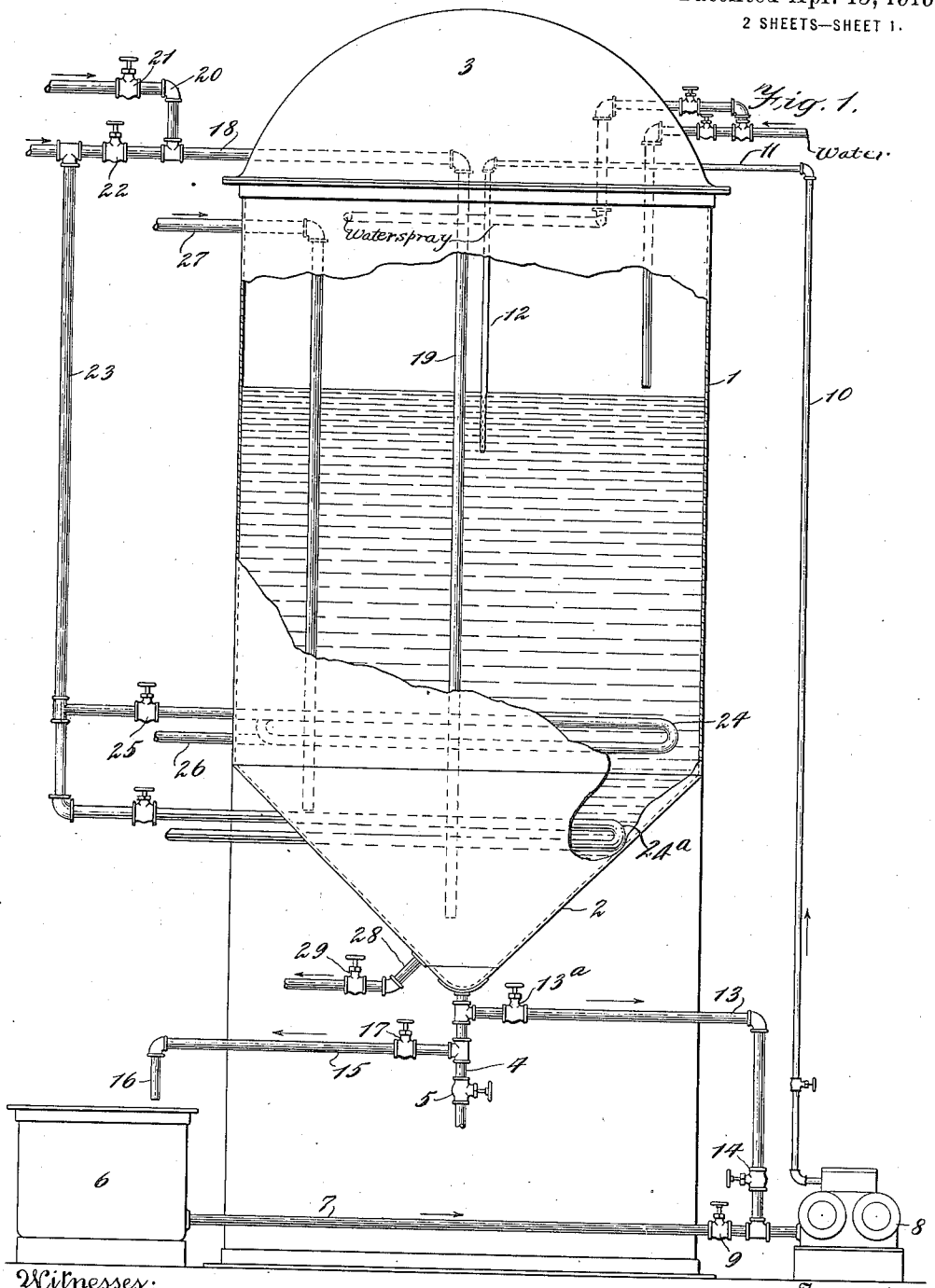
APPLICATION FILED SEPT. 11, 1915.

1,300,816.

Patented Apr. 15, 1919.

2 SHEETS—SHEET 1.

Fig. 1.



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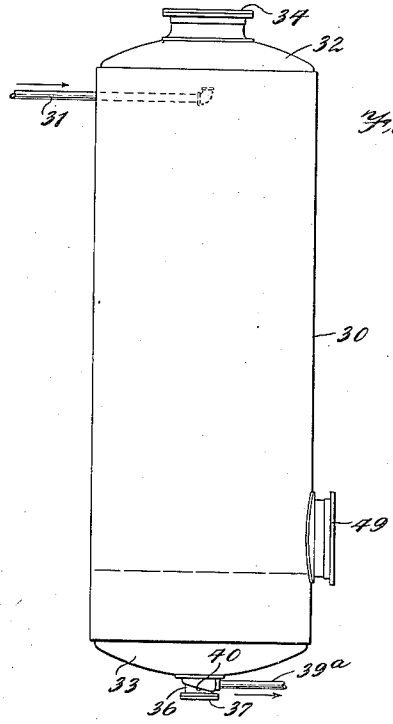
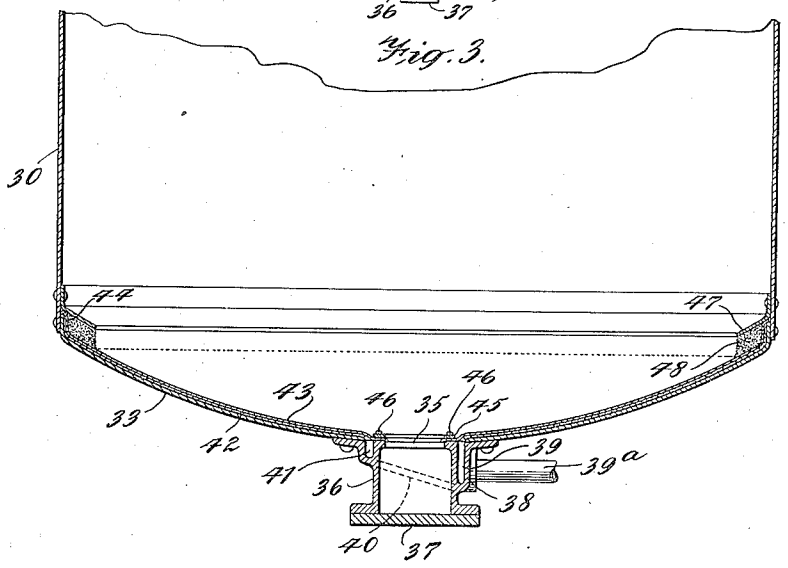


Fig. 2.

Fig. 3.



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UNITED STATES PATENT OFFICE.

ERNEST B. COBB, OF JERSEY CITY, NEW JERSEY, ASSIGNOR TO STANDARD OIL COMPANY, A CORPORATION OF NEW JERSEY.

PROCESS OF DESULFURIZING PETROLEUM-OILS.

1,300,816. Specification of Letters Patent. Patented Apr. 15, 1919.

Application filed September 11, 1915. Serial No. 50,177.

To all whom it may concern:

Be it known that I, ERNEST B. COBB, a citizen of the United States, residing at Jersey City, in the county of Hudson and State of New Jersey, have invented certain new and useful Improvements in Processes of Desulfurizing Petroleum-Oils, of which the following is a specification.

My invention relates to new and useful improvements in processes for the removal of elementary sulfur from petroleum oils. By elementary sulfur I mean that sulfur which exists in the oil in its elementary forms, such as brimstone, flowers of sulfur and all other modifications of elementary sulfur held in physical solution in the oil. The invention is applicable to and covers the removal of elementary sulfur primarily existing as such in the oil, and also elementary sulfur resulting from acid treatment of the oils and other processes of refining and chemical treatment. The presence of elementary sulfur in petroleum oils may be ascertained by first testing the oil by any of the well-known tests for sulfureted hydrogen (H_2S) and removing the same if any be present by any of the well-known processes for this purpose, after which a piece of bright copper or silver is immersed in the oil freed of sulfureted hydrogen (H_2S) and the oil heated; if any elementary sulfur is present it will act to tarnish or blacken the copper or silver. The removal of sulfureted hydrogen from the test oil is a necessary preliminary because it also darkens copper and silver. But in the treatment of the main body of oil, as hereinafter described, it is unnecessary to remove the sulfureted hydrogen by preliminary treatment.

I have discovered that elementary sulfur existing in petroleum oils, either primarily, or as the result of treatments or reactions with other compounds, or elements, may be removed by treatment, preferably under agitation, with alkali metal sulfids, and also by treatment with sulfids of the alkaline earths. By sulfids I refer particularly, although not necessarily, or by way of limitation, to monosulfids—that is to say, for example, sodium sulfid (Na_2S), calcium sulfid (CaS), etc.

It is well known that higher sulfids of these metals, such as sodium and calcium, exist, and the chemical action in using sulfids thereof, as contemplated by my invention, is to cause removal of the elementary sulfur apparently by simple addition, the sulfur combining with the low sulfid of the alkali metal or alkaline earth metal to produce higher sulfids. It sometimes occurs that the oil may contain sulfureted hydrogen in addition to elementary sulfur, in which case the addition of an alkali metal or an alkaline earth metal in the form of the hydroxid will first form monosulfid with the sulfureted hydrogen, and the monosulfid thus formed, will remove the elementary sulfur.

My invention, therefore, contemplates the treatment of the oil with an alkali metal sulfid or sulfids of the alkaline earth metals whether the sulfid is applied to the oil in that form, or is formed by adding to the oil the alkali metals or alkaline earth metals and permitting the same to react with sulfureted hydrogen existing primarily in, or injected into the oil, to form the sulfid of the alkali metal or alkaline earth metal.

In referring to alkali sulfid I include sulfids of the alkali metal group including ammonia, potassium, sodium and other elements of said group. In practice I prefer to employ sodium, as it is most abundant and lower in price. Whether the oil is to be treated with alkali metal sulfids or whether it is to be treated with sulfids of the alkaline earth metals depends to some extent on the character of the oil to be treated, the character of the finished products and the individual preference, but, to a large extent, the alkali metal sulfids and the sulfids of the alkaline earth metals are interchangeable. By sulfids of the alkaline earth metals I mean sulfids of the alkaline earth metal group, but in practice I preferably use sulfids of lime, although I do not necessarily exclude any of the sulfids of the two groups contemplated. By "alkaline sulfid" as used herein and in the appended claims, I include the sulfids of the alkali metal group and the alkaline earth metal group.

The invention is capable of being practised by a variety of apparatus, but, in the

accompanying drawings, I have illustrated two types of apparatus which have been successfully used by me.

Figure 1 of the drawings is a view in elevation partly in section of one type of apparatus particularly useful in the practice of the invention when employing sulfids of the alkali metal group.

Fig. 2 is a view in side elevation of a type of apparatus useful in the practice of the invention when employing sulfids of the alkali earth group.

Fig. 3 is an enlarged detail section through the bottom portion of the apparatus shown in Fig. 2.

I will first describe the apparatus illustrated in Fig. 1 of the drawings, and then the method of desulfurizing carried out thereby, after which I will describe the apparatus of Figs. 2 and 3 and the method performed thereby.

Referring particularly to Fig. 1:

1 designates a cylinder or receptacle adapted to receive the oil to be treated, and having a conical bottom 2 and a dome-shaped top or cover 3. The conical shaped bottom 2 is provided at its apex with an outlet pipe 4 having a valve 5 at its lowermost portion through which pipe the contents of the cylinder may be flowed when the valve is open, as will be hereinafter described. 6 designates a receptacle or tank of any suitable construction adapted to receive the supply of chemical with which the oil is to be treated, said tank being connected by an outlet pipe 7 with the inlet side of a circulating pump 8, said pipe containing a valve 9 for cutting off and establishing flow through the same to the pump. Connected to the outlet side of the pump is a feed pipe 10 extending upward from the pump and provided with a horizontal portion 11 entering the side of the cylinder 1 and provided at its end within the cylinder, with a depending pipe 12 having its lower end closed, but its sides perforated so as to distribute the chemical in fine streams within the cylinder to insure proper admixture of the same with the oil contents of the cylinder. The pipe 7 is connected at a point between the valve 9 and the inlet of the pump to one end of a pipe 13, the opposite end of which is connected to the pipe 4 at a point above the valve 5, heretofore mentioned. The pipe 13 is provided with controlling valves 13^a, 14 by means of which communication through said pipe 13 to the pump is controlled. Connected at one end to the pipe 4 between the valve 5 and the point of connection of the pipe 13 is an outlet or drain pipe 15 provided with an outlet neck 16 discharging into the tank 6, heretofore described. The pipe 15 is provided with a controlling valve 17 for controlling flow therethrough.

18 designates a steam inlet pipe entering through the dome 3 and provided with a depending outlet portion 19 by means of which live steam may be admitted to the interior of the cylinder, an air inlet pipe 20 being connected with pipe 18 and provided with a valve 21 for a purpose to be presently described. The pipe 18 may be provided with a valve 22 for controlling the flow of the steam to the same to the interior of the cylinder, said pipe 20 being connected with the pipe 18 between the valve 22 and the outlet end of said pipe 18. Also connected to the steam pipe 18 is a pipe 23 leading to a closed heating coil 24, of any suitable form, located within the bottom portion of the cylinder, said coil being provided with a control valve 25 for controlling the flow therethrough. The outlet end of the steam coil is shown at 26.

The inlet pipe for feeding the oil to be treated, to the cylinder, is shown at 27, the said pipe entering the cylinder adjacent the upper portion thereof and extending to a point preferably within the area of the cone-shaped bottom. The treated oil may be withdrawn from the cylinder through an outlet pipe 28, controlled by a valve 29, said pipe being located adjacent to, but above, the lowermost portion of the cone-shaped bottom.

I do not desire to be limited in any way to an apparatus such as described, having only described the same in detail so as to insure an adequate understanding of the process embodying my invention.

I will now proceed to describe the process of treating the petroleum oils with sulfids of the alkali metal group, this treatment being particularly applicable, but not necessarily confined, to paraffin wax, kerosene oil, and white paraffin oil for medicinal use, and I will describe the invention for the sake of illustration for the removal of elementary sulfur from partially finished white medicinal oil.

Previous to treatment this oil may contain .03 per cent. sulfur, of which .02 per cent. is elementary sulfur and .01 per cent. is in the form of inodorous sulfur, not elementary, and in this form unobjectionable in oils for the use stated and contained in sulfur compounds left after treatment with sulfuric acid, said oil being pumped into the vessel or cylinder 1 through the pipe 27. When a sufficient amount of the oil has been charged into the receptacle 1—for instance, in practical operations I have treated 100 barrels of 50 gallons each, when about two-thirds full—steam is admitted into the heating coil 24, and is continued until the temperature of the oil rises to a point where the chemical or chemicals to be added to the oil are active. It will be understood that this is done because chemicals, such as are

employed, act slowly at normal temperatures and rapidly at higher temperatures, and, if the temperature is too low, the operation will become too tedious and, if, on the other hand, the temperature is too high, the oil may become scorched, giving rise to objectionable odor and taste. I prefer to employ a temperature between 160° F. and 190° F., which temperature will usually be reached within an hour after steam is first admitted to the heating coil, but the time depends largely upon the area of the heating coil.

While the preliminary heating of the oil is going on, the chemicals used in the treatment of the sulfur-bearing oil may be mixed in the tank 6 and, for this purpose, I preferably employ the following proportions, which I have found to give excellent results, but it will be understood that they may be varied as conditions and qualities of the oil may require, or may be deemed expedient, without departing from the spirit of my invention.

Sulfid of soda (commercial) Na_2S9H_2O	265 pounds
Caustic soda	70 pounds
Water	458 pounds

I employ the caustic soda for three purposes—namely, (1) to neutralize any acid bodies left in the oil from previous refining processes, (2) for the purpose of insuring alkalinity to the solution, and (3) because the solution appears to be more active in its action upon the elementary sulfur contained in the oil when decidedly alkaline.

More water may be added than is indicated, but a longer time will then be necessary to complete the operation. If less water is added, the difficulty of getting a thorough incorporation of oil and the treating solution is increased.

When the chemical solution above described has been effected, it is of about the same temperature as the oil—namely, 160° F. to 190° F. and this solution is then injected into the oil within the cylinder. In order to accomplish this, the chemical is drawn through the pipe 7 to the pump 8 and is discharged from the latter through the pipes 10, 11, and perforated spray nozzle 12, into the oil. It is important, although not essential, to have the chemical in the pipes 10, 11 and spray nozzle 12 under pressure which will be continuous through said pipes up to the perforations in the nozzle, so that the jets of the chemical issuing from the latter will strike the oil with considerable force and effect a thorough mingling of the oil and the chemical solution.

The chemical solution injected into the oil in the manner described will gradually find its way by gravity through the body of oil to the bottom of the agitator, and, during the initial treatment, I maintain the valves 13ª, 5 and 17 closed, so that the solution, which has been partially used, will accumulate in the bottom of the agitator, and the pumping is continued until all, or the desired amount, is drawn from the tank 6 and injected into the agitator. When the desired amount of chemical solution has been fed to the oil, the valves 13ª and 14 are opened and the valves 5, 9 and 17 closed, and the pump is then operated to circulate the solution through the body of oil being treated, the pipe 13, the pump, the pipes 10, 11, and spray nozzle 12. During this circulation the temperature of the oil being treated is maintained by means of the coil 24 at a temperature of from approximately 160° F. to approximately 190° F. During the treatment described test samples of the oil are taken from time to time, said samples being washed with water and filtered through filter paper to remove the last traces of moisture, and are then placed in a test glass with a piece of bright copper and heated to about 175° F. for about one hour. When the test samples cease to show any discoloration or tarnishing of the copper, this stage of the process is considered finished. It may require from one to three hours, because the solution seems to be more active sometimes than at others, for some reason I have been unable to ascertain.

When the test samples cease to discolor the copper, as above described, the chemical solution is allowed to settle in the conical bottom of the vessel, and the settling is continued for a period of from six to ten hours in order to insure all of the solution being separated from the treated oil. When the maximum separation of the solution is assured by adequate settling, the solution may be drawn off from the vessel and returned to the tank 6 through the pipe 4, the pipe 15 and the discharge 16, and said solution reserved for further use in the treatment of oil.

I then treat the oil to remove therefrom any residual alkaline sulfid which may still be suspended in the oil. I prefer to accomplish this by treating the oil with what is known as a "still wash" either by playing water from a hand-hose onto the surface of the oil, drawing the water off continuously at the bottom of the vessel as the water may settle, or the water may be applied by pumping it through a permanent spray pipe S arranged at the top of the cylinder. This treatment may be followed up by an injection of live steam through the pipes 18, 19. This washing process, including the water wash and the steam, may extend over a period of four hours, but may be done in less or greater time, according to circumstances.

Instead of injecting live steam from a boiler into the base of the receptacle, I may pump clear, pure water into the bottom of the receptacle and generate steam therefrom, while in direct contact with the oil by means of a heating coil 24ª similar to the coil 24. This latter method is sometimes preferable because ordinary boiler steam may contain impurities which will be detrimental to the oil being treated. The oil is then allowed to stand for about ten to twelve hours and the water is carefully drawn off and discharged to any suitable point, as, for instance, a sewer, through the pipe 4. It may be that the treated oil still shows a cloud of moisture, but this may be removed by cutting off the steam flowing through the pipes 18, 19, and injecting air from the pipe 20 into the pipes 18 and 19 and into the body of oil. This step of the process may continue for a period of from approximately one to approximately three hours, whereupon the oil is usually found bright and is considered finished.

In employing sulfids of the alkali metals, it is preferable to use the same in solution, in order to obtain the best results, and the apparatus shown in Fig. 1, is well adapted for the application of the solution to the oil.

In the above description of the method, I have described the application of an alkali metal sulfid because the oil treated does not contain sulfureted hydrogen and, therefore, a previously prepared sulfid must be used. If the oil contained sulfureted hydrogen in sufficient amount, I would proceed by treating with a solution of alkali metal in the form of the hydroxid, for example, NaOH, in which case the alkali metal would react with the sulfureted hydrogen to produce the monosulfid and water, and the monosulfid so formed would act to remove the elementary sulfur.

Instead of treating with a solution of the previously prepared monosulfid as described, I may also treat oil not containing sulfureted hydrogen, with a solution of the hydroxid, for example, NaOH, and produce the sulfid by injecting sulfureted hydrogen into the body of the oil to react with the hydroxid of the alkali metal. In both of these last-mentioned methods, the amounts of chemical used *i. e.* the hydroxid, are chemically determinable in accordance with the directions heretofore given for the use of the previously prepared mono-sulfid, and in accordance with the amount of H_2S contained in the oil, and in case the oil contains no H_2S and the latter is to be supplied, the amount thereof, and of the hydroxid necessary to produce the required amount of alkaline sulfid are also determinable in accordance with the said receipe.

In Figs. 2 and 3, I show an apparatus for carrying out the process with sulfids of the alkaline earth metals, the form shown being employed because it is preferable to use the alkaline earth metal group in the solid form. This apparatus includes a vertically disposed cylinder or tank 30, adapted to contain the oil to be desulfurized, a feed pipe 31, entering the upper portion of the cylinder to feed the oil to the latter. The cylinder is provided with an upper head 32, and a lower head 33, the former being provided with a manhole 34. The lower head is provided with a central opening 35 discharging into a neck 36, bolted to said head, and closed at its lower end by a removable cover plate 37. The body of the neck is of less diameter than the opening 35, for a purpose to be described, and is provided with an external flange or shell 38 forming with said neck an annular passage 39, having an inclined bottom 40, said passage being accessible to the interior of the cylinder through the annular space 41 afforded between the upper portion of the neck and the edge of the opening 35. The upper edge portion of the flange 38 provides convenient means by which the neck may be bolted to the cylinder. A suitable outlet pipe 39ª leads from the passage 39.

The bottom head of the cylinder is provided with a false bottom consisting of a layer of wire mesh 42, preferably completely covering said head, and overlying this wire mesh is a layer of canvas 43, or other suitable material, the edges of the latter extending upward for a distance about the circumference of the lower head as at 44, for a purpose to be presently set forth. Both the mesh and the canvas covering are cut away at the center, as shown, the inner edge of the mesh preferably terminating slightly short of the annular passage 39, while the inner edge of the canvas is carried over said passage and secured to said neck by a clamping ring 45 and bolts 46.

The wall of the cylinder is provided with an inwardly projecting annular flange 47, overlying the outer edges of the canvas and wire mesh layers, the space between the said flange and the canvas being packed with cotton or wool waste packing, as at 48. Adjacent its lower end portion the cylinder is provided with a manhole 49 for a purpose to be presently set forth.

In practising the invention, using sulfids of the alkali earth groups, I proceed as follows:

800 pounds of freshly burned lime are placed preferably in an open pan or receptacle, into which is poured a mixture of 600 pounds of commercial sulfid of soda and 50 gallons (417 pounds) of water. As the lime slacks there is a decomposition of the sulfid of soda, thereby forming sulfid of lime and caustic soda. Upon the termination of the

slacking action the material, *i. e.* the sulfid of lime and caustic soda should be granular and somewhat coarse. The material is then placed in the chamber of the tank 30 and spread evenly over the false bottom thereof to the proper height, as indicated by the dotted line in Fig. 2 of the drawings. When the material is packed in the tank the impure oil to be desulfurized is pumped in at the top of the tank through the pipe 31, and is permitted to percolate down through the filter-like bed of sulfid of lime. The oil in passing through the sulfid of lime is completely desulfurized by reaction of the sulfur with the sulfid of lime by simple addition to produce higher sulfids, as has been previously set forth. The degree of desulfurization may be determined by the copper test described on samples of the oil taken from the outlet pipe 39ª. The purification in this case may be continued until test samples show no blackening of copper when tested as described, whereupon the exhausted sulfid is removed and the tank is recharged with a fresh supply of sulfid.

The filtering method, above described, effects contact between the oil and solid sulfid as distinguished from contact of the oil and liquid sulfid in the alternative process. The two methods are largely interchangeable, but the filtration method may be used when the chemical and physical character of the oil make it appear desirable to treat the oil with a solid rather than with a liquid, as for example, when a sample of the oil tends to emulsify when treated in the water solution. The filtering process provides for a systematic use of the active agent; that is, as the operation progresses the raw oil comes in contact with partially exhausted sulfid first, and on passing to the bottom of the filter it meets sulfid of a less and less degree of exhaustion. If desired or necessary, I may place a layer of water-moistened porous material such as burlap on the canvas 43 beneath the sulfid in order to remove any odors which may be introduced by or result from the use of the sulfid. The use of the water moistened porous material is desirable when the active agent is calcium monosulfid prepared from sulfid of soda of commerce, and an excess caustic soda. It frequently happens that the commercial sulfid of soda contains volatile sulfurous impurities which impart to the oil an unpleasant odor resembling sulfureted hydrogen which is removed by moisture through absorption.

In the false bottom construction, the canvas supports the sulfid of lime without allowing it to escape, while the wire mesh provides a proper space to permit the oil to flow to the outlet. The angle-iron or flange 47 and the packing 48 prevents leakage of the chemical employed about the outer edges of the canvas and wire mesh. The construction of the neck casting 36, provides for convenient removal of the sulfid from the cylinder without disturbing the false bottom or injury to the same.

What I claim and desire to secure by Letters Patent of the United States is:—

1. The process of removing elementary sulfur from petroleum oil, which consists in subjecting said oil to an alkaline sulfid.

2. The process of removing elementary sulfur from petroleum oil, which consists in subjecting said oil to an alkaline sulfid and continuing the treatment until the treated oil ceases to have a darkening effect on metallic copper.

3. The process of removing elementary sulfur from petroleum oil, which consists in treating said oil with an alkaline sulfid accompanied by heat at a temperature of from 160° F. to 190° F.

4. The process of removing elementary sulfur from petroleum oil, which consists in subjecting said oil to an alkaline sulfid and under alkaline conditions.

5. The process of removing elementary sulfur from petroleum oil, which consists in subjecting said oil to a solution of an alkaline sulfid.

6. The process of removing elementary sulfur from petroleum oil, which consists in subjecting said oil to a solution of an alkaline sulfid, and circulating said solution through the body of petroleum oil.

7. The process of removing elementary sulfur from petroleum oil, which consists in subjecting said oil to a solution of an alkaline sulfid, and circulating said solution through the body of petroleum oil until the treated oil ceases to have a darkening effect on metallic copper.

8. The process of removing elementary sulfur from petroleum oil, which consists in subjecting said oil to a circulating stream of a solution of alkaline sulfid and a substance insuring alkalinity of said solution.

9. The process of removing elementary sulfur from petroleum oil, which consists in subjecting said oil to a solution of alkaline sodium sulfid in the proportion of about 265 parts by weight of said sulfid to about 458 parts by similar weight of water.

10. The process of removing elementary sulfur from petroleum oil, which consists in subjecting said oil to a solution of alkaline sodium sulfid in the proportion of 265 parts by weight of said sulfid to 458 parts by similar weight of water to which is added 70 parts by weight of caustic soda.

11. The process of removing elementary sulfur from petroleum oil, which consists in neutralizing any acid present in said oil and treating the oil with a solution of alkaline sulfid.

12. The process of removing elementary

sulfur from petroleum oil, which consists in subjecting said oil to a solution of sodium sulfid and caustic soda.

13. The process of removing elementary sulfur from petroleum oil, which consists in subjecting said oil to a solution of alkaline sodium sulfid in the proportion of approximately 265 parts by weight of said sulfid to approximately 458 parts by similar weight of water to which is added a neutralizing agent.

14. The process of removing elementary sulfur from petroleum oil, which consists in subjecting said oil to a solution of alkaline sulfid and caustic soda.

15. The process of removing elementary sulfur from petroleum oil, which consists in heating said oil for approximately one hour, subjecting the same to a solution of an alkaline sulfid for from approximately one hour to approximately three hours, separating the sulfid from the oil and after-treating the oil to remove residual sulfid suspended in the oil.

16. The process of removing elementary sulfur from petroleum oil, which consists in heating said oil for approximately one hour, subjecting the same to a solution of an alkaline sulfid for from approximately one hour to approximately three hours, while maintaining the same at a temperature of from about 160° F. to 190° F., separating the sulfid from the oil and after-treating the oil to remove residual sulfid suspended in the oil.

17. The process of removing elementary sulfur from petroleum oil, which consists in heating said oil to a temperature of from about 160° F. to 190° F., subjecting the same to a solution of an alkaline sulfid, separating the sulfid from the oil and after-treating the oil to remove residual sulfid suspended in the oil.

18. The process of removing elementary sulfur from petroleum oil, which consists in treating said oil with an alkaline sulfid accompanied by agitation.

19. The process of removing elementary sulfur from petroleum oil, which consists in treating said oil with an alkaline sulfid accompanied by agitation and heat.

In testimony whereof I have hereunto signed my name in the presence of two subscribing witnesses.

ERNEST B. COBB.

Witnesses:
C. G. HEYLMUN,
ARTHUR G. DANNELL.