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PROCESS OF PURIFYING HYDROCARBONS

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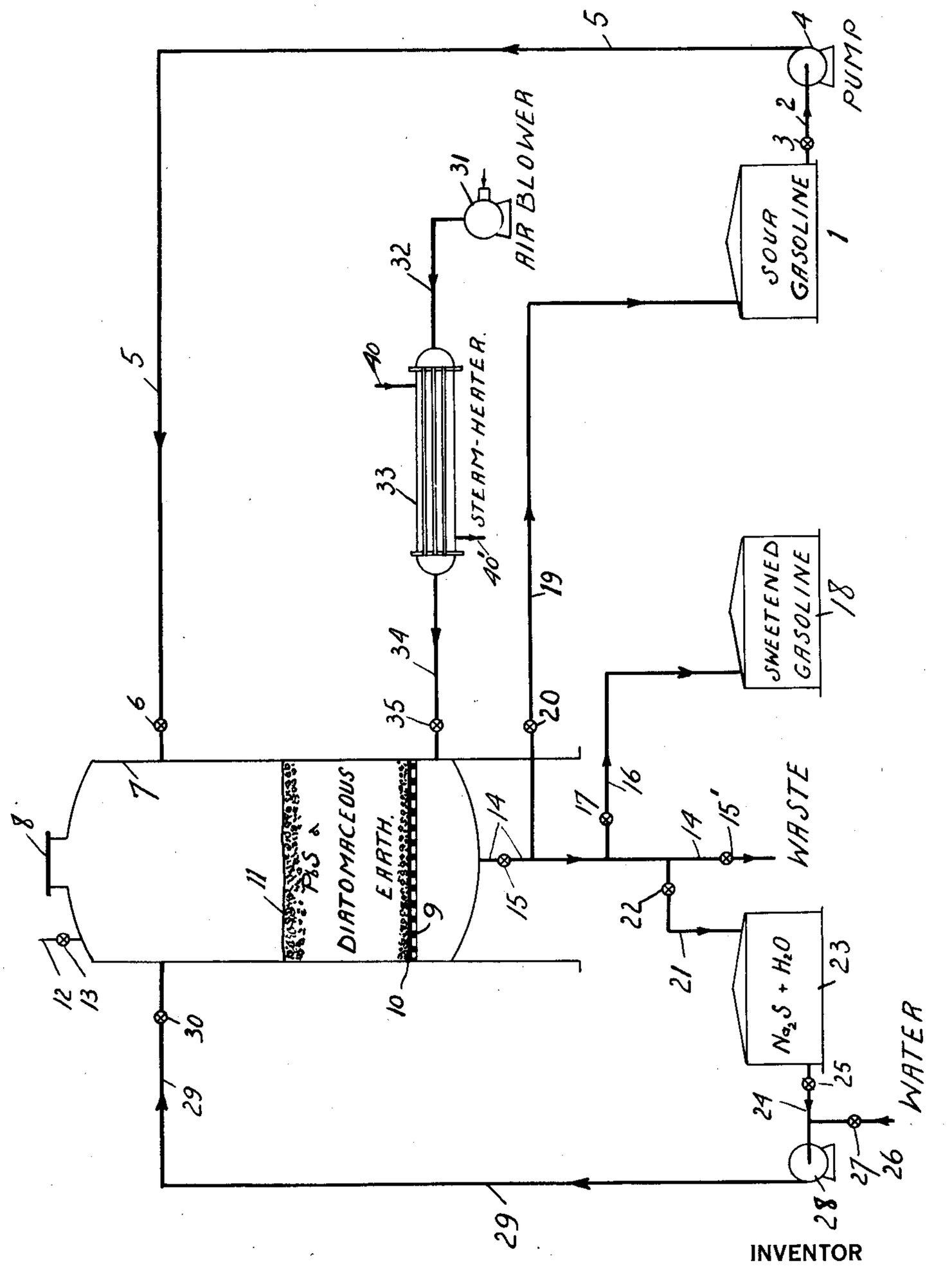

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PROCESS OF PURIFYING HYDROCARBONS

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This invention relates to the purification of hydrocarbons, and while not necessarily confined thereto, it more specifically refers to the treatment of naphtha or gasoline synthetically produced by the cracking of hydrocarbon oils such as petroleum or shale oil, or distillates derived from relatively high sulphur bearing crude oil in which mercaptans or other sulphur bearing hydrocarbons may be formed during said distillation or cracking operation, or present in the final distillation, rendering the stock "sour" to the "doctor test."

The object of this invention is to produce a stable and "sweet" gasoline stock by treating a gasoline or naphtha stock which contains mercaptans or other sulphur bearing hydrocarbons commonly called "sour" gasoline or naphtha stock with dry lead sulphide, particularly in a fine state of division to render the treated gasoline "sweet" to the "doctor test" by a sequence of operations in which the lead sulphide may be kept in an active state by intermittent revivification operations.

I am aware that it is common knowledge that the precipitate formed by treating a "sour" gasoline with "doctor solution" and sulphur, technically known as "black-strap," is itself a fairly good sweetening agent for some gasoline in the presence of a water solution of caustic soda. I have discovered, however, that a more efficient sweetening agent may be made by the employment of dry lead sulphide prepared by precipitating lead sulphide from a water solution of a lead salt, using hydrogen sulphide or a water soluble sulphide, washing the precipitate to remove soluble impurities and drying at a temperature of approximately 110° C. The gasoline stock sweetened by my invention is more stable in color than by the process where "black-strap" alone is used. I have also discovered that the lead sulphide may be kept in an active state by intermittent treatments with a water solution of sodium sulphide. The gasoline stock to be treated is preferably one which has had a preliminary caustic soda treatment or other treatment which will remove hydrogen sulphide, and may be one which has had a preliminary treatment with sulphuric acid and caustic soda. Mercaptans are among those substances which cause a gasoline stock to show a "positive" "doctor test" and it is to the treatment of this class of compounds that this invention is particularly adapted, although it is to be understood that this invention is not limited thereto.

My process in general consists in bringing dry gasoline into contact with pure dry lead sulphide by filtration or percolation through a material containing lead sulphide. The time of contact depends somewhat on the amount of lead sulphide contained by the filter medium and its fineness. The filter medium employed may be any dry inert carrier such as asbestos fiber, diatomaceous earth, fuller's earth and the like.

In the sweetening process as carried out by my invention, the lead sulphide appears to act in a catalytic manner, changing the mercaptans into dialkyl disulphides. I have determined that a small amount of lead sulphide will sweeten a large amount of "sour" gasoline and that the lead sulphide may be used for a relatively long period of time without revivification, and that the revivification may be accomplished by intermittent treatments of the spent sulphide with a water solution of sodium sulphide.

The lead sulphide employed may be prepared by passing hydrogen sulphide into a water solution of any of the well-known lead salts such as lead acetate, lead chloride, and the like.

With the foregoing preliminary explanation, the preferred form of our invention will now be more fully explained by reference to the accompanying drawing, which is a diagrammatical representation of an apparatus in which the invention may be performed.

In the drawing, 1 represents generally a tank for holding the "sour" gasoline to be treated. A pipe 2 controlled by the valve 3 connects the gasoline stock tank to a pump 4. The pipe 5 controlled by the valve 6 connects the pump 4 to the filter 7. Connected at the top of filter 7 is a man hole 8 through which the filter medium of lead sulphide and diatomaceous earth may be charged into

the filter. The figure 11 represents the charge of lead sulphide and diatomaceous earth interposed on the grate 9. 10 represents a filter cloth covering the grate 9. A pipe 12, controller by the valve 13, is connected to the filter 7 near the top. A pipe 29 controlled by the valve 30 connects the filter 7 to the discharge side of a pump 28. A pipe 24 controlled by a valve 25 connects the tank 23 to the suction side of pump 28. A pipe 26 controlled by a valve 27 is connected to the pipe 24, an leads to a source of water supply not shown. Pipe 21, controlled by the valve 22 connects tank 23 at the top to the pipe 14. A pipe 14, controlled by valves 15 and 15′ is connected to the filter 7 at the bottom. A branch pipe 19, controlled by a valve 20 connects the pipe 14 to the "sour" gasoline tank 1. A pipe 16, controlled by the valve 17, connects the pipe 14 to the sweetened gasoline tank 18. The pipe 34 controlled by the valve 35 connects the filter 7 below the filter grate 9 to steam heater 33. The pipe 32 connects the steam heater 33 to air blower 31. The pipe 40 is connected to the steam heater 33 and leads to a source of steam not shown. A pipe 40′ is connected to the steam heater 33 and leads to a source of waste steam not shown.

The preferred process as carried out with the apparatus described is as follows: A filter 7 is charged to the required height with a mixture of lead sulphide and diatomaceous earth and the gasoline or naphtha stock to be treated contained in the gasoline stock tank 1 is discharged by the pump 4 into the filter 7 passing through the pipes 2 and 5 controlled by the valves 3 and 6. As soon as the filter 7 has been charged with a sufficient amount of the gasoline stock to be treated, the valves 3 and 6 are closed and the operation of the pump 4 discontinued. The valves 15 and 17 are now open, keeping the valves 15′, 22 and 20 closed, which permits the gasoline coming through the filter to flow into the sweetened gasoline storage tank 18. The pump 4 is intermittently operated discharging the gasoline to be treated into the filter 7 as described, so as to keep a sufficient column of gasoline above the filter bed 11. As soon as the gasoline passing into the sweetened gasoline storage tank 18 commences to show a "positive" test to the "doctor" solution, valve 17 is closed and valve 20 is open by means of which the filter 7 is drained of its gasoline stock. The lead sulphide is now revivified by treating the same preferably with a water solution of sodium sulphide, followed by a water wash and then drying the filter mass with heated dry air. This is accomplished by operating the pump 28 and opening the valves 25 and 30, the valves 17, 20 and 15 being closed. As soon as a sufficient quantity of the water solution of sodium sulphide has been introduced into the filter 7 the operation of pump 28 is discontinued and the valve 25 closed and the valves 15 and 22 are opened, permitting the water solution of sodium sulphide after passing through the filter bed to pass back into the tank 23. As soon as a sufficient amount of the water solution of sodium sulphide has passed through the filter bed 11 to revivify the lead sulphide, the filter mass is washed with water which is accomplished by again operating the pump 28 opening the valves 27 and 30 which permits a flow of water to pass into the filter 7. The valve 22 is now closed and valves 15 and 15′ are opened, permitting the water passing through the filter to run to waste. As soon as the water passing through the filter bed 11 shows no appreciable amount of sodium sulphide, the introduction of water into the filter 7 is discontinued and the valves 30 and 27 closed. As soon as the filter 7 has been drained of its water content, the valves 15 and 15′ are closed and the valves 13 and 35 are opened. The filter mass is now dried, which is accomplished by blowing air through the filter bed in which operation the air from blower 31 passes through the steam heater 33 entering the filter 7 below the grate 9. The heated air passes upward through the bed 11 and out through the pipe 12. As soon as the filter bed 11 is substantially dry the operation of the air blower 31 is discontinued, the valves 35 and 13 are closed, and the filter 7 is again charged with the "sour" gasoline stock to be "sweetened."

As a specific example, in the treatment of gasoline stocks derived from cracking California petroleum oils, it was found that the amount of lead sulphide necessary to remove all sourness to the "doctor test" ranged from 1/10 to 5 pounds per barrel of gasoline stock treated, before it was found necessary to revivify the lead sulphide.

By the term "sour," we mean a petroleum oil containing mercaptans, or other hydrocarbons which produce a "positive" test to a standard "doctor" solution, and by the term "sweet" we mean a petroleum oil substantially free from the above named constituents.

By the term "doctor test" we means that well-known test employed by chemists to determine a "sour" or "sweet" petroleum oil stock, the term "negative" to the "doctor test" meaning that the oil stock is "sweet," and "positive" to the "doctor test" meaning that the oil is "sour."

It is also to be understood that any gasoline stock or petroleum oil distillate may be treated by our invention and rendered "sweet," and that any petroleum oil distillate may or may not have had prior treatments known in the art, such as treatments with acid and caustic soda, before being sweetened by my invention.

In the preferred embodiment of this invention, I have described an operation in which

heated air is employed after the revivifying operation to dry the lead sulphide. It is to be understood, however, that superheated steam or other hot inert gases may be employed for this purpose.

While the process herein described is well adapted for carrying out the object of the present invention, it is to be understood that various modifications and changes may be made without departing from the spirit of the invention and the invention includes all such changes and modifications as come within the scope of the appended claims.

What I claim is:

1. A process of treating gasoline stock, comprising filtering the same through a filter bed containing dry comminuted lead sulphide and dried by contact with air, prepared by reacting on a water solution of a lead salt with a water soluble sulphide, and intermittently revivifying the lead sulphide by treating the same with a water solution of a soluble alkali sulphide.

2. A process of treating gasoline stock derived from cracking petroleum oils to render the same "sweet" to the "doctor test," comprising filtering the same through comminuted dry lead sulphide and dried by contact with air, prepared by reacting on a water solution of a lead salt with a water soluble sulphide, and intermittently revivifying the filter mass by treating the same with a water solution of a soluble sulphide.

3. A process of treating gasoline which is "sour" to the "doctor test" to render the same "sweet" to the "doctor test" comprising contacting the same through a filter bed containing comminuted dry lead sulphide and dried by contact with air, prepared by reacting on a water solution of a lead salt with a water soluble sulphide, for a period of time sufficient to render the gasoline "sweet" and intermittently revivifying the lead sulphide by treating the same with a water solution of an alkali sulphide.

4. A process of treating gasoline stock which contains mercaptans to render the same "sweet" to the "doctor test" comprising filtering the same through a mass containing comminuted dry lead sulphide and dried by contact with air, prepared by reacting on a water solution of a lead salt with a water soluble sulphide, to render the same "sweet" to the "doctor test" and intermittently treating the filter mass with a water solution of an alkali sulphide.

5. A process of treating gasoline stock which is substantially free of water and hydrogen sulphide to render the same "sweet" to the "doctor test," comprising contacting the same with comminuated lead sulphide and dried by contact with air, prepared by reacting on a water solution of a lead salt with a water soluble sulphide, for a period of time sufficient to render the gasoline "sweet" to the "doctor test" and intermittently revivifying the lead sulphide by treating the same with a water solution of an alkali sulphide.

In testimony whereof I affix my signature.

WILSON H. LOW.