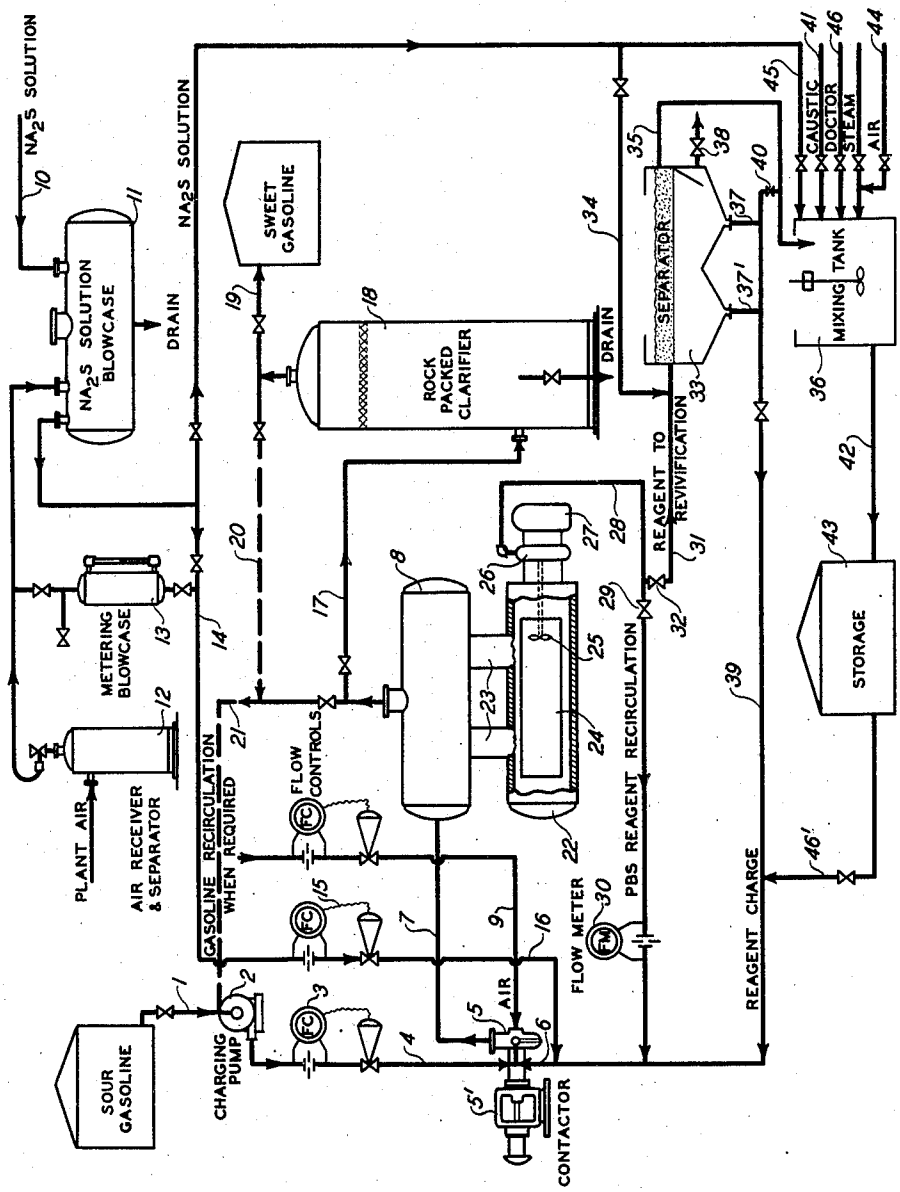
July 23, 1940. E. E. LYDER 2,208,591

PROCESS OF REFINING PETROLEUM DISTILLATES

Filed Oct. 11, 1937



INVENTOR
Ernest E. Lyder.

BY

ATTORNEY

Patented July 23, 1940

2,208,591

UNITED STATES PATENT OFFICE

2,208,591

PROCESS OF REFINING PETROLEUM DISTILLATES

Ernest E. Lyder, Richmond, Calif., assignor to Standard Oil Company of California, San Francisco, Calif., a corporation of Delaware

Application October 11, 1937, Serial No. 168,313

9 Claims. (Cl. 196—30)

This invention relates to a process of refining hydrocarbon oils and especially to a process of sweetening petroleum distillates containing mercaptans. The invention involves a process of the type disclosed in United States Patent No. 2,049,423 granted to Brown et al. August 4, 1936 and is more particularly concerned with maintaining the lead sulfide catalyst utilized in such a process in an active condition.

Accordingly, an object of the invention is to provide an improved process for sweetening petroleum hydrocarbons.

Another object of the invention is to provide an effective method for reactivating a lead sulfide catalyst for use in sweetening processes.

A further object of the invention is to provide a process for reactivating or regenerating a lead sulfide treating agent in processes which require that the treating agent be maintained in a "balanced" condition, i. e. substantially free from either soluble sulfides or soluble lead compounds.

The drawing is a diagrammatic illustration of an apparatus for carrying out the process and attaining the objects of the invention.

In the type of process with which the invention is primarily concerned, a petroleum distillate is intimately contacted with an aqueous caustic treating solution containing insoluble lead sulfide in suspension. The proportions of caustic soda and lead sulfide present in the treating agent may vary through a considerable range of proportions. The aqueous solution of alkali preferably comprises a 20 to 30° Bé. caustic soda solution, although as low a concentration as 1° Bé. is operative. The more dilute caustic solutions give a slower sweetening reaction rate. This slower rate is particularly noticeable and often objectionable when the hydrocarbons being treated have a relatively high mercaptan content. The amount of lead sulfide in suspension in the caustic solution may vary from 0.1 to 2.0 pounds of lead sulfide per gallon of reagant. The preferred proportions are from 0.5 to 1 pound of lead sulfide per gallon. Alkali hyroxides other than sodium or potassium may be used in the aqueous portion of the treating agent. Additional ingredients, such as agents which reduce the interfacial tension between oil and water, may also be present in the treating agent. The sodium salts of phenols or other acidic bodies present in petroleum are an example of such interfacial tension reducing agents.

This treating agent alone will sweeten large quantities of hydrocarbon distillates without the addition of extraneous air or oxygen when the hydrocarbon distillates being treated contain less than approximately .02–.03 percent of mercaptan sulfur. When the distillate to be treated contains greater amounts of mercaptan sulfur, the introduction of air or other oxygen containing gas is generally required. However, the amount of air added in the treating zone should be carefully controlled so that the treating agent is maintained in a balanced condition.

By the term "balanced" condition it is intended to signify a treating agent free from substantial amounts of either water-soluble metal sulfide compounds or water soluble lead compounds. Although a very small amount of water soluble lead compounds is desirable in some instances, for example approximately .003 pound of lead per gallon of reagent when the distillate being treated is relatively high in mercaptan content, the treating agent should generally be kept free from all but traces of soluble lead. It should be understood that the treating agent is to be regarded as in an essentially balanced condition when it contains no more than approximately .003 pound of soluble lead compounds per gallon. Similarly, only traces of soluble sulfides should be permitted in the balanced reagent to avoid the presence of free or corrosive sulfur in the treated gasolines.

Amounts of air required for sweetening gasoline distillates containing 0.1 to 0.12% of mercaptan sulfur usually comprise about 0.8–.10 cubic feet per gallon of oil treated. These proportions illustrate the careful control of amounts of air, which is essential to maintaining the treating agent in a balanced condition.

If an excess of air should be added by accident or if for some other reason the reagent becomes unbalanced and contains either an excess of soluble lead compounds or an excess of soluble sulfides, the treating agent can be brought back into a balanced condition by addition of either a proper amount of doctor solution to remove the soluble sulfides or a proper amount of sodium sulfide, hydrogen sulfide or other soluble sulfides to react with soluble lead and precipitate the same as insoluble lead sulfides. The technique of maintaining the treating agent in a balanced condition is disclosed in detail in United States Patent No. 2,049,423, previously mentioned.

In operating the above type of process it has been found that the lead sulfide eventually loses its catalytic activity. This is particularly true when cracked gasolines are being treated. The present invention provides a method for main-

taining the lead sulfide in an active condition by reactivating or regenerating the same. The reactivating process comprises the following principal steps:

(1) Adding sodium sulfide or other soluble sulfide to the caustic solution until there is a slight excess of soluble sulfide present;
(2) Separating the lead sulfide from the caustic solution;
(3) Thoroughly steaming and/or water-washing the separated lead sulfide;
(4) Again suspending the treated lead sulfide in a caustic solution to obtain an effective and active treating agent.

In some cases it is also found desirable to throw the reagent entirely "off balance" by blowing the lead sulfide while suspended in strong caustic solution with an excess of air at elevated temperatures. This blowing operation oxidizes the lead sulfide and converts the same to soluble lead compounds which dissolve in the cautic solution. This last type of treatment is generally utilized in addition to the above mentioned steaming and/or washing operations, although it can be adopted in lieu thereof. The air blowing is preferably continued until at least a major portion of the lead sulfide is oxidized and is therefore fundamentally different from air blowing operations in which the reagent is kept in an essentially balanced condition and where only a very small portion of the PbS is accidentally oxidized. The "unbalanced' reagent is then again balanced by addition of sodium sulfide in the proportion required to precipitate all of the soluble lead as lead sulfide. Excess sodium sulfide is, of course, avoided as is always done where a balanced reagent is desired.

Referring to the drawing:

Sour distillates such as gasoline flow from storage through valve controlled conduit 1 to charging pump 2, and flow control 3 in line 4 to contactor 5 driven by suitable means such as an electric motor 5'. Treating agent from conduit 6 is thoroughly contacted with the sour gasoline in contactor 5 and the mixture passed through line 7 to settler 8. Air from conduit 9 may also be introduced into contactor 5 to aid in the sweetening reaction.

Sodium sulfide is supplied to the system through pipe 10 to blowcase 11. Compressed air from receiver 12 enables the removal of the sodium sulfide solution from blowcase 11, and metering blowcase 13 permits the careful control of quantities of solution supplied to line 14. Sodium sulfide solution flows from line 14 through flow control device 15 and conduit 16 into the reagent supply pipe 6. The amount of sodium sulfide introduced at this point is very carefully controlled in order to maintain the treating agent in a balanced condition.

As has previously been stated, the gasoline and treating agent mixture is introduced into settler 8 after thorough agitation in contactor 5. The sweetened gasoline separates to the top of settler 8 and is removed through conduit 17 to rock packed clarifier 18.

Clarifier 18 is packed with rock of any suitable type and removes final traces of caustic soda solution and oil-wetted lead sulfide which are suspended in the oil and carried over from settler 8. The rock effectively removes the suspended lead sulfide and caustic soda solution, presumably by a coalescing action, and retains these constituents on the rock surface from which they subsequently drain. Various types of rock resistant to alkali may be used in the clarifier. Weathered rock such as found in gravel deposits is very satisfactory and is more efficient than crushed rock which has not been subjected to weathering action. Quartz is also a satisfactory packing material.

The clarified gasoline passes from the top of clarifier 18 through valve controlled line 19 to storage. Conduits 20 and 21 are provided for recirculating gasoline from the top of clarifier 18 or from the top of settler 8 to charging pump 2, when desired.

Settler 8 is provided with a lower drum 22 and is connected therewith through restricted passages 23. The sweetening system is operated so that the greater portion of the treating agent separates to the bottom portion 22 of settler 8 and so that the gasoline-caustic soda interface, that is the dividing line between the settled treating agent and the separated gasoline, is within the lower portion 22 of the settler.

Drum 22 is equipped with agitating means comprising an inner circulation tube 24 at one end of which is provided a circulation screw impeller 25 for the purpose of maintaining a flow velocity down the central tube and through the annular space between the circulation tube and the outer shell of the drum at sufficient velocity to bring about adequate turbulence in the fluid for maintaining a homogeneous mixture of lead sulfide, caustic solution and oil. Pump 26 driven by motor 27 is in communication with drum 22 and recirculates the homogenized treating agent through line 28 controlled by valve 29 and flow meter 30.

The agitating means provided in drum 22 is desirable for the reason that it has been found that the lead sulfide becomes "oil-wetted" and a portion thereof tends to gather at the oil-caustic soda solution interface. If an ordinary settler is utilized and the treating agent withdrawn from a region below the interface, it is apparent that a considerable portion of the PbS will not be effectively recirculated and will therefore not be utilized in the sweetening zone. At the beginning of operations, drum 22 is charged with the proper amount of 32° Bé. caustic solution containing lead sulfide. At this initial stage of operations the caustic should fill no more than approximately half of drum 22. As the sweetening is continued water is generated by the sweetening reaction and gradually dilutes the caustic soda solution, thereby increasing its volume and raising the caustic level in drum 22. Dilution also occurs from the addition of the solution of soluble sulfide. Thus it is seen that the caustic may be diluted to a considerable extent without raising the level of the interface above the agitating zone in drum 22. No claim is made in the present application to this agitating feature per se, since it comprises the invention of another. However, this feature in combination with the revivification or activation features of the present invention enables more efficient operation of lead sulfide sweetening processes.

As will be readily understood from previous discussion, the treating agent is continuously recirculated through line 28 to contactor 5 for long periods of time and effects a satisfactory sweetening action. The relative proportions of oil and sweetening agent entering the mixing zone in contactor 5 may vary considerably. Amounts of treating agent from 10 to 60% by volume of the naphtha are satisfactory, and in general it is found that higher rates of recirculation are de-

sirable where higher mercaptan content in the distillate being sweetened is encountered.

Even with very careful control of the quantities of air used and of the soluble lead or soluble sulfide content of the treating agent, the lead sulfide catalyst eventually loses some of its activity and if recirculated long enough without any reactivation treatment the catalyst may become entirely inactive. In order to maintain the catalyst in active form the treating agent may be passed through conduit 31 controlled by valve 32 to separator 33. Sufficient sodium sulfide is introduced through valve controlled line 34 to provide a slight excess in the treating agent and precipitate all soluble lead compounds which may be present. The separator as illustrated is of the gravity type and is provided with three outlets. As has been previously mentioned, a certain amount of the lead sulfide becomes oil-wetted and tends to float on the caustic soda solution. For this reason it is necessary to provide a conduit 35 at the top level of the caustic solution to remove this floating lead sulfide which passes to mixing tank 36. A portion of the lead sulfide also gravitates to the bottom of the separator and is removed therefrom through lines 37 and 37'. Caustic soda solution with the lead sulfide removed therefrom may be withdrawn through valve controlled line 38. This caustic solution may be passed to tanks and again mixed with the lead sulfide after the latter has received its reactivation treatment. The caustic may also be given a purification and concentration treatment when desired, as for example by heating and boiling off a substantial portion of the water present therein, which will simultaneously remove certain organic materials dissolved in the reagent.

Attention is directed to the fact that the term "oil-wetted" lead sulfide is used herein to designate that form of lead sulfide which has the property of floating on the caustic soda solution rather than of remaining dispersed therein. The exact cause of this property has not been ascertained, and it may be due to adsorption of constituents other than oil. In any event the lead sulfide in this form, though heavier than the caustic soda solution, will remain on the surface by reason of some surface tension phenomenon.

The lead sulfide from line 35 or line 37 or both is treated in mixing tank 36 to reactivate the same. The lead sulfide is first washed with hot water or steam or both at temperatures within the range of approximately 180 to 240° F. After this washing treatment the lead sulfide may again be suspended in caustic soda solution of the proper strength admitted through line 41. This caustic soda solution may be either a fresh supply or the caustic soda solution removed from separator 36 with or without a purification and concentration treatment is desired.

This reactivated treating agent can be returned to the system through conduit 42. An intermediate storage tank 43 is provided in line 42 so that a supply of active lead sulfide may be kept on hand at all times.

On those occasions where it is found that the lead sulfide catalyst is particularly resistant to reactivation, it is necessary to throw the reagent off balance by blowing with air supplied through line 44. This air blowing operation is carried out at elevated temperatures, such as 120° F. or above, and preferably above 180° F. while the lead sulfide is suspended in strong caustic soda solution. The lead sulfide-caustic suspension should be blown with air until at least a substantial portion of the PbS has been oxidized and converted to soluble lead dissolved in the aqueous phase. Preferably, all of the lead sulfide is so oxidized and dissolved. Before introducing the treating agent into the sweetening system after the air blowing step, the soluble lead is reprecipitated in active form and the entire agent converted to a balanced condition by addition of sodium sulfide through conduit 45. The doctor solution supply conduit 46 is also provided in order that the reagent may be balanced by precipitation of the soluble sulfides as lead sulfide in the event that an excess of sodium sulfide should be accidentally introduced.

It is apparent that the reactivation process can be operated concurrently with the sweetening operation merely by splitting the reagent into two portions, one flowing through valve 29 and the recirculation conduit including flow meter 30 to the sweetening zone, and the other portion flowing through valve 32 and line 31 to separator 33 for reactivation treatment. In general, it is more desirable to shut off recirculation by closing valve 29 entirely and removing the old treating agent from the system. While the old treating agent is being removed, fresh active lead sulfide suspended in caustic may be supplied from storage 43 through valve controlled line 46 to the sweetening system.

It should be noted that the drawing comprises merely a diagrammatic representation of the apparatus to be used with no attempt to show obvious or well known details.

Although certain specific proportions of ingredients and other specific features have been disclosed herein, it is to be understood that all such changes and modifications as come within the scope of the appended claims are embraced within the spirit and teaching of this invention.

I claim:

1. In a process of sweetening petroleum distillates with lead sulfide suspended in a treating agent in a balanced condition, said agent comprising an aqueous solution of an alkali hydroxide substantially free of water-soluble lead compounds, whereby said lead sulfide normally becomes at least partially poisoned and loses some of its catalytic activity, a process of maintaining the lead sulfide in active condition which comprises separating lead sulfide from the aqueous solution, treating the lead sulfide with H_2O at elevated temperatures above approximately 180° F., suspending the lead sulfide in an aqueous solution of an alkali hydroxide, converting the last mentioned solution of alkali hydroxide to an unbalanced condition by heating said solution to elevated temperatures and blowing with air while said lead sulfide is suspended therein, balancing the treating agent by addition of a soluble sulfide to precipitate dissolved lead formed by the air-blowing process and recirculating the balanced treating agent with the petroleum distillate to be sweetened.

2. In a process of sweetening petroleum distillates with lead sulfide suspended in a treating agent in a balanced condition, said agent comprising an aqueous solution of an alkali hydroxide substantially free of water-soluble lead compounds, whereby said lead sulfide normally becomes at least partially poisoned and loses some of its catalytic activity, a process of reactivating the lead sulfide which comprises adding a soluble sulfide to the aqueous solution in an amount sufficient to produce an excess thereof, separating lead sulfide from said aqueous solution, treating

the separated lead sulfide with water and steam at elevated temperatures, suspending the lead sulfide in an aqueous solution of an alkali hydroxide, converting said treating agent to an unbalanced condition by heating to elevated temperatures and blowing with air in the presence of said suspended lead sulfide, and balancing the treating agent by addition of a soluble sulfide to precipitate dissolved lead formed by the air-blowing process.

3. In a process of sweetening petroleum distillates with lead sulfide suspended in a treating agent in a balanced condition, said agent comprising an aqueous solution of an alkali hydroxide substantially free of water-soluble lead compounds, whereby said lead sulfide normally becomes at least partially poisoned and loses some of its catalytic activity, the improvement of reactivating the lead sulfide which comprises blowing the lead sulfide with air while out of contact with said distillate and suspended in hot caustic solution to throw the treating agent off balance and oxidize a substantial portion of lead sulfide to soluble lead compounds, and balancing the treating agent by adding sufficient soluble sulfide to precipitate the soluble lead compounds so formed.

4. In a process of sweetening petroleum distillates with lead sulfide suspended in a treating agent in a balanced condition, said agent comprising an aqueous solution of an alkali hydroxide substantially free of water-soluble lead compounds, whereby said lead sulfide normally becomes at least partially poisoned and loses some of its catalytic activity, a process of reactivating the lead sulfide which comprises separating lead sulfide contained in caustic suspension from the sweetening zone, suspending the separated lead sulfide in strong alkali solution, heating said suspension to an elevated temperature, blowing said suspension with an excess of air while at said elevated temperature and while out of contact with the oil being sweetened, and balancing the treating agent by adding sufficient sodium sulfide to precipitate the soluble lead compounds formed by the air-blowing operation.

5. In a process of sweetening petroleum distillates with lead sulfide suspended in a treating agent comprising an aqueous solution of an alkali hydroxide, the improvement of reactivating the lead sulfide which comprises passing the suspension through a separating zone and allowing oil-wetted lead sulfide to accumulate at the surface of the alkali solution and float thereon, removing the floating lead sulfide from said surface, thoroughly washing said lead sulfide with H_2O at elevated temperatures above approximately 180° F., and again suspending the lead sulfide in an aqueous solution of an alkali hydroxide.

6. In a process of sweetening petroleum distillates with lead sulfide suspended in an aqueous solution of an alkali hydroxide, the improvement of reactivating the lead sulfide which comprises converting at least a major portion of the lead sulfide to soluble lead compounds while suspended in hot caustic solution by blowing the suspension with air while out of contact with said distillate, and precipitating the soluble lead compounds so formed by adding a soluble sulfide to the solution, prior to recirculating the treated agent to a petroleum sweetening zone.

7. A process of maintaining in active condition a treating agent for sweetening petroleum distillates, said agent comprising lead sulfide suspended in an aqueous solution of an alkali hydroxide containing no more than approximately .003 pound of water-soluble lead compounds per gallon, said process comprising converting at least a major portion of the lead sulfide to soluble lead compounds while suspended in hot caustic solution by blowing with air while out of contact with the distillate to oxidize the insoluble lead sulfide, precipitating the lead in the soluble lead compounds so formed by adding a soluble sulfide to the solution, and recirculating the treated agent to a petroleum sweetening zone.

8. A process of treating petroleum distillates which comprises: intimately contacting a sour distillate in a sweetening zone with a catalytic treating agent comprising lead sulfide suspended in an aqueous solution of an alkali hydroxide; separating the distillate from said treating agent; recycling said treating agent to said sweetening zone; maintaining said treating agent in a substantially balanced condition when in said sweetening zone, whereby said recycled treating agent does not cause color reversion in the distillate being processed but becomes poisoned to the extent that it loses at least some of its catalytic activity; restoring catalytic activity to said poisoned treating agent, without causing color reversion in distillate to be treated, by blowing said lead sulfide with air while suspended in hot caustic solution to oxidize a substantial portion of said lead sulfide to soluble lead compounds and balancing said air-blown suspension by adding soluble sulfide to precipitate the soluble lead compounds; and returning said balanced treating agent to said sweetening zone.

9. A process of reactivating a lead sulfide catalytic sweetening agent which has accumulated catalyst poisons of the type produced by catalytic sweetening of petroleum distillates with a balanced treating agent comprising lead sulfide suspended in an aqueous solution of an alkali hydroxide, said reactivating process comprising blowing said lead sulfide with air while suspended in hot caustic solution, to oxidize a substantial portion of said lead sulfide to soluble lead compounds, and balancing the resulting solution by adding a soluble sulfide in an amount not substantially greater than necessary to precipitate the soluble lead compounds as a reactivated lead sulfide sweetening catalyst.

ERNEST E. LYDER.

CERTIFICATE OF CORRECTION.

Patent No. 2,208,591. July 23, 1940.

ERNEST E. LYDER.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 32, for "0.8-.10" read --.08-.10--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 19th day of November, A. D. 1940.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)