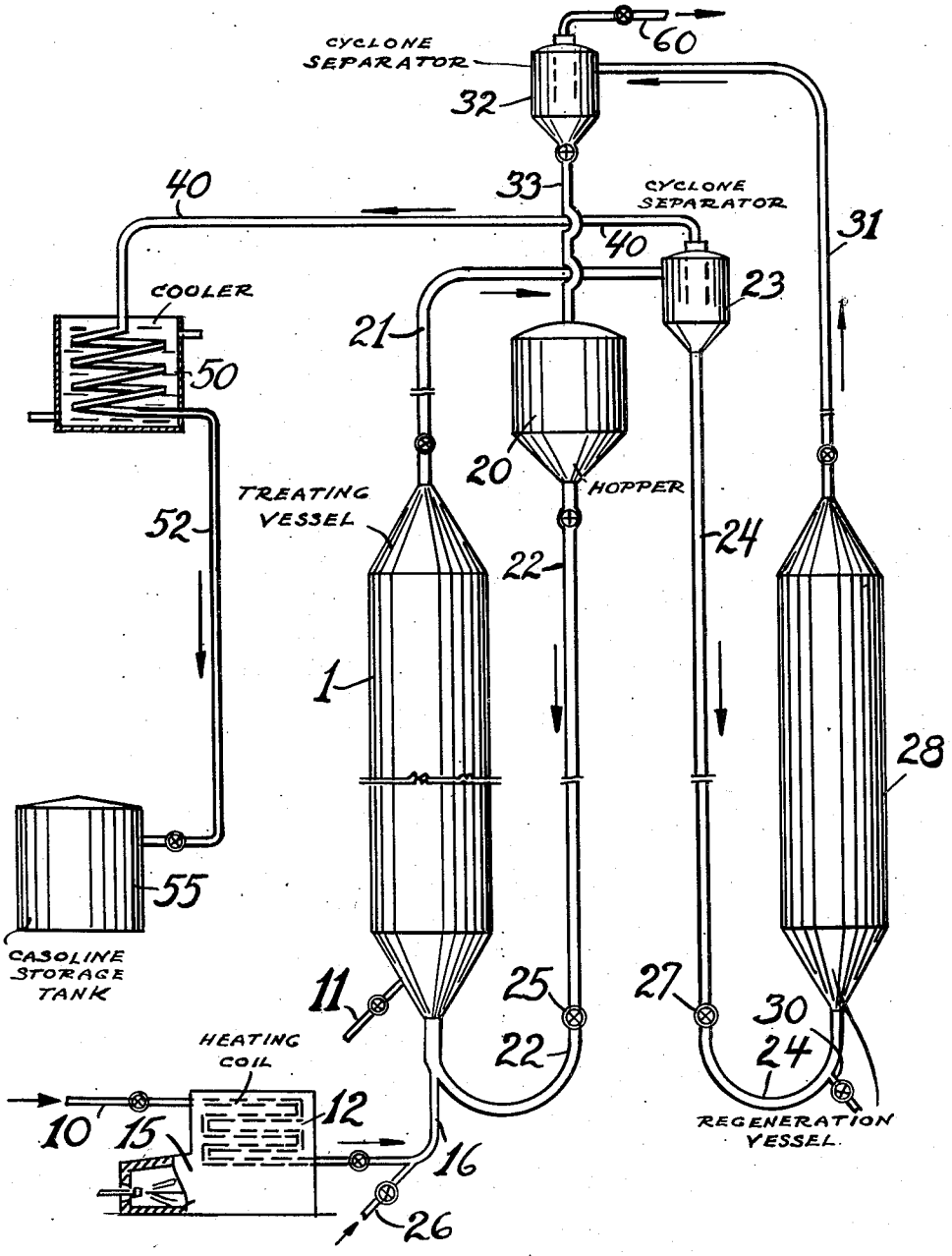
Nov. 7, 1944. E. V. MURPHREE ET AL 2,362,296

METHOD FOR REMOVING SULPHUR FROM SULPHUR-BEARING HYDROCARBONS

Filed June 21, 1941



Egger V. Murphree
Charles W. Tyson
Donald L. Campbell
Homer Z. Martin
Inventors

By P. L. Young Attorney

Patented Nov. 7, 1944

2,362,296

UNITED STATES PATENT OFFICE

2,362,296

METHOD FOR REMOVING SULPHUR FROM SULPHUR-BEARING HYDROCARBONS

Eger V. Murphree and Charles W. Tyson, Summit, Donald L. Campbell, Short Hills, and Homer Z. Martin, Elizabeth, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

Application June 21, 1941, Serial No. 399,048

3 Claims. (Cl. 196—28)

The present invention relates to improvements in the art of refining petroleum fuels and more particularly it relates to the method of treating hydrocarbons with a metal compound to remove sulphur therefrom.

Prior to our invention numerous proposals had been made by others for removing the offensive odor of sulphur-containing compounds from hydrocarbons, such as gasoline and other motor fuels. In the oil industry, a gasoline or other petroleum product which possesses an undesirable odor caused by the presence of certain sulphur compounds is said to be "sour" and methods for removing or minimizing the undesirable odor are commonly referred to as "sweetening" processes. One common method for sweetening sour gasoline or other fuel is the so-called "lead doctor" process in which process, after the removal of hydrogen sulphide and other easily removable sulphur-containing compounds, the gasoline or other fuel is treated with sodium plumbite and sulphur whereupon the mercaptans present in the motor fuel are oxidized to the corresponding disulphides. The fuel is improved in odor in that the offensive sulphur-containing compounds, such as mercaptans, are converted to a form in which they are less odoriferous. However, in this type of process the sulphur content of the treated fuel is usually substantially not less than in the untreated fuel.

Our process, on the other hand, relates to a treatment of fuels in which the sulphur content of the fuel is actually lowered by the treatment and, therefore, one principal object of our invention is to treat a gaseous or liquid hydrocarbon such as a sour or odoriferous gasoline with a metal or metal compound under conditions such that the fuel is sweetened and rendered less offensive from the standpoint of odor and, at the same time, to reduce the sulphur content of the hydrocarbon substantially.

A more limited object of our invention is to treat a sulphur-bearing fuel continuously in the presence of a copper compound under conditions of temperature, pressure and time of treatment so as to produce a refined petroleum fuel which is satisfactory from the standpoint of odor and is enabled to pass the so-called "doctor test," as well as not to impair the quality of the gasoline otherwise, such as to increase its corrosiveness toward copper and other metals.

Other and further objects of our invention will appear from the ensuing description and claims.

Our invention will be best understood by reference to the accompanying drawing which shows diagrammatically one form and arrangement of apparatus elements by means of which our invention may be carried into practical effect in the treatment of a sour gasoline.

To illustrate our invention the drawing will be described in connection with an illustrative example of our process.

Referring in detail to the drawing, 1 represents a treating tower or vessel which may be in the form of a vertical vessel having a substantially cylindrical intermediate section and conical upper and lower sections. The precise shape of the vessel is not critical and various forms may be employed. Sour gasoline to be treated is introduced into the system through line 10 and passed through a heating coil 12 disposed in a furnace 15. The oil is heated preferably at about 1 atmosphere gauge pressure, in the furnace to a temperature of say 200° F. to 700° F., with a range of from 300° F. to 400° F. being preferred, and the oil thus heated is withdrawn from the furnace through line 16 and discharged into the bottom of treating vessel 1. The gasoline is therefore preferably either vaporized or is in the form of a mist. A solid treating agent, say copper oxide, which is stored in a hopper 20 is withdrawn from the hopper 20 through line 22 and discharged into line 16 and thereafter, together with the gasoline, into the vessel 1 in the form of a suspension of the treating agent in the vapors. The hopper 20 is elevated sufficiently above vessel 1 so as to develop considerable static pressure, that is to say, hopper 20 may be elevated so that pipe 22 (shown broken) extends say 120 ft. or more above the top of vessel 1 so as to provide, in substance and effect, a system analogous to the ordinary stand-pipe employed to force water from a reservoir to the houses served in a municipal water system. To control the rate of flow in pipe 22 the latter is provided with a slide valve 25.

The operating conditions within vessel 1 are such that the oil is at a temperature, as previously indicated, of from 200° F. to 700° F., while the pressure prevailing in vessel 1 may be varied from atmospheric to 500 lbs. per square inch. It may be necessary to cause upward flow of the treating agent and oil where the latter is partially liquid by means of an added gasiform substance such as flue gas or steam. The flue gas or steam may be discharged into pipe 16 from pipe 26 and thence with the gasoline into the reactor. The oil remains resident in the vessel in contact with the copper compound for a period of from say 5 to 15 seconds. Under the condi-

tions stated, the mercaptans and other sulphur compounds present in the oil react with the added treating agent to form sulphides.

The amount of treating agent used to treat a given quantity of sour motor fuel depends upon the amount of sulphur present in the untreated oil, and ordinarily a preliminary test should be made to determine the amount of such sulphur in the untreated oil. Thereafter where the treating agent is say, copper oxide, at least the stoichiometric amount of copper oxide to form copper sulphide, from the sulphur present in the oil should be added to said oil. Preferably, however, it is advisable to use an excess of the copper compound over that stoichiometrically required to combine with all the sulphur in the oil.

The oil and copper compounds pass through reactor 1 and are withdrawn from vessel 1 through line 21 and delivered to a cyclone separator 23 where the larger portion of the copper compound is separated from the gasoline vapors. The copper compound is withdrawn from cyclone separator 23 through line 24 containing flow control slide valve 27 and discharged into a regeneration vessel 28 through which it flows upwardly with air, introduced into vessel 28 through line 30. The temperature of the entering air is sufficient to cause a burning of the copper sulphide and its conversion to copper oxide. Ordinarily an air inlet temperature of 600° F. to 800° F. is sufficient to cause combustion of the copper sulphide and the formation of copper oxide. The pressure prevailing in vessel 28 may be atmospheric, or pressures as high as 500 lbs. per square inch may be employed, the effect of pressure being to lower the ignition temperature and to cause more rapid consumption of the sulphur and, consequently, to enable decrease in the size of vessel 28. The copper oxide and gas is withdrawn from vessel 28 through line 31, discharged into cyclone separator 32 and the copper is recycled to hopper 20 by conduit 33.

Referring to the gasoline vapors in separator 23, the same are withdrawn through line 40, thence passed through a cooling coil 50 and finally delivered by line 52 to a storage vessel 55. It is pointed out that in order to remove copper oxide still in the vapors in line 40, the said vapors may be passed through a second or even a third cyclone separator to insure the complete removal of the copper compounds.

Referring again to separator 32, the excess air and oxidation products, including oxides of sulphur, are withdrawn from the separator through line 60 and these may be rejected from the system. Before such rejection, they may be passed through a waste heat boiler to recover at least a portion of their sensible heat or they may be treated with air or oxygen to form sulphuric acid which may be concentrated and recovered in known manner, either or both of which processes may be performed in apparatus well known but not illustrated.

Referring more particularly to the treating agent, the same is preferably in the form of a powder having say a particle size of from 200 to 400 mesh, although larger or smaller particle sizes may be employed. Compopnds may be used in our process which include copper, iron, nickel, bismuth, antimony, mercury, lead, cadmium and silver, chlorides, sulphates, nitrates, iodides, or oxides or the metals themselves or any metal compound which will form a sulphide upon contact with a hydrocarbon containing combined sulphur. However, we prefer to use a copper compound mixed with an acid-treated clay, such as a Montmorillonite clay or other inert carrier solid, by dissolving say copper nitrate or copper sulphate in water and forming a slurry with the clay. The slurry is then dried and finally heated in the presence of oxygen to a temperature of about 350° F. to 900° F., sufficient, in any event, to convert the copper nitrate or sulphate substantially to copper oxide. The clay containing the copper oxide intimately mixed therewith is thereafter pulverized or ground to produce the proper degree of fineness, i. e. to a size of from 200 to 400 mesh.

Referring again to treating vessel 1, it is pointed out that our invention includes the feature of supplying to treating vessel 1 a limited amount of oxygen or air introduced into the reactor through line 11. The presence of oxygen in reaction vessel 1 facilitates the reaction between the copper compound and the sulphur compounds of the oil. Obviously, the amount of air employed should not be sufficient to cause extensive oxidation of the hydrocarbons present in the vapors during the treatment. Good results are obtained by employing from 5 to 50 volumes per cent of air per volume of hydrocarbon vapor.

The present process is characterized by the feature that the copper or other compounds in vessel 1 may remain resident therein for controlled periods of time by regulating the linear velocity of the oil vapors. Thus, where a suspension of copper compounds in the vapors in vessel 1 weighs from 5 to 25 pounds per cubic foot, the linear velocity of the suspension may be from about 1.5 to 4 feet per second, and hence where the average length of the path traversed, through the reactor by the copper compound is about 30 feet, the compound will remain in the vessel 1 to 20 minutes or perhaps longer, the time being greater than that of the residence time of the vapors within the reactor. By increasing the linear velocity, the resident time of the treating compound in the treating vessel may be reduced.

To recapitulate, our invention resides in employing in a sulphur removal from a hydrocarbon process, a method of feeding the treating agent, such as, a copper compound preferably in powdered form, to the treating zone from a hopper, considerably elevated above the treating zone together with hydrocarbons to be treated, and so manipulating or controlling the flow of suspension of treating compound and the hydrocarbon in the treating zone that the flow of treating compound and gasoline is concurrently upward, but due to slippage of the treating compound in the treating zone the compound remains therein for a longer period of time than does the hydrocarbon. The hopper containing the treating compound which is fed to the treating zone is in communication with said treating zone by means of a pipe or conduit means, and due to the elevation of said hopper the copper compound will be under static pressure at the point where it enters the treating zone. According to our process gasoline, kerosene, gas oil, range oil, domestic heating oils, normally gaseous hydrocarbons and the like may be treated to remove sulphur therefrom.

It is pointed out that an important feature of our invention resides in employing the sensible heat of the regenerated treating compound by returning the latter to the treating zone substantially at the temperature it possesses as it leaves the regeneration zone. In other words, our present invention includes so manipulating

the process that it embodies the use of the sensible heat of the copper or other oxide recovered from the regeneration zone to supply at least a portion of the preheat imparted to the oil treated in the treating vessel.

While the apparatus shown in the accompanying drawing indicates the flow of catalyst from the hopper 20 to the treating vessel 1 or from the cyclone separator 23 to the regeneration vessel 28 as proceeding downwardly and then around a bend and upwardly before it mixes with the vapors or gas at the respective mixing points, an alternate form of the invention involves directing the flow of catalyst perpendicularly or angularly downward until it reaches the point of mixing with the vapors or gas in question. In other words, pipe 22 without the lower bend may terminate in the lower conical portion of treater 1 in which case pipe 21 would be a substantially straight pipe projecting from hopper 20 into treater 1 at a point just above the inlet end of pipe 16. Neither form of the apparatus, however, is intended to be limiting on the invention.

Many modifications of our invention will suggest themselves to those skilled in this art and these modifications will fall within the spirit of our present invention.

What we claim is:

1. A method for removing sulphur from sulphur-bearing hydrocarbons which comprises passing a stream of said hydrocarbons in vapor form upwardly through a desulphurizing zone, imposing a positive pressure on the hydrocarbon vapors passing through said zone at least sufficient to overcome the pressure drop therethrough, maintaining a vertical column of finely divided solid desulphurizing compound of a height sufficient to develop a pressure at the base thereof greater than the pressure imposed on said hydrocarbon vapors, discharging desulphurizing compound from the base of said column into said stream of hydrocarbon vapors, controlling the velocity of the hydrocarbon vapors passing upwardly through said desulphurizing zone to maintain said compound within said zone for a period materially greater than the period said vapors are maintained therein, keeping the hydrocarbon vapors in contact with said desulphurizing compound within said desulphurizing zone for a period and at a temperature sufficient to remove a substantial portion of the sulphur therefrom, and thereafter separating the treated hydrocarbon vapors from said compound.

2. A method of removing sulphur from sulphur-bearing hydrocarbons which comprises passing a stream of hydrocarbons in vapor form upwardly through a desulphurizing zone, continuously introducing a stream of finely divided solid desulphurizing compound into said stream of hydrocarbon vapors passing through said zone, regulating the velocity of the hydrocarbon vapors passing through said zone to maintain the finely divided desulphurizing compound within said zone for a period materially greater than the period said vapors are maintained therein, keeping said hydrocarbon vapors in contact with said desulphurizing compound under desulphurizing conditions for a period sufficient to remove a substantial portion of the sulphur from said hydrocarbon vapors, thereafter separating the treated hydrocarbon vapors from the finely divided compound, discharging the finely divided compound so separated into a stream of regeneration gas, passing said stream through a regenerating zone, subjecting said compound to regeneration within said regenerating zone, thereafter separating the regenerated compound from the regeneration gas, discharging the regenerated compound so separated into the top of a vertical column of said finely divided desulphurizing compound, maintaining said column at a height sufficient to develop a pressure at the base thereof greater than the pressure on the hydrocarbon vapors at the point of introduction of said desulphurizing compound into said stream of vapors, and discharging finely divided compound from the base of said column into said stream of hydrocarbon vapors.

3. A method of removing sulphur from sulphur-bearing hydrocarbons which comprises passing a stream of said hydrocarbons in vapor form upwardly through a desulphurizing zone, imposing a positive pressure on the hydrocarbon vapors passing through said desulphurizing zone at least sufficient to overcome the pressure drop through said zone, maintaining a vertical column of finely divided desulphurizing compound of a height sufficient to develop a pressure at the base thereof greater than the pressure imposed on said hydrocarbon vapors, discharging the finely divided desulphurizing compound in a continuous stream into said hydrocarbon vapors, controlling the velocity of the hydrocarbon vapors passing upwardly through the desulphurizing zone to maintain said finely divided compound within said zone for a period materially greater than the period said hydrocarbon vapors are maintained therein, keeping said hydrocarbon vapors in contact with said desulphurizing compound within said desulphurizing zone for a period sufficient to reduce the sulphur contained therein, thereafter separating the finely divided desulphurizing compound from the treated vapors, passing a stream of regeneration gas through a regeneration zone, imposing a positive pressure on said regeneration gas greater than the drop in pressure through said regeneration zone, maintaining a vertical column of finely divided desulphurizing compound separated from said hydrocarbon vapors of a height sufficient to develop a pressure at the base of said column greater than the pressure imposed on said regeneration gas, conducting compound separated from said hydrocarbon vapors to the top of said last-named column, discharging the finely divided compound from the base of said last-named column into said stream of regeneration gas, subjecting said compound to regeneration during passage through said regeneration zone, thereafter separating regenerated compound from the regeneration gas and conducting regenerated compound so separated to the top of said first-named column for return to said stream of hydrocarbons.

EGER V. MURPHREE.
CHARLES W. TYSON.
DONALD L. CAMPBELL.
HOMER Z. MARTIN.