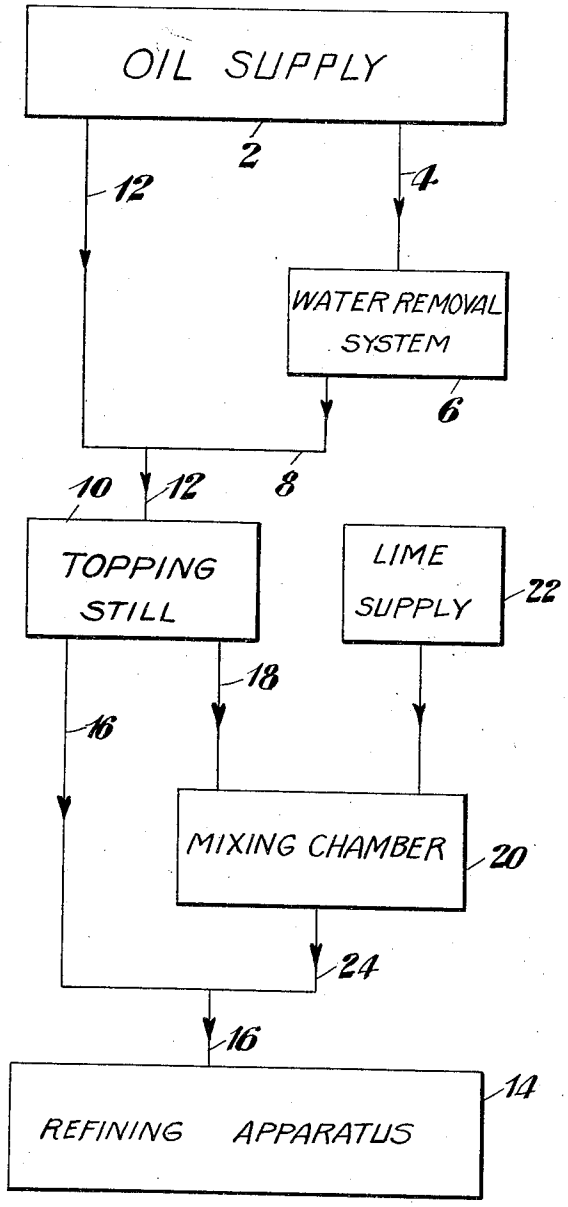
Aug. 23, 1932. W. G. LAIRD 1,873,136

PROCESS FOR PREVENTING CORROSION IN OIL REFINING EQUIPMENT

Filed Nov. 27, 1926



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Patented Aug. 23, 1932 1,873,136

UNITED STATES PATENT OFFICE

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PROCESS FOR PREVENTING CORROSION IN OIL REFINING EQUIPMENT

Application filed November 27, 1926. Serial No. 151,040.

This invention relates to a process for preventing corrosion in oil refining apparatus.

To those familiar with the operation and maintenance of oil refining equipment in modern refinery practice, it is well known that the life of the apparatus, particularly such parts as are exposed to oil vapors, is comparatively short due to the rapid corrosion taking place. Various means and methods have been resorted to in order to offset or retard this corrosion but so far no practical solution of the problem seems to have been found. Some special steel alloys have been proposed for the construction of oil refining equipment but their present cost is almost prohibitive. At the same time the loss in replacing corroded parts and that incident to having a unit shut down for frequent repairs is not a small item on the refiner's expense account, without considering the danger to life and property which would result from a fire or explosion caused by a corroded vapor line or furnace tube.

Certain types of petroleum are known to contain as high as 5 per cent sulphur while others contain very little or no sulphur and it is generally understood that certain sulphur compounds formed during the cracking or distilling operation are at least in part responsible for the corrosion referred to above. However it has been found that the combined action of water, free oxygen and the sulphur content of petroleum is responsible for the excessive corrosion of oil refining equipment. All crude petroleums contain varying amounts of water and in many cases the water is a solution of salts such as magnesium chloride which dissociates to give hydrochloric acid. Even the high boiling distillates used in cracking are steam distilled or have been exposed to the atmosphere from which they have absorbed moisture. In addition to water all natural petroleums, as well as the distillates such as gas oil, fuel oil, kerosene, etc., which have been exposed to the atmosphere after distillation, contain free oxygen. Furthermore it has been found that the solubility of oxygen or air in petroleum is about seven times that in water and that its absorption is facilitated by the action of sunlight or even diffused daylight, so the usual free oxygen content of petroleum is increased when it is exposed to light and air in storage or transit. The use of air under high pressures when pumping petroleum according to the "air lift" principle and in "air-wells" in order to increase the oil yield in adjacent "pumping wells" necessarily saturates the petroleum with oxygen, thereby rendering oil handled in this manner more corrosive than otherwise would be the case.

The combined action of these constituents (water, sulphur compounds and oxygen) may be represented as follows: Oxygen in the presence of moisture (H_2O) reacts with iron and similar metals to produce oxides commonly known as rust. This reaction occurs on the inner surface of the metal stills or associated equipment, and sulphur, particularly hydrogen sulphide, formed in the cracking operation, reacts with the iron oxide formed to yield iron sulphide and set free the oxygen to react with more of the iron or other metal of the apparatus. Hence instead of having merely the action of the oxygen and water alone, the corrosion is accelerated by the presence of sulphur which liberates the oxygen for additional corrosion right at the point of liberation. This is, undoubtedly, the cause of the deep pots found in corroded pipe taken from pipe still furnaces and vapor treating equipment.

These reactions will take place at a fairly rapid rate at ordinary temperatures but under the high temperatures and pressure used in cracking oil their rate is increased many times.

Accordingly the primary object of the present invention is to provide a process for

the preliminary treatment of petroleum oil whereby corrosion of the equipment used for refining such oil will be prevented or greatly reduced.

A further object is to provide a process whereby the corrosive constituents absorbed by, or naturally present in the oil to be cracked or distilled may be removed from the oil before it is subjected to the refining treatment or have their corrosive properties annulled during refining, for example, during the cracking operation, or to remove certain of said constituents and annul the corrosive action of others.

In order to accomplish these ends the oil to be refined may first be treated by any known settling or dehydrating process for removing the bulk of its water content, however, if the oil contains only a small amount of water this step may be omitted. The oil freed of most of its water content is next subjected to a topping operation in which a current of gas is passed through the oil as it is being heated whereby the last traces of moisture together with the absorbed oxygen and the gasoline fraction are swept out of the oil, the gasoline being recovered in the usual manner. This topping step is carried out in such a manner as to leave the oil entirely dry and free from any trace of free oxygen or other corrosive gas. The oil is then taken while hot or cold, as desired, from the topping plant and passed directly to the refining apparatus, provided it is an oil containing very little or no sulphur, however, if the oil contains any appreciable amount of sulphur it is first passed from the topping plant into a mixing chamber where lime or some alkali-earth metal carbide or oxide is intimately mixed with the oil and the mixture then passed into the refining apparatus, for example, through the cracking tube or tubes of a furnace where the lime (CaO) or calcium carbide (CaC_2) takes up sulphur from the oil, which together with the absence of water and oxygen prevents the corrosion of the cracking equipment.

The invention will now be described in detail, reference being had to the accompanying drawing in which

The figure is a diagrammatic sketch or flow sheet of the process.

In accordance with the invention the oil which is to be cracked or distilled and which may be either an asphaltic or paraffin base crude oil or a distillate thereof is passed from any convenient source of supply 2 by conduit 4 into a suitable apparatus 6 where the greater portion of the water content of the oil is removed by any of the well-known methods now in use. From the water removal system 6 the oil is conducted by conduit 8 into topping still 10. If the oil to be treated contains only a small amount of water it may be conducted directly from the supply 2 to the topping still 10 by the conduit 12 without passing through the water removal system.

The topping still 10 may be of any approved type but it is preferred to use a column still in which the oil entering the still is heated through a diaphragm by the vapors produced in the still itself so that the only heat loss from the still is by radiation, that required to vaporize the water and gasoline removed and the heat content of the topped oil drawn therefrom. Such a column still is shown in pending application Serial No. 125,893, filed July 30, 1926. One of the important features of this still comprises the use of a gas circuit wherein the gas circuit and the oil to be treated are passed in parallel through a still on the opposite sides of a diaphragm wherein the vapors of the oil which have been distilled are being fractionally condensed. A sufficiently large volume of gas is used to provide a partial pressure effect to substantially reduce the temperature of the distillation and condensation in the still below the temperatures of the ordinary distillation at atmospheric pressures. This low temperature evaporization and condensation avoids the excessive corrosion, and, furthermore, the gas on each side of the diaphragm tends to keep the materials in active agitation or ebullition so that the corrosion is minimized.

In the topping still 10 the oil is preferably heated only to a sufficient temperature to vaporize any water or moisture present and also the gasoline fraction in case a crude oil is being used. The vaporized water and gasoline together with the oxygen or other corrosive gases absorbed in the oil are swept from the oil in the column by passing a gas therethrough. The gas used for this topping step is preferably natural gas or a purified hydrocarbon gas, for example cracking still gases freed from sulphur containing gases, oxygen and carbon dioxide. The gas may be heated before being introduced into the column and may even be used as the sole means for heating the oil or may be passed with the oil into the column as disclosed in the application cited.

The gasoline, water and gases removed from the oil are passed through a condenser and the gasoline recovered in the usual manner, while the removed gases may be absorbed from the carrier gas, leaving it relatively pure so that it may be returned to the system if desired.

It is obvious that in case a distillate such as gas oil is to be treated in still 10, no gasoline will be recovered but the moisture and absorbed oxygen will be removed.

If the oil being treated contains relatively little or no sulphur it is passed while hot, directly from the column 10 to the refining apparatus 14 by the conduit 16 or if it is not.

desired to refine or crack it immediately, it may be put in storage. But where the oil contains appreciable quantities of sulphur it is passed from the column 10 by the conduit 18 into a mixing chamber 20, where it is intimately mixed with dry lime (CaO) or carbide from the supply 22. Instead of lime or calcium carbide other oxides or carbides of the calcium group or hydroxides of the alkali metal group may be used. From the chamber 20 which may be a combined grinding and mixing chamber in which the lime and oil may be intimately mixed by being ground together, the mixture is passed by the conduit 24 into the refining apparatus 14.

The amount of lime or other compound used in the process should at least be equivalent to the sulphur content of the oil but it is preferred to use two or three equivalents per equivalent of sulphur. The refining apparatus may comprise any of the well-known systems in which oil is heated to a distilling or cracking temperature in a heating coil, tube or tubes mounted in a furnace and then passed to a vaporizer or reaction chamber from which vapors pass through a dephlegmator and so on. If reflux condensate is returned from the dephlegmator to the heating zone, as is done in many cases, it may, if it still contains any appreciable quantity of sulphur or sulphur compounds, be introduced into the mixing chamber 20 where an additional quantity of lime may be added to fix its sulphur content in the subsequent heating step.

In the operation of the process described above oils which contain large amounts of brine are very corrosive and are treated to remove the brine and in certain cases may be washed with fresh water before the oil is admitted to the topping column where the last traces of water is removed. The removal of the salts contained in the brine eliminates the possibility of corrosive substances being formed therefrom in the heating, nevertheless if small amounts of hydrochloric acid, for example, is formed it quickly unites with the oxide or carbide present in the cracking mixture so that too much care need not be taken to wash out all the salts.

Because of the very corrosive effect of petroleum vapors in the vapor space of ordinary stills and in vapor heat interchangers it is preferred to use the type of column still described in the application referred to above for effecting the pre-treatment of the petroleum oil. In this type of column still the liquid oil is so completely mingled with the gas and vapor that the metal surfaces are protected to a large extent by the liquid. Furthermore if additional water is mixed with the entering oil along with the gas, the water by being vaporized will aid in the removal of oxygen and have a diluting effect on any corrosive constitutents present in the vapors.

Oxygen and water both of which are constituents of ordinary air are responsible for much of the corrosion of industrial equipment, and since petroleum oils naturally contain these constituents and absorb additional oxygen on being exposed to the atmosphere, it is important that these constituents be removed. Accordingly the oil is heated to a temperature sufficient to evaporate the water and a dry gas free from corrosive constituents is passed through the oil to sweep out the water vapor and absorbed oxygen and other gases. The gas in this step of the process acts to reduce the partial pressure of the corrosive gas content of the oil including moisture and furthermore acts to replace these constituents in the oil and remove them from the system. When oils which contain a gasoline fraction are subjected to the treatment the gasoline is also removed along with the water and absorbed oxygen or air so that a maximum amount of gasoline will be formed in cracking, since according to the law of "mass action", the presence of gasoline in the charging stock will hold back the formation of that much gasoline during the cracking operation.

For oils containing little or no sulphur further treatment of the oil before cracking will be unnecessary and even with high sulphur oils the removal of water and absorbed oxygen decreases the rate of corrosion several times. In a five day test with naphtha solutions of sulphur compounds, which included hydrogen sulphide, no action on iron was noted at ordinary temperatures while in cases where water was added corrosion resulted. Furthermore it has been found that rise in temperature accelerates the rate of corrosion. Therefore in accordance with the invention the dry and oxygen free oil which contains an appreciable amount of sulphur, is mixed with dry lime or its equivalent prior to its introduction into the refining apparatus such as the tube or tubes of a heating furnace. As sulphur compounds are formed in the cracking or distilling apparatus they immediately react with the highly reactive CaO or CaC_2 to form calcium sulphides and consequently are prevented from reacting on the walls of the equipment. An excess of lime or other compound, above that required to react with the sulphur in the oil, is used in order to make sure that all the sulphur which would ordinarily cause corrosion is taken up.

When a carbide is used as a sulphur fixing agent in the process the reaction, for example, between calcium carbide and hydrogen sulphide is as follows:

$$CaC_2 + H_2S = CaS + C_2H_2 + \text{heat}$$

Besides acting as a fixing agent for the sulphur, a combustible gas, acetylene is also formed from the carbide and serves to aug-

ment the supply and B. t. u. value of the gas formed from the oil.

Under certain circumstances it may be necessary to provide storage for the oil leaving the column still 10, for example where several cracking units are being supplied with non-corrosive oil or in case of a shut-down. The storage tanks used in this event, are air-tight and previously deleted of all air, oxygen or moisture by replacing these gases with purified hydrocarbon or other inert gases so that the oil in storage will have no opportunity to absorb anything but non-corrosive gases.

From the above description of the invention it will be seen that the present process provides an effective method of preventing corrosion in oil refining equipment and at the same time provides a novel oil product free of corrosive constituents, being adapted for use as a cracking or distilling stock.

While the invention has been described in detail with respect to the means and manner of removing absorbed corrosive constituents and traces of water from petroleum oils to be cracked, it is not to be understood that the invention is in any way limited thereby since it is obvious that other means and methods may be used for this purpose, for example absorption by chemicals. Likewise the use of lime or calcium carbide are merely examples of substances used to fix the sulphur of the sulphur compounds present in or formed from the oil during the heating and refining thereof. Obviously the invention is equally applicable to oils and other liquids other than petroleum oil where it is desired to eliminate corrosion in the equipment in which such oils or liquids are to be handled, used or treated.

Having thus described my invention, what I claim is:

1. The method of preventing corrosion in oil distilling apparatus, which comprises treating the oil to be distilled to remove excess water, passing the treated oil together with a hydrocarbon gas through a still to distil off the gasoline and to remove absorbed oxygen and remaining water therefrom, mixing the resulting oil while hot with a quantity of dry lime equivalent to at least twice the amount of sulphur in the oil and passing the mixture into the distilling apparatus.

2. The method of preventing corrosion in oil refining stills, which comprises passing the oil to be cracked into a topping still, passing a hydrocarbon gas into intimate contact with the oil in said still whereby gasoline, water and absorbed oxygen are removed from said oil, withdrawing topped oil from said still and mixing therewith a quantity of lime in excess of the amount of sulphur in said oil and passing the mixture to the refining still.

3. The process of treating a petroleum oil distillate, which comprises intimately contacting the same with cracking still gases substantially freed of free oxygen and sulphur-containing gases under non-cracking conditions, and thereafter mixing the treated distillate with lime.

4. The process of treating a petroleum oil which comprises intimately contacting the oil with cracking still gases substantially freed of free-oxygen and sulfur-containing gases under non-cracking conditions, and thereafter mixing the treated oil with lime.

In testimony whereof I affix my signature.

WILBUR G. LAIRD.