

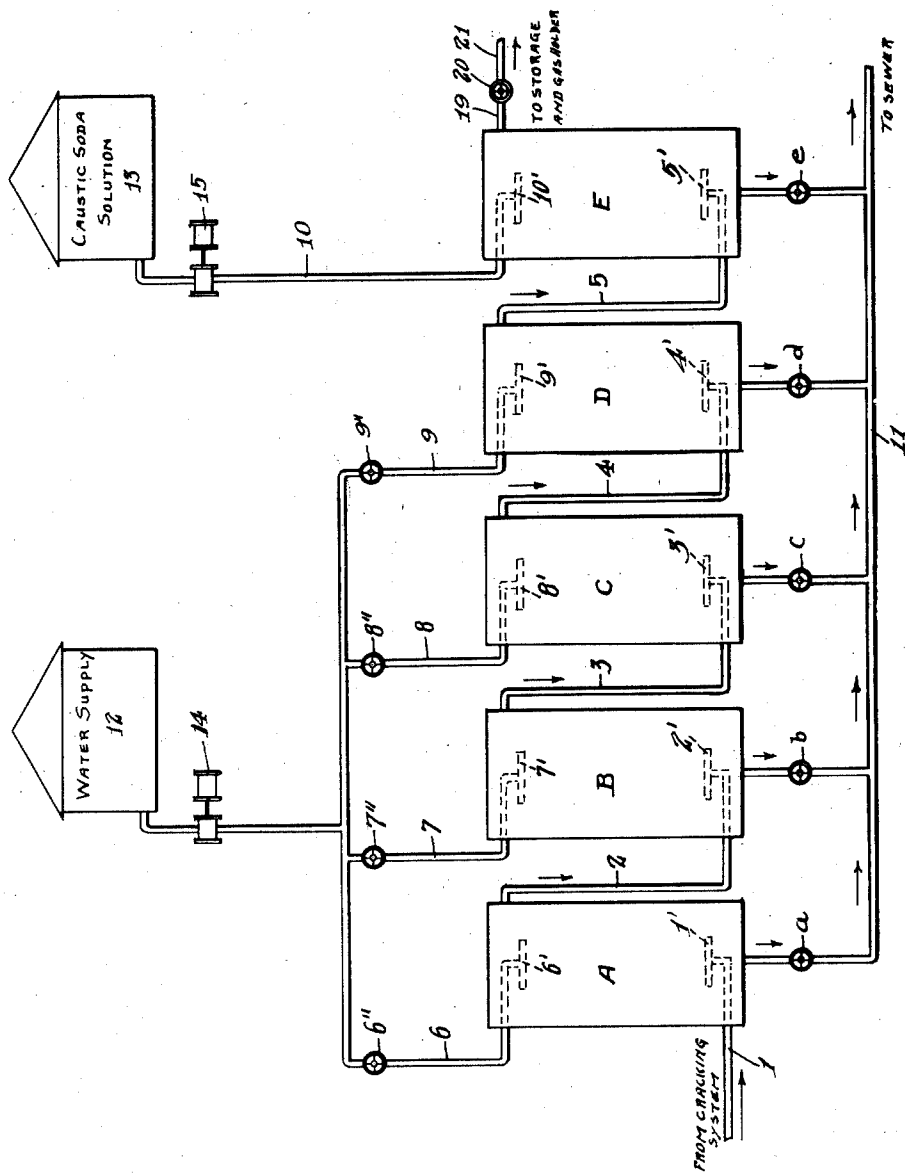
March 5, 1929.

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1,704,246

TREATMENT OF DISTILLATES FROM PROCESSES OF CRACKING PETROLEUM OILS

Filed Oct. 4, 1923



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TREATMENT OF DISTILLATES FROM PROCESSES OF CRACKING PETROLEUM OILS.

Application filed October 4, 1923. Serial No. 666,496.

This invention relates to the art of treating distillates which are formed during the cracking or destructive distillation of petroleum oils.

5 Such destructive distillation or cracking is usually carried out with the use of pressure and temperature, and for the purpose of producing from relatively high-boiling-point oils relatively low-boiling-point oils. These
10 low-boiling-point oils will, for purposes of brevity, in these specifications, be termed a pressure distillate. This pressure distillate, when properly refined and treated, is commonly employed as a motor fuel.

15 During the cracking operation there is formed in addition to the pressure distillate a considerable quantity of relatively fixed or noncondensable gas and provision is made for the withdrawal or removal thereof from the
20 system. There is also formed along with the easily condensable products a considerable quantity of desirable products which have under atmospheric pressure a boiling or vaporizing temperature so low that when the
25 pressure distillate is released from the pressure of the cracking system, these desired products vaporize and escape from the resulting liquid or remaining pressure distillate. The loss of these volatile constituents becomes
30 greater the longer the pressure distillate remains in storage and is subjected to the familiar process called "weathering."

In order to conserve these desirable volatile products it has been a custom to install gas
35 recovery equipment which may comprise a compression, or absorption, or a compression and absorption system whereby, when the pressure distillate is released from the pressure of the cracking system, these more volatile constituents which escape from the pressure
40 distillate are made to unite with an absorption stock for the formation of a comparatively stable liquid which may be used as a motor fuel. This process of recovering in
45 liquid state this desirable gas is analogous to the production of natural-gas gasoline or casing-head gasoline.

Whether or not such recovery of gas is practiced, it is a common practice to store the
50 resulting pressure distillate until such time as it may be convenient to treat it for the pro-

duction of a finished motor fuel. During this storage, some water settles out of the pressure distillate, and the removal of this water is an advantage in that there is less weakening by dilution of the sulfuric acid used in
55 subsequent treatment. Such storage before treatment, however, has certain limitations and disadvantages as will be pointed out later and is not always practiced, in which
60 case the pressure distillate may be immediately treated for a finished product, which treatment usually takes place after the release of the pressure distillate from the pressure
65 of the cracking system.

During the cracking process or operation there is formed a considerable quantity of hydrogen sulfide gas which was not present in the original charging stock fed to the cracking system. This hydrogen sulfide has
70 heretofore been a source of great trouble in the refining or treating of the pressure distillate for a satisfactory marketable product. When the pressure distillate is held in storage for a period before treatment it causes
75 excessive and severe corrosion of the storage equipment, which offsets the advantage of storing the pressure distillate before treatment for the settling out of the water and makes it imperative to apply the acid treat-
80 ment immediately with a consequent larger acid requirement.

When a recovery process is used for the conservation of the easily volatile products which accompany the pressure distillate, this
85 hydrogen sulfide causes severe and troublesome corrosion of recovery equipment, especially in the compression equipment, and the resulting recovered liquid product is so foul that its treatment to produce a satisfactory
90 marketable product is very unsatisfactory, if not practically useless.

Furthermore, due to the presence of the hydrogen sulfide there are formed during the subsequent acid treatment, and by the reaction of the sulfuric acid on the hydrogen sulfide, both water and sulfur. The water causes
95 dilution of the acid and increases the quantity of acid required while the sulfur fouls the product formed.

In addition to the hydrogen sulfide formed
100 during the cracking operation there are

formed a number of polymerized and complex products not definitely understood, which are acid in character. These products, which we will term "acid oils," can be substantially removed by either alkalies or by sulfuric acid. When, however, they are allowed to remain in the oil until the sulfuric acid treating stage is reached it has been found that the quantity of sulfuric acid required is materially greater than the sulfuric acid equivalent of caustic soda if said caustic soda is used for the removal of these "acid oils". Furthermore, it has also been found that when sulfuric acid is used to remove these acid oils, there are formed by the reaction of the sulfuric acid on the "acid oils", certain reaction products, not clearly understood, which produce a very poor quality of finished product.

I have found that by the removal of the hydrogen sulfide and the so-called "acid oils" prior to the sulfuric acid treatment of the pressure distillate many material advantages are obtained which are otherwise unattainable and heretofore unattained. These advantages include:

- (a) The elimination of corrosion of equipment during storage of the pressure distillate and therefore a permitting of such storage.
- (b) Less sulfuric acid required for treatment of the pressure distillate.
- (c) Better quality of finished product.
- (d) The making possible of a satisfactory recovery of the more volatile constituents which tend to escape from the pressure distillate when the same are released from the pressure of the cracking system.

I have also discovered certain new and novel methods of removing these products from the pressure distillate before the same is released from the pressure of the cracking system wherein the pressure distillate is produced.

My invention will be better understood by reference to the accompanying drawing which illustrate an apparatus in which may be performed a preferred embodiment of my invention. The indicated apparatus is given for illustrative purposes only, it being understood that the arrangement therein shown may be widely varied without departing from the scope or spirit of my invention.

In the drawing A, B, C, D, and E represent closed vertical tanks or treating vessels. Pressure distillate, direct from the cracking system wherein it is formed, while under substantially the same pressure as the cracking system, and while the same contains in liquid state the wet gases or highly-volatile and low-boiling-point constituents, is conveyed through a pipe or conduit 1 into the vessel A and discharged from spray nozzles 1' or other suitable distributing devices, located near its lower end. The pressure distillate is conveyed from vessel A through pipe 2 leading

from a point near the top of the vessel to vessel B where it is discharged through spray nozzles 2' or other spreading devices located near the bottom of said vessel. In a similar manner pipes 3, 4, and 5 convey the pressure distillate from vessels B, C, and D respectively into vessels C, D, and E respectively. It will thus be seen that the pressure distillate passes in series flow through the several vessels. From the last vessel E of the series the pressure distillate passes through pipe 19, thence through a pressure relief valve 20 and then through pipe 21, by which it is conducted to storage and the escaping gas, comprising the volatile and low-boiling constituents conducted to gas holding equipment. By means of this pressure relief valve 20 the pressure of the operation may be controlled and the pressure distillate, etc., undergoing treatment at all times maintained under substantially the same pressure as the cracking system.

From a supply tank 12 water at ordinary temperature is conveyed by pump 14 to the vessels A, B, C, and D through lines 6, 7, 8, and 9 respectively. These lines are valved at 6'', 7'', 8'', and 9'' so as to regulate the supply of water to each vessel. Either salt water or fresh water may be used. This water is discharged from spray nozzles or other spreading devices, 6', 7', 8', 9', located in the top of the respective vessels A, B, C, D. From a supply tank 13 a caustic soda solution is conveyed by a pump 15 through a pipe 10 to the vessel E and discharged through spray nozzle 10' located near the top of the vessel.

A pipe or conduit 11 connects with each of the vessels A to E, inclusive, through valves *a*, *b*, *c*, *d* and *e*, conveying the spent wash water from vessels A to D, inclusive, and the spent caustic soda solution from vessel E to a sewer or other suitable place for disposal, the valves *a*, *b*, *c*, *d*, and *e* being used to control the flow of spent liquids from the respective vessels.

In the operation of this process there is a partial extraction, from the pressure distillate, of the hydrogen sulfide by the water washing which takes place in vessels A to D, inclusive, the remaining hydrogen sulfide being removed by the caustic soda treatment in vessel E, and there is substantially a complete removal of the acid oils from the pressure distillate by the caustic soda treatment taking place in vessel E.

For a pressure distillate obtained from a charging stock which has been prepared in accordance with the method, as set forth in U. S. Patent #1,408,698, granted to R. W. Hanna March 7, 1922, and U. S. Patent #1,419,378, granted to R. W. Hanna, June 13, 1922, and which has been produced by the methods of cracking as therein described or as described in U. S. Patents #1,449,226 and

1,449,227, granted to R. W. Hanna on March 20, 1923, I have found it preferable to pass a quantity of salt water through each of the vessels A, B, C, and D equal to about two or
5 two and one-half times the volume of pressure distillate which is sent through the system. This will give a total volume of salt water used which is equal to about eight or ten times the volume of pressure distillate
10 treated.

When the water which is thus used is brought into contact with the pressure distillate, there is a transfer of a part of the hydrogen sulfide gas, which is held in the pressure
15 distillate, from the pressure distillate to the water. This transfer takes place in accordance with a well known law whereby, when a gas is soluble in either of two liquids, if one of the liquids, free from this gas, is brought
20 into contact with the other liquid which holds the gas in solution, the first liquid will extract gas from the second and this transfer of the gas from the one liquid to the other will take place until the ratio of the concentration of
25 the gas in the one to the concentration of the gas in the other has reached a certain constant value. In accordance with this law, it will be seen that it is impossible to remove, by this water washing, all of the hydrogen
30 sulfide gas from the pressure distillate. It is to be noted also that caustic soda is an agent which by itself will effectively remove all of the hydrogen sulfide from the pressure distillate and that the pressure distillate is
35 contacted with this agent in treater E. If, however, the hydrogen sulfide were to be removed in its entirety by such agent, the cost would be prohibitive. Therefore, this invention comprehends the use of the water
40 washing process as before referred to and described for the purpose of reducing the hydrogen sulfide content to such a degree that the amount of caustic required to remove the remainder of the hydrogen sulfide is not prohibitive in cost.

When such water washing is carried out, not only can the remaining hydrogen sulfide be economically removed in the caustic soda treater E, but opportunity is given to further
50 employ the caustic soda treatment in vessel E for the removal of the acid oils from the pressure distillate, thereby giving a product which is free from corrosive agents and which can, therefore, be held in storage until the
55 settling out of the water takes place. The possibility of carrying water into the subsequent acid treater and diluting the sulfuric acid used later is thus precluded. Less sulfuric acid is therefore required for the
60 treatment of the pressure distillate and the gas, which is evolved on the release of the pressure, would be sweet and in marketable condition ready for compression, absorption or other recovery process, in a gasoline re-
65 covery plant.

It will be noted that in the treating vessels A, B, C, D, and E, the pressure distillate travels in a direction which is counter to the direction of flow of the treating reagent employed, i. e.: to the direction of the flow of
70 the water or of the caustic soda solution. Because of the density of the pressure distillate being much less than that of the water and the caustic soda solution and because of the pressure distillate being discharged near
75 the bottom of each treating vessel, such counter current flow is made possible. By virtue of such process of counterflow, substantially every particle of treating reagent in each of the several vessels A, B, C, D, and E, during
80 its passage through its respective treater, continually comes into contact with a progressively increasing fresher pressure distillate or one which has been treated to a less degree through its respective treater, continu-
85 ally comes into contact with particles of pressure distillate which have a progressively increasing amount of hydrogen sulfide or "acid oils". It will therefore be seen that throughout the entire path of the reagent or
90 so long as it is in contact with the pressure distillate, this reagent will possess potential strength or potential treating power with reference to the pressure distillate with which it comes in contact. There will, therefore, be
95 a continual transfer of the hydrogen sulfide or "acid oils," from the pressure distillate to the water or caustic soda solution throughout the entire passage of the treating reagent and the maximum attainable strength
100 is obtained from the reagents used.

While a very high degree of efficiency is obtained through the use of such a counter-current flow of pressure distillate and treating reagents, I do not wish to limit my process to such a means of contacting the pressure
105 distillate with the water or alkali solution used, it being understood that any method by which an effective contact is obtained between the reagents employed and the pressure distillate, while said pressure distillate is held under substantially the same pressure as the cracking system wherein it is produced, may be employed without departing from the spirit of my invention.

It is to be noted that the products of the cracking operation have been first subjected to condensation in the cracking system before introduction into the vessel A; also that such
120 raw, untreated products of the cracking operation are so subjected to a process embodying my invention before any commercial or chemical treatment of such products except the usual condensation. It is also obvious that many of the advantages of my invention
125 may be secured even though there is a partial release of the pressure of the cracking system and a withdrawal of the wet gases produced by the cracking operation.

It will be further noted that the advantages 130

of my invention may also be secured if, prior to the treatment with water and with alkali, or with either, the pressure distillate is subjected to a pressure greater than that of the cracking system wherein the pressure distillate is produced and the treatments as herein described are carried out under such increased pressure. An example of a typical pressure used in the process may be 100 pounds per square inch although higher pressures such as 200 or 300 pounds per square inch may be applied and the drop of pressure between the cracking operation and the treating steps is preferably small, being only that drop of pressure which will facilitate the passage of the liquids through the several treating vessels and this differentiation in pressure between the cracking steps and the last treating step may be as low as 5 to 15 pounds per square inch.

My invention is particularly applicable to pressure distillates and wet gases produced by cracking operations, which distillates or gases have a sulfur content of more than 2 per cent.

In one embodiment of my invention the process may be utilized only for the removal of the hydrogen sulphide from the wet gases of the cracking operation. With such an embodiment of my invention, the wet gases of the cracking operation are withdrawn from the cracking system separate from the pressure distillate condensate without releasing from said gases the degree of pressure evolved in the cracking distillation operation substantially below the degree of pressure reduction requisite for the evolution of said wet gases from the pressure distillate as condensed in the cracking distillation operation.

I claim:

1. The process of treating petroleum oil pressure distillate having a sulfur content in excess of two-tenths of one per cent, which consists in washing the same with water directly after condensation thereof without releasing the distillate from the degree of pressure evolved in the cracking distillation operation substantially below the degree of pressure reduction requisite for the evolution of the wet gases from the pressure distillate and then without substantial release of said pressure contacting the same with a solution of alkali.

2. The process of treating the wet gases which evolve from a pressure distillate having a sulfur content of more than two-tenths of one per cent, which consists in washing said gases with water directly as received from the condenser of cracking operation and then contacting said gases with a solution of alkali, without releasing from said gases the degree of pressure evolved in the cracking distillation operation substantially below the degree of pressure reduction requisite for the evolution of said wet gases from said pressure

distillate as condensed in the cracking distillation operation.

3. In a process of treating the wet gases which evolve from a pressure distillate having a sulfur content of more than two-tenths of one per cent, that step which consists in washing said gases with water directly as received from the condenser of a cracking operation without releasing said gases from the degree of pressure evolved in the cracking distillation operation substantially below the degree of pressure reduction requisite for the evolution of said wet gases from the pressure distillate as condensed in the cracking distillation operation.

4. The process of treating a pressure distillate obtained from petroleum oil after the pressure distillate has been subjected to condensation and while in a raw untreated state, which includes flowing the pressure distillate continuously through a treating vessel without releasing the distillate from the degree of pressure evolved in the cracking distillation operation substantially below the degree of pressure reduction requisite for the evolution of the wet gases condensed in the pressure distillate from the cracking distillation operation, and simultaneously causing water to flow continuously through the same treating vessel but in a direction opposite or counter to that of the flowing pressure distillate, thereby removing hydrogen sulfide from the pressure distillate.

5. The process of treating a pressure distillate obtained from the petroleum oil after the pressure distillate has been subjected to condensation, which consists in flowing the pressure distillate continuously through a treating vessel, without releasing said distillate from the degree of pressure evolved in the cracking distillation operation substantially below the degree of pressure reduction requisite for the evolution therefrom of the wet gases condensed therein from the cracking distillation operation, and simultaneously causing a solution of alkali to flow continuously through the same treating vessel but in a direction opposite or counter to that of the flowing pressure distillate, thereby removing hydrogen sulfide from the pressure distillate.

6. The process of treating a pressure distillate obtained from petroleum oil after the pressure distillate has been subjected to condensation and while in a raw untreated state, which consists in flowing the pressure distillate continuously through a treating vessel, and simultaneously causing water to flow continuously through the same treating vessel but in a direction opposite or counter to that of the flowing distillate, separating the pressure distillate from the water, then passing the pressure distillate to a second treating vessel, and simultaneously causing a solution of alkali to flow continuously through

the same treating vessel but in a direction counter to that of the flowing pressure distillate, thereby removing hydrogen sulfide and acid oils from the pressure distillate, such treatment being carried out without releasing said pressure distillate from the degree of pressure evolved in the cracking distillation operation substantially below the degree of pressure reduction requisite for the evolution of the wet gases condensed therein 10 from the cracking distillation operation.

Signed at Richmond, California, this 28th day of September, 1923.

RALPH A. HALLORAN.