Feb. 23, 1943. E. W. McNEALY 2,312,112

PROCESS FOR ACID TREATING PETROLEUM OILS

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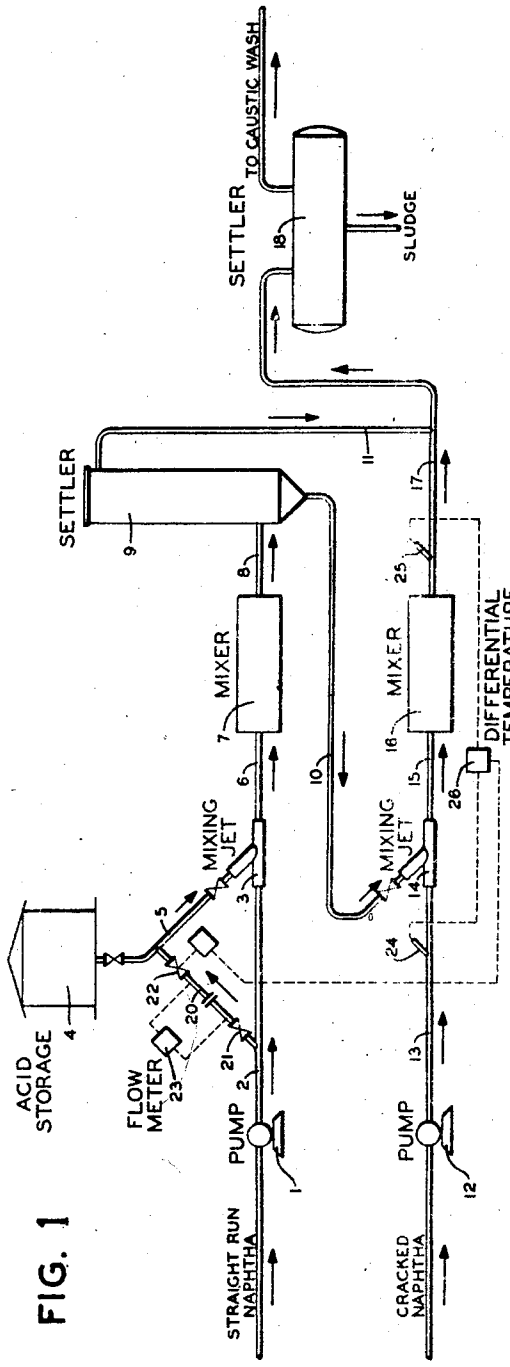


FIG. 1

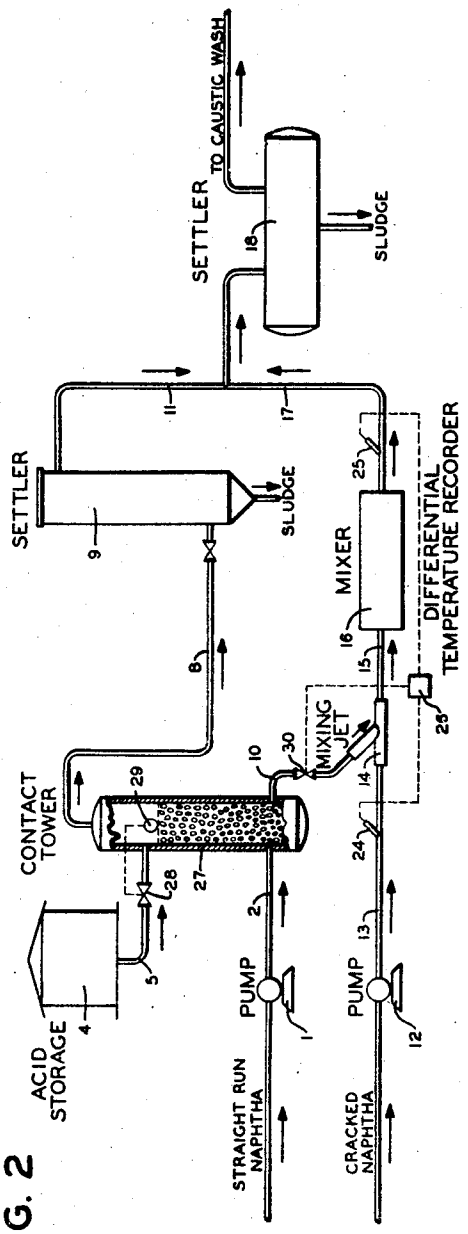


FIG. 2

EDDINS W. McNEALY
INVENTOR

BY R. J. Dearborn
Daniel Stryker
HIS ATTORNEYS

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PROCESS FOR ACID TREATING PETROLEUM OILS

Eddins W. McNealy, San Antonio, Tex., assignor, by mesne assignments, to The Texas Company, New York, N. Y., a corporation of Delaware

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8 Claims. (Cl. 196—31)

This invention relates to the process for treating petroleum hydrocarbon oils with acids to remove sulfur and gum-forming constituents. The invention particularly relates to an improved method of controlling the addition of acid to cracked petroleum oils in a continuous treating process. In its more specific aspects the invention relates to a method of controlling the introduction of acid in the process for the acid treating of both straight run and cracked petroleum oils disclosed in the U. S. application of R. F. Dorsch, Serial No. 364,027, filed of even date herewith.

In treating cracked petroleum oils such as cracked naphthas with an acid such as sulfuric acid it is desirable to control the reaction carefully in order to prevent loss of hydrocarbons due to polymerization and other side reactions. In continuous processes for the acid treatment of cracked oils wherein the acid is passed into contact with a flowing body of the oil, it is difficult to keep the acid flow constant or to vary it in the desired degree because of variations in the acid line due to clogging and erosion or corrosion of the pipes and valves employed. For economic reasons it is customary to employ for the acid treatment of hydrocarbon oils, recovered black acids containing various percentages of sulfuric acid. These acids contain impurities such as coke and the like and inorganic salts such as sodium sulfate. Since the acids are generally flowed in small streams, deposition of salts and clogging is liable to result.

In accordance with the present invention the difficulties previously experienced in controlling the flow of an acid treating agent to a flowing stream of a cracked petroleum hydrocarbon oil are overcome in a simple and efficient manner by controlling or varying the flow of acid treating agent in accordance with variations in the temperature differential between two points in the flowing stream of oil, one of which is located at a point where substantial mixing of the oil with the acid treating agent has been effected. The other point is preferably located before the introduction of acid treating agent into the moving body of oil. The invention is based upon the discovery that this differential temperature provides an accurate measure of the amount of acid being introduced into the system and that it is available to determine the flow of acid treating agent without regard to failures and weaknesses which may develop in the line carrying the acid treating agent or the control devices such as valves which may be disposed therein. This method of control may be operated either automatically or manually.

As indicated above, the present method is especially valuable when employed in connection with the process for the acid treating of both straight run and cracked petroleum oils to remove sulfur and gum-forming constituents disclosed in the previously referred to U. S. application of R. F. Dorsch. This process involves treating a straight run petroleum hydrocarbon oil, such as straight run naphtha, with relatively strong acid such as recovered 98 per cent sulfuric acid, removing from the resulting mixture of acid and oil the straight run acid sludge substantially as rapidly as formed, and introducing the acid sludge into a flowing stream of the cracked petroleum hydrocarbon oil. In applying the present invention to this process, the differential temperature between two points in the flowing stream of cracked oil is determined. One of these points is located where substantial mixing of the straight run acid sludge and the cracked oil has occurred, and the other is preferably located in the cracked oil line prior to the addition of the acid sludge. The flow of acid to the straight run system is then controlled in accordance with this differential temperature. It will be understood, of course, that the optimum differential temperature will have been determined in advance by analytical tests and the flow of acid is controlled so as to maintain the differential at the predetermined optimum.

In order that the invention may be understood more fully reference should be had to the accompanying drawing in which Figure 1 represents a system adapted to be employed in the use of applicant's method, and Figure 2 represents a modified system for this purpose. The operation of the systems disclosed in these figures will be described in connection with the treatment of straight run and cracked naphthas but it will be understood that the invention is not limited to the treatment of such oils.

Referring to Figure 1, straight run naphtha is forced into the system by pump 1, through line 2 and passes from this line through a jet 3, which is provided with a restricted orifice not shown. In jet 3 the naphtha is contacted with strong sulfuric acid, such as recovered 98 per cent black sulfuric acid, from acid storage vessel 4 through line 5, in a manner described more fully below. The mixture of naphtha and acid flows through line 6 to a mixer 7, which may be of any suitable construction such as a pipe mixer, for example, and from the mixer the mixture

flows through a line 8 into the lower portion of the settler 9. In this settler the straight run acid sludge settles to the bottom and is removed as rapidly as formed through a line 10 leading to the cracked naphtha system. The treated straight run naphtha passes from the top of settler 9 into a line 11, through which it is conducted into admixture with cracked naphtha containing acid sludge. Cracked naphtha is forced into the system by means of pump 12 and passes through line 13 leading to a mixing jet 14, which is similar to jet 3. In mixing jet 4, the cracked naphtha is mixed with straight run acid sludge and the resulting mixture passes through line 15 into mixer 16 and thence through line 17 leading to settler 18. Line 11 carrying acid treated straight run naphtha leads into line 17 and the mixture of straight run naphtha, cracked naphtha, and acid sludge passes into settler 18 where the sludge settles and is drawn off. From this settler the combined naphthas are passed to a caustic washing system and to any further treatment desired.

The method of effecting the introduction of acid into the straight run naphtha line is a feature of the present invention. Connecting line 2 and line 5 there is disposed a line 20 provided with valves 21 and 22 and a flow-meter 23. As the process is usually operated, the pressure in the naphtha line is greater than the pressure on the acid at the point that line 20 joins with line 5. With valves 21 and 22 open no acid would flow to the jet. In operating the process valve 22 is partially closed and the flow of naphtha in line 20 is controlled so that a regulated mixture of naphtha and acid flows to jet 3, the total amount of liquid entering this jet through line 5 being determined, of course, by the naphtha flow through the jet from line 2. This method of controlling the flow of acid into the system is advantageous from several aspects. Because the volume of liquid flowing to the jet is relatively large, clogging difficulties are avoided. Also it is more efficient to regulate the naphtha flow by means of valve 22 than it would be to effect this control by manipulation of one of the valves in the acid line.

The ultimate control of the introduction of acid into the system is effected in the following manner. In the cracked naphtha system there are disposed two means for measuring the temperature of the flowing stream in the line. As shown, a thermometer 24 is located in line 13 between the pump 12 and the jet 14 and a thermometer 25 is located after mixer 16; i. e., at a point in the line where thorough mixing of the cracked naphtha and straight run acid sludge has been accomplished. In this connection it will be understood that these means for determining temperature could be located at other points provided they were sufficiently separated in the line that the flowing stream measurably increased in temperature from one point to the other. It is known that the reaction between acid and a cracked petroleum oil, such as cracked naphtha, generates heat and, therefore, between the points in the system where means 24 and 25 are located, there is a measurable rise in temperature. In accordance with the present invention this rise in temperature is measured and is employed for controlling the flow of acid into the straight run naphtha system. This may be accomplished by the use of a differential temperature recorder 26. In controlling the flow of acid the valve 22 in line 20 may be manipulated manually by reference to differential temperature recorder 26. If desired, however, the variations in the differential temperature may be employed to control the operation of valve 22 automatically. The specific mechanical means for carrying out this automatic control forms no part of the invention since any suitable control mechanism may be employed.

It will be seen, therefore, that the method described above offers a simple and efficient means for accurately controlling an acid treating process of the type in question. The differential temperature is determined on the cracked naphtha line at a point in the system distant from the point where the acid is introduced and any variations in the acid flow are immediately determined and may be corrected.

To illustrate the operation of the present method more specifically the following example is given. In this example, the process is operated for the treatment of about 74 barrels per hour of straight run naphtha containing about 0.12 per cent total sulfur and about 95 barrels per hour of cracked naphtha obtained by thermal cracking and containing about 0.22 per cent sulfur. The straight run system is adjusted so that the pressure on pump 1 is 60 to 18 pounds per square inch and the valve 22 is at first adjusted so that about seven pounds of recovered 98 per cent sulfuric acid are fed into the jet 3 for each barrel of straight run naphtha. The resulting mixture is passed to mixer 6 and then into settler 8, the contact time, calculated from the time the mixture leaves the jet until it enters the settler, being about 46 seconds. The straight run acid sludge is removed from the settler as rapidly as it is formed and is introduced into the cracked naphtha line through jet 14. The pressure on the cracked naphtha pump 12 is also about 60 to 80 pounds per square inch. In the jet 14, the cracked naphtha is joined by the acid sludge in the proportion of about 4.7 pounds of acid sludge for each barrel of cracked naphtha. The mixture of cracked naphtha and straight run sludge is passed through mixer 16 and then into line 17 where it is joined by the acid treated straight run naphtha from settler 9. In settler 18 the sludge settles out and is withdrawn, and the combined naphthas are passed to a caustic wash and are further treated to obtain a finished gasoline. The time of contact between the straight run acid sludge and the cracked naphtha, calculated from the time of mixing the two in jet 14 until the combined naphthas and sludge enter settler 18, is about 31 seconds.

In this process the temperature of the cracked naphtha, determined prior to the addition of the acid sludge, is 95° F., and the temperature of the mixture of cracked naphtha and straight run acid sludge, after passing through the mixer 16, is 102° F., these two temperatures being determined at the points in the line where temperature measuring means 24 and 25 are located. Thus, the differential temperature between these points is 7° F. As the process is continued and variations in the flow of acid to the straight run system tend to develop, these variations are indicated by a change in the differential temperature and are corrected by making the necessary change in valve 22, either manually or automatically. It will be understood, of course, that at the start of the operation of the process, the proper amount of acid for addition to the system has been determined experimentally, and the differential temperature for this amount

has been recorded. When the process is started up, the differential temperature provides an accurate check on the amount of acid entering the system and also provides a means for determining variations in the acid flow.

The modified system disclosed in Figure 2 of the drawing provides means for increasing the contact time between the straight run naphtha and the acid. In this figure the numbers indicate corresponding elements in Figure 1. This system includes a contact tower 27 which is filled to within a predetermined distance from the top with means such as Raschig rings for effecting mixing of liquids passing therethrough. As disclosed, the straight run naphtha passes into the tower at a point near the bottom thereof, passes upwardly through a body of sulfuric acid, and leaves the tower through an overflow line 8 leading to settler 9. Acid from storage vessel 4 enters the tower through line 5, which is provided with float-controlled valve 28. Straight run acid sludge which forms in the tower is removed from the bottom thereof as rapidly as formed through line 10 leading to jet 14 in the cracked naphtha system. A float 29, which is sufficiently heavy to sink in the acid-treated naphtha and yet float on the body of acid is disposed in the tower at the interface between the body of acid and the naphtha. This float acts to control valve 28 and thereby vary the flow of acid into the tower. Sludge line 10 is provided with a valve 30 which is controlled by differential temperature recorder 26 in the manner of valve 22 in the apparatus disclosed in Figure 1. While the operation of the apparatus disclosed in Figure 2 is believed to clear from what has been stated, it may be of advantage to point out that by controlling the flow of sludge through line 10, the level of acid in tower 27 is varied and changes in this level are operative by means of float 29 and valve 28 to vary the flow of acid through line 5. Thus, on reducing the rate of flow of acid sludge through line 10, the acid level in the tower tends to rise and this rise is effective to change the setting of valve 28 so as to reduce the flow of acid into the tower. This system, therefore, similarly to that disclosed in Figure 1, provides means whereby the differential temperature between two points in the cracked naphtha line is employed to control the introduction of acid into the straight run naphtha system. The settler 9 in Figure 2 is employed for the purpose of removing any sludge which may be carried over from tower 27. If the separation of sludge is substantially complete in the tower, this settler need not be used.

Although the present method of control has been discussed particularly in connection with the combined process of treating both straight run and cracked hydrocarbon oils, it may be employed with advantage in other processes wherein a cracked petroleum hydrocarbon oil, especially a cracked naphtha, is contacted with an acid treating agent such as sulfuric acid or sulfuric acid sludge. For example, the method may be used in a process wherein a cracked naphtha is reacted directly with sulfuric acid (e. g., 93 per cent recovered acid). In this case, the differential temperature would be employed for controlling the flow of acid to the cracked naphtha stream.

Since changes may be made in the processes described above without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. In a process wherein a flowing stream of a cracked petroleum hydrocarbon oil is continuously contacted with an acid treating agent, the method of controlling the addition of said acid treating agent which comprises determining the differential temperature of the flowing stream of the cracked petroleum hydrocarbon oil between two points in said stream, at least one of said points being beyond the point of contact of said stream with said acid treating agent and sufficiently beyond the other of said points in the stream flow to enable the measurement of a temperature rise in said stream between said points resulting from the heat of reaction of said acid treating agent and said oil, and controlling the addition of said acid treating agent in accordance with vibrations in said differential temperature.

2. In a process wherein a flowing stream of a cracked naphtha is continuously contacted with a sulfuric acid treating agent, the method of controlling the addition of said acid treating agent which comprises determining the differential temperature of the flowing stream of cracked naphtha between two points in said stream, at least one of said points being beyond the point of contact of said stream with said acid treating agent and sufficiently beyond the other of said points in the stream flow to enable the measurement of a temperature rise in said stream between said points resulting from the heat of reaction of said acid treating agent and said oil, and controlling the addition of said acid treating agent in accordance with variations in said differential temperature.

3. In a process wherein a flowing stream of a cracked naphtha is continuously contacted with a sulfuric acid treating agent, the method of controlling the addition of said acid treating agent which comprises determining the differential temperature of the flowing stream of cracked naphtha between two points in said stream, one of said points being located before the point of contact of said stream with said acid treating agent and the other of said points being located at a point where substantial mixing of said cracked naphtha and said acid treating agent has occurred, and controlling the addition of said acid treating agent in accordance with variations in said differential temperature.

4. In a process for acid treating both straight run and cracked petroleum hydrocarbon oils wherein sulfuric acid is flowed continuously into contact with a moving body of the straight run petroleum hydrocarbon oil to produce an acid-treated straight run petroleum hydrocarbon oil and a straight run acid sludge, the straight run acid sludge is separated continuously from the acid-treated straight run petroleum hydrocarbon oil, and the straight run acid sludge is flowed continuously into contact with a flowing stream of the cracked petroleum hydrocarbon oil, the improvement which comprises controlling the flow of sulfuric acid into the straight run petroleum hydrocarbon oil by determining the differential temperature of the flowing stream of cracked petroleum hydrocarbon oil between two points in said stream, at least one of said points being beyond the point of contact of said stream with the straight run acid sludge and sufficiently beyond the other of said points in the

stream flow to enable the measurement of a temperature rise in said stream between said points resulting from the heat of reaction of said acid sludge and said oil, and controlling the flow of acid to the straight run petroleum hydrocarbon oil in accordance with variations in said differential temperature.

5. In a process for acid treating both straight run naphtha and cracked naphtha wherein sulfuric acid is flowed continuously into contact with a moving body of the straight run naphtha to produce an acid-treated straight run naphtha and a straight run acid sludge, the straight run acid sludge is separated continuously from the acid-treated straight run naphtha, and the straight run acid sludge is flowed continuously into contact with a flowing stream of the cracked naphtha, the improvement which comprises controlling the flow of sulfuric acid into the straight run naphtha by determining the differential temperature of the flowing stream of cracked naphtha between two points in said stream, at least one of said points being beyond the point of contact of said stream with the straight run acid sludge and sufficiently beyond the other of said points in the stream flow to enable the measurement of a temperature rise in said stream between said points resulting from the heat of reaction of said acid sludge and said cracked naphtha, and controlling the flow of acid to the straight run naphtha in accordance with variations in said differential temperature.

6. In a process for acid treating both straight run naphtha and cracked naphtha wherein sulfuric acid is flowed continuously into contact with a moving body of the straight run naphtha to produce an acid-treated straight run naphtha and a straight run acid sludge, the straight run acid sludge is separated continuously from the acid-treated straight run naphtha, and the straight run acid sludge is flowed continuously into contact with a flowing stream of the cracked naphtha, the improvement which comprises controlling the flow of sulfuric acid into the straight run naphtha by determining the differential temperature of the flowing stream of cracked naphtha between two points in said stream, one of said points being located before the point of contact of said stream with said straight run acid sludge and the other of said points being located at a point where substantial mixing of said cracked naphtha and said straight run acid sludge has occurred, and controlling the flow of acid to the straight run naphtha in accordance with variations in said differential temperature.

7. In a process for acid treating both straight run naphtha and cracked naphtha wherein sulfuric acid is flowed continuously into contact with a moving body of the straight run naphtha to produce an acid-treated straight run naphtha and a straight run acid sludge, the straight run acid sludge is separated continuously from the acid-treated straight run naphtha, and the straight run acid sludge is flowed continuously into contact with a flowing stream of the cracked naphtha, the improvement which comprises effecting the introduction of the sulfuric acid into the flowing stream of straight run naphtha by dividing said stream into a subsidiary stream and a main stream, passing the main stream through a zone of restricted flow to create suction, passing the subsidiary stream of naphtha into contact with an acid stream flowing to the main stream of naphtha due to the suction created in said main stream, the pressure on said subsidiary stream of naphtha being normally greater than the pressure on said acid, and regulating the pressure on said subsidiary stream to regulate the flow of acid to said main stream, the regulation of pressure on said subsidiary stream being controlled by determining the differential temperature of the flowing stream of cracked naphtha between two points in said stream of cracked naphtha, at least one of said points being beyond the point of contact of said stream of cracked naphtha with the straight run acid sludge and sufficiently beyond the other of said points in the stream flow to enable the measurement of a temperature rise in said stream between said points resulting from the heat of reaction of said acid sludge and said cracked naphtha, and regulating the pressure on said subsidiary stream of straight run naphtha in accordance with variations in said differential temperature.

8. A process for acid treating both straight run naphtha and cracked naphtha with a sulfuric acid treating agent which comprises continuously passing a stream of straight run naphtha in counter-current contact with a body of sulfuric acid contained in an enlarged zone, to produce an acid-treated straight run naphtha and a straight run acid sludge, continuously flowing said acid-treated straight run naphtha from the upper portion of said enlarged zone, continuously passing said straight run acid sludge from the lower portion of said enlarged zone into a flowing stream of cracked naphtha, maintaining a constant volume of sulfuric acid in said enlarged zone by introducing sulfuric acid into said enlarged zone at a rate equal to the rate of passage of straight run acid sludge into said flowing stream of cracked naphtha, determining the differential temperature of the flowing stream of cracked naphtha between two points in said stream, at least one of said points being located where substantial mixing of said cracked naphtha and said straight run acid sludge has occurred and sufficiently beyond the other of said points in the stream flow to enable the measurement of a temperature rise in said stream between said points resulting from the heat of reaction of said acid sludge and said cracked naphtha, and controlling the rate of passage of said straight run acid sludge from said enlarged zone into said flowing stream of cracked naphtha in accordance with variations in said differential temperature.

EDDINS W. McNEALY.

(Seal) Acting Commissioner of Patents.

CERTIFICATE OF CORRECTION.

Patent No. 2,312,112. February 23, 1943.

EDDINS W. McNEALY.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 27, for "18 pounds" read --80 pounds--; page 3, first column, line 36, after the word "to" insert --be--; and second column, line 21, for "vibrations" read --variations--; 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 13th day of April, A. D. 1943.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)