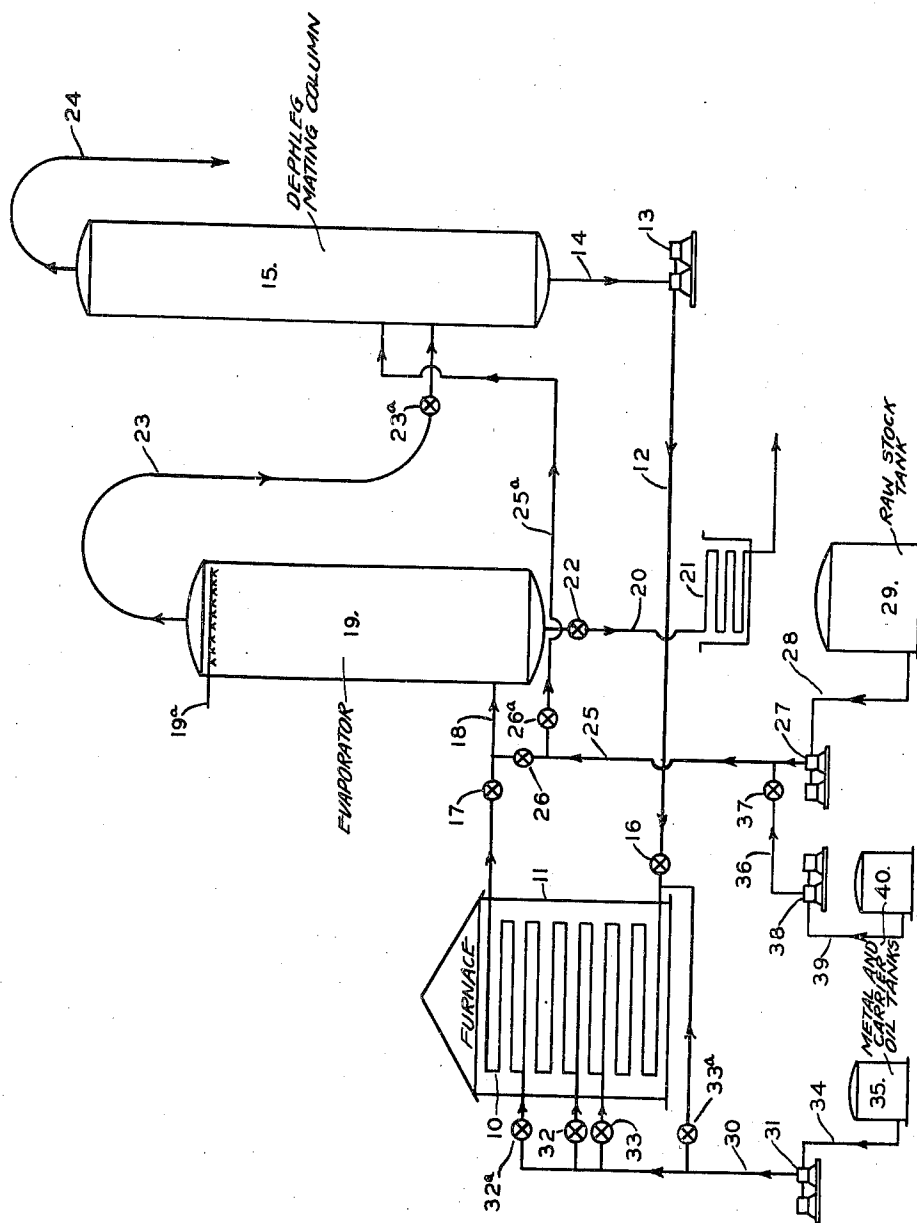


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PROCESS FOR PREVENTING THE CORROSIVE ACTION OF
SULPHUR-BEARING PETROLEUM HYDROCARBONS
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WITNESS

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PROCESS FOR PREVENTING THE CORRO-
SIVE ACTION OF SULPHUR-BEARING
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2 Claims. (Cl. 196-1)

My invention relates to a process for treating hydrocarbons, and more particularly to a process for treating sulphur-bearing petroleum hydrocarbons in the presence of finely divided metal or metallic alloy.

An object of my invention is to prevent the corrosive action of sulphur or sulphur compounds originally present or formed during the heat treatment of petroleum oils towards the metal of the apparatus in which such oils are commonly treated; such corrosive action commonly occurring in the heating tubes, vapor lines, separating columns, condensers and receivers of the apparatus.

During cracking of oils containing sulphur a portion of the latter constituent or its compounds attacks the walls of the apparatus. The sulphur compound thus produced, admixing with carbon, forms an agglomerate closely adhering to the heating tube walls and reaction chamber, causing overheating of the former and generally forestening the run. An object of my invention is to inhibit the formation of such agglomerate and thus prolong the operating cycle and life of the apparatus.

Distillates from sulphur bearing oils subjected to my process are also more readily refined to commercially acceptable standards for sulphur and corrosion; in many instances requiring no further treatment to comply with such standards.

I am aware that finely divided metals have been used in the refining art chiefly as catalysts in conjunction with the addition of hydrogen to the oil being processed, and that the use of various metallic oxides as desulphurants is also a well-known practice. My invention, however, differs from the prior art in providing for the continuous injection of a finely divided desulphurizing metal or metals, either separately, or in physical mixture, or in alloy form into the oil being processed preferably at the critical corrosive temperature of the latter and under certain temperature differentials subsequently described. While any finely divided metal or metallic alloy infusible and capable of acting on the sulphur or sulphur compound contained in the oil at the temperature involved may be used, such as iron, copper, nickel, etc., I preferably employ iron on account of its cheapness and ready accessibility, and in a state of diminution from filings to a colloidal form; the latter state being the more effective. The quantity employed will vary with the nature of the sulphur or its compounds present and the temperatures involved, i. e., with the critical corrosive temperature of the oil being processed or the tempera-

ture at which the existent sulphur or its compounds begin their most deleterious action toward the metal of the apparatus. In some oils such action is most intense during simple distillation and in others extends through the entire active cracking, separating and condensing stage. The approximate lower and upper corrosive temperature limits for most oils subjected to my process appear to lie between 200-1200° F. The metal (or metals) employed, advantageously predispersed in a carrier oil of relatively low sulphur content such as recycle oil, is preferably injected into the main body of the oil undergoing treatment at a predetermined point or points in the heating system, although the injection may be effected at other points and by other carriers as subsequently described. It appears preferable and the invention comprehends the introduction of the carrier oil with its dispersed metal at a substantial temperature differential from the main body of oil being processed. For example, in a cracking operation where it had been previously established that the critical corrosive temperature of the oil processed was 720° F., i. e., that active sulphur corrosion began at such temperature, it was found most advantageous to inject the carrier oil with its dispersed metal (finely divided iron) at a temperature of 750°-850° F., the carrier oil being conveniently preheated before injection through heat exchange or direct means. It has also been found that the carrier oil may be introduced with fair results at a temperature below the main body being processed. Direct admixture of a portion of the finely divided metal with the raw stock is frequently of advantage where disengagement of hydrogen sulphide occurs at a relatively low temperature. Preadmixture of the finely divided metal with the entire stock subjected to heat treatment while effective, requires a much greater quantity of metal to achieve the same result than where the latter is introduced by a carrier stream. Where employed in such carrier stream the quantity of metal required is ordinarily substantially atomically equivalent to the sulphur present in the oil, whereas if the metallic element be preadmixed with the main body of oil to be treated before the critical corrosive temperature is reached, a substantial excess of metal over the atomic sulphur equivalent is required; in either case the metal introduced being maintained in contact with the body of oil during its entire heat treatment and any unchanged metal together with sulphur compounds thereof formed being drawn off with the residuum and separated there-

from according to standard practice such as stagnation, filtration or the like if required.

In order that the invention may be more clearly understood, reference is made to the accompanying drawing depicting in diagrammatic form one type of apparatus suitable for carrying out the invention, wherein 10 represents a heating coil disposed in a conventional furnace 11, such coil being supplied with cycle oil through the line 12 by the pump 13 taking suction through the line 14 from the dephlegmating column 15. Valve 16 controls the inlet pressure and valve 17 the outlet pressure of the coil 10, the latter discharging through line 18 to the vessel 19 from which residuum is withdrawn from the system through line 20 and cooling coil 21 as controlled by valve 22, while the vapors escape through line 23 as controlled by valve 23a to the dephlegmating column 15. Dephlegmated vapor from the latter passes through line 24 to a condenser (not shown) wherein vapor is condensed according to standard practice and recovered. Raw stock is introduced to the system through lines 25 and 25a, as controlled by valves 26 and 26a, by pump 27 taking suction through line 28 from raw stock supply tank 29. Carrier oil, in which the metal employed is dispersed, is injected into coil 10 at a predetermined critical temperature, i. e., that at which sulphur or sulphur compounds become active, through the line 30 by the pump 31 as controlled by valves 32, 32a, 33 and/or 33a; the pump 31 taking suction through line 34 from the carrier oil tank 35, which is provided with a mixing device (not shown) for incorporating the finely divided metal with the carrier oil. A different, or the same metal may be introduced with the raw stock through line 35, as controlled by valve 37, by pump 38 taking suction through line 39 from tank 40, which like tank 35 is provided with a mixing device (not shown). The carrier oil with its dispersed metal may be heated by any desirable means (not shown) preferably to a tempera-

ture in excess of that of the oil processed at the point of injection.

The process is not limited to the method of injection or to the points of introduction of the finely divided metal, nor in general to the particular apparatus shown which is to be understood in practice would be equipped with various indicating and/or recording devices for temperature, pressure and automatic controls commonly employed in the art. The invention is further not limited as to any pressure or to the temperatures mentioned, which are given by way of example only, and what I claim is new and desire to protect by Letters Patent is:

1. Process for preventing the corrosive action of sulphur-bearing petroleum hydrocarbons towards the metal of the apparatus in which such hydrocarbons are treated which comprises continuously injecting into said hydrocarbons upon attainment of an initial critical corrosive temperature specific to said hydrocarbons finely divided iron dispersed in a carrier oil of relatively low sulphur content heated to a temperature approximately 150° F. in excess of said initial corrosive temperature and maintaining such contact while said hydrocarbons exist at a corrosive temperature.

2. Process for preventing the corrosive action of sulphur-bearing petroleum hydrocarbons towards the metal of the apparatus in which such hydrocarbons are treated which comprises continuously injecting into said hydrocarbons upon attainment of an initial critical corrosive temperature of approximately 700° F. finely divided iron dispersed in a carrier oil of relatively low sulphur content heated to a temperature approximately 150° F. in excess of said initial corrosive temperature and maintaining such contact while said hydrocarbons exist at a cracking temperature.

THOMAS L. MCGEE.