

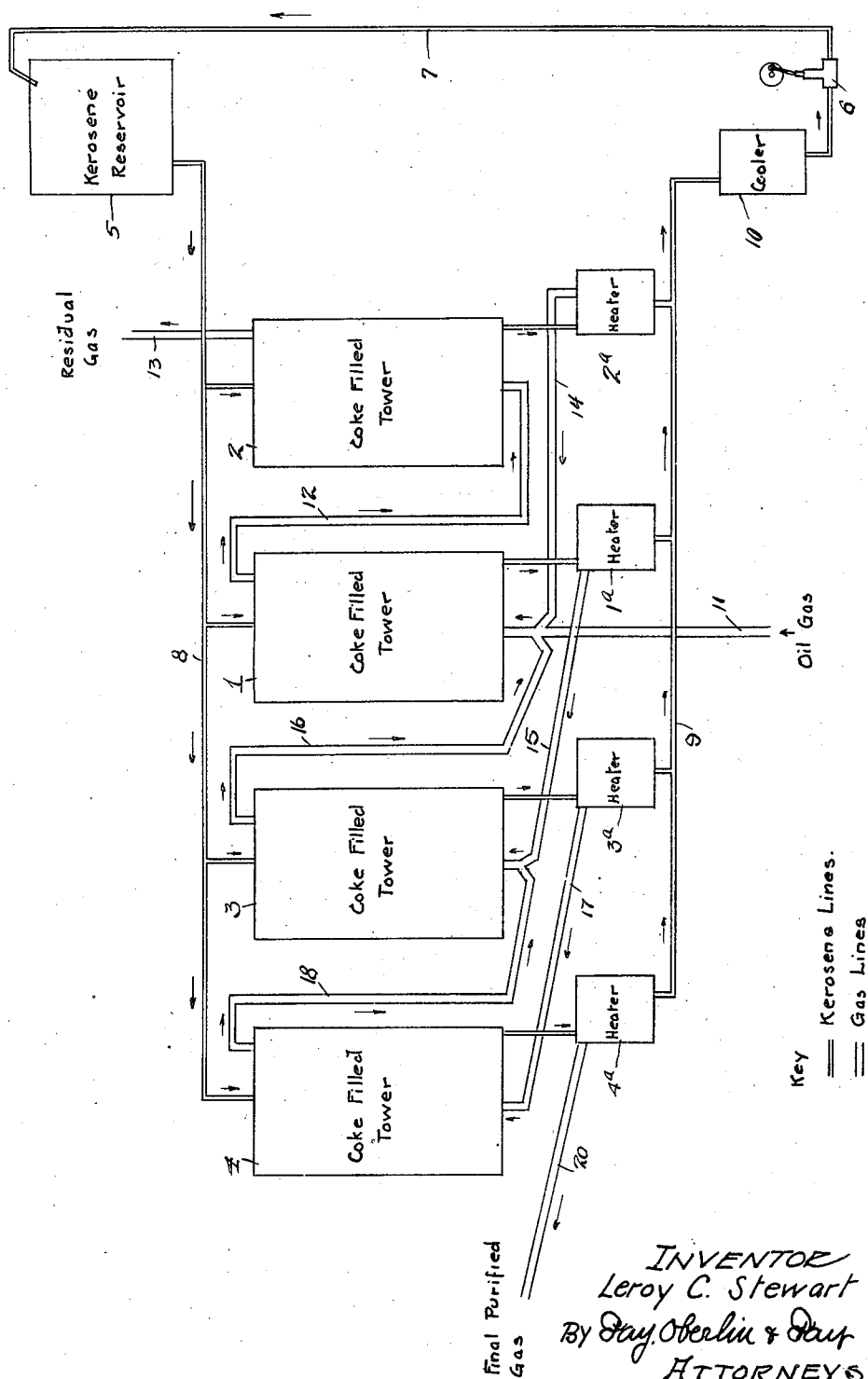
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METHOD OF SEGREGATING OLEFINS

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METHOD OF SEGREGATING OLEFINES.

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To all whom it may concern:

Be it known that I, LEROY C. STEWART, a citizen of the United States, and a resident of Midland, county of Midland, and State of Michigan, have invented a new and useful Improvement in Methods of Segregating Olefines, of which the following is a specification, the principle of the invention being herein explained, and the best mode in which I have contemplated applying that principle, so as to distinguish it from other inventions.

The production of olefines by cracking kerosene or other petroleum oil, that is by passing it through heated tubes, into heated retorts or similar apparatus, has been known and practiced for some time. When the temperature in such cracking process is properly regulated, an oil gas can be produced which will contain about fifty per cent of olefines, the remaining fifty per cent consisting of hydrogen, methane and other saturated hydrocarbons; while by varying the cracking conditions, such olefines may be made to consist almost entirely of ethylene, or of only some thirty or forty per cent ethylene, and the balance propylene and other higher members of the series.

Oil gas obtained in the manner just described has been found a convenient basis for the production of ethylene or glycol chlorhydrin ($\text{CH}_2\text{OH.CH}_2\text{Cl}$), as also for the production of other similar chlorine derivatives, such as propylene chlorhydrin ($\text{CH}_3\text{.CH}_2\text{Cl.CHOH}$), but for such use the gas must be quite rich in olefines, that is it is desirable that it contain not more than twenty per cent of impurities. The present improved method or process has as its object the segregation of the higher olefines, i. e. those above ethylene in the series, so that the chlorhydrins may be correspondingly segregated, or rather be entirely separately made.

To the accomplishment of the foregoing and related ends, the invention, then, consists of the steps hereinafter fully described and particularly pointed out in the claims, the annexed drawing and the following description setting forth in detail certain means and one mode of carrying out the invention, such disclosed means and mode illustrating, however, but one of various ways in which the principle of the invention may be used.

In said annexed drawing:—

The single figure there appearing represents diagrammatically an apparatus suitable for carrying out my improved process.

Such process is based on the wholly unexpected discovery that certain oils and specifically kerosene, will absorb propylene more readily than ethylene so that by washing an oil gas of the character in question with cold kerosene, for an example, in an amount that would be more than saturated if it absorbed or dissolved all of the olefines in the gas mixture, there will be a tendency for the kerosene to take up more propylene than ethylene. In this way, accordingly, by a series of washings with such kerosene in properly regulated amount, such propylene and related higher olefines may be satisfactorily separated, for all practical purposes, from ethylene and the other constituents of the gas. A certain amount of saturated hydrocarbons, such as butane, pentane, hexane, etc., will remain with the propylene fraction, but the separation is very good, giving a propylene which can be used at once for making chlorhydrin. The ethylene with the hydrogen, methane, ethane, etc., constituting the residual gas, will pass out of the vent of the system provided, as will now be described, for thus separating out the propylene fraction; and from such residual gas the ethylene can be recovered by suitable means, such as absorption in a different solvent, or by direct reaction with chlorine to form ethylene dichloride.

The apparatus diagrammatically shown in the drawing as suitable for carrying out my improved method or process, comprises a series of coke filled scrubbing towers 1, 2, 3, 4, with heaters 1^a, 2^a, 3^a, 4^a, respectively connected to receive the absorbing liquor from each such tower. Means comprising a reservoir 5, pump 6, and suitable connections 7, 8 and 9, are adapted to circulate such liquor through such towers and connected heaters in parallel. A cooler 10 is desirably inserted in such connection 9 so as to reduce the temperature of the circulating liquor to the proper degree before it is returned to reservoir 5.

The oil gas, i. e. the gas received from the furnace or retort in which the kerosene or other petroleum oil is cracked, is conducted by means of pipes 11 and 12 through towers 1 and 2 in series, the residual gas being dis-

charged from such last mentioned tower through a vent pipe 13. Heater 2^a, connected with the second of the series of towers through which the oil gas is thus passed against a counter-current of scrubbing liquor, specifically kerosene, is connected by means of a pipe 14 with pipe 11, so that the gas driven off from the kerosene passing through such heater is continuously returned to be rescrubbed in tower 1. Heater 1^a on the contrary, is connected by means of a pipe 15 with tower 3, so that the gas given off therefrom is scrubbed in this tower, the residue after such scrubbing being returned by means of pipe 16 to the bottom of tower 1 where it joins the incoming oil gas and the gas driven off, as just stated, from heater 2^a. The gas driven off from heater 3^a is conducted by means of pipe 17 to tower 4, the unabsorbed residue being returned by means of pipe 18 to tower 3 where it joins the gas driven off, as previously described, from heater 1^a.

The gas which is absorbed by the kerosene in such final tower 4 of the series, consists practically entirely of propylene and related higher olefines, so that when the kerosene from this tower is passed through heater 4^a, the gas driven off therefrom through discharge duct 20 constitutes the final purified product.

The general operation of the apparatus just described has been sufficiently indicated in the description of the construction and arrangement of such apparatus. By means of the connections shown, the propylene fraction initially separated out is, it will be seen, subjected to repeated scrubblings, only the gas that is absorbed following the last such scrubbing being included in the final product. The residual gas passing out through duct 13 will similarly be seen to consist of the residue left over after successive scrubblings of the original oil gas, as introduced into the system, and of the gas absorbed in the first towers of the system after it is subsequently driven off in the corresponding heaters connected with said towers. The result is that the propylene fraction is practically completely segregated from the ethylene, so that these respective constituents of the original oil gas may be utilized in subsequent manufacturing operations, without the presence of the one interfering with the reactions it is desired to secure in the other. Thus for example I am enabled, by means of the present process, to obtain a chlorhydrin product from the propylene fraction, which is substantially free from any ethylene or glycol chlorhydrin.

Other modes of applying the principle of my invention may be employed instead of the one explained, change being made as regards the steps herein disclosed, provided

the steps stated by any of the following claims or the equivalent of such stated steps be employed.

I therefore particularly point out and distinctly claim as my invention:—

1. In a method of segregating olefines from a gaseous intermixture of the same, the step which consists in bringing such intermixture into contact with a cold petroleum oil capable of absorbing propylene and the higher members of the series in preference to ethylene, whereby such propylene and higher members are separated from such ethylene, substantially as described.

2. In a method of segregating olefines from a gaseous intermixture of the same, the steps which consist in bringing such intermixture into contact with a cold petroleum oil capable of absorbing propylene and the higher members of the series in preference to ethylene and heating such oil to drive off the absorbed gases, consisting of such propylene and higher members, whereby they are obtained separately from such ethylene.

3. In a method of segregating olefines from a gaseous intermixture of the same, the step which consists in bringing such intermixture into contact with cold kerosene whereby propylene and the higher members of the series are absorbed preferentially to ethylene, substantially as described.

4. In a method of segregating olefines from a gaseous intermixture of the same, the steps which consist in bringing such intermixture into contact with cold kerosene whereby propylene and the higher members of the series are absorbed preferentially to ethylene, and then heating such kerosene to drive off the absorbed gases.

5. In a method of segregating olefines from a gaseous intermixture of the same, the steps which consist in scrubbing such intermixture with kerosene, thereupon heating such kerosene to drive off the absorbed gases, again scrubbing the latter with kerosene, and then heating as before.

6. In a method of segregating olefines from a gaseous mixture of the same, the steps which consist in scrubbing such mixture with kerosene, thereupon heating such kerosene to drive off the absorbed gases, again scrubbing the latter with kerosene, and then heating as before, the residual gases from such second scrubbing being added to those in the first scrubbing.

7. In a method of segregating olefines from a gaseous mixture of the same, the steps which consist in scrubbing such mixture with kerosene in a series of steps, heating the kerosene from each such step to drive off the absorbed gases, and adding the gases thus driven off from the kerosene passing through each subsequent step to those passing through the first step of the series.

8. In a method of aggregating olefines from a gaseous mixture of the same, the steps which consist in scrubbing such mixture with kerosene in a series of steps, heating the kerosene from each such step to drive off the absorbed gases, adding the gases thus driven off from the kerosene passing through each subsequent step to those passing through the first step of the series, and separately scrubbing the gases thus driven off from the kerosene passing through such first step.

9. In a method of aggregating olefines from a gaseous mixture of the same, the steps which consist in scrubbing such mixture with kerosene in a series of steps, heating the kerosene from each such step to drive off the absorbed gases, adding the gases thus driven off from the kerosene passing through each subsequent step to those passing through the first step of the series, and separately scrubbing the gases thus driven off from the kerosene passing through such first step, the residual gases from such last-mentioned scrubbing being likewise added to those passing through such first step.

10. In a method of segregating olefines from a gaseous mixture of the same, the steps which consist in scrubbing such mixture with kerosene in a series of steps, heating the kerosene from each such step to drive off the absorbed gases, adding the gases thus driven off from the kerosene passing through

each subsequent step to those passing through the first step of the series, separately scrubbing the gases thus driven off from the kerosene passing through such first step, the residual gases from such last-mentioned scrubbing being likewise added to those passing through such first step, heating the kerosene passing over such last-mentioned step, and re-scrubbing the gases thus driven off.

11. In a method of segregating olefines from a gaseous mixture of the same, the steps which consist in scrubbing such mixture with kerosene in a series of steps, heating the kerosene from each such step to drive off the absorbed gases, adding the gases thus driven off from the kerosene passing through each subsequent step to those passing through the first step of the series, separately scrubbing the gases thus driven off from the kerosene passing through such first step, the residual gases from such last-mentioned scrubbing being likewise added to those passing through such first step, heating the kerosene passing over such last-mentioned step, re-scrubbing the gases thus driven off, adding the residual gases to those in the preceding scrubbing, and heating the kerosene from such re-scrubbing to drive off the finally purified gases.

Signed by me, this 7th day of January, 1920.

LEROY C. STEWART.