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METHOD OF PURIFYING AN ACID TREATED LIGHT HYDROCARBON OIL

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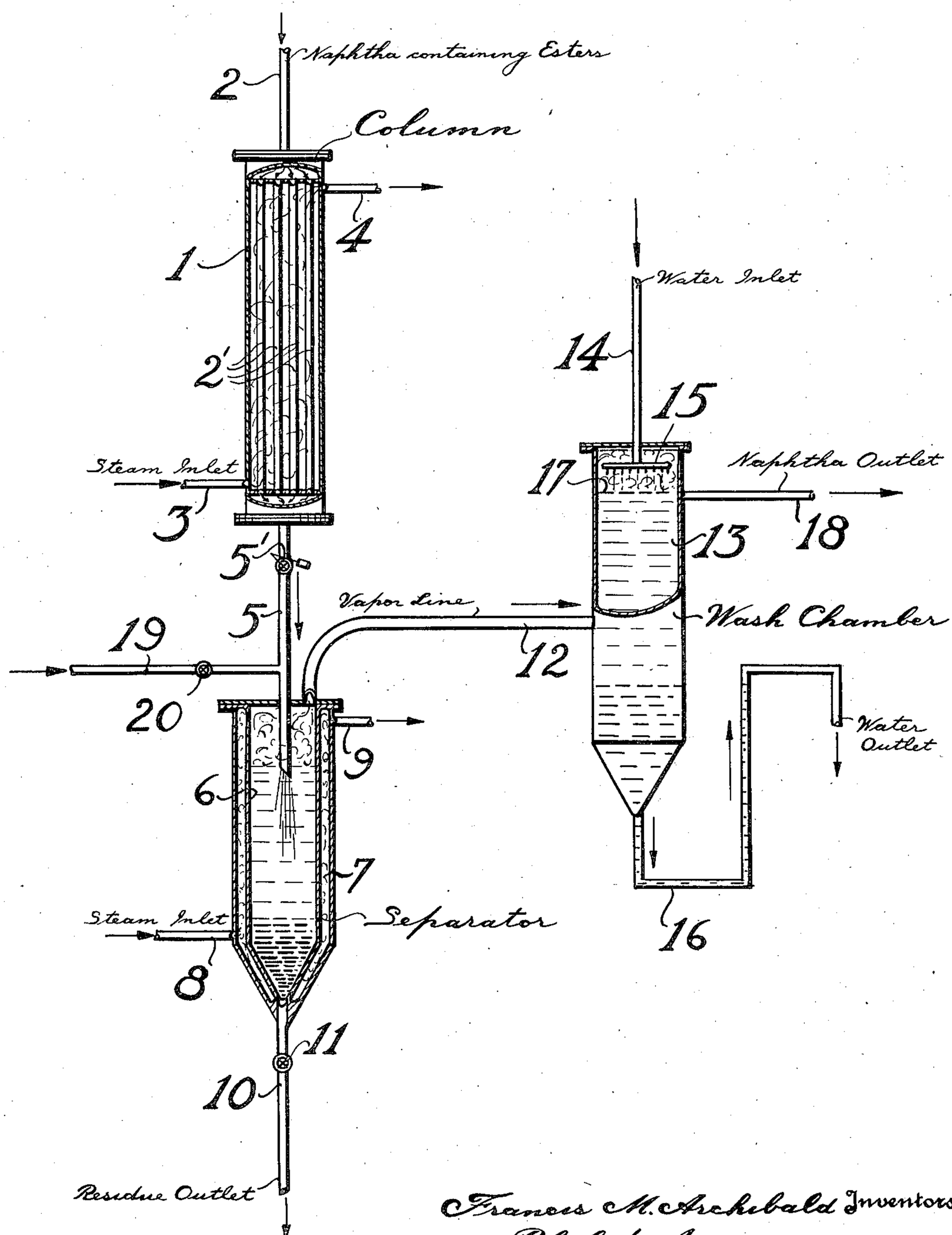

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METHOD OF PURIFYING AN ACID-TREATED LIGHT HYDROCARBON OIL

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5 Claims. (Cl. 196—148)

This invention relates to the process of purifying naphtha recovered as a residue after the extraction of olefins by sulphuric acid in the manufacture of secondary butyl and amyl alcohol. Such naphtha contains sulphuric esters and polymers which often prevent its use as a blending agent for gasoline. The sulphuric esters are bodies which on aging, on hydrolysis, or on evaporation of the naphtha, give rise to acidity which is partly, if not all, sulphuric and sulphurous acid.

The sulphuric esters are objectionable chiefly because they increase the sulphur content of gasoline with which the naphtha is blended. They also tend to cause corrosion in storage tanks. The polymers are heavy ends produced by the action of the sulphuric acid during the olefin extraction, and are detected by distillation or by evaporation of a sample of the naphtha on a steam bath and comparing the residue with the residue of the original material. The polymers are objectionable when present in large quantities, because they limit the amount of naphtha that can be blended with gasoline without excessively raising the end point of the gasoline.

Both esters and polymers may be removed by distilling the recovered naphtha in a still over caustic soda. That process is expensive and the present method relates particularly to a new development on a new principle which allows economies in equipment size, refrigeration, heating cost, and caustic soda cost.

The present invention will be fully understood from the following description and drawing which indicates suitable apparatus for carrying out the process. The drawing is a diagrammatic view in sectional elevation of an apparatus constructed according to the invention and indicates the flow of various materials in the process.

Referring to the drawing, reference numeral 1 indicates a steam heated column through which naphtha recovered from the sulphuric acid treatment of olefins is passed under pressure by means of pipes 2 and 2'. Column 1 is heated by the circulation of superheated steam through inlet 3 in the lower part of column 1 and outlet 4 in the upper part of column 1. The naphtha upon being heated to about 80° to 150° C. and at a pressure of about 30 to 70 pounds per square inch, is passed by opening pressure reducing valve 5' on pipe 5 into separating chamber 6. Separating chamber 6 maintained at a pressure of about 5 to 25 pounds per square inch, is heated by means of steam jacket 7 through which superheated steam is circulated through inlet 8 and outlet 9. Pipe 10 provided with valve 11 is used to pass the oil polymers from chamber 6. Pipe 19 provided with valve 20 and connected to pipe 5 above the separating chamber 6 may be used to pass a 2 to 10% water solution of sodium hydroxide into the naphtha passing into chamber 6.

We have found that when a light naphtha containing esters is heated at a moderate temperature (80° to 150° C.), it deposits a dark colored fluid which is high in acidity. This dark colored deposit or residue is a good catalyst for the decomposition of esters, yielding more of the residue as well as sulphur dioxide.

In chamber 6 the naphtha deposits on the sides and the bottoms such a dark colored fluid or residue, together with the oil polymers which are high in acidity. This dark deposit or residue acts as a catalyst for the decomposition of the esters. The dark colored fluid and oil polymers are continuously withdrawn to storage through pipe 10 controlled by valve 11, care being taken that the volume is kept comparatively low. The naphtha vapors pass through pipe 12 to wash chamber 13. Water or a sodium hydroxide water solution of 4 to 10% strength is passed through pipe 14 to sprayer 15, where it is sprayed over the naphtha and condenses the vapors. A bottom outlet pipe 16 for the removal of the water or sodium hydroxide solution is provided at the lowest part of wash chamber 13. Pipe 16 is U shaped in form, with the outer leg being raised so that a quantity of water or sodium hydroxide water solution is retained in the lower part of chamber 13. The condensed naphtha settles out in a layer to the level of 17 and is removed to storage by outlet pipe 18.

In a typical operation according to the present invention, spent naphtha is passed under a pressure of about 30 to 70 pounds per square inch through steam heated chamber 1. From chamber 1 the naphtha is released through throttle valve 5 to steam heated separator 6, and the pressure reduced to about 5 to 25 pounds per square inch. The residue separating is drawn off continuously from separator 6, only a small quantity of residue being retained in the separator, and the vapors pass off to the wash chamber 13. A spray of water condenses the naphtha and washes out the sulphur dioxide at the same time in wash chamber 13. The resulting naphtha removed is white in color, free of esters and acid, and showing only small fractions of polymer content.

The following data are given from an experimental run in this apparatus:

Feed rate	8 gals. per hr.
Residue separated	0.7 gals. per hr.
Temperature of naphtha in column	70° to 80° C.
Temperature of naphtha in separator	100° to 150° C.

	Acidity	Ester	Polymer
Spent naphtha feed	0.02	0.3	7.5
Recovered naphtha	0.001	0.003	3.0

The polymer is expressed in grams per 100 cc. The ester and acidity are in grams of sulphuric acid per 100 cc.

Sulphur determination on blending with gasoline

	Percent
Base stock naphtha	.109
Base stock+5% finished naphtha	.100
Base stock+15% finished naphtha	.090

There is no gas lost in this process so that a complete material recovery is made. A 2 to 10% water solution of sodium hydroxide may be introduced into the separator through valved line 19 to aid the removal of the ester and sulphur dioxide formed. A 2 to 10% water solution of sodium hydroxide may be used instead of water in the wash chamber where the quantity of sulphur dioxide formed is high.

The present process is not limited to naphtha recovered from the sulphuric acid treatment of olefins. It is applicable to any acid treated light distillate of hydrocarbon oils such as naphtha or gasoline containing esters. It will be necessary to heat gasolines to a higher temperature, such as up to 250° C. to complete the separation.

The foregoing description is merely illustrative and various changes and alternative arrangements may be made within the scope of the appended claims in which it is our intention to claim all novelty inherent in the invention as broadly as the prior art permits.

We claim:

1. Method of purifying acid-treated light hydrocarbon oil distillate to remove sulfuric esters, which comprises subjecting it in one chamber to the approximate temperature limits of 80° to 150° C. and a pressure of 30 to 70 pounds per square inch, releasing it into a second chamber and subjecting it to a temperature of approximately 100° to 150° C. under a pressure of approximately 5 to 25 pounds per square inch.

2. Method according to claim 1, in which a 2 to 10% aqueous solution of sodium hydroxide is introduced into the second chamber to help remove impurities.

3. Method of separating sulphuric esters from naphtha comprising the steps of subjecting a naphtha containing sulphuric esters to heat and pressure, reducing the pressure while subjecting the naphtha containing sulphuric esters to heat in the presence of previously separated impurities which catalytically promote the liberation of further quantities of impurities and separately removing the vapors containing the naphtha and liquid residue containing the sulphuric esters and their decomposition products.

4. Method according to claim 3, in which the naphtha, while being subjected to heat under reduced pressure, is treated with 2 to 10% of a water solution of sodium hydroxide.

5. Method of purifying an acid-treated light hydrocarbon oil to remove sulfuric esters, which comprises subjecting it to flash distillation in the presence of previously separated sulfuric esters which catalytically promote the liberation of further quantities of sulfuric esters, whereby purified oil distillate and sulfuric esters are separately removed.

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