

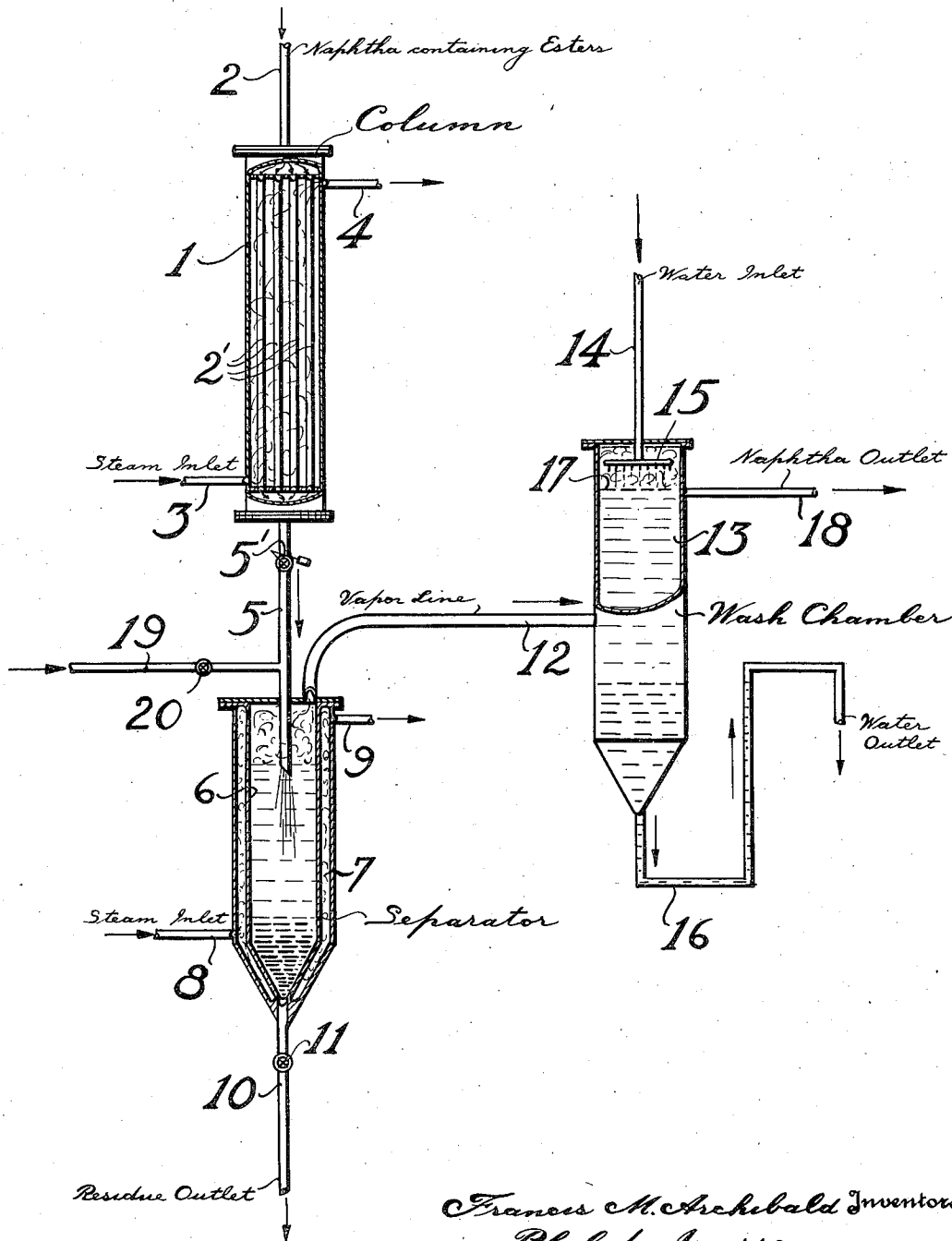
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METHOD OF PURIFYING AN ACID TREATED LIGHT HYDROCARBON OIL

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METHOD OF PURIFYING AN ACID-TREATED
LIGHT HYDROCARBON OILFrancis M. Archibald, Roselle, and Philip Janssen,
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5 Claims. (Cl. 196—148)

This invention relates to the process of purify-
ing naphtha recovered as a residue after the
extraction of olefins by sulphuric acid in the
manufacture of secondary butyl and amyl alco-
hol. Such naphtha contains sulphuric esters and
polymers which often prevent its use as a blend-
ing 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 sul-
phurous acid.

The sulphuric esters are objectionable chiefly
because they increase the sulphur content of gas-
oline 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 quan-
tities, because they limit the amount of naphtha
that can be blended with gasoline without ex-
cessively 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 de-
velopment on a new principle which allows econ-
omies 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 con-
structed 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 treat-
ment of olefins is passed under pressure by means
of pipes 2 and 2'. Column 1 is heated by the cir-
culation 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 super-
heated 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 hy-
droxide into the naphtha passing into cham-
ber 6.

We have found that when a light naphtha con-
taining esters is heated at a moderate tempera-
ture (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 de-
composition of esters, yielding more of the resi-
due 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 bot-
tom 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 pres-
sure of about 30 to 70 pounds per square inch
through steam heated chamber 1. From cham-
ber 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 quan-
tity of residue being retained in the separator,
and the vapors pass off to the wash chamber 15.
A spray of water condenses the naphtha and
washes out the sulphur dioxide at the same time
in wash chamber 13. The resulting naphtha re-
moved 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.
5 Temperature of naphtha in column	70° to 80° C.
Temperature of naphtha in separator	100° to 150° C.

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

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

25 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.

30 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.

40 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 5 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 15 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 20 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 25 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 30 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 35 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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