

UNITED STATES PATENT OFFICE

1,965,828

NITROGEN BASE AND METHOD OF MAKING
SAMEDenis L. Fox, Berkeley, Calif., assignor to Stand-
ard Oil Company of California, San Francisco,
Calif., a corporation of DelawareNo Drawing. Application March 2, 1929,
Serial No. 344,098

11 Claims. (Cl. 260—38)

This invention relates to the recovery of nitro-
gen compounds from oil and particularly from
hydrocarbon oils such as petroleum.

It is well known that most petroleum oils,
shale oils and similar hydrocarbon oils contain
nitrogen compounds in various quantities. It
has been known that these nitrogen compounds
could be extracted, in part at least, from the
oils by means of dilute sulphuric acid or other
mineral acids. I have also found that extracts
obtained by treating oils with liquid sulphur di-
oxide contain a complex mixture of nitrogen
compounds of varying strengths as bases, some
of said compounds even appearing to be neutral.
From this it may be seen that the stronger the
acid used in the extract of nitrogen compounds,
the larger will be the quantity of nitrogen bases
removed, but even with the strongest acids there
are nitrogen compounds weakly basic or neutral
which are not removed.

An object of this invention is to disclose and
provide a process of removing and separating
nitrogen compounds from oils.

Another object is to disclose and provide a
process of extracting and removing nitrogen bases
from petroleum oils.

Another object is to disclose and provide a
process of obtaining nitrogen bases in relatively
pure condition from petroleum oils.

A still further object is to disclose and provide
a method whereby nitrogen compounds and bases
may be completely removed from oils in a rela-
tively pure condition.

Another object of this invention is to provide
nitrogen bases and compounds in concentrated
form.

A still further object is to provide, as an article
of manufacture, nitrogen bases of particularly
desirable characteristics.

An object of this invention is to provide, as an
article of manufacture, mixtures of nitrogen
bases having particularly desirable properties.

The nitrogen compounds occurring in most
petroleum oils, shale oils and the like are volatile
at the temperatures employed in distillation, and
consequently they may be found in the distillates.
I have discovered that all, or nearly all, of the
nitrogen bases in cracked petroleum distillates
are of relatively low molecular weight and are
stronger in general, as bases, than those origi-
nally occurring in petroleum.

These compounds, or bases, may be removed
completely, or nearly so, by means of dilute acid
solutions.

When liquid acids are used such as liquid sul-

phur dioxide and concentrated sulphuric acid,
however, large amounts of oil bodies are also
extracted from the oil and difficulties are en-
countered in separating the extracted nitrogen
compounds from the oil bodies. Furthermore,
when aqueous acid is used, all of the acid in
the water can not be made to combine with the
nitrogen bases because of the hydrolysis of the
resulting salts and consequent resolution of the
bases in the oil. When aqueous acids are used,
as much as one hundred per cent excess of acid
is required in some cases to hold the bases in the
water solution as salts, and this excess is all
wasted since, in order to obtain the free bases, all
of the acid must be neutralized. By carrying out
the extract in accordance with the process em-
braced by this invention, all of the disadvantages
recited hereinabove are obviated.

I have discovered that the nitrogen compound
present in oils can be more readily removed by
the use of gaseous acids such as hydrogen
chloride or sulphur dioxide, than by the use of
liquid acids such as sulphuric acid or liquid sul-
phur dioxide. By using gaseous reagents it is
possible to extract the nitrogen compounds with-
out removing oil bodies or impurities and there-
fore a subsequent separation is not required for
the separation of the nitrogen compounds from
the oil bodies or impurities. When oils are treated
with sulphur trioxide or with liquid sulphur di-
oxide numerous impurities are removed or pre-
cipitated from the oil, and the nitrogen bases are
so intimately mixed with and included with the
impurities that it is impractical to separate them
from the oil bodies.

As has been stated above, hydrolysis of nitrogen
base salts occurs when acid solutions are used
for extraction, but when an anhydrous acid in
gaseous state is used, in accordance with this in-
vention, no water is present, and consequently no
hydrolysis of the salts formed occurs. A great
saving in acid is made possible by this process in
that no excess of acid is required beyond that
needed to combine with the bases.

Furthermore, by employing acid in the an-
hydrous state, the nitrogen bases are obtained
directly as relatively pure salts and not in the
form of dilute aqueous solutions. This greatly
reduces the volume of material to be handled.
If an aqueous solution saturated with sulphur
dioxide is employed, it is so weak that only a
small proportion of the bases is removed from an
oil.

I have also found that distillates obtained by
cracking petroleum oils containing nitrogen com-

pounds are particularly suitable as sources of nitrogen compounds or as raw material for use in my process.

Any suitable apparatus may be employed in carrying out the process described herein, and I am not to be limited to any particular form of apparatus. The process may be carried out either by the batch method or by a continuous counterflow method. Apparatus for use in counterflow methods is well known in the art and the arrangement of various well known units so as to carry out the process does not of itself involve invention.

The oil to be treated in accordance with the process of this invention may be placed in an agitator or other suitable receptacle and anhydrous acid, or acid anhydride in gaseous form, then bubbled through the oil at moderate temperatures, or temperatures somewhat lower than those ordinarily employed. Sulphur dioxide or hydrogen chloride may be employed. As stated hereinabove, the desired contact between the gaseous acid and the oil may be accomplished by counterflow methods if desired. The treatment with acid is continued until the acid gases have reacted with all, or substantially all, of the nitrogen bases present therein. Most of the nitrogen bases are precipitated by the action of the acid gas in the form of salts of nitrogen bases and may be separated from the residual oil by sedimentation, filtration or other methods.

When cracked naphtha is used as the oil stock in accordance with this process, it has been found that only about 0.007 pound of hydrogen chloride gas and/or about 0.008 pound of sulphur dioxide per gallon of naphtha is necessary to effect the extraction of substantially all the nitrogen bases present in such naphtha. These quantities are merely illustrative and will vary with the character of the oil being treated, from about 0.002 pounds to 0.008 pounds of hydrogen chloride or sulfur dioxide per gallon.

A certain proportion of the salts of nitrogen bases remains in solution or suspension in the oil and such salt may be recovered separately, by extraction with an aqueous solvent. For example, the salts remaining in solution or suspension in the oil, being water soluble may be removed from the oil by extraction with water. The salts may be used directly in the form of a water solution or they may be neutralized with alkali so as to precipitate the nitrogen bases.

The salts of nitrogen bases which are precipitated from the oil by treatment with a gaseous acid, or acid anhydride, may be used as such or they may be neutralized to form nitrogen bases. The products obtained by this process are complex mixtures of nitrogen bases and it has been discovered that these bases and salts thereof have toxic properties which make them particularly useful in the preparation of insecticides. The nitrogen compounds and bases prepared in accordance with this invention may be used in the form of the solution of the salts in water or as a solution of the free bases in oil or an emulsion of bases in oil and the salts in water or the nitrogen bases may be embodied in a dust or powder.

Obviously these toxic salts and bases when used for insecticidal purposes may be used alone or together with other ingredients and insecticides.

While the process has been described as being applied to petroleum oils, it is to be understood that the process is also applicable to other nitrogen-bearing hydrocarbon oils and is not limited to the particular details described herein, but embodies all the changes and modifications which

come within the scope of the appended claims.

I claim:

1. A process of recovering nitrogen bases from oils comprising treating oil containing nitrogen compounds with substantially dry gaseous sulphur dioxide, without oxidizing the oil to remove impurities therefrom, separating salts of nitrogen bases precipitated from the oil by such treatment, and extracting suspended salts of nitrogen bases from the treated oil.

2. A process of recovering nitrogen bases from oils comprising treating a distillate obtained by cracking oil containing nitrogen compounds with gaseous sulphur dioxide to form salts of nitrogen compounds without oxidizing the oil to remove impurities therefrom, separating salts of nitrogen bases precipitated by such treatment from the oil, and extracting suspended salts of nitrogen bases from the treated oil.

3. A mixture of salts of nitrogen bases substantially free from hydrocarbon oils precipitated from petroleum oils by treating a petroleum oil containing nitrogen compounds with a material selected from the group consisting of substantially anhydrous gaseous sulfur dioxide and hydrogen chloride.

4. In a method of recovering nitrogen bases from petroleum oils, the steps of treating a petroleum oil with a substantially dry gaseous material selected from the group consisting of sulfur dioxide and hydrogen chloride, without oxidizing the oil to remove impurities therefrom, to form salts of nitrogen compounds present in said oil, and then separating such salts from the oil.

5. In a method of recovering nitrogen bases from petroleum distillates, the steps of treating a petroleum distillate containing nitrogen compounds with a substantially anhydrous gaseous material selected from the group consisting of sulfur dioxide and hydrogen chloride to precipitate salts of nitrogen bases without oxidizing the petroleum distillate to remove the impurities therefrom, and separating the precipitated salts of nitrogen bases from the distillate.

6. In a method of recovering nitrogen bases from petroleum distillates, the steps of treating a petroleum distillate containing nitrogen compounds with a substantially anhydrous gaseous material selected from the group consisting of sulfur dioxide and hydrogen chloride to precipitate salts of nitrogen bases without oxidizing the petroleum distillate to remove impurities therefrom, separating the precipitated salts of nitrogen bases from the distillate, and extracting suspended salts of nitrogen bases from the treated distillate.

7. In a method of recovering nitrogen bases from petroleum distillates, the steps of treating a petroleum distillate containing nitrogen compounds with a substantially anhydrous sulfur dioxide in gaseous state to precipitate salts of nitrogen bases without oxidizing the petroleum distillate to remove impurities therefrom, and separating the precipitated salts of nitrogen bases from the distillate.

8. In a method of recovering nitrogen bases from petroleum distillates, the steps of treating a petroleum distillate containing nitrogen compounds with a substantially anhydrous hydrogen chloride in gaseous state to precipitate salts of nitrogen bases without oxidizing the petroleum distillate to remove impurities therefrom, and separating precipitated salts of nitrogen bases from the distillate.

9. In a method of recovering nitrogen bases

from petroleum distillates, the steps of treating a petroleum distillate containing nitrogen compounds with a substantially anhydrous hydrogen chloride in gaseous state to precipitate salts of nitrogen bases without oxidizing the petroleum distillate to remove impurities therefrom, separating precipitated salts of nitrogen bases from the distillate, and separately extracting suspended salts of nitrogen bases from the treated distillate.

10. A mixture of substantially solid nitrogen

compounds precipitated from petroleum oil by treating an oil containing nitrogen compounds with substantially anhydrous sulfur dioxide in gaseous state.

11. A mixture of salts of nitrogen bases substantially free from hydrocarbon oils precipitated from petroleum oil by treating a petroleum oil containing nitrogen compounds with substantially anhydrous hydrogen chloride in gaseous state.

DENIS L. FOX.

15	90
20	95
25	100
30	105
35	110
40	115
45	120
50	125
55	130
60	135
65	140
70	145
75	150