

UNITED STATES PATENT OFFICE

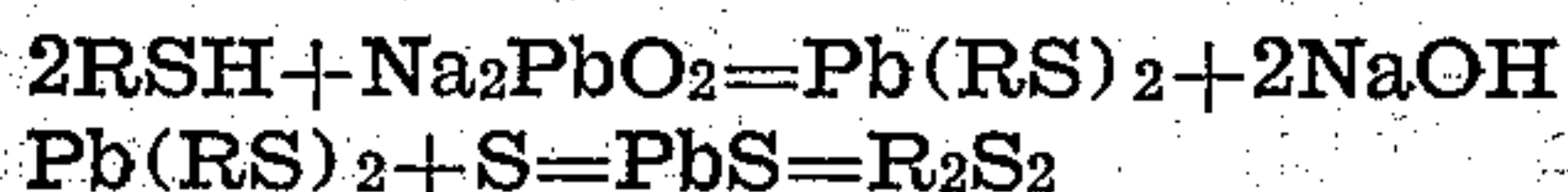
2,011,954

METHOD OF SWEETENING
HYDROCARBON OILCharles F. Teichmann, New York, N. Y., assignor
to The Texas Company, New York, N. Y., a cor-
poration of DelawareNo Drawing. Application January 27, 1932,
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6 Claims. (Cl. 196—33)

My invention relates to the refining of hydro-
carbon oils and particularly to a process of in-
creasing the reactivity of suspensions of lead
compounds in alkaline solutions used for sweeten-
ing hydrocarbon oils.

Most light mineral oil distillates such as gaso-
line or kerosene contain sulfur compounds which
impart disagreeable odors to the oil. It has been
common practice to remove these sulfur com-
pounds from the oils by agitating them with an
alkaline solution of an alkali metal plumbite such
as sodium plumbite, prepared by dissolving lead
oxide in an excess of sodium hydroxide. This
treatment causes a reaction between the sulfur
compounds such as mercaptans and the plumbite
solution with the formation of colored lead com-
pounds such as lead mercaptides. In order to
decompose these lead compounds, it is necessary
to add free sulfur, whereupon the lead is pre-
cipitated as the insoluble lead sulfide which per-
mits of its being removed. This operation is
commonly called "sweetening" and may be typi-
fied by the following reactions:

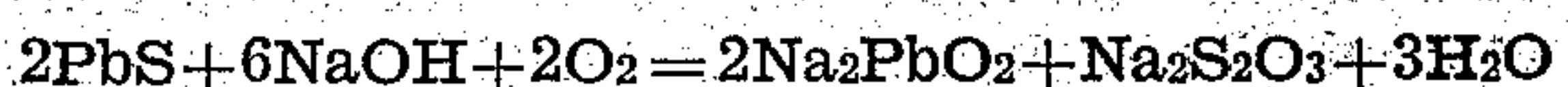


Although the sodium plumbite and sulfur
method of sweetening naphthas is recognized as
being the most efficient as regards the high qual-
ity of the product resulting from its use, the ex-
ceptionally high cost introduces a serious disad-
vantage. It is known that in the case of high
sulfur naphthas, as much as one pound of litharge
per barrel of gasoline may be consumed in the
operation.

Several new methods of sweetening have been
proposed in order to circumvent the difficulties
of an alkali plumbite-sulfur method of treating.
Most of these methods feature a vigorous direct
oxidation of the sulfur compounds by means of
oxidizing agents. It has been found by the in-
ventor that in the case of certain light hydro-
carbons these methods of desulfurizing may re-
sult in undesirable reductions in color stability
and decreases in the anti-knock values of the
finished products due to the fact that the oxida-
tion cannot be limited to the sulfur compounds
alone but extends to a vigorous action on those
unstable hydrocarbon compounds which by their
very nature contribute desirable characteristics
to the hydrocarbon products in which they are
present.

It has also been proposed to agitate light hy-
drocarbon oil distillates with a suspension of
lead sulfide in a solution of caustic alkali. In

order to activate the suspension it is subjected
to the action of air. It may be necessary in this
process when treating light hydrocarbon oils con-
taining extremely stable sulfur compounds to
bleed in quantities of oxygen or oxygen-contain-
ing gases while the hydrocarbon oils are being
agitated with the treating solution. The reac-
tion which occurs is considered by some to be
as follows:



This process is of value, and finds ready appli-
cation in the treatment of straight run distillates
and some cracked petroleum products. With
some of the naphthas obtained by cracking, dif-
ficulties have arisen in its application, which dif-
ficulties are directly traceable to the presence
of stable high-molecular weight mercaptans re-
quiring disproportionately long agitation with
the treating solution. The stability of some of
these mercaptans is such that they remain un-
changed even when contacted with the treating
solution and oxygen or oxygen-containing gases.
Such naphthas require after-treatment with al-
kali plumbite and sulfur to make them satis-
factory for commercial purposes. The use of air
in direct contact with the oil is extremely un-
desirable since it reduces the stability of the oil,
increases substantially the fire hazard and brings
about high evaporation losses which in turn in-
crease the load on the gasoline absorption plant.

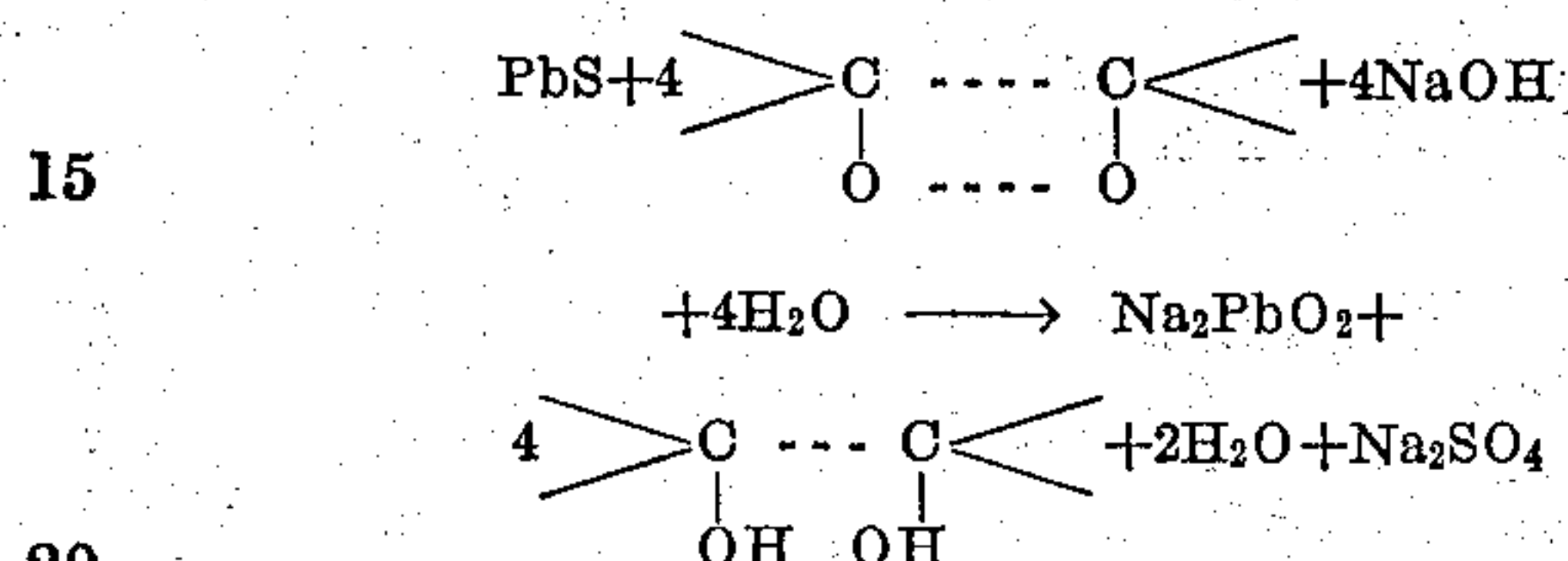
By the application of my invention I am en-
abled to share in the advantages of all of the
above mentioned processes while avoiding their
respective disadvantages.

I have discovered that when small quantities
of organic or inorganic peroxides are added to a
suspension of lead sulfide in an alkaline solution,
the high-molecular weight mercaptans which are
not acted upon by the ordinary lead sulfide sus-
pensions in caustic solutions, are readily attacked
and removed. I have likewise found that the
life of my treating solution is longer than any
other proposed to date. The naphthas treated
therewith are stable to light and storage and
the time necessary for reaction is greatly de-
creased.

To explain the extraordinary results obtained
with this treating solution, I advance the follow-
ing theoretical explanation to the correctness of
which I do not intend to limit myself.

When an unsweetened naphtha is treated with
a suspension of lead sulfide in sodium hydroxide,
said treating solution having been activated pre-
viously by the introduction of oxygen or oxygen-

containing gas, it is observed that the low-molecular weight mercaptans are readily oxidized to disulfides. There is also usually a slight discoloration of the naphtha which can be removed by the introduction of a small quantity of elementary sulfur. An analysis of the peroxide content of the naphtha before and after treatment indicates that the peroxide content has been materially decreased. It is believed that the organic peroxides react with the lead sulfides suspended in the sodium hydroxide according to the following reaction:

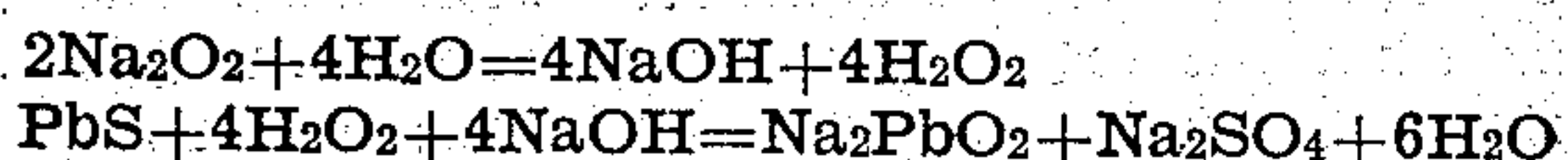


The sodium plumbite formed in this way is then available for reacting with the high-molecular weight mercaptans in the usual manner.



By increasing the concentration of the organic peroxides to such a value as to make the available oxygen content equivalent to the sulfur content of the high-molecular weight mercaptans, it is possible to completely sweeten the naphtha by means of a suspension of lead sulfide in sodium hydroxide. Sulfur is necessary for decomposing the lead mercaptides formed as a result of the reaction.

I have found that inorganic peroxides when added to a suspension of lead sulfide in sodium hydroxide give a reaction similar to that obtained with the organic peroxides. The reaction of the inorganic peroxides may be considered as follows:



The sodium plumbite formed in this manner is available for reaction with the stable mercaptans, reacting with them according to the equation set down heretofore. It is of interest to note that when using my process, sulfur is necessary in order to decompose the lead mercaptides that are formed.

I have noted that mercaptans react very slowly with peroxides. This explains why naphthas containing both these compounds do not become "sweet" on storage due to the decomposition of the mercaptans. However, in the presence of lead sulfide in an alkaline solution the reaction goes very readily and is almost quantitative. I have also observed that the surface of the granular lead sulfide used as a starting material in my process gradually becomes eroded, eventually losing its solid character and becoming flocculent.

As a specific example of the practice of my invention I give below the constitution of a treating solution which may be used for sweetening a cracked naphtha containing approximately 0.20% of high-molecular weight mercaptans, which do not react perceptibly with a suspension of lead sulfide in sodium hydroxide:

100 bbls. of 15° Baumé sodium hydroxide solution.
1500 lbs. of lead sulfide.
35 lbs. of sodium peroxide.

While I have shown sodium hydroxide in the above composition, it is understood that solutions

of alkaline or caustic compounds or mixtures of these may be used in its stead. Among these may be identified solutions of ammonium hydroxide, potassium carbonate, calcium hydroxide, sodium carbonate, potassium hydroxide, trisodium phosphate and similar compounds of alkaline reaction.

The sodium peroxide may be replaced by equivalent amounts of hydrogen peroxide, barium peroxide, sodium perborate or any such inorganic substances which decompose to yield hydrogen peroxide in aqueous solutions.

Organic peroxides, such as acetic peroxide, benzoyl peroxide, methyl-ethyl ketone peroxide or any organic compound that is a potential source of hydrogen peroxide or nascent oxygen may be substituted for or used in conjunction with the inorganic peroxides.

My invention readily lends itself to continuous operation, in which case the hydrocarbon oil to be sweetened is intimately mixed with the suspension of lead sulfide in alkaline solution to which has been added the correct quantity of the suitable peroxide. After thorough agitation the mixture is conducted through one or more settling chambers, where the velocity of flow is reduced to such a rate as to allow the separation of the oil from the treating solution. The separated oil is then contacted with the proper amount of sulfur to bring about the decomposition of the lead mercaptides into the corresponding organic disulfides and lead sulfide.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. An improved method of sweetening hydrocarbon oils which comprises reacting the oil with a suspension of lead sulfide in an alkaline solution containing inorganic peroxides.

2. A method of sweetening hydrocarbon oils which comprises reacting the oil with a suspension of lead sulfide in an alkaline solution containing dissolved inorganic peroxides and then reacting said oil with elementary sulfur.

3. A method of sweetening hydrocarbon oils which comprises reacting the oil with a treating suspension consisting of lead sulfide, an aqueous alkaline solution and a peroxide, separating the treated oil from the treating suspension and then reacting the treated oil with elementary sulfur.

4. A method of sweetening hydrocarbon oils which comprises reacting the oil with a treating suspension consisting of lead sulfide, an aqueous alkaline solution and an organic peroxide, separating the treated oil from the resulting suspension and then reacting the treated oil with elementary sulfur.

5. A method of sweetening hydrocarbon oils which comprises reacting the oil with a treating suspension consisting of lead sulfide, an aqueous alkaline solution and an inorganic peroxide, separating the treated oil from the treating suspension and then reacting the treated oil with elementary sulfur.

6. A method of sweetening hydrocarbon oils which comprises reacting the oil with a treating suspension consisting of lead sulfide, an aqueous solution of sodium hydroxide and sodium peroxide, separating the treated oil from the treating suspension and then reacting the treated oil with elementary sulfur.

CHARLES F. TEICHMANN.