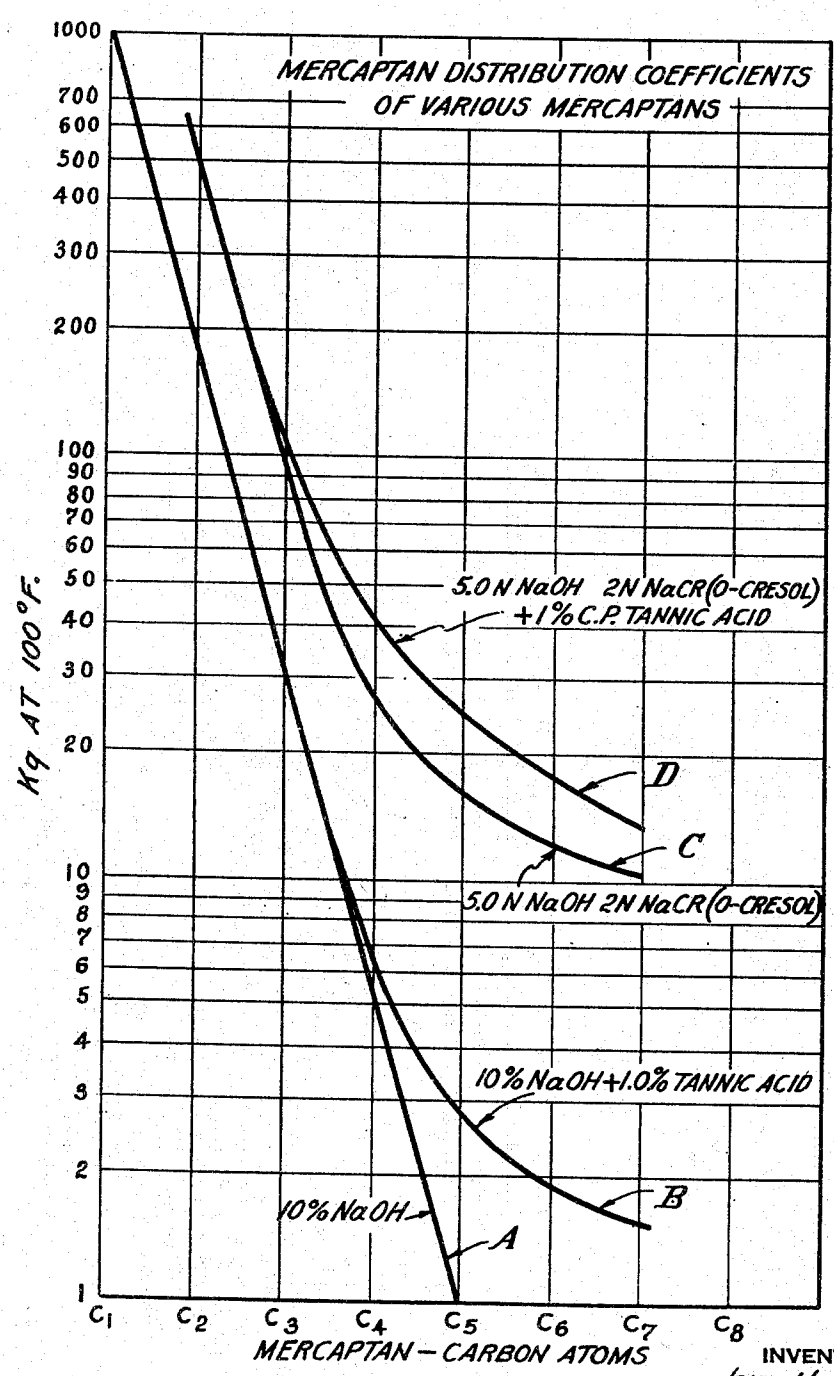
Nov. 2, 1948. J. HAPPEL ET AL 2,453,067

METHOD FOR REDUCING THE MERCAPTAN SULFUR CONTENT OF HYDROCARBON OILS

Filed June 11, 1943



INVENTORS
JOHN HAPPEL
STEPHEN P. CAULEY

BY Myron Bunbird

ATTORNEY

Patented Nov. 2, 1948

2,453,067

UNITED STATES PATENT OFFICE

2,453,067

METHOD FOR REDUCING THE MERCAPTAN SULFUR CONTENT OF HYDROCARBON OILS

John Happel, Brooklyn, and Stephen P. Cauley, Jackson Heights, N. Y., assignors to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

Application June 11, 1943, Serial No. 490,492

5 Claims. (Cl. 196—30)

1

This application is a continuation-in-part of our co-pending application Serial No. 463,602, filed October 28, 1942, now abandoned, for the Treatment of hydrocarbon oils.

This invention is directed to the treatment of hydrocarbon oils for the reduction of the mercaptan sulfur content thereof, particularly intended to provide a finished gasoline fraction which is either "sweet" to the "doctor" test or is sufficiently low in sulfur to be acceptable under specifications wherein the doctor test is not used and total sulfur content is determined.

In treating hydrocarbons, such as straight run gasoline, natural gasoline, cracked gasoline and the like, to render them sweet to the "doctor" test, the objective is to remove materials of the nature of hydrogen sulfide, mercaptans or the like or to convert them to innocuous compounds. Washing with aqueous solutions of strong alkalies, such as caustic soda will remove most of the hydrogen sulfide and some, but not all, of the mercaptans. Washing with aqueous caustic to which some material has been added as a "solutizer," or solubility promoter, enables the caustic to dissolve and remove more or all of the mercaptans. Butylene glycols, butyric acids, and phenolic material are so used. Older methods make use of sodium plumbite formed by dissolving litharge in caustic soda, the effect here being to convert mercaptans to mercaptides and later to disulfides, which are innocuous to the doctor test, by addition of free sulfur.

In general, all processes of this kind leave something to be desired, and this field, one of the oldest in petroleum refining, is still the subject of active research.

This invention has for its object the provision of a method for treatment of light petroleum hydrocarbons of the nature of gasoline, natural gasoline, cracked gasoline, kerosenes, solvents and the like, capable of effecting very considerable reductions in the mercaptan sulfur content of the material so treated.

This invention is based upon the discovery that if small percentages of tannic acid be added to caustic solutions containing other quite competent solutizers, a very considerable increase in the mercaptan dissolving power of the reagent occurs.

These desired objects may be effected by such a process when conducted as explained in the following discussion, certain features of which are shown in the drawing attached hereto, the single figure of which drawing presents in graphic form certain features of the process. In preparation for the discussion of the process, it may be pointed

2

out that the criterion of removal of material from the oil phase to the reactant phase in a liquid-liquid treating operation is the distribution coefficient K_d which coefficient in the present case is arrived at by dividing the concentration of mercaptans in the reagent by the concentration of mercaptans remaining in the gasoline after the reagent and gasoline have been brought in contact to a sufficient degree and for a sufficient time to arrive at equilibrium.

Turning to Figure 1 of these drawings, we find curves A, B, C and D, in which the distribution coefficient is shown upon the vertical scale at the left and the number of carbon atoms in the mercaptan is shown along the scale at the bottom. Curve A shows the distribution coefficients, that is, the efficiency in removal of mercaptans of a 10% caustic solution. It is found to be quite high with low molecular weight mercaptans but decreases rapidly to rather impractical limits with mercaptans containing more than six carbon atoms, aptly illustrating the reason why treatment with straight caustic solutions has never been particularly effective upon certain types of gasoline.

In curve B the same 10% caustic solution is used except that to the caustic there has been added 1% of tannic acid. As shown, this reagent is nearly three times as effective for the removal of C_5 mercaptan as is the straight caustic solution and this reagent retains a fairly good effectiveness even for much heavier mercaptans.

Curve C illustrates the effect of a solutizer material such as, for example, o-cresol, the reagent used in curve C being a 5.0 normal sodium hydroxide solution which also contains sufficient additional sodium and o-cresylic acid to provide a strength of 2 normal sodium o-cresylate. As may be observed, this reagent shown in curve C is immeasurably more effective than straight caustic and particularly in the case of higher molecular weight mercaptan, being 16 times as effective as a straight 10% caustic for the removal of a C_5 mercaptan.

Curve D shows the effect of an addition of 1% of tannic acid to this same reagent as used in curve C. The removal efficiency is considerably increased. For example, for a C_5 mercaptan the new solution is more than 50% more effective.

These results are contrary to those which might be expected from study of the capability of tannic acid in caustic alone. In caustic alone in the absence of other solutizers, tannic acid does not at all increase the capability for the removal

of C_3 mercaptans, yet it increases the capability of the solutizer solution about 15%. For C_4 mercaptans the efficiency of caustic alone is increased about 19%, while the solutizer reagent efficiency is increased around 46%. With C_5 mercaptans where tannic acid was capable of effecting almost a tripling of the removal efficiency of plain caustic, it increased the solutizer solution efficiency about 56% and with heavier mercaptans, where its increase in the efficiency of plain caustic is most pronounced, the percentage of increase with solutizers is less marked. Thus we have the rather surprising fact that while tannic acid apparently does not enhance the activity of straight caustic for removal of lower molecular weight mercaptans, it is in this same area where it effects its most marked increase in the efficiency of solutizer-caustic solutions.

Consequently, the present invention advances the fact that the presence of a small amount of tannic acid will very considerably increase the extraction power of an alkali metal hydroxide solution in the presence of added solubility promoters such as cresylic acid, isobutyric acid and the like, enabling a very material reduction in the amount of sulfur in the gasoline since the treating reagent after treatment may be physically separated from the gasoline. The caustic reagent used and the added solutizer therein may be any of those already widely known. In general, the caustic solution which is used may be one of relatively high concentration, such as solutions containing from 10–45% of caustic soda together with sufficient of the solubility promoter or solutizer to achieve a desired effectiveness in mercaptan removal. For example, a preferred reagent utilizing isobutyric acid will be a 40° Bé. caustic solution to which has been added 20% by weight of isobutyric acid. In the case of a cresol containing reagent, a 5 normal caustic, 2 normal sodium cresylate reagent appears to be highly useful.

The caustic solution may be either sodium hydroxide or potassium hydroxide and it will usually be a solution of a concentration between about 10% caustic and 45% caustic. From the standpoint of efficiency, potassium hydroxide is to be preferred, since mercaptan solubility promoters are more effective in solutions of this alkali. However, cost relationships will probably more usually indicate sodium hydroxide as the alkali to be used. The mercaptan solubility promoters to be used are any of the well known materials developed for this use and in the form in which they appear in the reagent are usually the alkali compounds of the named promoters. Among solubility promoters which may be used are: ethylene glycol, ethanolamine, propanol amine, phenyl acetic acid, alpha hydroxy Valeric acid, butyric acid, isobutyric acid, propionic acid, isobutylene glycol and alkyl phenolic acids. The amount of these solubility promoters which can be used depends only upon the solubility of the promoter itself in the caustic alkali in which it is to be used. In general, the beneficial effect of the solubility promoter is increased by an increase in concentration of the mercaptan solubility promoter, or of the alkali or of both. These mercaptan solubility promoters constitute a class of reagents which by this time are quite well known for the purpose. As will be observed from the list they fall into several kinds of chemical compounds. However, it is believed that materials of this kind are sufficiently well known to the art that they may be generically defined herein and in the following claims as solubility promoters capable of increasing the solubility of mercaptans in alkali metal hydroxide reagents.

The tannic acid may be C. P. tannic acid, commercial tannic acid, tannin or any of the usual forms in which tannin appears upon the market.

The term tannic acid or tannin is understood to cover those substances generally so grouped. Most of them are substances widely distributed in the vegetable kingdom. They are soluble in water, possess an acid, astringent taste, are colored dark blue or green by ferrous salts, precipitate gelatin, and form leather when applied to animal hides. The constitution of many tannic acids is still somewhat obscure. Some appear to be glucosides of gallic acid, and decompose into gallic acid and sugar upon boiling with dilute acids. Others contain phloroglucin. Upon fusing with KOH these mostly form protocatechuic acid and phloroglucin. Among the tannic acid compounds there may be named gallo-tannic acid, digallic acid, gallyl-gallic acid, and the various tannin materials derived from oak-bark, quinine-bark, coffee, moringa-tannin, cutch, chestnut, logwood, sumac, and many other natural sources. Many such compositions appear to contain compounds of the nature of polyhydroxyflavpinacols, yielding, upon fusion with alkali, polyhydroxy benzenes such as phloroglucin, resorcinol, or pyrogallol, and polyhydroxy benzene carboxylic acids such as protocatechuic or gallic acid. All such compounds are considered to be equivalent and embraced by the term tannic acid as herein used.

The concentration of tannin in the treating solution may vary. It has been found that from 1% to 3% by weight appears to be the most effective concentration, although concentrations as low as 0.1% may be used. On the upper end, concentrations higher than 5.0% appear at present to yield diminishing returns.

The treating solution may be contacted with the oil to be treated in any conventional treating system, such as in a packed tower or any system providing countercurrently arranged contacting stages. The amount of solution to be used may be varied to the individual treating requirements, but in general, will be from 1–50% by volume of the oil being treated. The treating temperature may vary. The removal effect appears to be at a minimum at 70° F. and increases at temperatures above and below this temperature, at least within the limits of 32° F. and 100° F. For practical operation, a temperature of 75–100° F. is recommended. Since this is quite a usual atmospheric temperature or readily attainable around an oil refinery, this phase of the operation presents no difficulties.

We claim:

1. That method of treating a light petroleum fraction to reduce the mercaptan sulfur content thereof comprising contacting the petroleum fraction with an aqueous alkali metal hydroxide to which there has been added a solubility promoter other than tannic acid capable of increasing the ability of the hydroxide to dissolve mercaptans, and to which there has also been added a small amount of tannic acid sufficient to further increase the mercaptan removal ability of the hydroxide more than additive and separating the oil from the mercaptan containing reagent

2. That method of treating a light petroleum fraction to reduce the mercaptan sulfur content thereof comprising contacting the petroleum fraction with an aqueous alkali metal hydroxide to which there has been added a solubility promoter

other than tannic acid capable of increasing the ability of the hydroxide to dissolve mercaptans, and to which there has also been added a small amount, not in excess of about 5% by weight, of tannic acid sufficient to further increase the mercaptan removal ability of the hydroxide more than additive and separating the oil from the mercaptan containing reagent.

3. That method of treating a light petroleum fraction to reduce the mercaptan sulfur content thereof comprising contacting the petroleum fraction with an aqueous alkali metal hydroxide to which there has been added a solubility promoter other than tannic acid capable of increasing the ability of the hydroxide to dissolve mercaptans, and to which there has also been added a small amount, from about 1% to about 5% by weight, of tannic acid sufficient to further increase the mercaptan removal ability of the hydroxide more than additive and separating the oil from the mercaptan containing reagent.

4. That method of treating light petroleum fractions to reduce the mercaptan-sulfur content thereof which comprises contacting a petroleum fraction with an aqueous solution of alkali metal hydroxide containing alkali metal cresylate and tannic acid, the distribution coefficient of said solution being greater than the sum of the distribution coefficient of aqueous alkali metal hydroxide containing the same amount of cresylate and the distribution coefficient of aqueous alkali metal hydroxide containing the same amount of tannic acid, and separating the petroleum fraction from the mercaptan-containing reagent.

5. That method of treating light petroleum fractions to reduce the mercaptan-sulfur content thereof which comprises contacting a petroleum fraction with an aqueous solution of alkali metal hydroxide containing potassium isobutyrate and tannic acid, the distribution coefficient of said solution being greater than the sum of the distribution coefficient of aqueous alkali metal hydroxide containing the same amount of potassium isobutyrate and the distribution coefficient of aqueous alkali metal hydroxide containing the same amount of tannic acid, and separating the petroleum fraction from the mercaptan-containing reagent.

JOHN HAPPEL.
STEPHEN P. CAULEY.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,228,028	Brower	Jan. 7, 1941
2,228,041	Yabroff et al.	Jan. 7, 1941
2,297,621	Henderson et al.	Sept. 29, 1942
2,315,530	Loyd	Apr. 6, 1943
2,316,092	Loyd	Apr. 6, 1943
2,316,966	McNamara et al.	Apr. 20, 1943
2,369,771	Bond	Feb. 20, 1945