

Jan. 7, 1941.

D. L. YABROFF ET AL

2,228,041

PROCESS FOR THE SWEETENING OF HYDROCARBON DISTILLATES

Filed Jan. 28, 1939

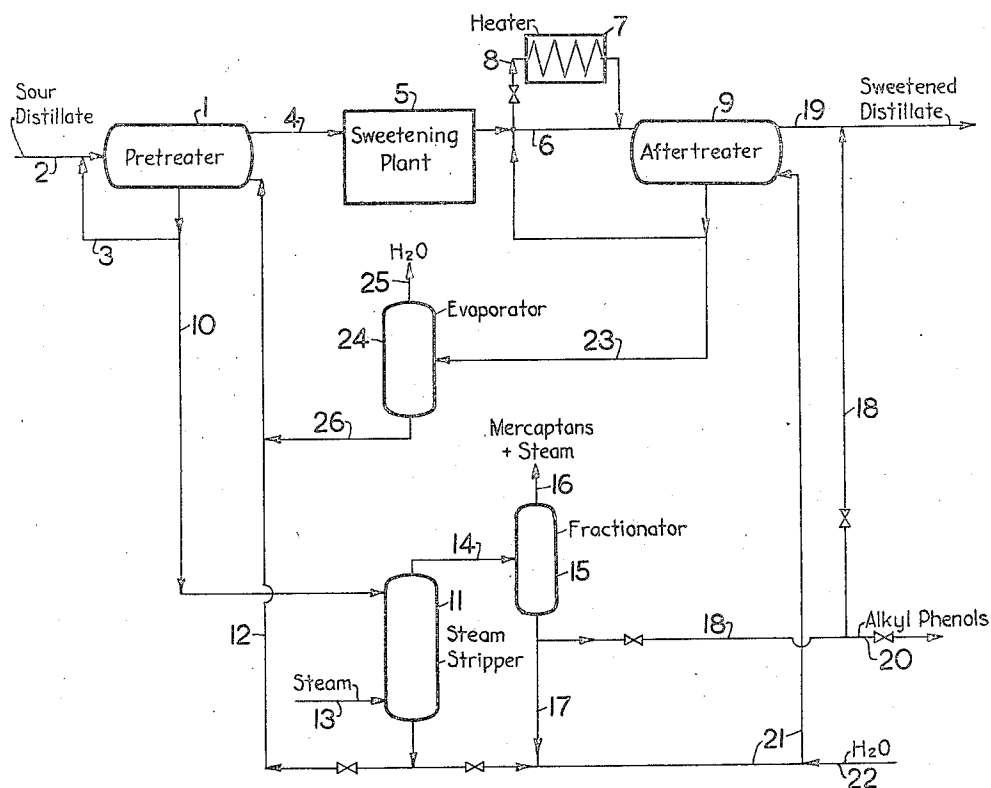


Fig. 1

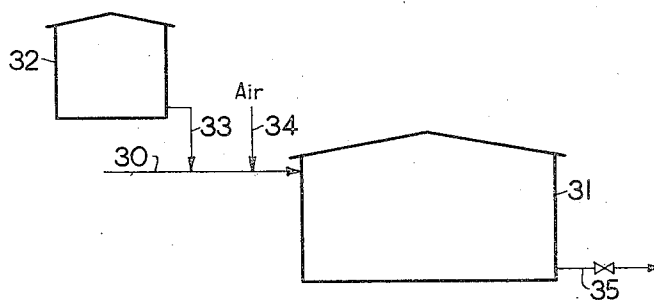


Fig. 2

Inventors: David L. Yabroff

Alan C. Nixon

By their Attorney: *E. W. Zublin*

UNITED STATES PATENT OFFICE

2,228,041

PROCESS FOR THE SWEETENING OF HYDROCARBON DISTILLATES

David Louis Yabroff and Alan C. Nixon, Berkeley, Calif., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

Application January 28, 1939, Serial No. 253,366

3 Claims. (Cl. 196—29)

This invention deals with the removal of mercaptans from liquid hydrocarbons containing same, and more particularly is concerned with the sweetening of sour hydrocarbon distillates such as gasolines.

Sweetening of sour hydrocarbon oils by oxidizing the obnoxious mercaptans to odorless disulfides is well known. A large number of different processes have been developed to effect this oxidation. One of the oldest and most widely used is the so-called doctor sweetening process in which sodium plumbite and free sulfur are used as the active chemical reagents. Other processes comprising oxidation with air or oxygen in the presence of various catalysts such as certain metals as copper, lead, nickel, cobalt, iron, etc., or their oxides or sulfides; or copper salts as CuCl_2 , if desired, in the presence of absorptive clays; or oxidation with easily reducible metal oxides or salts such as PbO_2 or sodium plumbate MnO_2 , hypochlorite, etc. While these processes are all or more or less effective, they have the common disadvantage of failing materially to reduce the sulfur content of the hydrocarbon liquid, and to form disulfides which are objectionable for several reasons, for example, in that they reduce the octane numbers and lead susceptibilities of gasolines, increase the sludging of electric oils, produce harmful SO_2 in the combustion of burning oils, etc.

It is a purpose of this invention to produce from sour distillates sweet oils containing a minimum amount of disulfides; it is another purpose to pretreat sour hydrocarbon distillates in a manner materially to facilitate conversion of mercaptans to disulfides; and it is a further purpose to so condition sour distillates that they can readily be sweetened by a novel method of effecting the oxidation of mercaptans to disulfides. Other advantages will become readily apparent from the following description.

Our process comprises treating a sour hydrocarbon oil containing weak organic acids, such as mercaptans and natural gum inhibitors, with an aqueous solution of a caustic alkali which contains dissolved a substantial amount of a solubility promoter for weakly acidic organic acids, under conditions to extract at least a major portion of these organic acids, separating the aqueous solution containing the extracted weak organic acids from the treated hydrocarbon oils, and subjecting the resulting oil to a mild oxidation just enough to convert remaining mercaptans to disulfides. The separated aqueous solution may then be steamed to remove mercaptans. This steaming may be accomplished under conditions to retain substantially all of the extracted gum inhibitors in the aqueous solution or to take a portion of them overhead together with the mercaptans.

A portion of the extracted gum inhibitors may be returned to the sweetened distillate to give it added stability. The method by which the return is effected depends to some extent on the above conditions of the steaming. If the gum inhibitors have been retained in the steamed aqueous alkaline solution, we may contact the sweetened hydrocarbon oil with the steamed solution under conditions to effect a transfer of the dissolved inhibitors from the aqueous to the oil phases. This may be had by maintaining during this contact a temperature which is higher than the temperature of the above-described treatment of the sour oil; or by diluting the steamed aqueous solution with a substantial amount of water; or, if the solubility promoter is volatile, by removing a portion thereof from the aqueous solution by distillation. Any one or a combination of these expedients will cause the desired return of part of the extracted gum inhibitors to the sweetened gasoline. On the other hand, gum inhibitors taken overhead together with mercaptans in the course of the steaming may be separated from the latter in some convenient manner as by fractional distillation, fractional absorption in weak caustic alkali, etc., as disclosed in the co-pending application Serial No. 235,572, filed October 18, 1938, and may then be recovered and returned to the sweetened gasoline. Alkyl phenols recovered in this manner are the most weakly acidic components of the alkyl phenols contained in petroleum distillates, and are known to be the most powerful natural gum inhibitors.

The advantages of our treatment comprise a material reduction of the content of organic sulfur compounds; an amount of disulfides in the sweetened oil which normally is harmless; a reduction in the amount of chemicals required in the oxidation of mercaptans to disulfides; a material prolongation of the life of oxidation catalysts if catalysts are used, due to a reduction of gum and tar formation; and if an alkaline medium is used, such as doctor solution, longer life and easier and more complete regeneration. Moreover, the removal of a large portion of both mercaptans and gum inhibitors so facilitates the oxidation of mercaptans to disulfides that it enables this oxidation to be carried out in an exceedingly simple and novel manner; i. e., by merely dissolving in the pretreated but distinctly sour oil a trace of a soluble catalyst in an amount less than that which is known to be harmful, and saturating the resulting solution with air, the oil so treated may be completely sweetened.

The aqueous solution used in the pretreating step comprises a strong base, preferably an alkali metal hydroxide, although other strong bases such as ammonia, alkali metal carbonates, quaternary ammonium bases, etc., may be applicable,

in which base is dissolved a suitable solubility promoter for weak organic acids. To be suitable, a solubility promoter must be substantially insoluble in the hydrocarbon oil and must be readily soluble in strong aqueous solutions of the base. To be materially effective, the concentration of solubility promoters in the aqueous solution should be between about 15% and 85%, and preferably from 25% to 75%. The aqueous solution should preferably contain 15% or more water, not only to reduce the solubility of the promoter in the hydrocarbon oil to a minimum, should it be materially soluble therein, but also to make possible the regeneration by simple steam stripping of the spent aqueous solution containing mercaptides. Moreover, the promoter must be chemically inert to the action of the strong base, even at the elevated temperatures of the steam stripping.

Suitable solubility promoters are, for example, aliphatic alkanolamines and amino alkylamines in which the alkyl radicals contain two to three carbon atoms; diamino alcohols, glycols and amino glycols of three to five carbon atoms; alkyl glycerines in which the number of carbon atoms in the alkyl radicals is from one to four, diamino, dihydroxy or amino hydroxy alkyl ethers or thioethers in which the alkyl radicals have from two to three carbon atoms; alkali metal and particularly potassium salts of fatty acids having from one to six carbon atoms, amino or hydroxy fatty acids having from two to seven carbon atoms, phenyl acetic acid, hydroxy or amino phenyl acetic acids, alkyl phenols; mixtures of the above, etc.

In treating the sour oil with the alkaline aqueous solution containing the solubility promoter, we usually use 5 to 100 volume percent of the solution. We may treat in a single stage, though preferably we employ a multi-stage countercurrent treating system or a countercurrent packed tower. The temperature of the prior treatment is preferably kept between about 0 and 60° C., although temperatures outside of this range may be used if desired. At temperatures lower than 0° C., there is often danger of causing a portion of the solubility promoter to precipitate, and the high viscosity of the alkaline solution may cause serious operating difficulties. At temperatures above about 60° C., the extraction efficiency drops rapidly.

Depending upon the conditions of the treatment, the amount and nature of the mercaptans contained in the distillate and the boiling range of the latter, it is usually possible to reduce the mercaptan sulfur content of the extract distillate to below .01% and normally below .005%. For example, by treating full range West Texas gasolines which are notoriously difficult to sweeten due to their relatively high content of high boiling mercaptans, with aqueous solutions of potassium hydroxide containing potassium isobutyrate, we have been able consistently to reduce mercaptan sulfur contents to below .005%.

The pretreated gasoline or other distillate may now be sweetened by any suitable method to oxidize remaining mercaptans to disulfides. When sweetening with conventional doctor solution, it has been found that, since the pretreatment has resulted in a far-reaching removal of alkyl phenols and other acidic components of the gasoline, the doctor solution becomes less contaminated, remains active for periods many times its normal life, and when eventually spent,

its regeneration by the conventional air blowing is greatly facilitated, being much quicker and more complete than normal.

The effect of alkyl phenol accumulation in doctor solution on the regenerability of the latter is interesting. It seems that the presence of a small amount of alkyl phenolates in doctor solution of the order of about 1-2%, for example, is beneficial, the time for air blowing required to regenerate the solution being materially reduced by this small amount. This improvement is believed to be due to a lowering of the surface tension of the doctor solution, which lowering permits a much more thorough contact with the air. However, when amounts of alkyl phenols substantially larger than the above are allowed to accumulate in the doctor solution, gasoline is retained in appreciable amounts, both in true solution and in suspension. Ordinary separating means such as settling or centrifuging are insufficient to completely remove the retained gasoline, and even distillation is frequently ineffective because of excessive foaming. Retained gasoline makes regeneration by air blowing very difficult, if not impossible, the gasoline either preventing thorough contact of the air and aqueous solution or acting as an inhibitor, or both. Whichever the true reason may be, regeneration can proceed smoothly only after most or all of the retained hydrocarbons have been removed. Our pretreating method completely overcomes these regeneration difficulties.

When sweetening by air oxidation in the presence of a catalyst such as lead sulfide, nickel sulfide, copper compounds or the like, we have found that not only can we accomplish the reaction with a much smaller amount of catalyst than is usually necessary, but also the amount of air required may be reduced to such an extent substantially to avoid losses of light hydrocarbon components, which components are normally carried away by unreactive portions of the air. For example, we have found that by merely dissolving from .00001% to .0005% copper in the pretreated gasoline, adding to the resulting solution an amount of air preferably not substantially in excess of that which is required to saturate it at atmospheric pressure, and allowing the mixture to stand for several hours, may convert the remaining mercaptans to disulfides. Occasionally, this conversion proceeds rather slowly, particularly if the gasoline is a straight run gasoline and may not take place at all if the amount of residual mercaptan sulfur substantially exceeds .005%, e. g., .01%. The addition of olefines or of an olefinic hydrocarbon distillate such as a cracked gasoline materially accelerates the reaction. Organic peroxides do not seem to have an influence on the rate of reaction in this method of sweetening. For example, the addition of benzoyl peroxide fails to have a noticeable influence. The presence of many gum inhibitors, however, particularly those of the amino phenol type, may inhibit this particular reaction. On the other hand, small amounts of natural gum inhibitors, i. e., alkyl phenols which may have been left over from the pretreatment in quantities sufficient to prevent rapid deterioration of the pretreated distillate as by formation of peroxides, do not normally retard the mercaptan conversion to any great extent.

Amounts of dissolved copper of the order of

.001% in gasoline are known to be harmful. For example, in processes in which sour hydrocarbon distillates are sweetened by contact with copper or compounds thereof, it is usually necessary to eliminate dissolved copper by an after-treatment with a metal sulfide such as sodium or zinc sulfide, because dissolved copper adversely affects the stability of the gasoline. Analyses of copper containing gasoline after the treatment with a sulfide have shown that about .0002% copper remains dissolved. This amount is definitely known, therefore, to be harmless. Moreover, analysis of many gasolines taken from gasoline stations have shown that they contain an average of .0001% to .0005% dissolved copper and yet are satisfactory. Hence, it appears that .0005% dissolved copper may still be regarded as harmless.

Since the amount of natural gum inhibitors left in the gasoline after our pretreatment with an alkaline aqueous solution containing solubility promoters is usually very small, there is danger that peroxide formation may set in if a pretreated gasoline is allowed to remain in contact with oxygen or substances capable of liberating oxygen. Traces of oxygen may be present almost everywhere, and it is therefore advisable to effect the sweetening almost immediately following our pretreatment, especially in all those cases in which the content of natural gum inhibitors has been depleted to below safe limits, i. e., to induction periods by the oxygen-bomb stability test of less than about one hour. As soon as possible after sweetening has been accomplished, an amount of inhibitors should be added to raise the induction period of the sweetened gasoline to at least the accepted standard which at present is four hours or higher.

Thus, while time within which the several steps of pretreating with caustic alkali containing solubility promoter, conversion of residual mercaptans to disulfides, and addition of gum inhibitor are completed, may be of considerable importance, normally a leeway of several hours is permissible. However, in all those cases in which the induction period of the distillate after the pretreatment is less than one hour, the permissible time between pretreatment and return of gum inhibitors is less than about 24 hours.

While gum inhibitors from any source may be added, we prefer to utilize at least a portion of the natural gum inhibitors which previously had been removed in the pretreatment. Methods by which extracted natural gum inhibitors can be returned to the sweetened gasoline have already been described.

The attached flow diagrams further illustrate our process. Fig. 1 shows an arrangement involving the sequence of the steps of pretreating, sweetening and stabilizing. Fig. 2 illustrates the sweetening by adding traces of dissolved copper and saturating with air. In Fig. 1, sour distillate, for example, a gasoline, enters pretreater 1 through line 2 from a source not shown. In the pretreater it is treated with an aqueous solution of a strong base such as an alkali metal hydroxide containing dissolved relatively large amounts of suitable solubility promoters for mercaptans and other weak organic acids. This solubility promoter may be added to the aqueous solution from an outside source or may comprise alkyl phenols accumulated from the treatment itself as by recirculation of the aqueous solution through line 3 or preferably through lines 10 and 12 and steam

stripper 11. In this pretreatment, the major portion of mercaptans and alkyl phenols originally contained in the distillate are removed. The resulting pretreated oil, which is still distinctly sour to the doctor test, is then immediately conveyed through line 4 to the sweetening plant 5 where residual mercaptans are converted to disulfides. The sweetened gasoline proceeds at once through line 6 or through heater 7 in line 8 to after-treater 9 in which a portion of the alkyl phenols removed in the pretreating step are returned to the sweetened gasoline in one of several manners, as will be described later.

Spent base solution from pretreater 1 containing both mercaptans and alkyl phenols passes through line 10 to steam stripper 11 in which mercaptans are driven off by live steam introduced through line 13 from a source not shown. Steam, mercaptans and a minor portion of the alkyl phenols are withdrawn through vapor line 14, and the resulting vaporous mixture may then be fractionated in fractionator 15 to separate alkyl phenols from the mercaptans. Mercaptans are removed through line 16, while alkyl phenols may be returned to the stripped aqueous solution through line 17 or may be introduced directly through line 18 into the sweetened distillate in line 19. Excess alkyl phenols may, if desired, be taken out of the system through line 20, stripped aqueous base solution may either be returned to pretreater 1 through line 12 as stated before, or may proceed through line 21 to after-treater 9 to be contacted with sweetened gasoline for the purpose of giving off a portion of its alkyl phenol contained to the latter. In order that this may be achieved, it is necessary that the condition during the contact in after-treater 9 be such to reduce the solubility of alkyl phenols in the aqueous phase as much as possible. Diluting the aqueous solution with water or maintaining relatively high temperature or both has this desired effect. Hence we may introduce water through line 22 into the stripped aqueous solution base through line 21. Moreover, we may heat the sweetened distillate in heater 7 on its way from the sweetening plant to after-treater 9, as described before.

Diluted aqueous base solution which has given up a portion of its alkyl phenol content to the distillate in after-treater 9 is withdrawn through line 23. A part thereof may be recirculated through lines 24 and 26 or lines 24 and 28 and heater 7, the remainder proceeding to the evaporator 24 where the water of dilution is removed by vaporization, steam going out through line 25 and reconcentrated solution returning through lines 26 and 12 to the pretreater 1.

In Fig. 2, which shows a specific embodiment of a sweetening plant, pretreated gasoline stripped of most of its acidic components containing less than .01% and preferably not more than .005% mercaptan sulfur is conveyed through line 30 to tank 31. Tank 32 contains a solution of an oil-soluble copper compound such as copper naphthenate, oleate, etc., in an oil-miscible solvent such as gasoline, benzene, alcohol, etc. An amount of this solution is introduced through line 33 into the gasoline in line 30 to produce a mixture containing between about .00001% and .0005% dissolved copper. Into this mixture is then introduced through line 34 air in an amount which is preferably not in excess of that required just to saturate the gasoline. The gasoline so treated then enters tank 31 where it is allowed to digest, preferably at ordinary atmospheric

temperature or slightly above, for a time sufficient to convert the mercaptans contained therein to disulfides. Sweet gasoline may be withdrawn through line 35 to be blended with a suitable gum inhibitor as described.

As previously pointed out, it is very desirable that the gasoline in which a trace of copper is dissolved contain a small amount of alkyl phenols to prevent its rapid deterioration due to formation of peroxides. This may be accomplished by using in the pretreatment a solubility promoter comprising or consisting of alkyl phenols, or by returning to the gasoline immediately after the pretreatment a small amount of alkyl phenols.

The following examples further serve to illustrate our invention:

Example I

A California sour cracked full range gasoline containing about .02% mercaptan sulfur was extracted in one stage with 1.5% by volume of an aqueous solution of 6N KOH+3.1 N potassium butyrate. The mercaptan content of the gasoline was reduced to .003%. Copper oleate was dissolved in the pretreated gasoline in an amount to result in a solution containing .0001% copper. The gasoline was then saturated with air. After 10 hours standing at 35° C. the gasoline had become sweet. When dissolving one-tenth only of the above amount, i. e., .00001% copper, the time required for sweetening was 40 hours.

The same gasoline prior to the pretreatment could not be sweetened with an amount of dissolved copper less than that which is known to be harmful.

Example II

Full range California gasoline similar to that of Example I was pretreated with an aqueous solution of 6N KOH+3.1 N potassium isobutyrate under conditions to result in a mercaptan sulfur content of .0031%. The induction period of the pretreated gasoline was of the order of about one hour. .0001% by weight of copper in the form of copper oleate was dissolved in the gasoline. The resulting solution was saturated with air and was divided into three portions. To one portion .05% alkyl phenols were added, giving the gasoline an induction period of about three hours. To another portion .01% of a commercial gum inhibitor comprising amyl para-amino phenol was added, which also gave the gasoline an induction period of about three hours. All three portions were allowed to stand at 25° C. and the times required for sweetening were measured. They were as follows:

Gum inhibitor	Time to sweeten, hours
None.....	29
0.05% alkyl phenols.....	29
0.01% commercial inhibitor.....	575

The portion to which no gum inhibitor had

been added had lost more than one point in octane rating during the period required for the sweetening, apparently due to formation of peroxides. The portion to which alkyl phenols had been added became sweet in the same time and lost no octane rating during this period. By adding additional gum inhibitors immediately after sweetening, it was possible to raise its induction period to the minimum four hours required.

Example III

Sour gasoline containing .07% mercaptan sulfur was sweetened with air in the presence of PbS before and after extraction with caustic alkali containing solubility promoter. The times required to effect sweetening were as follows:

Pretreatment	Mercaptan sulfur in gasoline	Time required to sweeten
None.....	0.070	3.6 hours.
Pre-extracted with caustic alkali containing solubility promoter.	0.005	1 minute.

Similar comparative results were obtained when sweetening this gasoline with aqueous solutions of cupric chloride. Before pretreatment 1.1 hours were required to effect sweetening. After the pretreatment, the gasoline was sweet in less than 20 minutes.

The analytical method by which the mercaptan sulfur contents as herein disclosed have been determined is that of Tamele and Ryland, reported in "Industrial Engineering Chemistry," Analytical edition VIII, pages 16-19 (1936). The mercaptan sulfur content of a sweet hydrocarbon distillate as measured by this method is .0004 maximum.

We claim as our invention:

1. In the process of sweetening a sour hydrocarbon distillate containing mercaptans, the steps comprising treating said distillate with an aqueous solution of a strong base containing dissolved a substantial amount of a solubility promoter for said mercaptans which is insoluble in said distillate and inert to said base, under conditions to absorb a major portion of said mercaptans in said aqueous solution and to form two liquid layers, an aqueous layer containing mercaptans and a treated sour distillate layer containing not more than .005% residual mercaptan sulfur, separating the layers, dissolving in said treated gasoline an oil-soluble copper salt in an amount such that the content of dissolved copper in the distillate is less than 0.0005% by weight, and treating the resulting solution with an amount of air at least sufficient to convert said residual mercaptans to disulfides.

2. The process of claim 1 in which the amount of dissolved copper is between 0.00001% and 0.0002% by weight.

3. The process of claim 1 wherein the amount of air is not substantially in excess of that required to saturate the distillate.

DAVID LOUIS YABROFF.
ALAN C. NIXON.