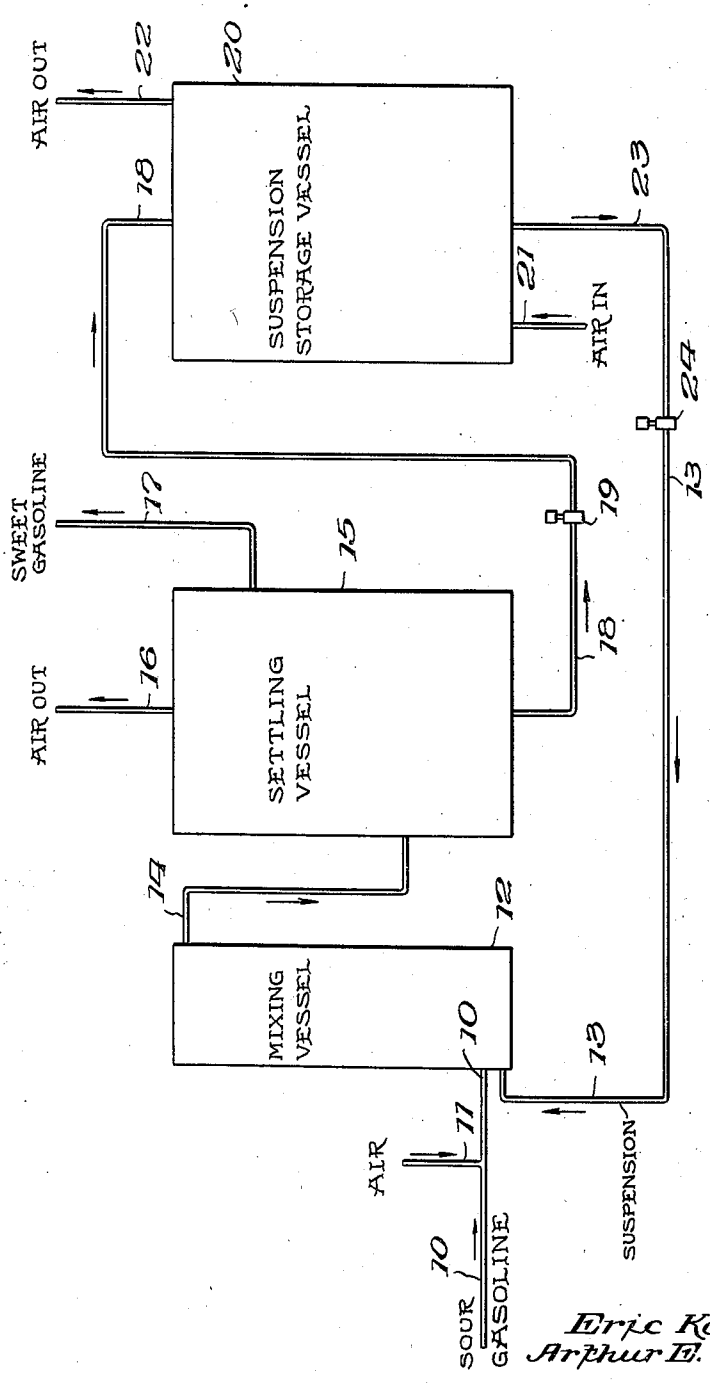
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PROCESS FOR SWEETENING SOUR HYDROCARBON OILS

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PROCESS FOR SWEETENING SOUR HYDROCARBON OILS

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This invention relates to a process for sweetening sour hydrocarbon oils, more particularly light petroleum products, such as natural and synthetic gasolines, naphthas, kerosenes, and furnace oils; and it comprises contacting a sour hydrocarbon oil with a suspension of ferric hydroxide and lead sulfide in an aqueous caustic alkali solution; all as more fully hereinafter set forth and as claimed.

Crude gasolines and the like are generally "sour" and have an offensive odor. The sourness and odor of such products is due to the presence therein of sulfur impurities such as mercaptans or hydrogen sulfide or both. The hydrogen sulfide is easily removed by an alkaline wash, such as caustic soda solution. However, no economical and effective process for the removal of mercaptans is known. Consequently, most refiners resort to some process for conversion of the mercaptans to inoffensive alkyl disulfides.

The most common of such conversion or "sweetening" processes is the widely known "doctor" method. This method consists of treating a sour oil with sulfur and a solution of sodium plumbite in aqueous caustic soda. The reactions which are believed to occur are as follows:

(1) $2RSH+Na_2PbO_2 \rightarrow (RS)_2Pb+2NaOH$

(2) $(RS)_2Pb+S \rightarrow R—S—S—R+PbS$

wherein R represents an alkyl radical or a mixture of such radicals. The mercaptans (RSH) are converted into alkyl disulfides (R—S—S—R), which remain in the gasoline but are not objectionable. The added lead is precipitated as lead sulfide.

Although the doctor process of sweetening is effective in convertng mercaptans, it has serious disadvantages. One important disadvantage of the process is that it involves the consumption of substantial amounts of sulfur and lead oxide, as is evident from the above equations. Moreover, in actual practice an excess of sulfur over that called for by Equation 2 is employed. The function of this excess sulfur appears to be that it accelerates the precipitation of the freshly formed lead sulfide. This excess cannot be conveniently recovered; it therefore adds to the expense of the doctor treatment. Moreover, the excess sulfur remains, at least in part, in the sweetened product, where its presence is objectionable. For example, it causes the product to be corrosive.

Not only does the doctor method of sweetening involve considerable expenditure of chemicals, but it also has the disadvantage that, in the case of gasoline, it produces a sweetened gasoline having a substantially lower octane number and, frequently, a poorer response to tetraethyl lead then the unsweetened gasoline and a reduced oxygen stability.

It has been sought in the art to discover improved methods of sweetening light petroleum products, particularly gasoline; that is, processes which do not consume chemicals and do not injuriously affect the product. Such methods as have been previously known are not, however, wholly satisfactory. One method, for example, involves agitating sour oil with air and a suspension of lead sulfide in caustic soda solution. In practicing this method, however, it is usually necessary to add sulfur; either as such, or in the form of some compound. This addition of surfur, or sulfur compounds is especially necessary when it is desired to conduct the process over extended periods of time and when charging stocks which are difficult to sweeten are employed. Sodium sulfide is usually used except when handling light oils which are extremely difficult to sweeten; in which case, free sulfur is used. In this prior art process, as in the doctor process, the addition of sulfur, or sulfur compound, is necessary to secure a "break"; that is, the conversion of lead mercaptide to alkyl disulfide, as shown above by Equation 2. The use of a sulfur compound, such as sodium sulfide, does not deleteriously affect the quality of the sweetened product substantially, but the quantity of such compound used must be accurately controlled. The quantity must be sufficient to cause a "break," but if any substantial excess is used the sweetening power of the mixture will be destroyed. Thus, for a given plant, if it is desired to handle a variety of stocks at various charging rates, the control of the rate of addition of the sulfur compound is a serious problem.

It is an object achieved by this invention to provide a superior process of sweetening sour gasoline and other like sour petroleum oils, particularly a process which obviates the necessity of wasting purchased chemicals.

It is also an important object achieved by this invention to provide a sweetening process which results in less deterioration of the product, such as lessening the lead response and lowering the octane member of the product, and causing the product to be corrosive or have a reduced oxygen stability.

We have discovered that a suspension of ferric hydroxide and lead sulfide in caustic alkali solution constitutes an excellent sweetening agent;

one which produces a better product than that produced by the doctor process and which moreover can be used in a manner which avoids the expenditure of substantial quantities of purchased chemicals.

In accordance with the procedure of our invention, a sour hydrocarbon oil is contacted until sweetened with a suspension of ferric hydroxide and lead sulfide in caustic alkali solution. The sweetened oil is separated from the suspension. The used suspension has a somewhat diminished sweetening power, so that it may or may not be feasible to use it in sweetening further quantities of oil, depending upon the degree to which it has been exhausted in the prior sweetening. However, the used suspension can be regenerated and re-used. Thus, we have found that contacting the used suspension with air or other oxygen-containing gas effects a regeneration of the used suspension, and by employing sufficient air, the sweetening power of the suspension can be substantially fully restored.

We find it advantageous to adopt a procedure whereby sour hydrocarbon oil is continuously sweetened and the used suspension is continuously regenerated for re-use in sweetening. This may be accomplished, for example, by continuously contacting the sour oil with suspension, separating the sweetened oil from the suspension, blowing the recovered suspension with air to regenerate it, and recycling the regenerated suspension to the sweetening zone for contact with further quantities of sour oil. The same result may also be accomplished by introducing part or all of the air needed for regeneration of the suspension into the sweetening zone; that is, contacting the sour oil simultaneously with both air and suspension. The sweetened oil is separated, and the recovered suspension, blown with a further quantity of air if necessary to complete the regeneration, is used for sweetening further quantities of sour oil.

In a typical embodiment of our procedure, a suspension of lead sulfide and ferric hydroxide is prepared by adding sufficient sodium sulfide to a sodium plumbite solution to precipitate all the lead as lead sulfide, then ferric chloride is added to precipitate ferric hydroxide, or hydrated ferric oxide. However, other methods of forming the suspension may be employed. For example, preformed lead sulfide and ferric hydroxide may be added directly to a caustic alkali solution. It is desirable that the suspension be free from lead oxide and sodium sulfide because suspensions containing free lead oxide or sodium sulfide do not sweeten as satisfactorily.

The sour charge is mixed with the suspension and the mixture may be brought into contact with air or other oxygen-containing gas. We find that it is advantageous to admit at least a part of the air during the step of mixing sour oil with the suspension, because an intimate contact between oil, suspension and air is thereby rapidly effected. However, other procedures may be employed.

The total quantity of suspension, and of suspended lead sulfide and ferric hydroxide therein, recommended for sweetening will vary from case to case, depending upon the nature of the distillate, particularly upon its mercaptan content.

Either caustic soda or caustic potash solutions may be employed in our procedure. For that matter, a solution containing both alkalis may be employed. However, caustic soda is much cheaper and is very satisfactory. Its use, therefore, is advantageous. The concentration of the caustic alkali may be varied considerably, but in general, in using caustic soda, we find it advantageous to confine the concentration to between about 10° and about 40° Bé. For each 100 barrels of such caustic soda solution employed as suspending medium, from 800 to 1100 pounds of lead sulfide and from 500 to 1000 pounds of ferric hydroxide are advantageously used.

The recommended period of contact between the light oil and suspension will depend in large measure upon the sourness of the oil and the proportion of suspension to oil. The more sour the charge, the longer will be the necessary period of contact to produce a sweet product. The greater the proportion of suspension to oil, the less will be the necessary period of contact. We have found, however, that even with very sour gasoline, when using one volume of suspension to four volumes of gasoline, a period of 8 to 15 minutes generally suffices to yield a sweet product.

The visual phenomena accompanying our sweetening procedure are worthy of note. Thus, shortly after the commencement of agitation of a mixture of gasoline, suspension and air, the gasoline changes color, generally becoming pale green. Just before the gasoline becomes sweet, it tends to emulsify with the suspension. In the case of a very sour gasoline, the mixture may become gel-like or soupy at this stage. However, when the gasoline becomes sweet, the emulsion breaks and a clean separation of the sweet gasoline from the suspension can be readily effected.

The procedure of our invention results in a completely sweetened product. Moreover, in the case of gasoline, it results in less loss of oxygen stability, less lowering of response to tetra-ethyl lead, and less decrease in octane number than the doctor method. The color of light oils sweetened according to our invention is not impaired. In this respect, our process compares favorably with the doctor process. Our method also produces a product having a good copper strip test.

It is an important advantage of our invention that the suspension of lead sulfide and ferric hydroxide in caustic alkali solution can be used repeatedly, in fact almost indefinitely. It is only necessary to regenerate the suspension, for example, by blowing air through it, either from time to time or continuously. The blowing may take place after the suspension has been separated from the sweetened oil, or during the actual sweetening operations. We find it advantageous, however, to perform part of this regenerating operation during sweetening and part afterwards. It may also be advisable to bleed off small quantities of suspension and replace the same by additional quantities of fresh suspension to maintain the sweetening power thereof at maximum strength. Such rate of replacement, however, need be only very small.

The chemical nature of our sweetening process is not entirely clear. However, we believe that it can be explained in terms of the following equations:

(3) $PbS+2Fe(OH)_3 \rightarrow PbO+S+2Fe(OH)_2+H_2O$

(4) $PbO+2NaOH \rightarrow Na_2PbO_2+H_2O$

(5) $2RSH+Na_2PbO_2 \rightarrow (RS)_2Pb+2NaOH$

(6) $(RS)_2Pb+S \rightarrow R—S—S—R+PbS$

Thus, in effect the same sweetening reactions are believed to occur as occur in doctor treatment. However, the necessary sulfur and lead oxide are supplied by oxidation of the lead sulfide.

The ferric hydroxide serves as the oxidizing agent and is itself reduced to ferrous hydroxide. Therefore, it becomes necessary to regenerate the suspension by reoxidizing the ferrous hydroxide to ferric hydroxide. This is most conveniently done with air.

Whether or not this explanation is correct, it is a fact that a much more rapid and effective sweetening is produced in the presence of ferric hydroxide than in its absence. Further, the necessity for the use of free sulfur or such compounds as sodium sulfide is entirely eliminated.

In order that our invention may be clearly set forth and understood, we now describe, with reference to the drawing accompanying and forming part of this specification, a preferred form and manner in which our invention may be embodied and practiced.

In this drawing, the single figure is a diagrammatic elevational view of apparatus useful in the practice of our invention.

With particular reference to the sweetening of gasoline, the apparatus illustrated in the drawing operates as follows: Sour gasoline passes through pipe 10, is mixed therein with air entering through pipe 11, and enters a mixing vessel 12. A suspension of ferric hydroxide and lead sulfide in caustic soda solution also enters mixing vessel 12 through pipe 13. Mixing vessel 12 may be a packed tower or it may be any other convenient means of securing intimate contact between the gasoline, air and suspension. The mixture of fluids passes up through mixing vessel 12 and out through pipe 14 to settling vessel 15. The proportion of gasoline, air and suspension admitted to mixing vessel 12 and the rate of flow of the mixed fluids therethrough is advantageously such that the gasoline is sweet on entering settling vessel 15. In settling vessel 15 the mixture is allowed to separate by gravity into an upper layer of gasoline and air and a lower layer of aqueous suspension. Air is vented through pipe 16 and sweetened gasoline is withdrawn through pipe 17. This sweetened gasoline may be given a wash with water to remove traces of alkali. Suspension is pumped from the bottom of vessel 15 through pipe 18 by means of pump 19 into suspension storage vessel 20. Sufficient air is passed into vessel 20 through pipe 21 to reoxidize the ferrous hydroxide to ferric hydroxide. The air is then vented through pipe 22.

Regenerated suspension of ferric hydroxide and lead sulfide in caustic soda solution is withdrawn from tank 20 through pipe 23 and forced by means of pump 24 through pipe 13 into mixing vessel 12. It may be advisable to vent a small amount of suspension from the system, either continuously or from time to time, at any convenient point and replace it by fresh suspension. This will serve to maintain the full sweetening power of the suspension.

Instead of introducing part of the air into mixing vessel 12 and the remainder into the suspension storage vessel 20, all of the air necessary for sweetening and regeneration can be introduced into mixing vessel 12. However, it is advantageous to divide the air supply as shown in the drawing. For one thing, this avoids carrying the full volume of air through the mixing and settling vessels and thereby increases the capacity of a plant of given size. It also minimizes loss of gasoline by such being carried off with the vented air. Furthermore, we have found that introducing all the air into the mixing vessel results in over-oxidation of the lead sulfide and its consequent loss.

To completely avoid carrying off gasoline from settling vessel 15 by vented air, and to minimize over-oxidation of lead sulfide and also, in the case of gasoline exhibiting a tendency to form gum and deteriorate in color, to minimize these latter tendencies, it may be advisable to modify the procedure illustrated in the drawing in the opposite respect. This may be done by not introducing air at all into mixing vessel 12 and settling vessel 15, and instead introducing all the required air into vessel 20. Although in the case of unstable gasoline this modified procedure has important advantages, in the majority of cases we find that it is advantageous to operate as shown in the drawing.

The following specific examples of sweetening sour gasoline will serve to illustrate the practice and advantages of our invention. The procedure employed in these examples was the same as that shown in the drawing.

Example I.—A ferric hydroxide-lead sulfide-caustic soda solution suspension was made up by dissolving 1008 pounds of litharge in 100 barrels of 20° Bé. sodium hydroxide solution. To this solution was added 6.2 barrels of a 20° Bé. sodium sulfide solution. This quantity of sodium sulfide solution provided just sufficient sulfide to precipitate all of the lead as lead sulfide. 1200 pounds of ferric chloride were also added to the litharge solution. A flocculent mass of ferric hydroxide was precipitated. 50 barrels per hour of a very sour West Texas gasoline containing 0.042 per cent of mercaptan sulfur, about 8 barrels per hour of the above suspension, and approximately 100 cubic feet per hour of air were passed through a mixing vessel and into a settling vessel. The mixing vessel consisted of two vertical lengths of pipe, each 14 inches in diameter and 40 feet high, placed in series and packed with 2 inch by 2 inch pipe nipples. The settling vessel was a vertical tower, 12 feet in diameter and 40 feet high. Under these conditions, the gasoline entering the settling vessel was sweet according to the doctor test. The gasoline, air and suspension were separated in the indicated manner. The separated suspension was regenerated by blowing with air, the air serving as a means of agitation as well as providing oxygen, and recycled to the mixing vessel to sweeten further quantities of gasoline. The sweetened gasoline was given a water wash and was subjected to standard tests. The following table gives the results of these tests and a comparison to doctor sweetening. The first column of figures refers to the original charge, the second to the same gasoline sweetened by the above method, and the third to the same gasoline sweetened by the doctor method.

	Charge	$Fe(OH)_3$—PbS sweetened	Doctor sweetened
Mercaptain sulfur content percent	0.042	Nil	Nil
Gravity °API	66.6	66.3	66.4
Doctor test	Bad	Good	Good
Copper strip test	Good	Good	Good
Color, Saybolt	25+	25+	25+
Reid vapor pressure	11.0	10.8	11.0
Octane No. (CFR)	63.0	62.8	61.5
Distillation:			
Over point °F	91	96	94
End point °F	350	354	351
10% at °F	138	139	138
50% at °F	214	215	214

From the above table, it is apparent that the

ferric hydroxide-lead sulfide sweetening was considerably less detrimental to the octane number of the product than doctor sweetening.

Example II.—49 barrels per hour of a New Mexico straight run distillate, containing 0.048 per cent of mercaptan sulfur, and about 100 cubic feet per hour of air were admitted to a mixing vessel. A ferric hydroxide-lead sulfide-caustic soda solution suspension was also admitted, first at the rate of 1 barrel per 6 barrels of gasoline, later at the rate of 1 barrel per 4 barrels of gasoline. The mixture of gasoline, suspension and air was then passed into a settling vessel and the constituents were separated in the indicated manner. This process was continued for 24 hours, or until 1176 barrels of gasoline had been sweetened.

The mixing vessel was designed to give intimate contact between the suspension and gasoline and a contact period of about 10 minutes at the above rates of flow. The latter rate of flow of suspension, producing a higher ratio of suspension to gasoline, was found to be advantageous because it resulted in more complete sweetening in the mixing vessel. At times it was noted that the gasoline leaving the mixing vessel was slightly sour. The frequency with which this was noted was substantially less in the case of the 1:4 ratio than in the case of the 1:6 ratio of suspension to gasoline. However, even in the case of the 1:6 ratio, the gasoline was always sweet at and above the middle of the settling vessel.

The gasoline thus sweetened, 1176 barrels in all, had the following characteristics. The characteristics of the original charge and a sample of the same gasoline doctor sweetened are also given by way of comparison.

	Charge	$Fe(OH)_3PbS$ sweetened	Doctor sweetened
Mercaptan sulfur content, percent	0.048	Nil	Nil
Gravity, °API	67.6	67.0	66.9
Doctor test	Bad	Good	Good
Copper strip test	Good	Good	Good
Color, Saybolt	30+	30+	30+
Reid vapor pressure	12.4	12.0	12.0
Octane No. (CFR)	63.0	62.2	60.5
Distillation:			
Over point, ° F.	89	92	90
End point, ° F.	335	344	346
10% at, ° F.	135	134	136
50% at, ° F.	209	208	210
90% at, ° F.	294	295	298
Recovery, percent	95	96	95

As in Example I, a substantially better product from the standpoint of octane number was obtained by the ferric hydroxide-lead sulfide process than by the doctor process.

Example III.—A cracked gasoline containing 0.022 per cent of mercaptan sulfur was sweetened in the manner of Examples I and II. The product was tested according to the standard method for oxygen stability at 212° F. and found to have an oxygen stability of 510 minutes compared to 600 minutes for the original charge. The same gasoline, however, when sweetened by the doctor method, had an oxygen stability on the same scale of only 250 minutes.

Our invention has been described with particular reference to certain embodiments and specific examples, but it is not limited in scope to such embodiments and examples except as defined in the appended claims.

What we claim is:

1. A process of sweetening sour hydrocarbon oils which comprises contacting a sour hydrocarbon oil with a suspension of ferric hydroxide and lead sulfide in caustic alkali solution.

2. A process of sweetening sour hydrocarbon oils which comprises contacting a sour hydrocarbon oil with a suspension of ferric hydroxide and lead sulfide in caustic alkali solution and regenerating the used suspension.

3. A process of sweetening sour hydrocarbon oils which comprises contacting a sour hydrocarbon oil with a suspension of ferric hydroxide and lead sulfide in caustic alkali solution and regenerating the used suspension with an oxygen-containing gas.

4. A process of sweetening sour hydrocarbon oils which comprises contacting a sour hydrocarbon oil with an oxygen-containing gas and a suspension of ferric hydroxide and lead sulfide in caustic alkali solution.

5. A process of sweetening sour hydrocarbon oils which comprises contacting a sour hydrocarbon oil with a suspension of ferric hydroxide and lead sulfide in caustic alkali solution, separating the sweetened oil from the suspension, and regenerating the used suspension with air.

6. A process of sweetening sour gasoline which comprises contacting sour gasoline with air and a suspension of ferric hydroxide and lead sulfide in caustic soda solution.

7. A process of sweetening sour kerosene which comprises contacting sour kerosene with air and a suspension of ferric hydroxide and lead sulfide in caustic soda solution.

8. A continuous process of sweetening sour gasoline which comprises establishing a continuous, intimate contact between sour gasoline, air and a suspension of ferric hydroxide and lead sulfide in caustic soda solution, thereby sweetening the gasoline, separating used air and suspension from the gasoline, recovering the sweetened gasoline, regenerating the used suspension by contact with air, and re-using the regenerated suspension to sweeten further quantities of sour gasoline.

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