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PROCESS FOR SWEETENING HYDRO-CARBON OIL

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The present invention relates to the treatment of sour hydrocarbon oils or sour petroleum distillates, such as kerosene, naphtha and gasoline, for the purpose of sweetening them, and to the treatment of such oils and distillates for the purpose of removing corrosive agents, such as sulphur. The invention is applicable to the treatment of hydrocarbon oils and petroleum distillates derived both from naphthenic base crudes and paraffinic base crudes. Such oils and distillates are said to be sour when they respond positively to the so-called "Doctor Test" and they are said to be sweet when they respond negatively to said test. The act of treating a sour distillate, so that, after treatment, it is sweet is generally called "sweetening." The sour condition or sourness of a hydrocarbon oil distillate is generally attributed to mercaptans in dissolved condition in the hydrocarbon oils or distillates.

More particularly the present invention relates to the treatment of hydrocarbon oils or distillates, in the presence of a soap or other salt of a metal which forms soluble sulphides, and in the presence of uncombined oxygen, with the following reagents and mixtures of reagents in solid form: (a) solid alkali metal hydroxide (e. g., sodium or potassium hydroxide); (b) a mixture of solid alkali metal hydroxide (e. g., sodium or potassium hydroxide) and elemental sulphur; (c) a mixture of solid alkali metal hydroxide (e. g., sodium or potassium hydroxide) and solid alkali metal monosulphide (e. g., sodium or potassium monosulphide); and (d) a mixture of solid alkali metal hydroxide (e. g., sodium or potassium hydroxide), solid alkali metal monosulphide (e. g., sodium or potassium monosulphide) and elemental sulphur.

While the presence of a soap or other salt of a metal which forms soluble sulphides is necessary, the soap or salt itself appears to take no direct part either in the sweetening of the oil or distillate, or in the removal of corrosive agents, other than to promote contact between the other reagent or reagents and the oil or distillate being treated. The presence of uncombined oxygen inhibits the formation of undesired reaction products and enables the process to be more readily controlled. Like the soap or salt, it apparently takes no direct part in the reactions which bring about the sweetening of the oil and the removal of corrosive agents, but its presence during the treatment of the oil or distillate is necessary to prevent the sweetened oil from reverting to its sour condition.

When a sour hydrocarbon oil or distillate

which contains (1) free sulphur or (2) both hydrogen sulphide and free sulphur, in addition to mercaptans is flowed, for example, at an atmospheric temperature or at a temperature not above about 120° F., through a bed, layer or column of solid alkali metal hydroxide and a soap or salt of the type referred to, for example, flowed vertically upwardly through a column of solid sodium hydroxide, in lump, flake or granular form, having the lumps, flakes or granules coated, or partially coated with the soap or salt, the hydrocarbon oil or distillate passing out of the bed, layer or column of alkali metal hydroxide will be sweet to the Doctor test for only a comparatively short time after the flow of hydrocarbon oil or distillate is started. However, as the sour oil or distillate is continued to be passed through the bed, layer or column of alkali metal hydroxide, the alkali metal hydroxide loses its activity to completely sweeten the hydrocarbon oil or distillate. This loss in sweetening power of solid alkali metal hydroxide makes its appearance long before the total amount of alkali metal hydroxide is completely utilized in the sweetening. In fact, the alkali metal hydroxide begins to lose its power to completely sweeten the flowing hydrocarbon oil or petroleum distillate after only a small part of the sodium hydroxide has been used in sweetening. This is referred to herein as Case A.

When a sour hydrocarbon oil or distillate which contains (1) no free sulphur nor hydrogen sulphide, or (2) which contains free sulphur without hydrogen sulphide or (3) which contains free sulphur and hydrogen sulphide, or (4) which contains hydrogen sulphide without free sulphur, in addition to mercaptans, is flowed, for example, at an atmospheric temperature or at a temperature not above about 120° F., through a bed, layer or column of a mixture of elemental sulphur, solid alkali metal hydroxide and a soap or salt, the metal of which forms soluble sulphides, for example flowed vertically upwardly through a mixture of elemental sulphur and solid sodium hydroxide in lump, flake or granular form, in which the lumps, flakes or granules are coated or partially coated with the soap or salt, the hydrocarbon oil or distillate passing out of the bed, layer or column will be sweet to the Doctor test for only a comparatively short time after the flow of hydrocarbon oil has started. As the sour hydrocarbon oil or distillate is continued to be passed through the mixture, the mixture loses its activity to completely sweeten the hydrocarbon oil or distillate long before all the components of the mixture are completely made use

of in the sweetening done. This is referred to herein as Case B.

When a sour hydrocarbon oil or distillate which contains (1) free sulphur without hydrogen sulphide, or (2) free sulphur and hydrogen sulphide, in addition to mercaptans is flowed, for example, at an atmospheric temperature or at a temperature not above 120° F., through a bed, layer or column of a mixture of solid alkali metal hydroxide and solid alkali metal monosulphide, for example, flowed vertically upwardly through a column of a mixture of lump, flake or granular sodium hydroxide and lump, granular or flake sodium monosulphide, in which the lumps, flakes and granules are coated or partially coated with the soap or salt, the hydrocarbon oil or distillate passing out of the bed, layer or column of the mixture will be sweet to the Doctor test for only a comparatively short time after the flow of hydrocarbon oil or distillate has started. As the sour oil is continued to be passed through the mixture, the mixture loses its activity to completely sweeten the hydrocarbon oil or distillate in spite of the fact that the components of the mixture are only partly consumed. This is referred to herein as Case C.

Again, when a sour hydrocarbon oil or distillate which contains (1) no free sulphur nor hydrogen sulphide, or (2) which contains free sulphur without hydrogen sulphide, or (3) which contains free sulphur and hydrogen sulphide, or (4) which contains hydrogen sulphide without free sulphur, in addition to mercaptans is flowed, for example, at an atmospheric temperature or a temperature not above about 120° F., through a bed, layer or column of a mixture of solid alkali metal hydroxide, solid alkali metal monosulphide and elemental sulphur, for example flowed vertically upwardly through a column of a mixture of lump, flake or granular sodium hydroxide, lump, flake or granular sodium monosulphide and elemental sulphur, in which the particles of sodium hydroxide and sodium sulphide are coated or partially coated with the soap or salt, the hydrocarbon oil or distillate passing out of the bed, layer or column of the mixture will be sweet to the Doctor test for only a comparatively short time after the flow of the hydrocarbon oil distillate has started. As the sour oil is continued to be passed through the mixture, the mixture loses its activity to completely sweeten the hydrocarbon oil or distillate in spite of the fact that large portions of all components of the mixture still remain therein in unused condition. This is referred to herein as Case D.

The sour hydrocarbon oils or petroleum distillates treated in accordance with Cases A, B, C and D above, must of course contain those small amounts of water moisture which are necessary to initiate the chemical actions involved. This water moisture is usually provided by the water which is in solution in the hydrocarbon oil or by small amounts of water in suspension in the form of very small globules in the oil. The same water moisture conditions of the oil prevail in the hydrocarbon oils treated according to my process hereinafter described, except that in the case of hydrocarbon oils which do not carry water moisture in solution or suspension, or which are deficient in water moisture, for the purposes stated above, I intimately mix a very small amount of water or steam into the oil to supply the deficiency in moisture.

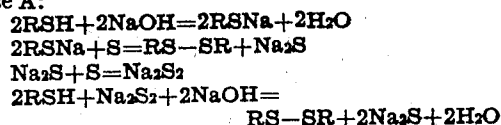
Now I have discovered that in Cases A, B, C

and D above, the objectionable properties of the reagents of losing their sweetening activity, in spite of the fact that they are present in large amounts in unused condition when the oil flowing from the layers, beds or columns of them is no longer completely sweet, can be overcome by adding air or oxygen to the hydrocarbon oil flowing to the said layers, beds or columns, or by introducing air or oxygen into the chambers containing the said layers, beds or columns at a point at which the air or oxygen will mix with the hydrocarbon oils before they enter the said layers, beds or columns of reagents.

I have further discovered that the above described ceasing or diminution of sweetening action is connected with the formation of sodium or potassium monosulphide as a product of the sweetening action or hydrogen sulphide removal by the alkali metal hydroxide, or with the formation of sodium or potassium monosulphide and the removal of hydrogen sulphide by the alkali metal hydroxide. As will be more fully explained below, the sweetening reactions in Cases A, B, C and D, and in the process of the present invention are accompanied by the formation of sodium or potassium monosulphide.

Representing the mercaptans as having the general formula RSH in which R is an organic radical containing carbon and hydrogen atoms, and using sodium as the example of the alkali metal, the hydroxide and monosulphide of which are referred to above, the fundamental reactions involved in the sweetening of the sour hydrocarbon oil in Cases A, B, C and D above are indicated below:

Case A:

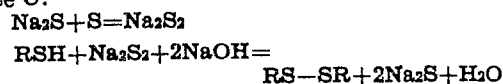


As will be seen, in this Case A there is removal of free sulphur from the hydrocarbon oil treated, and this sulphur removal is also accomplished when Case A is modified by the introduction of air or uncombined oxygen according to the present invention.

Case B:

In this case the reactions are the same as in Case A. In Case B, and in Case B as modified by the present invention, in order to obtain free sulphur removal from hydrocarbon oils having a high content of free sulphur, it will be necessary to proportion the free sulphur content of the mixture according to the free sulphur content of the oil and it may become necessary to entirely eliminate it from the mixture if the free sulphur content of the oil is very high, and in which latter event the process proceeds according to my modification of Case A. The purpose of adding the sulphur to the mixture is to provide sulphur for decomposing the sodium mercaptides in those instances where the oil treated contains no free sulphur or very little free sulphur.

Case C:



From the first equation above, it will be seen that free sulphur can or may be removed from an oil containing free sulphur, and such removal of free sulphur also occurs when air or

oxygen is introduced into the column along with the oil or distillate according to my invention.

Case D:

In this case the reactions are the same as in Case C above. In case D, and in Case D as modified by the introduction of air or oxygen according to the present invention, in order to obtain free sulphur removal from oils having a high content of free sulphur, it will be necessary to proportion the free sulphur content and sodium monosulphide content of the mixture according to the free sulphur content of the oil, and it may become necessary to entirely eliminate free sulphur from the mixture, in which latter event the process proceeds according to my modification of Case C.

From the foregoing chemical equations and explanations, taking into account also the reaction between the alkali metal hydroxide and the hydrogen sulphide content, if any, of the hydrocarbon oil treated, the person skilled in the art will readily be able to calculate, estimate, or adjust by trial the proportions of reagents in the mixture to give a sweet treated product free of free sulphur or one of reduced free sulphur content or one the free sulphur content of which is not substantially different from the free sulphur content of the untreated hydrocarbon oil.

When proceeding according to Cases B and D above without the use of oxygen, or according to Cases B and D above with the use of oxygen according to the present invention, the elemental sulphur (e. g., flowers of sulphur or finely ground sulphur) may be directly mixed with the solid alkali metal hydroxide on the one hand, and with the alkali metal hydroxide and alkali metal monosulphide on the other hand, before the sour oil is passed through or in contact with the mixture of reagents; or flowers of sulphur (or finely divided sulphur), at the beginning of the practice of the process, may be mixed with a small portion of the oil to be treated to form a slurry and this slurry mixed into the sour hydrocarbon oil just before, or a short distance before, it enters a layer, bed or column containing the soap and the flake or granular alkali metal hydroxide on the one hand, or of a mixture of alkali metal hydroxide, alkali metal monosulphide and the soap, on the other hand. In this latter manner, the sulphur forms in the one case a mixture with the alkali metal hydroxide, and in the other case a mixture with alkali metal hydroxide and alkali metal monosulphide. In the appended claims where I have referred to mixtures containing elemental sulphur I include mixtures formed in either of the above referred to manners.

The process of the present invention is further described in the following examples given by way of illustration.

Example 1

The apparatus used for practicing my process according to this example consisted of two vertical steel drums, three feet in diameter by twelve feet in height, each filled to a depth of eight feet with sodium hydroxide in flake form and sodium naphthenate. The drums were connected in series by pipes in such a manner that the sour petroleum distillate to be treated entered the bottom of one of the drums, flowed upwardly through the column of flake sodium hydroxide and soap or salt therein, discharged at the top of that drum into a pipe which carried the distillate to the bottom of the second drum, from which point it flowed upwardly through the col-

umn of flake sodium hydroxide and soap or salt in the second drum and then out through a pipe connected with the top of the second drum.

The distillate treated according to this example had the following characteristics:

Initial boiling point.....	Fahrenheit... 200°
End boiling point.....	do..... 400°
Beaumé gravity.....	41°
Lamp sulphur.....	Percent... 0.019
Octane number.....	72
Hydrogen sulphide.....	Considerable present but percent not determined
Mercaptans and other constituents giving a positive Doctor test... 3 mg. per 100 cc.	
Corrosion test.....	Bad
Color.....	30
Water.....	Slight haze

The temperature at which the distillate was treated was 90° to 95° F. However, temperatures as low as 50° F. or even lower, or temperatures up to about 120° F. may be used. Temperatures above about 120° F. should not be used as above about that temperature sulphides will be formed which are of such a nature that they will not take up sulphur. Also above about that temperature a change may take place in some of the soaps or salts which renders them less effective in the reaction.

The distillate was conducted into the bottom of the first drum at approximately uniform rate of flow at the rate of eight hundred barrels per twenty-four hours.

During the first twenty-four hours of operation, the distillate leaving the top of the second drum was sweet to the Doctor test and gave a negative corrosion test. However, at about the end of this twenty-four hour period of operation, the distillate leaving the top of the second drum gave a positive Doctor test, indicating that the treated distillate was no longer sweet.

Air was now admitted along with the distillate going to the first drum. After allowing time for displacement of distillate in the two drums, the distillate leaving the second drum gave a negative Doctor test. More than a million barrels of distillate have been treated according to this example. A constant supply of air was found necessary to maintain the distillate sweet at the outlet of the second drum.

The characteristics of the above specified distillate after treatment as above described, while using air in admixture with the ingoing distillate were:

Lamp sulphur.....	0.014%
Hydrogen sulphide.....	None
Doctor test.....	Negative
Octane number.....	75
Corrosion test.....	Negative
Boiling range.....	Unchanged

It will be noted that the treated distillate is lower in total sulphur content than the untreated distillate, that it gives a negative Doctor test and a negative corrosion test, and that the treated distillate gained three units in octane rating.

Example 2

The apparatus was the same as in Example 1, except that instead of only the flake sodium hydroxide and sodium naphthenate being charged in the two drums, a mixture of 50% flake sodium hydroxide and 50% granular sodium chloride was charged into the two drums

along with sodium naphthenate in an amount equal to about 2%. The sodium chloride prevents caking of the flake sodium hydroxide. The distillate treated had the same general characteristics of the untreated distillate in Example 1, mercaptans, free sulphur and hydrogen sulphide being present in the untreated distillate. A gaseous mixture of 99.5% oxygen and 0.5% nitrogen and other inert constituents of the atmosphere was used instead of the air in Example 1. The distillate entered the bottom of the first drum as in Example 1, at the same rate as in Example 1. Unless the mixture including the oxygen was introduced into the oil to be treated, the distillate leaving the second drum became sour. The treated distillate was sweet, gave a negative corrosion test and showed an improvement of two units in octane rating. The introduction of gaseous oxygen is preferably done continuously, although it may be done periodically, but the periods of introduction should not be so far separated as to permit the distillate leaving the second drum to become sour.

Example 3(a)

Two grades of naphtha were made from the same crude oil, one grade having the low end boiling point of 325° F. and the other grade having the high end boiling point of 400° F.

The grade having the low end boiling point of 325° F. was treated according to this example. It had the following specifications:

Beaumé gravity.....	54°
Water moisture.....	Slight haze
Hydrogen sulphide.....	Contained an appreciable amount, but percent was not determined
Free sulphur.....	Contained free sulphur, but percent was not determined
Mercaptans and other substances giving a positive Doctor test.....	4 mg. per 100 c. c.
Octane number.....	70
Color.....	30
Corrosion test.....	Positive
Initial boiling point.....	166° F.
End boiling point.....	325° F.

The apparatus consisted of one vertical steel drum five feet in diameter and fifteen feet high. This drum was filled to a depth of ten feet with a mixture consisting of 50% flake sodium hydroxide and 50% granular rock salt (sodium chloride) and sodium naphthenate. This mixture in the drum was placed on top of two feet of ½ to 1½ inch mesh gravel. The naphtha to be treated entered the very bottom of the drum, flowing upward and out of the top of the drum to finished storage. The naphtha entered the bottom of the drum as a continuous stream at the same rate as in Example 1.

Substantially pure gaseous oxygen was introduced into the drum along with the untreated naphtha. The oxygen was required to maintain the activity of the sweetening materials in the drum.

The treated distillate was sweet, and gave a negative corrosion test. Its color was 30, it was free of water moisture and it showed an improvement of two units in octane number.

Example 3(b)

The naphtha treated according to this example

is the high end boiling naphtha referred to in Example 3(a).

It had the following characteristics:

Beaumé gravity.....	42°
Initial boiling point.....	290° F.
End boiling point.....	400° F.
Hydrogen sulphide.....	None
Free sulphur.....	None
Water.....	No haze
Corrosion test.....	Negative
Mercaptans and other constituents giving a positive Doctor test.....	3 mg. per 100 c. c.
Octane number.....	59

The apparatus was the same as in Example 3(a), the drum likewise containing a mixture of flake sodium hydroxide, granular sodium chloride and sodium naphthenate in the same proportions of Example 3(a), and the drum was filled to the same extent. The stream of naphtha to be treated entered the bottom of the drum and flowed out of the top of the drum through a pipe as in Example 3(a).

Ten pounds of flowers of sulphur were made into the form of a slurry with some of the naphtha and fed into the stream of naphtha entering the bottom of the drum. The sulphur was taken up by the mixture in the drum by adhesion or filtration or both, whereby a mixture of solid sodium hydroxide and elemental sulphur was formed. This mixture sweetened the naphtha for a period of time, but unless gaseous oxygen was introduced into the untreated oil entering the drum, the oil leaving the drum would begin to show a positive Doctor test which would persist positive until gaseous oxygen was introduced into the oil to be treated.

The treated oil was sweet and also gave a negative corrosion test. It had an octane number of 61 (an increase of two units) and its color was 30.

In Examples 1, 2 and 3(a) the hydrogen sulphide contained in the distillate reacted during the treatment of the distillate with a portion of the sodium hydroxide to form a sodium sulphide, and in Example 3(b) the sulphur introduced as a slurry reacted with a portion of the sodium hydroxide to form a sodium sulphide so that in each instance the distillate was treated, in the presence of sodium naphthenate and air or oxygen, with a reagent including sodium hydroxide and a sodium sulphide.

Example 4

The distillate treated in this example was the same as that treated in Example 1, but before introducing the distillate into the drums they were filled to a depth of eight feet with a mixture containing approximately 89% sodium hydroxide in flake form, 9% sodium monosulphide, and 2% sodium naphthenate. The distillate was then introduced into the first column along with air and flowed upwardly through the mixture of sodium hydroxide, sodium sulphide and sodium naphthenate therein. The distillate was discharged at the top of that drum into a pipe which carried it to the bottom of the second drum. It flowed upwardly through the second drum through the sodium hydroxide, sodium sulphide and sodium naphthenate therein and was discharged at the top. The distillate leaving the second drum gave a negative corrosion test and a negative Doctor test, indicating that it had been sweetened. The distillate remained sweet

and showed no signs of reverting to its unsweetened condition.

The oxygen used as described above in the foregoing description and in the examples may be oxygen in the form of air, pure oxygen or mixtures of oxygen and inert gases richer in oxygen than the air of the atmosphere. The oxygen should be introduced into the oil to be treated in an amount or at such a rate to maintain the treated hydrocarbon oil or distillate sweet to the Doctor test. This may readily be accomplished by introducing the oxygen into the oil to be treated through a pipe provided with a regulating valve. The valve is then regulated to provide the necessary oxygen in accordance with Doctor tests made upon the treated oil. The oxygen may be introduced into the oil to be treated as a continuous stream or it may be introduced periodically. However, I prefer to introduce it as a continuous stream. If it is introduced periodically for some time, the periods of introduction should not be so far separated as to permit the treated oil to become sour.

The sodium naphthenate used in each example was prepared by mixing 20 parts of 1.20 specific gravity, or 19% sodium hydroxide solution with 10 parts of naphthenic acid having a carbon content of six to twenty-four atoms in twenty-five parts of the oil or distillate of the type to be treated. The mixture was thoroughly agitated and then let stand in a quiescent condition until it separated into three distinct layers. The top layer was the hydrocarbon oil or distillate, the middle layer was the sodium naphthenate and the bottom layer was the excess of sodium hydroxide solution. The mixing of the sodium hydroxide, the naphthenic acid and the hydrocarbon oil or distillate can take place at any temperature above that at which the sodium hydroxide would solidify up to a temperature of about 120° F.

The concentration of the sodium hydroxide solution used in preparing the sodium naphthenate may vary from about 15% to about 30%, but a concentration of about 19% is preferred because when an aqueous sodium hydroxide solution of that concentration is used the resulting sodium naphthenate will contain approximately 66.67% of oil and about 8% water, both by volume, will be almost transparent, and insoluble both in the oil which forms above it and the sodium hydroxide solution below it. Also the sodium naphthenate produced by using a 19% aqueous solution of sodium hydroxide is more reactive with the octane depressing constituents contained in hydrocarbon oils and distillates of various qualities, especially when used in the treatment of aviation gasoline. That is particularly important as the quantities of anti-knock constituents are low in untreated aviation gasoline and it is extremely difficult, and in some cases impractical, to treat aviation gasoline by the conventional methods without permanently injuring it.

If sodium hydroxide of a concentration higher than about 19% is used the sodium naphthenate which is formed will be more or less flocculent and when added to the treating drum and the oil or distillate passed therethrough, will tend to become dispersed in the oil or distillate and carried out of the drum. If the concentration of the sodium hydroxide is lower, the resulting sodium naphthenate tends to go into solution in the excess sodium hydroxide and forms a gel with the hydrocarbon oil or distillate and more sodium

hydroxide has to be added to take up excess water and to salt out the sodium naphthenate. In other words, if a sodium hydroxide solution of a concentration other than about 19% is used it subsequently will be necessary either to add water or anhydrous sodium hydroxide, depending upon whether the concentration was above or below about 19%, in order that the formed sodium hydroxide will be in its most effective condition to promote contact between the hydrocarbon oil or distillate being treated and the other conditioning reagents, and to bring about a sweetening of the oil and the removal of corrosive agents therefrom.

The balance between the hydrocarbon oil or distillate and the water present in the sodium naphthenate which is formed is important and depends on the concentration of the sodium hydroxide solution which is used. The permissible amount of water which may be present in the sodium naphthenate is from about 6% to about 10% although about 8% is preferred. During the treatment of the oil or distillate the anhydrous sodium hydroxide will withdraw a certain amount of the water from the soap or salt solution and if the amount of water contained in the oil or distillate and taken up by the soap or salt solution is not sufficient to compensate for water taken from the soap or salt solution by the sodium hydroxide, water, preferably in the form of steam, should periodically be added to the reagent mixture in the treating drums so that the water content of the soap or salt solution will be maintained approximately at 8%. The amount of hydrocarbon oil or distillate which the sodium naphthenate should contain may vary from about 60% to about 70% although about 66.67% is preferred. As indicated above, the use of an aqueous sodium hydroxide solution of about 19% will produce sodium naphthenate containing about 8% water and about 66.67% hydrocarbon oil or distillate. If a solution of sodium hydroxide of lower concentration, for example, a concentration of about 15%, is used the resulting sodium naphthenate will contain about 12% water and less hydrocarbon oil or distillate, the additional water displacing or driving out a part of the hydrocarbon oil or distillate. On the other hand, if the concentration of the sodium hydroxide is higher, for example, about 25% or 30%, the resulting sodium naphthenate will contain 1% or less of water and will be flocculent and disperse throughout the oil. In its flocculent state the sodium naphthenate has less wetting properties and accordingly does not as well promote contact between the hydrocarbon oil or distillate and the other reagents and does not promote those reactions which cause the hydrocarbon oil to be sweetened and the corrosive agents removed.

While specific reference has herein been made to sodium naphthenate for promoting the sweetening of the hydrocarbon oil or distillate and for promoting the removal of corrosive agents, it is to be understood that soaps or salts other than sodium naphthenate may be used for promoting the sweetening of the oil. The only essential seems to be that the soap or salt must be of metal which forms a soluble sulphide. If a soap or salt of a metal which forms an insoluble sulphide is used, it will react with sulphur present or the sodium sulphides present to form insoluble sulphides which will precipitate out and no sweetening of the oil will be obtained. I have found that soaps or salts formed by an alkali metal base

and any of the following acids are effective in promoting the sweetening of hydrocarbon oils or distillates: Gluconic, p-toluenesulfonic, sulfanilic, adipic, maleic, anthranilic, silicofluoric, arsenic, arsenous, glycolic, succinic, phthalic, salicylic, silicic, pyrophosphoric, benzoic, orthophosphoric thiocyanic, citric, stearic, oleic, abietic and naphthenic.

Likewise, it is not necessary that sodium naphthenate be used in order to promote those reactions which cause the removal of corrosive agents present in the oil being treated, although it does not appear that every soap or salt of a metal which forms soluble sulphides is effective in promoting the removal of corrosive agents. However, I have found that soaps or salts formed from alkali metal bases and sulfanilic, arsenic, glycolic, succinic, thiocyanic and naphthenic acids were effective both in promoting the sweetening of the hydrocarbon oil or distillate and in the removal of corrosive agents therefrom.

In each of the examples given, the soap or salt was first formed and added to the treating solution. However, it will not always be necessary to first form the sodium naphthenate or other salt and add it as such to the treating solution. If the hydrocarbon oil or distillate to be treated contains an acid which will react with the sodium hydroxide in the treating drums to form a soap or salt of a metal which forms a soluble sulphide, as, for example, when the oil or distillate is derived from a naphthenic base crude and contains naphthenic acid, it will not be necessary to first form the soap or salt and add it to the other reagent or reagents. In such a case it will be sufficient if the oil and the sodium hydroxide or the oil and the sodium hydroxide and other reagents are circulated through the treating drum until a sufficient amount of the soap or salt has been formed, by reaction between the sodium hydroxide and the acid content of the oil or distillate, to promote the sweetening of the oil or distillate, or both sweetening of the oil or distillate and the removal of corrosive agents. However, even in such cases it is desirable to first form the soap and add it to the other reagent or reagents, due to the length of time it may take to form a sufficient amount of the soap or salt to effectively promote the sweetening of the oil or distillate. But regardless of how the soap or salt is formed, the essential thing is that it, like the uncombined oxygen, should be present when the oil or distillate is contacted with the sodium hydroxide, or the sodium hydroxide, sodium sulphide and sulphur.

The treatment of the oil or distillate may be carried out at any temperature which normally would exist or at any temperature up to about 120° F. The temperature at which the oil or distillate is treated should not be permitted to rise above about 120° F. because it has been found that above about that temperature the sodium naphthenate or other soap or salt is less effective in promoting the sweetening of the oil or distillate and the removal of corrosive agents therefrom, probably due to the formation of undesirable polysulphides which have a very low affinity for free sulphur. At any rate, when sodium naphthenate which is formed above about that temperature is used the oil or distillate does not settle bright and clear and sulphur is not removed. The pressure under which the treatment takes place is immaterial. It may be at atmospheric or at a higher or lower pressure,

The amount of oxygen admitted to the treating drums, either as such, or as air, may vary within considerable limits, but ordinarily 0.01 cubic feed of oxygen per gram of the mercaptan previously determined to be present in the oil or distillate will be sufficient.

The relative amounts of the sodium hydroxide, sodium sulphide and sodium naphthenate or other soap or salt used in the treatment of the oil or distillate should be held in relatively narrow limits if the best results are to be obtained. A few percent of the soap or salt, for example, 1% to 3% ordinarily is sufficient and the sodium hydroxide and sodium sulphide should be present in a ratio of about 10:1 or 11:1. When the amount of sulphur contained in the oil or distillate is not sufficient to completely convert the mercaptans into sulphides an amount of sulphur sufficient to make up such deficiency should be added to the mixture of sodium hydroxide, and soap or salt, or sodium hydroxide, sodium sulphide and soap or salt in the treating drums.

Hydrocarbon oil distillates obtained from straight run distillation of petroleum, or from distillations following cracking of petroleum distillates or residues, can be treated according to the process of the present invention.

While the process of the present invention has been described in considerable detail and various examples have been given, it is to be understood that such detailed description is by way of exemplification and that various changes within the scope of the appended claims may be made without departing from the invention or losing any of the advantages thereof.

What is claimed is:

1. In a process for sweetening hydrocarbon oil in which the oil is contacted with solid alkali metal hydroxide under conditions which result in the formation of an alkali metal monosulphide as a product of the reactions involved in the treatment of the oil, the improvement which comprises performing said contact while the oil is in the liquid phase and in the presence of added, extraneous, uncombined oxygen and a salt, of a metal which forms water soluble sulphides, said contact taking place at a temperature not exceeding about 120° F.

2. The process of sweetening hydrocarbon oil which comprises contacting the oil in the liquid phase with solid alkali metal hydroxide at a temperature not exceeding about 120° F. and in the presence of free sulphur, added extraneous uncombined oxygen and a salt, the metal of which forms water soluble sulphides.

3. The process of sweetening hydrocarbon oil which comprises adding uncombined oxygen to the oil while the oil is in the liquid phase, and contacting the mixture of oil and oxygen in the presence of free sulphur with solid alkali metal hydroxide and sodium naphthenate at a temperature not exceeding about 120° F.

4. The process of sweetening hydrocarbon oil containing free sulphur which comprises contacting the oil in the liquid phase, and in the presence of added extraneous uncombined oxygen, with a mixture including solid sodium hydroxide, sodium naphthenate and a solid alkali metal monosulphide.

5. The process of sweetening hydrocarbon oil which comprises contacting the oil in the liquid phase at a temperature not exceeding about 120° F. and in the presence of free sulphur, added extraneous uncombined oxygen and a salt of a metal which forms water soluble sulphides, with

a mixture including a solid alkali metal hydroxide and a solid alkali metal sulphide.

6. The process of sweetening hydrocarbon oil which comprises adding uncombined oxygen to the oil in the liquid phase and contacting the mixture of oil and oxygen, at a temperature not exceeding about 120° F. and in the presence of sodium naphthenae, with a mixture including a solid alkali metal hydroxide, a solid alkali metal monosulphide and elemental sulphur.

7. The process of sweetening hydrocarbon oil which comprises contacting the oil in the liquid phase at a temperature not exceeding about 120° F. and in the presence of free sulphur, added extraneous uncombined oxygen and a salt of a metal which forms water soluble sulphides, with a mixture including solid sodium hydroxide and solid sodium sulphide.

8. The process of sweetening hydrocarbon oil which comprises adding uncombined oxygen to the oil while the oil is in the liquid phase and contacting the mixture of oil and oxygen, at a temperature not exceeding about 120° F., with a mix-

ture including elemental sulphur, a solid alkali metal hydroxide and a salt of a metal which forms water soluble sulphides, which soap contains from about 6% to 10% water.

9. The process of sweetening hydrocarbon oil which comprises treating the oil in the liquid phase at a temperature not exceeding about 120° F. and in the presence of added extraneous uncombined oxygen and sodium naphthenate containing about 8% water, with a mixture including elemental sulphur and solid sodium hydroxide.

10. The process of sweetening hydrocarbon oil which comprises contacting the oil in the liquid phase at a temperature not exceeding about 120° F. and in the presence of free sulphur, added extraneous uncombined oxygen and a soap, of a metal which forms water soluble sulphides and which contains from about 6% to 10% water, with a mixture including a solid alkali metal hydroxide and a solid alkali metal sulphide.

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