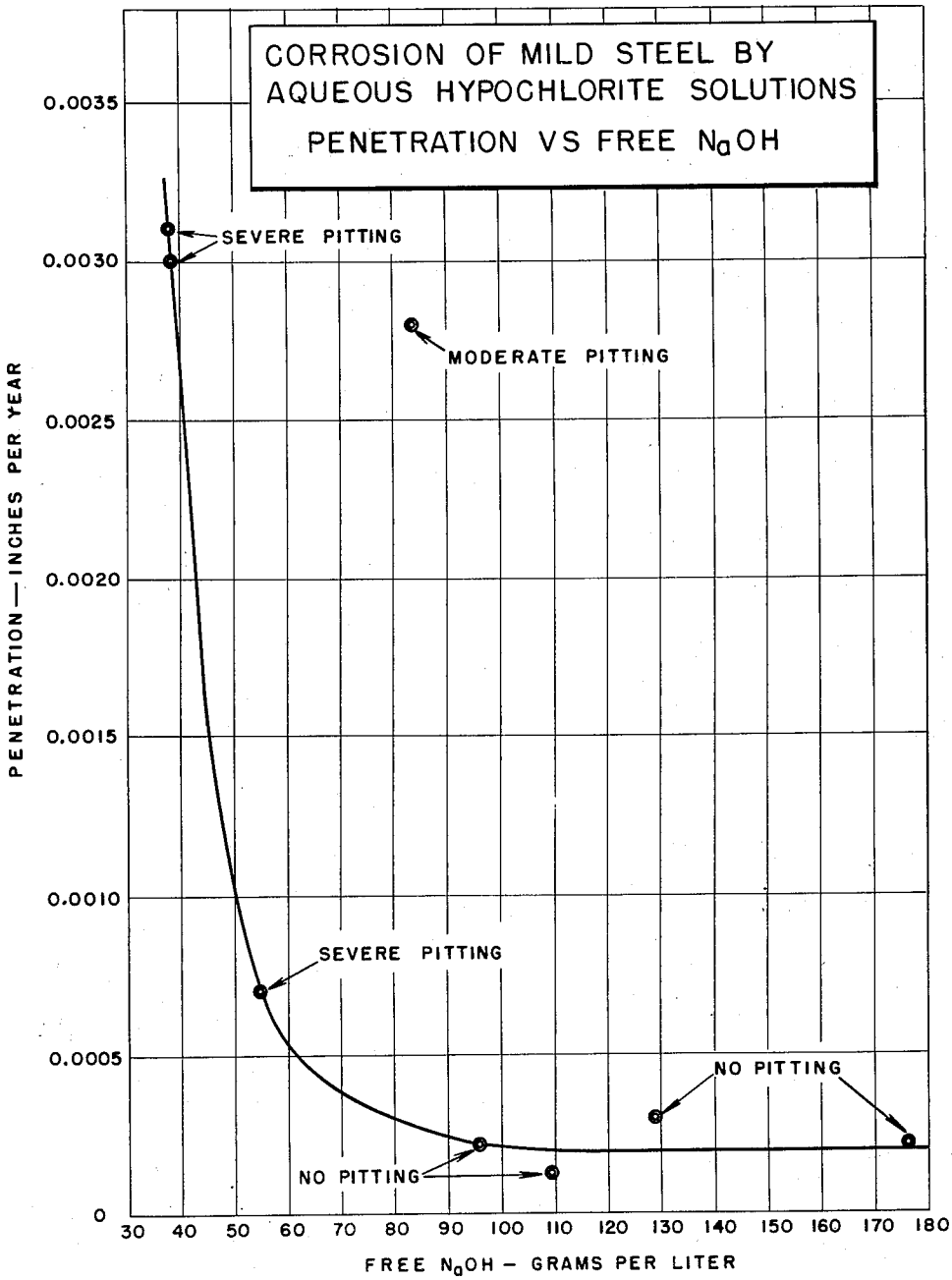
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METHOD FOR SWEETENING HYDROCARBONS

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METHOD FOR SWEETENING HYDROCARBONS

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The present invention is directed to a method for sweetening hydrocarbons. More particularly, the invention is directed to an improved method of sweetening sour petroleum distillates and in its more specific aspects is directed to sweetening sour petroleum distillates having a boiling point no greater than 700° F.

Prior to the present invention it has been known to sweeten hydrocarbons and particularly sour petroleum distillates with alkaline hypochlorite solutions. However, the methods of sweetening sour hydrocarbons with alkali metal hypochlorite solution as taught in the literature have many disadvantages. The process of the prior art is uneconomical because the sweetening agent is partly consumed in reactions other than sweetening. Another great disadvantage is that the prior art solutions have been exceedingly corrosive to steel equipment in which the treating procedures have been carried out. Besides the above disadvantages, the naphtha is chlorinated, which is undesirable. Furthermore, the powerful oxidizing tendency of hypochlorite causes any hydrogen sulfide present in the naphtha to be converted to free sulfur, which in turn causes the sweetened naphtha to fail to pass the copper strip corrosion test.

It is, therefore, the main object of the present invention to provide an improved sweetening process in which the disadvantages of the prior art are substantially eliminated.

Another object of the present invention is to provide an improved alkaline hypochlorite treating reagent which is substantially non-corrosive to steel equipment and which does not deleteriously affect hydrocarbons sweetened therewith.

A further object of the present invention is to provide an improved alkaline hypochlorite treating reagent in which the tendency toward undesired reagent consuming reactions is reduced to a minimum.

A still further object of the present invention is to sweeten sour petroleum distillates having boiling points no greater than 700° F. with a hypochlorite solution which does not cause chlorination of the naptha.

It has now been discovered that contrary to the teachings of the prior art, improved results may be obtained by employing alkaline hypochlorite solutions containing in excess of 90 grams of free alkali metal hydroxide per liter in sweetening hydrocarbons having boiling points no greater than 700° F.

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Thus, the present invention may be briefly described as involving the contacting of a sour hydrocarbon boiling up to 700° F. with an alkaline hypochlorite solution such as one containing sodium hydroxide in excess of 90 grams of free sodium hydroxide per liter and available chlorine in excess of 1 gram per liter. The sour hydrocarbon and the alkaline hypochlorite solution are contacted intimately, separated and the sweetened hydrocarbon recovered. The sweetened hydrocarbon may be subjected to a washing operation with water to remove any hypochlorite which may be suspended or entrained therein.

The temperature, at which the treating operation in accordance with the present invention may be conducted, may range from about 40° up to about 120° F. with temperatures in the range from 60° to 90° F. being preferred. When sweetening sour volatile hydrocarbons it may be necessary to superimpose pressure on the treating equipment to maintain the hydrocarbon in the liquid state.

The alkaline hypochlorite solution employed in the practice of the present invention may be prepared by any one of the well known methods of preparing hypochlorite solutions. A convenient method of preparing hypochlorite solution is merely to bubble chlorine gas into a solution of alkali metal hydroxide such as sodium hydroxide of proper strength to make the hypochlorite. While sodium hydroxide is the preferred alkali metal hydroxide, by virtue of its availability, it is within the scope of my invention to use other alkali metal hydroxides in lieu of sodium hydroxide; for example, potassium hydroxide and lithium hydroxide may be employed in the practice of my invention.

The type of hydrocarbon which may be treated in accordance with the present invention may range from the liquefied petroleum gases such as propane and butane up to and through sour hydrocarbons in the heating oil boiling range. For example, besides propane and butane, the hydrocarbons in the gasoline boiling range boiling from about 85° up to about 450° F., the hydrocarbons in the kerosene boiling range and those in the heating oil boiling range including hydrocarbons

boiling up to about 700° F. may be sweetened in accordance with the practice of the present invention. These hydrocarbons may be obtained from crude petroleum or from conversion operations such as thermal or catalytic cracking operations, and the like. Prior art workers have been unable to sweeten cracked stocks but my reagent may be successfully employed in sweetening such fractions.

The treating operation in which the hydrocarbons are contacted with the alkaline hypochlorite solution may be conducted in any one of several ways. For example, the alkaline hypochlorite and the sour hydrocarbon may be contacted by admixing the treating reagent and the hydrocarbons in mixing pumps, incorporators, vessels equipped with stirring devices such as propellers, and the like, constructed of ferrous metals or by jetting the sour hydrocarbon into a pool of alkaline hypochlorite solution. Mixing may be accomplished by circulating the alkaline hypochlorite solution and the naphtha from one vessel to another. Contacting may also be obtained countercurrently in a suitable contact tower equipped with equipment such as cascade trays, bell cap trays, and the like. There are many admixing devices on the market which may be used in the practice of the present invention. It is a feature of the present invention that my improved process and reagent may be used in ferrous metal equipment without destruction thereof.

In order to illustrate the invention further, sour kerosenes having copper numbers of 38 and 66, respectively, were treated with hypochlorite solutions containing available chlorine and free sodium hydroxide in amounts disclosed in the literature. The hypochlorite solutions and the sour kerosene were intimately contacted, separated after treatment and the treated kerosene subjected to tests. The results of these tests are given in the following table:

TABLE I

Hypochlorite sweetening of sour kerosenes

Hypochlorite solution, gms./lit.		Copper number of charge stock	Hypochlorite treat		Doctor test	Residual acidity of treated stock
Available Cl_2	Free NaOH		Vol. percent	Stoichiometric equivalents		
10.2	26	38	25	6.0	Neg.	2.19
10.2	2	38	25	6.0	Neg.	3.25
10.3	51	66	25	3.5	Neg.	2.80
10.2	26	66	25	3.5	Neg.	3.28
10.2	2	66	50	7.0	Neg.	5.52

It will be apparent from the data in the foregoing Table I and specifically from the number of stoichiometric equivalents of reagent required to obtain a doctor sweet product that a considerable number of side reactions were taking place in the solutions made up in accordance with the prior art. It will be apparent further that these side reactions consume hypochlorite and make the process quite expensive. The high residual acidities of the treated naphtha indicate chlorination of the naphtha is taking place, which is undesirable.

In order to demonstrate the corrosiveness of the hypochlorite solutions of the prior art to steel, steel specimens were immersed in hypochlorite solutions containing variable quantities of available chlorine and free NaOH for periods ranging from 19 to 25 days. The steel specimens, prior to immersion in the hypochlorite solution, were weighed and after the period of immersion stated were removed, washed and reweighed to determine the metal loss. Visual observations of the steel specimens with respect to the attack of the metal by the hypochlorite were also made. The results of these tests are given in the following table:

TABLE II

Steel strip corrosion test in hypochlorite solutions

Hypochlorite solution, gms./lit.		Average corrosion rate of steel strip, in./yr.	Test, days	Remarks
Available Cl_2	Free NaOH			
103	38	0.0031	25	Severe pitting.
89	55	.0007	25	Do.
84	38	.0030	19	Do.
64	83	.0028	25	Moderate pitting.

It will be noted from the data given in Table II that the hypochlorite solutions containing 83 and less grams of sodium hydroxide per liter showed marked effect in corroding the specimens of steel as evidenced by severe pitting. It will be noted that there seems to be no correlation of the effect of the available chlorine on corrosivity of the hypochlorite solution to the metal.

Besides the deleterious effects mentioned before, as shown by the data in Tables I and II, it has been found that hypochlorite solutions containing less than 90 grams of sodium hydroxide per liter when contacted with petroleum distillates containing H_2S result in the H_2S being converted to free sulfur which is well known to be detrimental to hydrocarbons to be employed as solvents, or as fuels.

In order to illustrate the practice of the present invention, a sour kerosene having a copper number of 38 was contacted with hypochlorite solutions containing approximately 92, 139 and 700 grams of free sodium hydroxide per liter. The amounts of available chlorine in these solutions were 11.7, 39.2 and 7.5 grams per liter respectively. After separation of the hypochlorite from the sweetened kerosene the kerosene was tested and the following results were obtained:

TABLE III

Sweetening of sour kerosene with high-alkalinity hypochlorite solution

Hypochlorite solution, gms./lit.		Copper number of charge stock	Hypochlorite treat		Doctor test	Residual acidity of treated stock [1]
Available Cl_2	Free NaOH		Vol. percent	Stoichiometric equivalents		
11.2	92.2	38	6.0	1.66	Neg.	0.30
39.2	139.0	38	2.0	1.85	Neg.	.20
7.5	700	38	7.5	1.33	Neg.	.30

[1] Mls. of 0.10 N KOH per mls. of treated stock.

It will be immediately apparent from the foregoing data that the stoichiometric equivalents of reagent required to obtain a doctor sweet product are considerably reduced over that of Table I, the amount being approximately one-fourth to one-half of that shown for Table I. It will also be apparent that the residual acidity of the

treated stock is approximately one-tenth of that shown in Table I and particularly where the copper number of the feed stock was the same. With the high copper number stock it will be apparent that the residual acidity in one case was approximately one-twentieth of that shown when the prior art reagents were employed.

In order to determine conclusively the superiority of the treating solutions of the present invention over the prior art solutions, the sour kerosenes used in obtaining the data of Table I were treated as in the examples of Table I with hypochlorite solutions containing available chlorine and free sodium hydroxide in amounts disclosed in the literature. Smaller amounts of reagent were used then in the examples of Table I. After contacting the sour kerosene and sweetening agent, and recovering the treated kerosene, it was tested and the following results were obtained:

TABLE IV

Hypochlorite solution, gms./lit.		Copper number of charge stock	Hypochlorite treat		
Available Cl_2	Free NaOH		Volume percent	Stoichiometric equivalents	Doctor test
10.2	26	38	10	2.4	Pos.
10.2	2	38	10	2.4	Pos.
10.2	2	66	25	3.5	Pos.

It will be apparent from this foregoing data that quantities of the prior art sweetening solutions amounting to 2.4–3.5 stoichiometric equivalents failed to produce doctor sweet products. It will be apparent also that the amount of the prior art sweetening solution used in these examples was 1.3 to 2.7 times the amount of my improved sweetening solution which was used in the examples of Table III in which doctor sweet products were obtained.

In order to illustrate the non-corrosivity of the solutions employed in the practice of the present invention, specimens of steel similar to that described in the preceding examples were immersed in hypochlorite solutions containing in excess of 96 grams of free sodium hydroxide per liter. These weighed specimens remained in the hypochlorite solution for periods of time ranging from 19 to 25 days, after which they were removed from the corrosive solutions, washed with water, dried and reweighed; the metal loss was calculated as inches per year. In addition, the condition of the metal was observed to determine whether or not it had become pitted. These results are shown in Table V as follows:

TABLE V

Steel strip corrosion tests of high alkalinity hypochlorite solutions

Composition of hypochlorite solution, gms./lit.		Average corrosion rate of steel strips, inch/yr.	Time on test, days	Remarks
Available Cl_2	Free NaOH			
45	109	0.0001	25	No pitting.
22	129	.0003	25	Do.
109	176	.0002	19	Do.
102	96	.0002	19	Do.

Comparing these results with those shown in Table II it will be immediately apparent that the solutions of the present invention give substantially improved results.

The features of the present invention will become even more apparent by reference to the single figure in which the data presented in Tables II and V are plotted. The amount of free sodium hydroxide in grams per liter has been plotted against the corrosion reported in inches per year. By reference to the drawing it will be seen that at 83 grams of free NaOH per liter only moderate pitting occurred. This amount of free NaOH in the hypochlorite solution resulted in a penetration of 0.0028 inch per year of the steel specimen. Further reference will show that at 96 grams of free NaOH per liter the corrosion rate was 0.0002 inch per year. It will be apparent that the hypochlorite solution containing 83 grams per liter of free NaOH caused moderate pitting of the steel specimen. Since only moderate pitting occurred at 83 grams of free NaOH per liter and no pitting occurred when a solution containing 96 grams of free NaOH was employed, it is safe to conclude that solutions containing in excess of 90 grams per liter will be substantially non-corrosive to steel and that these solutions may be safely used in steel equipment in which the treating reaction is conducted.

Besides the solutions of the present invention being non-corrosive, non-reactant with the naphtha and inexpensive to employ, they also do not convert hydrogen sulfide to free sulfur. It was found that free sulfur was not formed when solutions containing 96 grams of free NaOH per liter were employed in treating naphtha containing hydrogen sulfide.

A number of runs were made in which a mixture of cracked and crude petroleum naphtha was contacted with a hypochlorite solution containing 10 grams of available chlorine per liter of reagent and 139 grams of sodium hydroxide per liter of reagent. The naphtha had a copper number of 6 and was contacted with 2, 3 and 4 volume percent of the reagent. The stoichiometric equivalents of hypochlorite employed in the different treats were respectively 3, 4½ and 6. After the naphtha had been contacted with the solutions in the various amounts, the reagent was separated therefrom, washed with water and the treated naphtha tested for copper number. It was found that the copper number of the naphtha treated with 2 volume percent of the reagent had been reduced from 6 to 2, while the naphtha treated with 3 volume percent of the solution had a copper number of 1, a reduction of 5 units. The naphtha contacted with 4 volume percent of the hypochlorite solution mentioned before was doctor sweet as indicated by the aforementioned doctor test.

A high sulfur refined oil which was a sulfur dioxide extract of a kerosene fraction was then treated with the same hypochlorite solution, runs being made with 5, 10, 12 and 13 volume percent of the reagent. In these runs the stoichiometric equivalents of hypochlorite employed were respectively 0.8, 1.6, 1.9 and 2.1. After the reagent had been separated from the treated solvent extract, washed with water, the solvent extract was tested for copper number and was found to have copper numbers of 29, 10, less than 1 and finally the one contacted with 13 volume percent passed the doctor test. It will be apparent from these data that a marked reduction in copper number is obtained by using small quantities of the treating reagent of the present invention and furthermore it is possible to obtain a completely sweetened product.

It is possible to employ even smaller quantities of reagents than those employed in the foregoing examples. If it is desired to use smaller

quantities the amount of reagent may be decreased by employing a hypochlorite solution containing greater amounts of available chlorine than shown in the preceding examples. As an illustration thereof, the foregoing high octane number naphtha having a copper number of 6 was contacted with a hypochlorite solution containing 75 grams of available chlorine per liter of reagent and containing 140 grams of sodium hydroxide per liter. The high octane naphtha was contacted with 0.25, 0.5 and 0.6 volume percent of reagent which amounted respectively to stoichiometric equivalents of hypochlorite of 2.8, 5.6 and 6.7. After contacting with these amounts of the reagent the reagent was separated from the treated naphtha and the copper number of the treated naphtha after washing was determined and found to be respectively 2.5, 0.5 and the last sample was doctor sweet. It will be noted that the stoichiometric equivalents of hypochlorite in these runs were substantially identical to the stoichiometric equivalents of the previous runs indicating that the amount of treating reagent employed will depend to a large extent on the available chlorine in the hypochlorite solution.

Similar results may be obtained with the aforementioned solvent extract when employing a hypochlorite solution containing 75 grams of available chlorine per liter and 140 grams of sodium hydroxide per liter. In runs of this nature the volume percent of the reagent employed may be decreased from 5 to 1 in one instance and from 10 to 1½ in another instance, while providing substantially the same stoichiometric equivalent of hypochlorite and obtaining substantially the same reduction in copper number. Specifically, sweetening may be obtained with the latter reagent employing 2.25 volume per cent of solution and a stoichiometric equivalents of hypochlorite of 2.7, whereas in the previous runs where 13 volume percent of the reagent having 10 grams per liter of available chlorine and 2.1 stoichiometric equivalents were necessary to obtain a doctor sweet product.

From the foregoing it will be apparent that the treating reagent of the present invention should contain more than 90 grams of free alkali metal hydroxide per liter and may contain available chlorine in amounts ranging from about 1 to 150 grams per liter. It is specifically contemplated in the present invention that hypochlorite solutions may be employed containing free alkali metal hydroxide in the range from about 90 to 700 grams per liter and available chlorine in the range from about 1 to 150 grams per liter.

Besides the naphthas mentioned specifically before, it is contemplated that the present invention may be applied to treatment of pentane and pentylene fractions, light naphthas from crude petroleum, thermally and catalytically cracked fractions, kerosenes and solvent naphthas. For example, the present invention has particular application to sweetening solvent naphthas such as one obtained from crude petroleum. Such naphthas boil in the range from about 300 to 400 °F. and may contain aromatic and naphthenic hydrocarbons besides a predominant amount of paraffins.

In order to illustrate the invention further a solvent naphtha obtained from a mixture of Texas crude petroleums was contacted with an alkaline hypochlorite solution containing available chlorine in the amount between 3 and 5 grams per liter and free sodium hydroxide in the range between 100 and 170 grams per liter at a temperature ranging from about 80 to 85° F. This solvent naphtha had a copper number of less than 1 and was sweetened in contact with the alkaline hypochlorite solution without excess consumption of reagent and without chlorination of the solvent naphtha. The naphtha was contacted with the hyprochlorite solution at a rate of about 14,000 barrels per day. The solvent naphtha treated in accordance with this procedure was found to pass a copper strip corrosion test which is the ordinary A. S. T. M. copper strip test modified to the extent that the copper strip is immersed in the naphtha for half an hour at its boiling point.

As shown by the several examples it is possible to treat the hydrocarbons in accordance with the present invention and to eliminate only part of the mercaptan content with the treating reagent of the present invention. It is contemplated that my invention may be used in connection with other well known treating processes such as for example the doctor sweetening process. In some instances it may be undesirable to sweeten completly, that is to reduce the copper number to where the naphtha passes the doctor test. In those instances hypochlorite solution might be followed by a treatment with doctor solution and the numerous equivalents thereof in the prior art. Conversely, the present invention might also be used in connection with other well known sweetening processes, for example in the treating process of the prior art where sour hydrocarbons are contacted with alcoholic solutions of alkali metal hydroxide, it might be desirable to follow such a treatment with the improved reagent of the present invention. Likewise the operation with the improved treating reagent might be followed by contact with the alcoholic solution of sodium hydroxide if desirable.

The nature and objects of the present invention having been fully described and illustrated, what I wish to claim as new and useful and to secure by Letters Patent is:

1. A method for treating petroleum distillates which comprises contacting in a ferrous metal container a sour petroleum distillate having a boiling point below 700° F. with an alkaline hypochlorite solution non-corrosive to said metal container containing in excess of 90 grams of free alkali metal hydroxide per liter and available chlorine in the range between one and five grams per liter, removing said hypochlorite solution from contact with said distillate and recovering a sweetened distillate.

2. A method in accordance with claim 1 in which the alkali metal hydroxide is sodium hydroxide.

3. A method in accordance with claim 1 in which the alkali metal hydroxide is potassium hydroxide.

4. A method in accordance with claim 1 in which the alkali metal hydroxide is lithium hydroxide.

5. A method for treating petroleum distillates which comprises contacting in a ferrous metal container a sour petroleum distillate having a boiling point below 700° F. with a sodium hypochlorite solution non-corrosive to said metal container containing sodium hydroxide in an amount in the range between 100 and 170 grams per liter and chlorine in the range between 3 and 5 grams per liter, removing said solution from contact

with said distillate and recovering a sweetened distillate.

ROBERT M. LOVE.

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