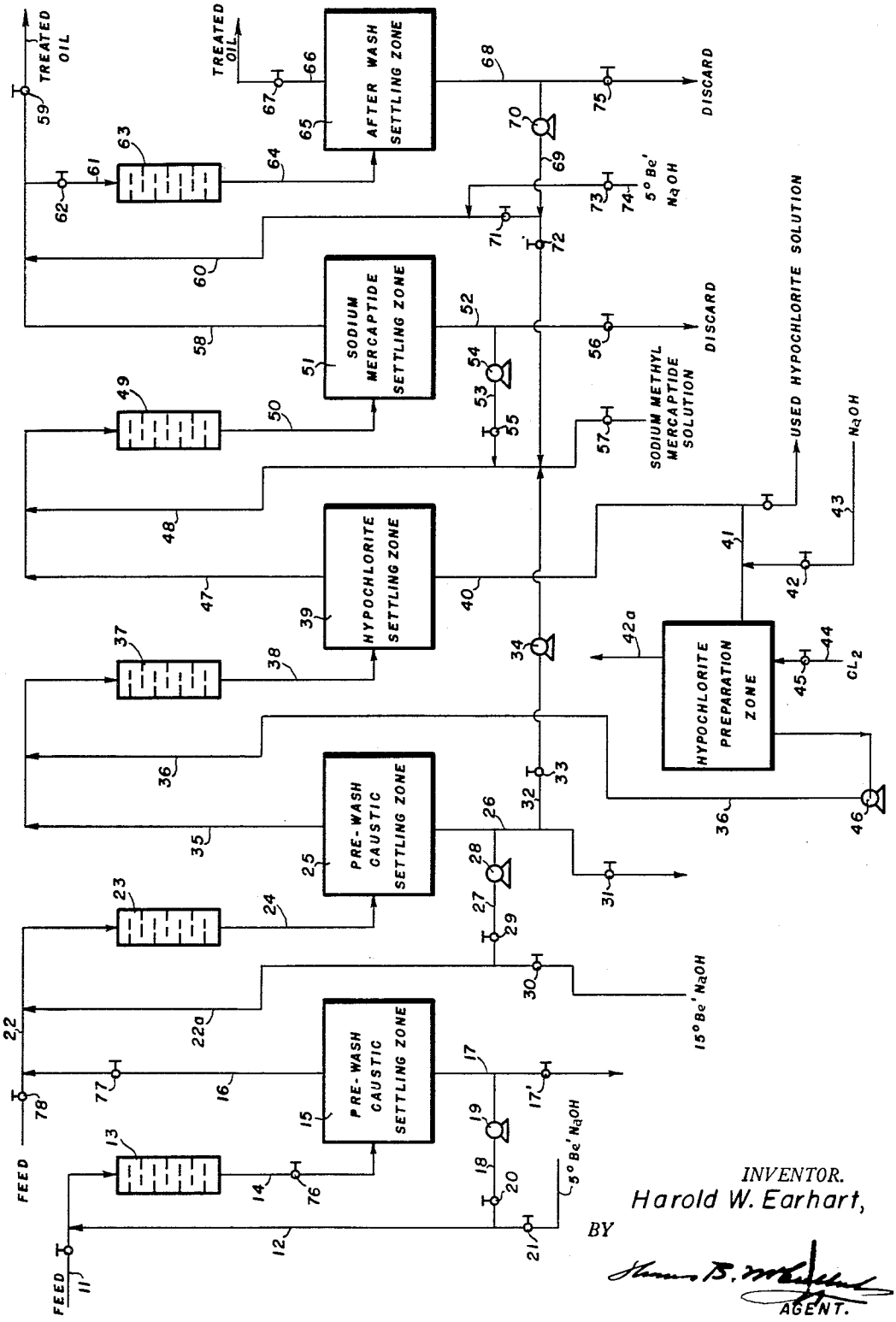
Oct. 18, 1955 H. W. EARHART 2,721,166

TREATMENT OF DISTILLATES WITH HYPOCHLORITE SOLUTION

Filed Oct. 23, 1952



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United States Patent Office 2,721,166 Patented Oct. 18, 1955

2,721,166

TREATMENT OF DISTILLATES WITH HYPOCHLORITE SOLUTION

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Application October 23, 1952, Serial No. 316,386

7 Claims. (Cl. 196—29)

The present invention is directed to a method for treating a hydrocarbon distillate. More particularly, the invention is directed to treating a petroleum distillate boiling below 750° F. which contains acidic chlorinated compounds. In its more specific aspects, the invention is directed to a method for treating a petroleum distillate with an alkaline hypochlorite solution following which the alkaline hypochlorite treated distillate is treated to convert acidic chlorinated compounds to innocuous compounds.

The present invention may be described briefly as involving treating a hypochlorite treated distillate boiling below 750° F. and containing acidic chlorinated compounds with a solution consisting of water, alkali metal hydroxide and an alkali metal mercaptide selected from the group consisting of aromatic mercaptides and aliphatic mercaptides having no more than 4 carbon atoms in the molecule.

The invention also includes the treatment of a hydrocarbon distillate boiling below 750° F. with an alkaline hypochlorite solution following which the alkaline hypochlorite solution is separated from the hydrocarbon distillate and the hypochlorite treated hydrocarbon distillate is then washed or contacted with an aqueous solution of an alkali metal hydroxide and an alkali metal mercaptide of the type illustrated for a sufficient length of time to convert acidic chlorinated compounds in the hydrocarbon distillate to innocuous compounds and to form in said distillate disulfides and in the solution of alkali metal hydroxide and alkali metal mercaptide an amount of alkali metal chloride and then employing the latter solution to contact additional quantities of the hypochlorite treated distillate containing acidic chlorinated compounds.

The mercaptans employed to make up the solution consisting of water, alkali metal hydroxide and alkali metal mercaptide may be an aliphatic mercaptan having no more than 4 carbon atoms in the molecule, such as methyl mercaptan, ethyl mercaptan, iso and normal propyl mercaptan and the butyl mercaptans, such as tertiary, primary and secondary butyl mercaptans or an aromatic mercaptan such as benzene thiol, a thiocresol such as ortho, meta, or para thiocresol, 2-phenyl 1-ethane thiol, 4 ethyl benzene thiol, methyl benzyl mercaptan, 2-naphthlene thiol, and 4-phenyl-1-benzene thiol.

The solution of alkali metal mercaptide may suitably be formed by extracting mercaptans from the feed stock prior to treatment with the hypochlorite solution provided hydrogen sulfide is removed from the feed stock prior to contact of the feed stock with an alkali metal hydroxide solution to form the alkali metal mercaptide. Removal of hydrogen sulfide may be accomplished by washing a feed stock containing hydrogen sulfide with a 5° Bé. aqueous sodium hydroxide solution or by distillation to remove hydrogen sulfide and light fractions. Preferably, hydrogen sulfide is removed with a sodium hydroxide solution.

After removal of hydrogen sulfide and/or other acidic material reactive with the hypochlorite solution the hydrogen sulfide-free feed stock is then contacted with a stronger aqueous sodium hydroxide solution, say one of about 15° Bé., to extract therefrom at least a portion of the mercaptans, particularly the low molecular weight mercaptans such as methyl, ethyl, propyl, and butyl mercaptans and also the aromatic mercaptans present. The higher mercaptans such as the pentyl and hexyl mercaptans may also be removed. Removal of such mercaptans is desirable since consumption of chlorine in the subsequent hypochlorite treating step is thereby reduced. The sodium mercaptide solution thus formed may then be used to treat the hypochlorite sweetened oil.

The alkali metal mercaptide solution may also be prepared by adding a mercaptan of the types illustrated to an equeous solution of alkali metal hydroxide.

When the alkali metal mercaptide solution is formed by extracting mercaptans from the feed stock, the solution may contain besides the alkali metal mercaptides, alkali metal phenolates, naphthenates, alkali metal salts of other carboxylic acids and unreacted alkali metal hydroxide and water. The presence of the salts of carboxylic acids and/or phenolates and naphthenates is not deleterious and does not affect the efficacy of the alkali metal mercaptide treat.

The hydrocarbon distillate employed as a feed stock in the present invention may be any hydrocarbon distillate such as a petroleum distillate boiling below 750° F. which may contain hydrogen sulfide, mercaptans and other acidic materials. Thus the feed stock to the present invention may be a liquefied normally gaseous hydrocarbon fraction, such as butane, or it may be a gasoline fraction boiling in the range from about 80° to about 450° F. or it may be a kerosene fraction boiling in the range from about 450° F. to about 650° F. or, as stated hereinbefore, the petroleum distillate may boil up to 750° F.

The solution employed to remove the acidity of the side reaction products which are present in the hypochlorite treated oil will consist of water, alkali metal hydroxide and alkali metal mercaptides. The alkali metal hydroxide may be present in an amount in the range from 1.0% by weight to 15% by weight and the alkali metal mercaptide may be present in an amount in the range from 50.0 to 600.0 mgs. (mgs. of RSNa–S per 100 ml.) with the remainder being water. Although it is preferred to use sodium hydroxide and hence a sodium mercaptide, it is within the purview of my invention to employ the other alkali metal compounds, such as those of lithium and potassium. Sodium hydroxide is preferred because of its economic availability.

In treating a hypochlorite treated oil with the treating reagent consisting essentially of water, alkali metal hydroxide and alkali metal mercaptide, an amount of treating reagent in the range from about 5% to about 30% by volume should be used with good results being obtained with about 20% by volume based on the hypochlorite treated oil.

The present invention will be conducted ordinarily at temperatures ranging from about 60° F. up to about 120° F. with temperatures within the range from about 75° F. to about 100° F. preferred. However, higher temperatures up to about 250° F. may be used under some conditions. When higher temperatures are used it may be desirable to superimpose pressure on the treating equipment to maintain the liquid phase.

The invention will be further illustrated by reference to the drawing in which the single figure is a flow diagram of a preferred mode.

Referring now to the drawing, numeral **11** designates a line through which is admitted a feed stock such as a sour hydrocarbon fraction as one in the gasoline boiling range containing, for example, mercaptans and hydrogen sulfide. The feed stock in line **11** has admixed with it by way of line **12** a solution of sodium hydroxide having, for example, a Bé. gravity of about 5°. The amount

of this caustic solution injected will be about 10% by volume based on the feed oil. The feed oil and the sodium hydroxide solution are intimately admixed in an incorporator or mixing device **13** which is shown as a baffle plate mixer but which may be any suitable mixing device, such as jets, agitators, contacting towers, centrifugal pumps and the like. Any contacting device which will give intimate admixture between the feed and the caustic may be suitable.

The admixture of feed and caustic solution is then discharged from incorporator **13** by line **14** into a first prewash settling zone **15** which may be any desirable form of settling tank. In pre-wash settling tank **15** the caustic pre-washed oil has substantially all of its hydrogen sulfide removed by the caustic and is discharged by line **16** for further treatment as will be described hereafter. The caustic solution is discharged from settling zone **15** by line **17** and preferably is recycled to line **12** by connecting line **18** containing a pump **19** and controlled by a valve **20**. From time to time it may be desirable to discard the caustic solution in part from line **17** and this may be done by opening valve **20**. When an amount of the caustic solution is discarded by opening valve **17'** in line **17** a similar amount of fresh caustic solution will be introduced into the system by opening valve **21** in line **12**.

The washed feed substantially free of hydrogen sulfide but still sour to the doctor test is withdrawn by line **16** and is admixed in line **22** with a caustic solution having a Bé. gravity of about 15° introduced by line **22***a* from a source which will be described in more detail hereinafter. The caustic washed feed in line **22** is then discharged thereby into a baffle-type incorporator **23** which is similar to the incorporator or mixing device **13**. In incorporator **23** intimate contact is effected between the caustic solution and the feed and the contacted mixture is then discharged by line **24** into a second prewash settling zone **25** which is of sufficient capacity to provide a suitable residence time for separation of the caustic solution from the caustic treated oil.

The first caustic washing operation with 5° Bé. sodium hydroxide solution removes hydrogen sulfide from the feed oil and the second caustic washing operation removes mercaptans, and also phenols, naphthenic and other carboxylic acids as well as other acidic bodies, if present in the feed. The solution resulting from the second caustic washing operation is free of sodium sulfide but does contain sodium mercaptide and may also contain sodium salts of the acidic materials mentioned and may be used as will be described further hereinafter.

The caustic solution from pre-wash settling zone **25** is discharged therefrom by line **26** and may be recycled by branch line **27** containing pump **28** and controlled by valve **29** to line **22***a* for admixture with the oil in line **22** for treating same as has been described. From time to time it may be necessary to add fresh caustic solution such as a 15° Bé. sodium hydroxide solution to the oil being treated in line **22**. This may be done by opening the valve **30** in line **22***a*. The caustic solution withdrawn from settling zone **25** in line **26** may be discharged in part from the system by opening valve **31** in line **26** but preferably is employed in a later stage of the process by discharging same into line **32** controlled by valve **33** and containing pump **34**. The subsequent employment of this caustic stream will be described in more detail hereinafter.

The pre-washed oil is removed from zone **25** by line **35** and has added thereto a hypochlorite solution which is introduced by line **36** from a source which will be described in more detail hereinafter. This hypochlorite solution may be a sodium hypochlorite solution or it may suitably be a calcium hypochlorite solution or any hypochlorite solution suitable for sweetening operations. The admixture of sodium hypochlorite solution and caustic washed oil in line **35** is discharged thereby into an incorporator **37** which is similar to incorporators **23** and **13**.

In incorporator **37** intimate contact is effected between the hypochlorite solution and the caustic washed feed and the contacted mixture is then discharged by line **38** into a hypochlorite settling zone **39** which is of sufficient capacity to provide a suitable residence time for separation of the hypochlorite solution from the hypochlorite treated oil.

The contacting of the oil in line **35** and incorporator **37** with the hypochlorite solution results in the formation in the oil of acidic chlorinated compounds of a type such as the sulfonyl and sulfenyl as well as the sulfinyl chlorides. These compounds are deleterious in motor fuel in that they affect the product quality of the finished motor fuel, such as the breakdown time or induction period (ASTM 525–46). In accordance with my invention, these acidic chlorinated compounds are converted to innocuous compounds as will be described further.

The hypochlorite solution separated from the treated feed in settling zone **39** is withdrawn therefrom by line **40** and routed by line **41** into a hypochlorite generation zone **42**. The hypochlorite solution flowing through line **41** may have added to it from time to time or continuously, if desired, an amount of sodium hydroxide which is accomplished by line **43** containing valve **42** connected to a source of caustic solution, not shown. Hypochlorite generation zone **42** is provided with a line **44** controlled by valve **45** connecting to a source of chlorine to allow formation in zone **42** of sodium hypochlorite solution which is withdrawn therefrom by line **36**, as has been described, containing pump **46**.

The hypochlorite treated oil is removed from settling zone **39** by line **47**; and there is admixed in line **47** with the hypochlorite treated oil a solution originally consisting essentially of water, sodium mercaptide and sodium hydroxide. The sodium mercaptide suitably may be sodium methyl mercaptide. This solution is introduced into line **47** by line **48** as will be described hereinafter. The admixture of sodium mercaptide solution and hypochlorite treated oil flows into an incorporating device **49** which is shown as a baffle-type incorporator but may be an incorporating device, such as incorporators **23**, **13**, or **37**, as has been described. The sodium mercaptide solution and the hypochlorite treated oil are intimately admixed in incorporator **49** and are then discharged by line **50** into a sodium mercaptide settling zone **51** which is similar to settling zones **39**, **25**, and **15**. After separation by gravity of the sodium mercaptide solution in zone **51**, the solution is withdrawn from zone **51** by line **52** and preferably is recycled to line **48** by branch line **53** containing pump **54** and controlled by valve **55**. The recycled solution contains as a result of the contacting operation sodium chloride and other reaction products resulting from conversion of the acidic compounds supra in the hypochlorite treated oil but does not contain any sodium sulfide. These compounds, which may be compounds such as sodium sulfonate and sodium thiol sulfonate, do not deleteriously affect the conversion of the acidic compounds supra.

From time to time it may be necessary to withdraw a portion of sodium mercaptide solution and this may be done conveniently by opening valve **56** in line **52**. When the sodium mercaptan solution is withdrawn from line **52** an amount of make-up solution equivalent to that withdrawn may be introduced by opening valve **57** in line **48**.

In lieu of extraneously prepared make-up solution, I may, and preferably do, employ part of the solution withdrawn from settler **25** by way of line **32**. This solution consists essentially of water, sodium hydroxide, and sodium mercaptides from the group consisting of sodium alkyl mercaptides having no more than 6 carbon atoms per molecule, and sodium aryl mercaptides, and is free of sodium sulfide.

When sodium methyl mercaptide or sodium ethyl mercaptide solution is used, there may be withdrawn from zone **51** by line **58** a treated oil which may be routed

to storage by opening valve 59. However, when other mercaptides of the types illustrated are employed in the treating solution it may be necessary to treat the treated oil further to remove mercaptans, such as propyl or butyl mercaptans, which may be in the treated oil phase by virtue of extraction from the sodium mercaptide solution through a mechanism which may involve hydrolysis. Under these conditions, I, therefore, admix with the oil in line 58 a quantity of sodium hydroxide solution, for example, which is introduced by line 60. The treated oil and sodium hydroxide solution then flow by way of branch line 61 controlled by valve 62 into an incorporating device 63 which may be of the baffle type and is similar to incorporator 49, 37, 23, and 13. The caustic solution and the treated oil are intimately admixed in incorporator 63 and are withdrawn therefrom by way of line 64 and discharged into an after-wash settling zone 65 which is like settling zones 51, 39, 25, and 15. Treated oil may then be withdrawn from the system for storage and further use by line 66 controlled by valve 67. The used sodium hydroxide solution is withdrawn from zone 65 by line 68 and may be recycled, in part, by branch line 69 containing pump 70 to line 60 on opening valve 71. The solution in line 69 may also be discharged in part into line 32 by opening valve 72. Line 32 discharges into line 48.

It is desirable and preferable in this latter described mode that at least a portion of the solution withdrawn from zone 65 by line 68 be employed as the source of the sodium mercaptide solution along with that from line 32. Since all of the caustic solution withdrawn by line 68 is not recycled to line 60, I, therefore, introduce an amount of make-up sodium hydroxide solution by opening valve 73 in line 74. Also I contemplate that it may be desirable from time to time to discard a portion of the sodium hydroxide solution from the system by opening valve 75 in line 68.

As a modification of my invention, I may by-pass completely the treating system including incorporator 13 and first pre-wash settling zone 15. Under these conditions valve 76 in line 14 is closed and valve 77 in line 16 is also closed, and valve 78 in line 22 is opened, allowing the feed stock to be introduced by line 22 into incorporator 23 for operation as has been described. Under these conditions the caustic solution introduced into line 22 by line 22*a* will serve to remove not only hydrogen sulfide but also the mercaptans having 6 and less carbon atoms in the molecule as well as the phenolic, naphthenic, and other carboxylic acid bodies. This caustic solution should not be recycled from line 26 to line 32 for use in line 48 since this solution would then contain sodium sulfide which is not as effective as the sodium mercaptide in treating the hypochlorite solution. When treating facilities including incorporator 13, feed line 11, and settling zone 15 are eliminated from the system I employ a sodium mercaptide solution such as a sodium aliphatic mercaptide solution or sodium mercaptide solution formed with an aromatic mercaptan. This solution would be introduced into the system by line 48 on opening valve 57. In operation in such a manner with the sodium mercaptide solution being introduced by line 48, I may also eliminate from the operation the treating facilities including the incorporator 63, settling zone 65, and the attendant lines, provided the solution introduced by opening valve 57 contains no mercaptide other than methyl and ethyl.

It may be seen from the foregoing description taken with the drawing that I have provided a process for converting the acidity of chlorinated compounds present in oils which have been treated with hypochlorite and this treatment has converted the acidic chlorinated compounds which are of the type mentioned before into innocuous compounds which do not deleteriously affect the product quality of the gasoline or the oil being treated for use as a motor fuel.

The invention will be further illustrated by a number of runs wherein the practice of the present invention is compared to washing the hypochlorite sweetened oil with other reagents, for example, aqueous sodium sulfide solution and an alkaline solution obtained in a petroleum refinery resulting from treating an oil containing mercaptans, H_2S, phenolic bodies, naphthenic acids and the like with a caustic solution.

In the first instance a heptane fraction was divided into two portions and one portion had added to it a sufficient amount of normal amyl mercaptan to provide a stock having a copper number of 100, while the second portion had added to it an amount of tertiary amyl mercaptan sufficient to provide a stock also having a copper number of 100.

The heptane fraction containing the normal amyl mercaptan was treated with sodium hypochlorite solution and the sodium hypochlorite treated heptane fraction was then divided into three portions. One portion of the hypochlorite treated heptane was inspected as is. The second portion was treated with 20% by volume based on the hypochlorite treated oil of an aqueous sodium sulfide solution containing 148 grams of sodium sulfide per liter. The third portion was treated with a solution containing 80 grams per liter of free sodium hydroxide and also sodium ethyl mercaptide to the extent of 600 mgs. of mercaptide sulfur per 100 ml.

The heptane fraction to which tertiary amyl mercaptan was added was treated in a manner similar to that of the above mentioned fraction in that one hypochlorite sweetened fraction was inspected as is, one was washed with sodium sulfide solution, and one was washed with sodium ethyl mercaptide solution. In all of these operations the hypochlorite treated oils were contacted with the several solutions for one minute contacting time.

The results of these runs are given in Table I.

Table I

Sweetening Method	Hypochlorite					
Stock Sweetened	Heptane Containing N-Amyl Mercaptan			Heptane Containing T-Amyl Mercaptan		
Type of Afterwash (20 Vol. Percent) [1]	None	Sodium Sulfide.	Sodium Ethyl Mercaptide.	None	Sodium Sulfide.	Sodium Ethyl Mercaptide.
Inspection of Treating Solution:						
Na_2S, g. p. l.		148	None		148	None.
Free NaOH, g. p. l.		0	80		0	80.
Mercaptide Sulfur, mgs./100 ml.		600				600.
Inspections on Treated Oil:						
Wt. Percent Cl_2	0.0129	0.000	0.000	0.1048	0.000	0.000.
Acidity, mls. of 0.1 N KOH/100 ml.	4.0	0.10	0.10	21.3	0.14	0.12.
Sulfur as Free Sulfur or Polysulfide Sulfur mgs./100 ml.	0	2.5	0.0	0	15.0	0.0.
Corrosion 3 hrs. at 212° F.	#4	#5	#3	#10	#6	#4.

[1] Reaction time of 1 min. employed.

With respect to the inspections employed in these experiments, it may be mentioned that the copper number is numerically the same as the milligrams of mercaptan sulfur present in 100 milliliters of 0:1. The corrosion number is an indication of the amount of free sulfur or equivalent material present in the oil. It is deter-

mined by A. S. T. M. test No. D130–50T. Briefly, the corrosion test consists of immersing a portion of a copper strip in a given quantity of sample and heating it at a temperature and for a time characteristic of the material being tested. In the present case, the strip was immersed in normal heptane at its boiling point under reflux conditions for three hours. The discoloration of a strip is indicative of the corrosiveness of the sample. It is rated by numbers which are determined by comparison with standard test strips. A number of zero indicates no tarnish; 4 is considered slightly corrosive, and greater than 4 indicates pronounced corrosion to an increasing extent.

The data in Table I show that the sodium mercaptide treated oil is free of sulfur as free sulfur and polysulfide sulfur, whereas the oil which has been hypochlorite treated and then washed with sodium sulfide contains considerable quantities of free sulfur or polysulfide sulfur. In short, my invention provides a hypochlorite treated product substantially free of sulfur in these forms. This is also reflected in the corrosion test in that my invention allows the obtaining of a lower corrosion number, which is also an indication of the absence of free or polysulfide sulfur, than is obtainable with the hypochlorite treated oil which was treated with sodium sulfide.

In order to illustrate further the benefits of my invention, a comparison was made using a heptane fraction which contained tertiary butyl mercaptan in an amount sufficient to provide a copper number of 200 in the heptane. This heptane having a copper number of 200 was treated with a sodium hypochlorite solution and the sodium hypochlorite treated heptane was divided into three portions. One portion of the hypochlorite treated heptane was inspected as is and the other two portions were treated, respectively, with a sodium normal butyl mercaptide solution containing sodium hydroxide and water, and with an alkaline solution resulting from treating a mercaptan- and hydrogen sulfide-containing oil with sodium hydroxide. Inspections on the solutions used to treat the hypochlorite treated heptane, and inspections on the heptane after treating with hypochlorite, hypochlorite and sodium normal butyl mercaptide solution, and with the alkaline solution obtained from the refining operations where the oil, as described, was treated, are given in Table II.

Table II

Sweetening Method Stock Sweetened	Hypochlorite N-heptane, Containing Tertiary Butyl Mercaptan		
Afterwash Used (20 Vol. percent)	None	N-butyl Mercaptide.	Plant Spent Treating Caustic.
Reaction Time	1 Minute	1 Minute	1 Minute.
Inspection on Treating Solution:			
Free NaOH, g. p. l.		81.8	61.0.
Na_2S Content, g. p. l.		None	78.3.
Mercaptide Sulfur Content, mgs./100 ml.		300	20.0.
Phenolic Compounds, Wt. Percent		None	0.5.
Inspections on Oil:			
Color, Saybolt	+13	+27	+30.
Acidity, mls. of 0.1 N KOH/100 ml.	26.0	0.06	0.12.
Wt. Percent Chlorine	0.125	<0.0008	<0.0008.
Sulfur as Free Sulfur or Polysulfide Sulfur, mgs./100 ml.	0	0	15.0.

It will be seen that the alkaline solution obtained from the refining operations contained sodium hydroxide, sodium sulfide and sodium mercaptide as well as some phenolic compounds and that the sodium normal butyl mercaptide consisted of sodium hydroxide, sodium normal butyl mercaptide and water. It will also be noted that the oil treated in accordance with my invention had a sulfur content as free sulfur or polysulfide sulfur of zero while that treated with the alkaline caustic solution contained 15 mgs./100 ml. of sulfur.

From the foregoing results presented in Tables I and II it will be seen that my invention gives improved results over that obtained when treating hypochlorite treated oils with sodium sulfide solution or alkaline solution containing both sodium sulfide and sodium mercaptide.

The hypochlorite solution employed in the practice of the present invention is preferably sodium hypochlorite but may be an alkaline earth hypochlorite such as calcium hypochlorite. It is contemplated that the other alkali metal hypochlorites may be employed such as lithium and potassium hypochlorites or that the hypochlorite solution may be a solution of an alkaline earth hypochlorite such as magnesium, calcium, and strontium hypochlorite.

The hypochlorite solution will ordinarily have an available chlorine content in the range from about 2 grams per liter to about 150 grams per liter; concentration of about 10 grams per liter gives good results.

The hypochlorite solution when it is sodium hypochlorite solution will preferably have an average sodium hydroxide content ranging from about 5 to about 750 grams of sodium hydroxide per liter. Ordinarily, the hypochlorite solution employed will contain free sodium hydroxide in the range from about 50 to 100 grams per liter. It may be stated, however, that the present invention has most applicability to treatment of naphthas which have been contacted with hypochlorite solutions having a low level of causticity since naphthas treated with sodium hypochlorite having a small amount of free sodium hydroxide are generally more unstable than those having a high level of free sodium hydroxide.

In practicing the present invention, it is desirable to maintain the alkalinity of the hypochlorite solution employed in the process at a high level in order to minimize consumption of hypochlorite and corrosion of equipment, since in employing hypochlorite solutions having an average sodium hydroxide content below about 90 grams per liter ferrous metal equipment is rapidly attacked by the hypochlorite. Therefore, it is contemplated that sufficient sodium hydroxide will be added to the process as described to maintain the causticity at above 90 grams per liter. It is further contemplated that sufficient chlorine will be added as make-up to replace that consumed or discarded. When employing high caustic content hypochlorite solution it is desirable to add sodium hydroxide and chlorine as make-up and to withdraw a portion of the hypochlorite solution to prevent build-up of sodium chloride in the system.

In the description taken with the drawing provision is made for discarding sodium mercaptide solution through line **52** controlled by valve **56**. This should be done when sodium chloride builds up in the solution as a result of the reaction of the mercaptide with the acidic compounds. The mercaptide solution should be discarded at least in part when the sodium chloride content builds up to such an extent that a salting-out effect occurs. The non-discarded portion of the solution withdrawn by line **52** may have added to it the particular mercaptan being used to convert some of the sodium hydroxide to sodium mercaptide but it is always desirable to leave a sufficient amount of caustic in the solution

to provide a solution consisting essentially of water, alkali metal mercaptide and alkali metal hydroxide and reaction products such as sodium sulfinate and sodium thiolsulfonate.

By way of explanation it will be desirable to recycle the solution from zone **65** to line **32** by way of line **69** when the solution in zone **65** becomes saturated with sodium mercaptide to the extent that it would no longer extract mercaptans from the oil in line **58**.

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

1. A method for treating a hypochlorite treated hydrocarbon distillate boiling below 750° F. containing acidic chlorinated compounds which comprises contacting said distillate with a solution consisting of water, alkali metal hydroxide and an alkali metal mercaptide selected from the group consisting of the aromatic mercaptides and aliphatic mercaptides having no more than 4 carbon atoms in the molecule.

2. A method for treating a hypochlorite treated hydrocarbon distillate boiling below 750° F. containing acidic chlorinated compounds which comprises contacting said distillate with a solution consisting of water, alkali metal hydroxide and an alkali metal mercaptide selected from the group consisting of aromatic mercaptides and aliphatic mercaptides, having no more than 4 carbon atoms in the molecule for a sufficient length of time to convert acidic chlorinated compounds in said hydrocarbon distillate and to form in said distillate disulfides and in said solution alkali metal chloride, separating said contacted distillate from said aqueous solution containing alkali metal chloride and employing said separated solution to contact additional quantities of hypochlorite treated hydrocarbon distillate containing acidic chlorinated compounds.

3. A method for treating a sour hydrocarbon distillate boiling below 750° F. which comprises contacting said distillate with an aqueous hypochlorite solution whereby acidic chlorinated compounds are formed, separating said contacted distillate from said hypochlorite solution, treating said contacted distillate with a solution consisting of water, alkali metal hydroxide and an alkali metal mercaptide selected from the group consisting of aromatic mercaptides and aliphatic mercaptides having no more than 4 carbon atoms in the molecule for a sufficient length of time to convert acidic chlorinated compounds in said contacted distillate and to form disulfides in said treated distillate and in said solution alkali metal chloride, separating said treated distillate from said aqueous solution containing alkali metal chloride and employing said separated solution to contact additional quantities of said hypochlorite treated distillate containing acidic chlorinated compounds .

4. A method for treating a sour hydrocarbon distillate boiling below 750° F. containing hydrogen sulfide and mercaptans which comprises removing hydrogen sulfide from said sour distillate, contacting the hydrogen sulfide free sour distillate with an aqueous caustic solution to form an aqueous solution containing alkali metal mercaptides, treating said last-contacted distillate with an aqueous hypochlorite solution, separating said treated distillate from said hypochlorite solution, contacting the treated distillate with a solution consisting of water, alkali metal hydroxide and an alkali metal mercaptide selected from the group consisting of the aromatic mercaptides and the aliphatic mercaptides having no more than 4 carbon atoms in the molecule, separating mercaptide solution from said treated distillate, and recovering said hypochlorite treated oil.

5. A method for treating a sour distillate boiling below 750° F. containing hydrogen sulfide and aliphatic mercaptans including mercaptans having at least six carbon atoms in the molecule which comprises removing hydrogen sulfide and said aliphatic mercaptans having six and less carbon atoms in the molecule from said sour distillate, treating the sour distillate, after removal of hydrogen sulfide and said aliphatic mercaptans, with an aqueous hypochlorite solution, separating the treated distillate from said hypochlorite solution, and contacting the treated distillate with a solution consisting of water alkali metal hydroxide and an alkali metal mercaptide selected from the group consisting of the aromatic mercaptides and the aliphatic mercaptides having no more than four carbon atoms in the molecule.

6. A method for treating a hypochlorite treated hydrocarbon distillate boiling below 750° F. containing acidic chlorinated compounds which comprises contacting said distillate with an aqueous solution consisting of sodium hydroxide, water, and an alkali metal mercaptide selected from the group consisting of the aromatic mercaptides and the aliphatic mercaptides having no more than four carbon atoms in the molecule.

7. A method for treating a hypochlorite treated hydrocarbon distillate boiling below 750° F. containing acidic chlorinated compounds which comprises contacting said distillate with an aqueous solution consisting of an alkali metal hydroxide, water, and an alkali metal mercaptide selected from the group consisting of methyl mercaptan, ethyl mercaptan, propyl mercaptans, butyl mercaptans, benzene thiol, thiocresols, 2-phenyl 1-ethane thiol, m-tolubenzyl mercaptan, 4-ethyl benzene thiol, methyl benzyl mercaptan, 2-naphthalene thiol, and 4-phenyl-1-benzene thiol.

References Cited in the file of this patent

UNITED STATES PATENTS

2,581,117 Love ---------- Jan. 1, 1952