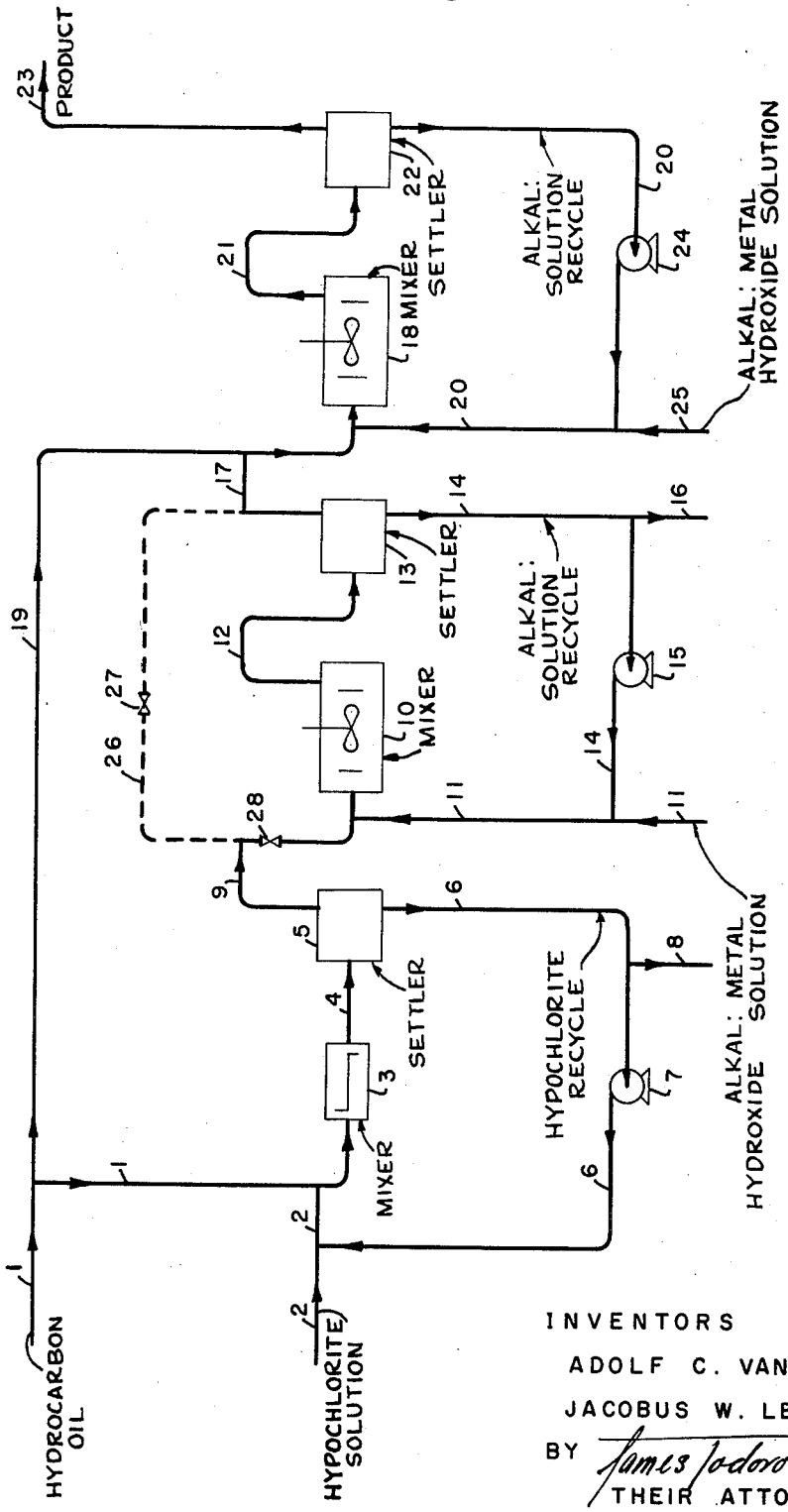
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PROCESS FOR SWEETENING HYDROCARBONS WITH ALKALI HYPOCHLORITES, ALKALI HYDROXIDES AND ALKALI MERCAPTIDES

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INVENTORS
ADOLF C. VAN BEEST
JACOBUS W. LE NOBEL
BY James Jodoroic
THEIR ATTORNEY

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PROCESS FOR SWEETENING HYDROCARBONS WITH ALKALI HYPOCHLORITES, ALKALI HYDROXIDES AND ALKALI MERCAPTIDES

Adolf C. van Beest and Jacobus W. Le Nobel, Amsterdam, Netherlands, assignors to Shell Development Company, New York, N.Y., a corporation of Delaware

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This invention relates to the treatment of hydrocarbon distillate oils, particularly to the removal of mercaptans therefrom.

It is known to treat hydrocarbon oils, particularly gasoline and kerosene, with an aqueous hypochlorite solution such as sodium or calcium hypochlorite solution in order to oxidize the mercaptans present in the hydrocarbon oil and also, if desired, to reduce the sulfur content of the hydrocarbon oil.

It has not been heretofore practicable to effect more than a minor degree of desulfurization by means of a hypochlorite solution without conducting the process under such severe conditions of temperature, time of contact, etc., that the finished hydrocarbon oil product is degraded because of deleterious side reactions.

It is a principal object of this invention to provide an improved process of hypochlorite treating of hydrocarbon oils, especially those boiling in the boiling range of gasoline and kerosene. A more particular object is to provide such a process wherein an improved hydrocarbon product is obtained, especially with respect to the degree of desulfurization obtained. These objects will be better understood and others will be apparent from the description of the invention, which will be made with reference in part to the accompanying drawing wherein the sole figure is a flow schematic of a preferred embodiment in which a mercaptan-containing hydrocarbon oil is sweetened and desulfurized.

It has been heretofore thought that a hypochlorite solution used in the treatment of hydrocarbon oils must contain a substantial concentration of free alkali, for example, uncombined sodium or calcium hydroxide. Contrary to this generally accepted view, it has been found that a hypochlorite solution which contains no, or substantially no, free alkali so that the pH of the solution is less than 9 not only can be used, but advantageously so, when combined with additional processing steps. The above objects are attained by treating a hydrocarbon oil distillate with such a hypochlorite solution of low alkalinity and, afterwards, treating the distillate with alkali metal mercaptides. The hypochlorite solution preferably has a pH of from about 8.2 to about 8.5.

The most important embodiment of the process according to the invention relates to the desulfurization of hydrocarbon oils, since it has been found that a much more complete desulfurization of hydrocarbon oils is obtained than has hitherto been possible with hypochlorite solution when the hydrocarbon oil is contacted with an alkali metal hydroxide solution in an intermediate step, i.e., after the treatment with hypochlorite solution but before the treatment with alkali metal mercaptides. By this combined treatment most of the sulfur-containing reaction products formed during the hypochlorite treatment are removed from the hydrocarbon oil. In order to accelerate this removal, one or more phenols or phenolates, alkyl phenols or alkyl phenolates may be added to the alkali metal hydroxide solution used in this intermediate step.

According to this process in three stages, viz. successive treatments with hypochlorite solution, alkali metal hydroxide solution and alkali metal mercaptides, it is possible to remove 75 to 90% by weight of the sulfur originally present in the hydrocarbon oil, while the quantity of sulfur which could be removed according to the processes applied hitherto is 35 to 50% by weight of the original sulfur in the oil.

It is preferable to wash the hydrocarbon oil with alkali metal hydroxide solution before the treatment with hypochlorite solution in order to remove any hydrogen sulfide present, as this gives rise to the formation of objectionable free sulfur in the hypochlorite treatment.

The treatment of the hydrocarbon oil with the hypochlorite solution is effected by mixing the two phases together. The hydrocarbon oil and the hypochlorite solution are kept in contact with each other for not more than 30 minutes, the period being dependent on the composition of the hypochlorite solution, the quantity thereof, the sulfur content of the hydrocarbon oil and the intensity of the stirring. A period of only 2 to 10 minutes is usually sufficient.

The hypochlorite content in the solutions is usually 0.005 to 1 mol per liter, preferably from about 0.01 to about 0.2 mol per liter. The quantity of hypochlorite in contact with hydrocarbon oil may vary within wide limits. In general an excess of hypochlorite is used with respect to the theoretical (i.e., the stoichiometric) amount, for example, from 2 to 15 times, particularly 5 to 10 times, the stoichiometric amount, based on the oxidation of the mercaptans present to disulfides.

The treatment of the hydrocarbon oil with hypochlorite solution takes place at ambient, somewhat elevated or somewhat reduced temperature. Temperatures between 0° C. and 50° C., and especially between 15° C. and 35° C., are suitable.

The aqueous alkali metal hydroxide solution with which the hydrocarbon oil is treated in the second stage during desulfurization usually contains 0.5 to 30% by weight, particularly 10 to 25% by weight, of alkali metal hydroxide. Sodium hydroxide is generally used. In this stage it is preferred to use an efficient mixing apparatus in order to ensure a good contact between the oil and the alkali phase for a sufficiently long period; for this period a turbo-mixer or a propeller mixer is used in particular. The temperature is generally 0° C. to 50° C., particularly 15° C. to 35° C.

The alkali metal mercaptides with which the hydrocarbon oil is treated in the last stage in order to remove the corrosive compounds still present may be added in aqueous solution or in alkali metal hydroxide solution. A preferred technique, however, is to contact the hypochlorite-treated hydrocarbon oil in the last stage with a mixture of an alkali metal hydroxide solution and a hydrocarbon oil which contains mercaptans but which is preferably free from hydrogen sulfide. Mercaptans will then pass into the alkali metal hydroxide solution and be converted therein into the corresponding mercaptides. An even more effective and convenient method is to contact the hypochlorite-treated hydrocarbon oil in the last stage with an alkali metal hydroxide solution in the presence of an untreated portion of the same pour oil which has been hypochlorite-treated. In this case the process then amounts to the splitting of a mercaptan-containing hydrocarbon oil into two parts, one part of which is treated as described above with the low-alkalinity hypochlorite solution in a first stage, and preferably then with an alkali metal hydroxide solution in a second stage, and finally mixing the hypochlorite-treated part in a last stage with the second, or untreated, part in the presence of an alkali metal hydroxide solution.

When employing the intermediate stage contacting of the hypochlorite-treated oil with an aqueous alkali metal

hydroxide, it is important that the aqueous solution used in this stage be separated from the hydrocarbon oil before the hydrocarbon oil is treated in the last stage because otherwise a lesser degree of desulfurization will be obtained. It is of course also essential to completely separate the hypochlorite solution from the oil after the first stage and before proceeding with the subsequent treatment of the oil.

In order to promote the reaction of the alkali metal mercaptides in the last stage, intense stirring is desirable. A suitable stirrer is the propeller mixer of the turbomixer. The reaction is generally complete after 3 to 30 minutes, and is carried out at room temperature, although higher or lower temperatures may also be used, if desired.

The quantities of the hypochlorite-treated hydrocarbon oil and of the mercaptan-containing hydrocarbon oil which are reacted with each other in the simultaneous presence of an alkali metal hydroxide solution may vary within certain limits. The lower limit of the quantity of the mercaptan-containing hydrocarbon oil is usually determined by the requirement that the potential acid number of the final product should not be more than 0.01. By potential acid number is meant the number of milligrams of KOH which must be added, in an alcoholic medium, per gram of hydrocarbon oil in order ot saponify and neutralize the sulfenyl and sulfonyl chlorides present in the hydrocarbon oil. The upper limit is usually determined by the requirement that the final product should give a negative doctor test, i.e., it should have a mercaptan sulfur content of not more than 0.0005% by weight. In the usual case especially good results will be obtained when the amount of mercaptans or corresponding mercaptides present is from about 5 to 100 mol percent, more especially from about 10 to about 30 mol percent, of the mercaptans originally present in the oil which is hypochlorite treated. When the source of the mercaptans is the original oil and the oil is split into two aliquot parts as before mentioned, the amount of the part of the oil by-passed around the hypochlorite treating stage (and the intermediate stage, if used) is therefore from about 5 to about 100 percent, more especially from about 10 to about 30 percent, of the part of the oil which is hypochlorite treated.

The quantity and concentration of the alkali metal hydroxide solution which is added in combination with the merctaptan-containing hydrocarbon oil to the hypochlorite-treated hydrocarbon oil may vary within wide limits. Aqueous solutions of sodium or potassium hydroxide in a concentration of 10 to 20% by weight are very suitable. Such solutions may be added in a quantity of 5 to 50, and particularly 10 to 20% by volume, calculated on the hydrocarbon oil phase.

If, after the said treatment, small quantities of corrosive components formed during the hypochlorite treatment are still present in the hydrocarbon oil, the corrosive effect thereof may be counteracted by adding to the hydrocarbon oil a small quantity, particularly 0.001 to 0.1% by weight, of a substituted or unsubstituted aliphatic or cyclo-aliphatic monocarboxylic acid having 12 or more carbon atoms, the water solubility of which is not more than 0.1 gram per liter at 20° C., e.g., oleic acid.

The process of the invention is applicable with good results to both heavy hydrocarbon oil distillate fractions such as gas oil and to light hydrocarbon oil distillate fractions such as gasoline and kerosene, although the light fractions are preferred. It is generally applicable to hydrocarbon oil distillates having final boiling points not exceeding 370° C. The preferred fractions are those which are substantially non-olefinic, for example, straight-run petroleum distillates.

The invention will be further illustrated with reference to the accompanying drawing. In the drawing, hydrocarbon oil to be treated is supplied via line **1**, while a hypochlorite solution is added via line **2**. The hydrocarbon oil and the hypochlorite solution are intimately mixed in the mixer **3** and the dispersion of both phases is introduced via line **4** into settler **5**, where the phases are separated. The hypochlorite solution is recycled via line **6** and pump **7** to supply line **2** so as to use the hypochlorite present as efficiently as possible. In order not to reduce too greatly the hypochlorite concentration in the mixer and to compensate the increase in volume as a result of supplying fresh hypochlorite solution, a quantity of spent hypochlorite solution is drawn off via line **8**. The hypochlorite-hydrocarbon oil is passed via line **9** to propeller mixer **10**, in which it is intimately mixed with an alkali metal hydroxide solution which is supplied to the line **9** via line **11**. The dispersion of oil and alkali phase is led from mixer **10** via line **12** to settler **13**, in which the two phases are separated. The alkali solution is recycled from settler **13** via line **14** and pump **15** to line **11**, while a part thereof is being drawn off via line **16**. The hydrocarbon oil is passed from settler **13** via line **17** to propeller mixer **18** where it is intimately mixed with untreated hydrocarbon oil which is supplied via line **19** to line **17**, and with an alkali metal hydroxide solution which is supplied via line **20**. The hydrocarbon oil thus obtained which is desulfurized and sweetened is led via line **21** into a settler **22** and separated therein from the alkali phase and drawn off via line **23**. The alkali solution is recycled via line **20** and pump **24** to line **17**, any fresh alkali being supplied via line **25**.

When it is desired to sweeten the hydrocarbon oil with only a minor degree of desulfurization, line **9** is directly connected to line **17**, via by-pass line **26** containing valve **27**, and valve **28** in line **9** is closed.

EXAMPLE I

Kirkuk gasoline was treated with sodium hypochlorite solution and then with untreated gasoline and sodium hydroxide solution by the flow scheme shown in the drawing, in which, however, valve **27** was open and valve **28** was closed so that the hypochlorite-treated hydrocarbon oil was not subjected to an intermediate treatment with alkali metal hydroxide. The treatment conditions and the properties of the gasoline before and after sweetening are shown in Table I.

Table I

Treatment conditions	Untreated Kirkuk gasoline	1st stage treatment with NaOCl	Last stage treatment with NaOH and untreated gasoline
Quantity of treatment solution, cc. per hour		420	
Quantity of gasoline introduced, cc. per hour		1,000	1,000
Quantity of untreated gasoline added in the last stage, cc. per hour			700
Quantity of NaOH present in the last stage, cc.			200
Ratio of recycled quantities of aqueous phase and gasoline, percent by volume		65	40
Residence time of gasoline, min.		7½	18
Temperature, ° C.		20	20
Volume of mixer, cc.		200	400
Properties of fresh treatment solutions:			
NaOH content, mol per liter		nil	2.80
NaOCl content, mol per liter		0.0497	
NaCl content, mol per liter		0.0497	
pH		8.5	
Properties of the treatment solutions used:			
NaOH content, mol per liter		nil	2.75
NaOCl content, mol per liter		0.0034	
NaCl content, mol per liter		0.0870	traces
Properties of the gasoline:			
Total sulfur content, percent by wt.	0.040	0.018	0.027
Mercaptan sulfur content, percent by wt.	0.0193	nil	0.0005
Disulfide sulfur content, percent by wt.	nil	0.0018	0.0114
Sulfide sulfur content, percent by wt.	0.019		0.011
Potential acid number, mg. KOH/g.		0.24	<0.001

EXAMPLE II

Kuwait gasoline was successively treated with sodium hypochlorite solution, sodium hydroxide solution and with untreated gasoline together with sodium hydroxide solution, by the flow scheme shown in the drawing, in which, however, valve 27 was closed and valve 28 was open so that the hypochlorite-treated oil from the first stage received the intermediate stage treatment with aqueous alkali metal hydroxide solution as well as the last stage treatment with mercaptides. The treatment conditions and the properties of the gasoline before and after the use of the process according to the invention are shown in Table II.

Table II

Treatment conditions	Untreated Kuwait gasoline	1st stage treatment with NaOCl	Intermediate stage treatment with NaOH	Last stage treatment with NaOH and untreated gasoline
Quantity of the treatment solution, cc. per hour		275	50	
Quantity of gasoline introduced, cc. per hour		1,000	1,000	1,000
Quantity of untreated gasoline added in 3rd stage, cc. per hour				120
Quantity of NaOH solution present in 3rd stage, cc				150
Ratio of recycled quantities of aqueous phase and gasoline, percent by vol		63	25	60
Residence time of gasoline, minutes		7½	9½	13
Temperature, ° C		20	20	20
Volume of mixer, cc		200	200	200
Properties of the fresh treating solutions:				
NaOH content, mol per liter		nil	5.99	7.54
NaOCl content, mol per liter		0.0502		
NaCl content, mol per liter		0.0502	nil	nil
pH		8.4		
Properties of the treatment solutions used:				
NaOH content, mol per liter		nil	5.94	7.38
NaOCl content, mol per liter		nil		
NaCl		0.0921	0.028	0.017
Properties of the gasoline:				
Total sulfur content, percent by weight	0.030	0.010	0.006	0.008
Mercaptan sulfur content, percent by wt	0.0125	nil	nil	0.0005
Disulfide sulfur content, percent by wt	nil	0.0020	0.0020	0.0026
Sulfide sulfur content, percent by wt	0.017		0.003	0.004
Potential acid number, mg. KOH/g		about 0.08	0.010	0.001
Lead susceptibility expressed in percent of that of the sulfur-free product	74		86	84

The above data show that after the treatment with the sodium hypochlorite solution all mercaptans are converted, but that the gasoline contains a fair amount of acid-reacting compounds. The content thereof is greatly reduced by the alkali treatment, the total sulfur content being decreased at the same time. By adding the untreated gasoline in the last stage the sulfur content of the final product becomes higher than that of the hydrocarbon oil obtained in the intermediate stage since the mercaptans present in the untreated gasoline are converted into disulfides which dissolve far more readily in the gasoline than in the alkali and which therefore remain in the final product, while the remaining sulfur compounds present in the untreated gasoline added also contribute to increase the sulfur content.

EXAMPLE III

The same Kirkuk gasoline as sweetened in Example I was desulfurized by the same process as that used on Kuwait gasoline according to Example II. The treatment conditions and the properties of the gasoline before and after desulfurization are shown in Table III.

Table III

Treatment conditions	Untreated Kirkuk gasoline	1st stage treatment with NaOCl	Intermediate stage treatment with NaOH	Last stage treatment NaOH and untreated gasoline
Quantity of the treatment solution, cc. per hour		420	50	
Quantity of gasoline introduced, cc. per hour		1,000	1,000	1,000
Quantity of untreated gasoline added in 3rd stage, cc. per hour				65
Quantity of NaOH solution present in 3rd stage, cc				130
Ratio of recycled quantities of aqueous phase and gasoline, percent by volume		65	27	48
Residence time of gasoline, minutes		7½	14	15
Temperature, ° C		20	20	20
Volume of mixer, cc		200	300	400
Properties of the fresh treatment solutions:				
NaOH content, mol per liter		nil	5.99	3.08
NaOCl content, mol per liter		0.0497		
NaCl content, mol per liter		0.0497	nil	
pH		8.5		
Properties of the treating solutions used:				
NaOH content, mol per liter		nil	5.84	3.04
NaOCl content, mol per liter		0.0034		
NaCl content, mol per liter		0.0870	0.042	traces
Properties of the gasoline:				
Total sulfur content, percent by weight	0.040	0.018	0.005	0.007
Mercaptan sulfur content, percent by weight	0.0193	nil	nil	0.0006
Mercaptan sulfur content, percent by weight	0.0193	nil	nil	0.0006
Disulfide sulfur content, percent by weight	nil	0.0018	0.0018	0.0024
Sulfide sulfur content, percent by weight	0.019		0.002	0.003
Potential acid, number mg. KOH/g		0.24	0.020	0.001
Lead susceptibility expressed in percent of that of the sulfur free product	70		87	84

EXAMPLE IV

The Kuwait gasoline referred to in Example II and the Kirkuk gasoline referred to in Examples I and III were subjected to the conventional treatment with sodium hypochlorite solution containing free sodium hydroxide, followed by a washing with alkali. The sodium hypochlorite solution used in this conventional treatment contained 0.05 mol of NaOCl and one mol of NaOH per liter and kept in intimate contact with the gasoline for 15 minutes at 20° C. The hypochlorite solution was then removed and the gasoline was washed for 24 hours with a 6 N NaOH solution. The results of this treatment are shown in Table IV in which, for the purpose of comparison, the results obtained according to Examples II and III are also included.

Table IV

	Kuwait gasoline			Kirkuk gasoline		
	Untreated	After conventional treatment	After treatment according to the invention	Untreated	After conventional treatment	After treatment according to the invention
Properties of the gasoline:						
Total sulfur content, percent by wt.	0.030	0.017	0.008	0.040	0.026	0.007
Mercaptan sulfur content, percent by wt.	0.0125	nil	0.0005	0.0193	nil	0.0006
Disulfide sulfur content, percent by wt.	nil	0.0040	0.0026	nil	0.0094	0.0024
Sulfide sulfur content, percent by wt.	0.017	0.012	0.004	0.019	0.014	0.003
Potential acid number, mg. KOH/g.		0.005	<0.001		about 0.08	0.001
Reduction in sulfur content:						
Total sulfur content, percent by wt.	0	43	75	0	35	84
Mercaptan and disulfide content, percent by wt.	0	68	75	0	51	84
Sulfide sulfur content, percent by weight	0	30	76	0	26	83
Lead susceptibility:						
Lead susceptibility in percent of that of the sulfur-free product	74	80	84	70	76	84
Gain in lead susceptibility, percent	0	6	10	0	6	14

The data in Table IV show that mercaptan and disulfide sulfur together are now removed to the extent of 75% and 84% respectively, as against 51% and 68% respectively, according to the process used hitherto in practice. For monosulfide sulfur these figures are 76 and 83% respectively, and 26 and 30% respectively. The total amount of sulfur is reduced by 75% and 84% respectively instead of by 35% and 43% respectively.

As this table also shows, as a result of the more complete desulfurization, the lead susceptibility of the products treated according to the invention is also increased.

We claim as our invention:

1. A process of desulfurizing a mercaptan-containing hydrocarbon oil distillate which comprises contacting the distillate with an aqueous alkaline hypochlorite solution having a pH of less than 9, separating the resulting hypochlorite-treated distillate, contacting the hypochlorite-treated distillate with an aqueous alkali metal hydroxide solution, separating the resulting hypochlorite-treated and caustic-washed distillate, and contacting the hypochlorite-treated and caustic-washed distillate with alkali metal mercaptides in an amount of from about 10 to about 100 mol percent of the original mercaptan content of the distillate.

2. A process in accordance with claim 1, wherein the pH of the aqueous hypochlorite solution is from about 8.2 to about 8.5.

3. A process in accordance with claim 2, wherein the hypochlorite content of the aqueous hypochlorite solution is from about 0.01 to about 0.2 mol per liter.

4. A process of desulfurizing a mercaptan-containing hydrocarbon oil distillate comprising the steps: (1) splitting the distillate into a first part and a second part of like compositions, the second part being from 10 to 100% of the first part; (2) contacting the first part with an aqueous hypochlorite solution having a pH of from about 8.2 to about 8.5 in an amount in excess of the stoichiometric amount for the oxidation of the mercaptans therein to disulfides; (3) separating the resulting hypochlorite-treated first part; (4) intimately contacting the hypochloride-treated first part with an aqueous alkali metal hydroxide solution; (4) separating the resulting hypochlorite-treated and caustic-washed first part; (5) mixing the hypochlorite-treated and caustic-washed first part with the second part still containing mercaptans; (6) contacting the resulting mixed treated and untreated distillate with an aqueous alkali metal hydroxide solution; and (7) separating a doctor-sweet hydrocarbon oil distillate product of reduced sulfur content.

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