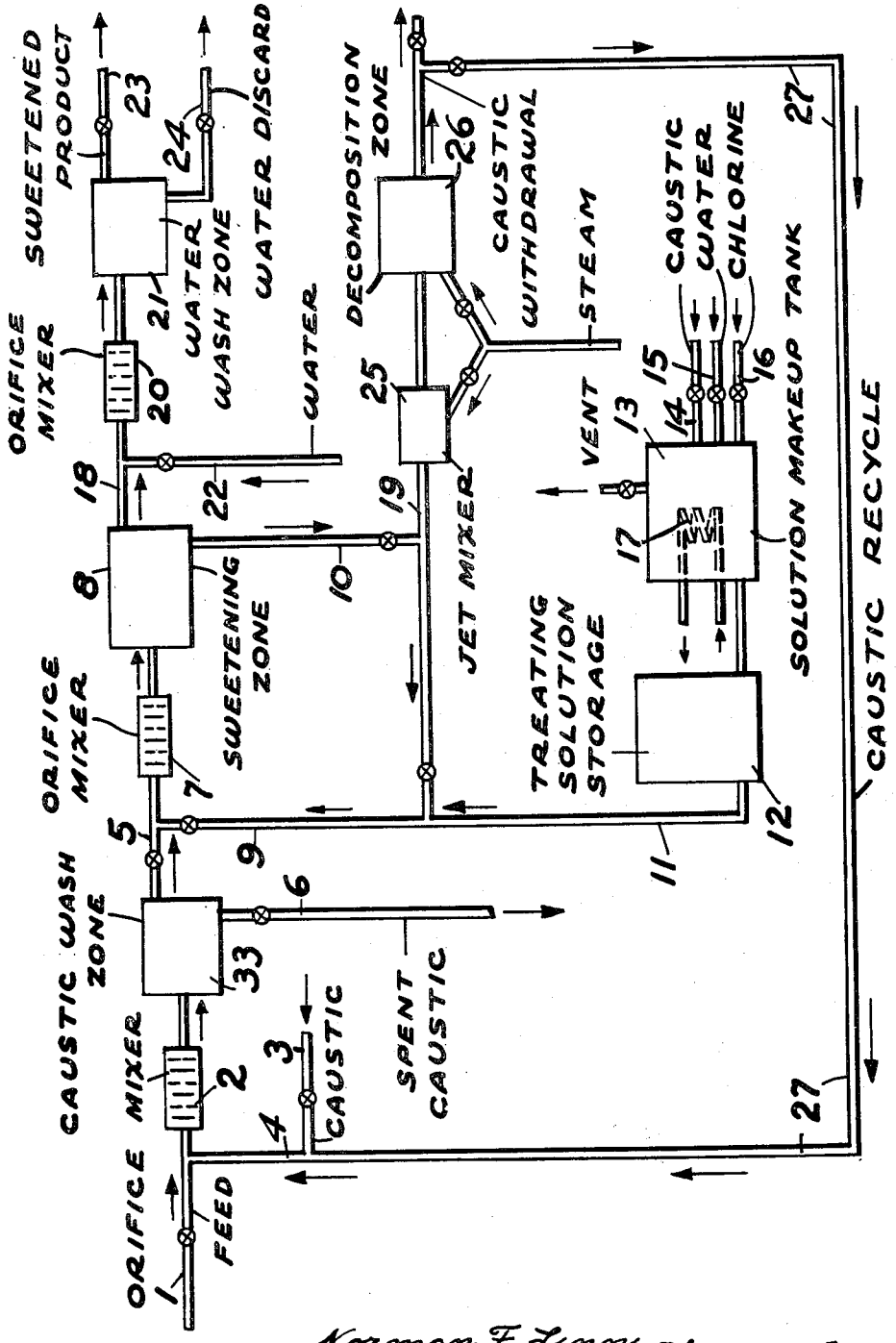
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HYPOCHLORITE SWEETENING PROCESS

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HYPOCHLORITE SWEETENING PROCESS

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This invention is concerned with an improved hypochlorite sweetening process in which particular operating features are involved and in which particular concentrations of treating agents are maintained. The invention is concerned with the conversion of mercaptan compounds present in petroleum oils using a treating reagent consisting of a hypochlorite solution containing high quantities of sodium hydroxide and sodium chloride. A novel feature of the process is the manner in which it is continuously conducted so as to provide for the recirculation of the main body of the treating reagent with provision for the discard of a portion of the agent and for the addition of makeup constituents so as to maintain optimum quantities of the treating constituents at all times. A particular advantage of the process is the economy of operation provided by a novel manner of treating spent hypochlorite solution so as to provide suitable sodium hydroxide solutions for preliminary caustic washing operations.

As disclosed in United States application No. 86,152 filed April 5, 1949, now U. S. Patent No. 2,550,668, improved sweetening results may be obtained by using a hypochlorite sweetening solution containing an excess quantity of sodium hydroxide and a high proportion of sodium chloride. Such a solution is operative to cause a marked reduction in sulfur content when using a comparatively small treat. The present invention is related to this type of operation by providing an improved procedural method for conducting this type of sweetening adapted for economic commercial utilization. It is therefore to be understood that while the identified application U. S. 86,152 broadly concerns the concentrations of constituents to be used in hypochlorite sweetening, this application relates to improved steps and procedures for conducting this type of sweetening.

In the refining of petroleum oils, a common refining step is to treat the oils by various procedures in order to remove objectionable compounds such as sulfur compounds therefrom. One manner of accomplishing this which has been known is to treat particular hydrocarbon fractions with a hypochlorite solution containing, for example, either sodium or calcium hypochlorite. Mercaptans present in the petroleum fraction react with the hypochlorite solution to form alkyl disulfides,

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a metal chloride, and water. The conversion of the mercaptans to disulfides has the effect of "sweetening" the petroleum fraction so as to eliminate the malodorous mercaptans and so as to form the relatively harmless disulfides.

This general type of sweetening operation using hypochlorite solutions has not been particularly attractive for a number of reasons. First, a prime disadvantage of the older method of sweetening with hypochlorite solutions containing only relatively minor amounts of free sodium hydroxide is that considerable amounts of chlorine are introduced into the hydrocarbons with a resulting degradation in product quality. Secondly, the corrosion of equipment has been severe so that high replacement rates and costs have discouraged the wide adoption of the hypochlorite process. Thirdly, in prior methods of sweetening with hypochlorite solutions containing minor amounts of free sodium hydroxide as in U. S. Patent 1,552,830, it was necessary to follow the sweetening operation with a caustic washing step in order to obtain a marketable product. By conducting the sweetening operation according to the improved process described hereafter, no caustic afterwash is required. It is therefore the principal object of this invention to provide an improved hypochlorite sweetening process in which relatively low treats of the treating reagent are required, in which product degradation is substantially reduced and in which the corrosivity of the treating solution is substantially eliminated.

A still more specific object of this invention is to provide an effective continuous process for conducting the sweetening operations in a manner to permit maintenance of the optimum quantities of sweetening reagents.

A still further object of the invention is to provide a recovery operation for treating the spent hypochlorite sweetening solution so as to economize the consumption of the treating reagent.

The manner in which these and other objectives of this invention are attained will be understood from the following description developed with relation to the accompanying drawing in which a suitable flow plan of the hypochlorite sweetening process of this invention is diagrammatically illustrated.

In accordance with the process of this inven-

tion, a sweetening solution is used consisting of particular proportions of hypochlorite, of sodium hydroxide, and of sodium chloride. The hypochlorite in the solution may consist of either sodium or potassium hypochlorite, although, other alkali metals or alkali earth metals having soluble hydroxides may be used, if desired. The amount of the hypochlorite solution employed is not critical and may vary appreciably in the ranges, for example, of about 2% to 50% and higher, based upon the volume of oil being treated. According to the preferred procedure, in order to maintain the quantity of treating solution as low as possible, the percent treat is maintained at about 5%. Similarly, the concentration of the hypochlorite in the sweetening solution may vary appreciably, and, to some extent, the concentration will be a function of the amount of solution utilized. Thus, while the concentration of the hypochlorite may be chosen from the range of about 1 to 60 grams of sodium hypochlorite or equivalent, per liter, it is preferred that the concentration be in the range of about 1 to 12 grams per liter of treating solution. More narrowly still, it is preferred that about 1 to 5 grams per liter of hypochlorite be utilized. These specific concentrations of hypochlorite limit the oxidizing power of the solution so as to minimize undesired reactions.

The concentration of sodium hydroxide maintained in the sweetening solution is a critical factor which must be assiduously maintained above 90 grams per liter. A preferred concentration of the sodium hydroxide is 100 to 300 grams per liter, and, more specifically, may be said to be about 200 grams per liter. The concentration of the sodium hydroxide is critically chosen in the range indicated for three reasons. First, the sweetening effect obtainable is critically related to the sodium hydroxide content, as indicated by the fact that improved sweetening results are obtained in the case in which an excess of sodium hydroxide is maintained over the case in which less than 50 grams per liter of sodium hydroxide is maintained. Secondly, by maintaining a high concentration of caustic, the equilibrium between hypochlorite and hypochlorous acid is controlled so that only a small concentration of hypochlorous acid will be present. This aids in limiting the oxidation potential of the treating solution so as to minimize undesired side reactions. In particular sour cracked stocks may be sweetened without danger of forming highly oxidized compounds or of introducing excessive amounts of chlorine into the hydrocarbon. Thirdly, the corrosivity of the sweetening solution is critically related to the concentration of the sodium hydroxide. Thus, it has been discovered that when the sodium hydroxide is present in concentrations of less than about 90 grams per liter, the sweetening solution begins to exhibit corrosive tendencies towards ferrous materials. However, when the concentration of the sodium hydroxide is greater than about 90 grams per liter, the sweetening solution is substantially non-corrosive to ferrous materials. Consequently, for these three reasons, the concentration of sodium hydroxide is maintained above 90 grams per liter, and preferably, at about 100 to 300 grams per liter so as to maintain the hydroxide content on the safe side of the corrosive limits and so as to maintain the hydroxide content in the range in which improved sweetening results may be obtained.

Similarly, the concentration of the sodium chloride maintained in the sweetening solution is a critical factor which is carefully controlled by the process of this invention. Thus, improved sweetening results are obtained by maintaining the sodium chloride content in the range of about 50 to 250 grams per liter, the upper limit being set by the solubility of sodium chloride. It is apparent that should reagents other than sodium hypochlorite and sodium hydroxide be used, the concentration of the corresponding salt should similarly be maintained below saturation conditions. In the preferred operation of this process, the sodium chloride content is maintained at about 100 grams per liter. This range is particularly preferred in order to keep the sodium chloride at a concentration level adapted for effective sweetening, but so as to maintain the sodium chloride content below the level at which the sodium chloride begins to precipitate from the sweetening solution. This precipitation point is at about 170 grams per liter of sodium chloride when the treating solution contains 200 g./l. of NaOH and 5 g./l. of NaOCl. A practical advantage of operating considerably below the saturation limit of sodium chloride, at about 100 grams per liter for example, is that localized salt build-ups may be tolerated without likelihood of salt precipitation.

Other operating parameters of the sweetening operation are not particularly critical and may be controlled within wide limits. Thus, the time of contact may be more or less arbitrarily chosen, but should preferably be below about 10 minutes to limit possibility of undesirable side reactions. A contact time of about 2 to 5 minutes is preferred. The temperature of treatment may be chosen from the range of about ambient temperatures to about 150° F. Any temperature greatly in excess of about 125° F. is undesirable since the sodium hypochlorite in the sweetening solution becomes unstable at higher temperatures.

With this general indication of the critical factor and principles of hypochlorite sweetening, the process of this invention may be appreciated by reference to the accompanying drawing. Referring to this drawing, the numeral 1 designates a feed introduction line for petroleum fractions to be treated in accordance with this invention. The fraction to be treated may broadly be any hydrocarbon fraction boiling below about 700° F. The process is of particular application to the treatment of uncracked hydrocarbon fractions although it is also effective in the sweetening of cracked stocks. The process is particularly applicable to those hydrocarbons boiling in approximately the kerosene boiling range, as, for example, in the range of about 300 to 600° F. It is to be understood that the fraction to be treated contains malodorous mercaptans to be converted by the sweetening operation. Consequently, a suitable feed stock is conducted through line 1 to a mixing zone 2, wherein the feed hydrocarbons are mixed with a caustic solution introduced through line 3. As illustrated, the caustic washing facilities may comprise the orifice mixers or equivalent mixing means indicated by the numeral 2 operated in conjunction with the separation zone 33. Suitable caustic washing will be provided by utilizing a single stage caustic contacting of the feed employing about 4 to 20 percent of a caustic solution containing about 3 to 20 percent of caustic. It is preferred to utilize about 10% of a caustic solution comprising about 5° Baumé caustic solution. This caustic washing is operative to remove hydrogen sulfide and a portion of

other sulfur compounds from the feed. The particular purpose of the caustic washing is to remove the hydrogen sulfide which otherwise could be converted to elemental sulfur in later sweetening steps.

The caustic washed feed hydrocarbons may be removed from the upper portion of separation zone 33 through line 5 while the spent caustic solution may be removed from the lower portion of zone 33 through line 6, containing the abstracted sulfur compounds. The caustic washed feed hydrocarbons are then conducted through line 5 to mixing zone 7 and sweetening zone 8. Again, the mixing means utilized in zone 7 may, if desired, consist of simple orifice mixers or equivalent means operative to thoroughly mix the feed hydrocarbons of line 5 with sweetening solution conducted through line 9. As will be developed, the sweetening solution of line 9 principally consists of the sweetening reagents withdrawn from the sweetening zone 8 through line 10 for recycle back to zone 8 through line 9. Makeup sweetening constituents are also introduced to line 9 from line 11 leading from storage zone 12. Thus, storage zone 12 contains a solution containing fresh hypochlorite, sodium hydroxide and sodium chloride. This solution may be made up in the solution makeup vessel 13 in which caustic, water, and chlorine are combined. Thus, caustic solution may be introduced to zone 13 through line 14 while water and chlorine are respectively introduced to zone 13 through lines 15 and 16. In a specific embodiment of this invention, caustic of about 50° Baumé is introduced through line 14 while sufficient water is introduced through line 15 to dilute the caustic to a concentration of about 29° Baumé. Sufficient chlorine is then introduced through line 16 to provide a desired concentration of sodium hypochlorite. As an example of preferred conditions, sufficient reagents are introduced to zone 13 so as to provide a sweetening solution consisting of 200 grams per liter of sodium hydroxide, 65 grams per liter of sodium hypochlorite and about 51 grams per liter of sodium chloride. Sodium chloride is formed as a by-product of the hypochlorite formation and subsequently in the sweetening zone is formed as a by-product of the sweetening reaction. It is important that cooling coils or equivalent means 17 be provided in zone 13 so as to maintain the temperature of the solution below about 125° F. The sweetening solution as made up may then be conducted to storage zone 12 for subsequent addition to sweetening zone 8, as will be described.

In the operation of sweetening zone 8, as indicated, the feed hydrocarbons to be sweetened are mixed with the sweetening reagents in mixer 7 and are then passed to the separation zone 8. Zone 8 may simply consist of a settling zone operated to permit withdrawal of sweetened hydrocarbons from the upper part thereof through line 18 and to permit the withdrawal of partially spent sweetening solution from the lower part of the zone through line 10. The temperature of zones 7 and 8 is maintained below about 150° F., preferably below 125° F. The contact of the indicated sweetening solution and the feed hydrocarbon converts mercaptans present to disulfides with the consequent formation of sodium chloride. Thus, the concentration of sodium chloride in line 10 will be greater than the concentration of sodium chloride in line 11. Similarly, the concentration of the sodium hypochlorite in line 10 will be lower than the concentration of sodium chloride in line 11. It is apparent that with continuous recycle of the sweetening solutions through line 10 back to the sweetening zone, the concentration of sodium chloride would build up to prohibitive levels, while the concentration of the sodium hypochlorite would drop to insufficient levels. Consequently, a portion of the solution of line 10 is periodically or continuously withdrawn through line 19 while a substantially equivalent amount of fresh sweetening solution is introduced to the system through line 11. In the preferred operation of this process, the withdrawal of sweetening solution through line 19 is maintained so as to hold the sodium chloride content of the solution at a desired level. Thus, for example, sufficient solution is withdrawn from line 10 through line 19 so that this solution has a composition of about 200 grams per liter of sodium hydroxide, about 3½ grams per liter of sodium hypochlorite, and about 100 grams per liter of sodium chloride. By this method of withdrawing partially spent sweetening solution while continuously adding fresh sweetening solution, it is possible to maintain the concentrations of sweetening reagents at optimum levels at all times. Thus, by the specific withdrawal and introduction of sweetening compositions having the concentrations indicated, at all times the sweetening reagents present in zone 8 will consist of a solution containing about 200 grams per liter of sodium hydroxide, from 3½ to 5 grams per liter of sodium hypochlorite, and from 98 to 100 grams per liter of sodium chloride. As will be developed, sweetening solutions of this composition are best adapted for the sweetening of hydrocarbons while having minimum corrosivity towards ferrous materials so that conventional steel tank and apparatus facilities may be utilized in the sweetening.

To complete the processing of the sweetened hydrocarbons removed through line 18, these hydrocarbons are preferably subjected to a water wash in mixer 20 and settling zone 21. For this purpose, about 30 volume percent of water may be introduced through line 22 for admixture with the hydrocarbons in mixer 20. The water washed sweetened product may then be removed through line 23 from the separation zone 21 while the water utilized may be discarded through line 24.

A particular feature of this invention is the manner in which the abstracted sweetening solution of line 19 is treated. The solution of line 19 is preferably contacted with steam in jet mixing zone 25 and is then conducted to decomposing zone 26. The contact of the spent sweetening solution with steam in zones 25 and 26 decomposes the greater part of the sodium hypochlorite. As indicated, the decomposition may be carried out by utilizing steam as a source of heat input provided the temperature be increased to about 200° F. Alternatively the solution of line 19 may be passed into decomposing zone 26 and there be contacted with steam to promote decomposition of residual sodium hypochlorite. The steam is also effective to dilute the sweetening solution sufficiently to prevent crystallization of salt present. It is preferred that the sweetening solution be maintained in zones 25 and 26 for a period about 10 minutes in order to permit satisfactory decomposition of the sodium hypochlorite to sodium chlorate and sodium chloride. The resulting solution, to be removed through line 27, will therefore consist of a sodium hydroxide solution

containing tolerable concentrations of sodium chlorate, sodium hypochlorite and sodium chloride. This caustic solution on suitable dilution may then be recycled through line 27 for utilization as the caustic washing agent employed in caustic washing zones 2 and 3. If desired, a portion of the sodium hydroxide solution of line 27 may be withdrawn for use as desired in other refining operations.

Having now fully described a preferred manner of conducting the process of this invention, examples of treating operations will be given to more clearly define the nature and scope of this invention.

EXAMPLE 1

An uncracked kerosene fraction containing mercaptans and boiling in the range from about 340 to 530° F. was contacted with hypochlorite solutions containing different quantities of sodium hydroxide for contact times of about 2 minutes.

The results of these operations are listed as follows:

Effect of concentration of sodium hydroxide in hypochlorite sweetening of kerosene in two minutes contact time

Operation	Hypochlorite Analysis		Treat, Vol. Percent	Doctor Test	Acidity, Ml.N/10KOH/100 ml.	Chlorine, Wt. Percent
	NaOCl, g./l.	NaOH, g./l.				
1	10.7	2.1	25	DNP		
2	10.7	2.1	50	pass	2.25	0.002
3	10.7	26	10	DNP		
4	10.7	26	25	pass	1.36	0.004
5	10.8	51	10	do	1.44	0.002
6	10.6	78	10	do	1.25	0.004
7	10.5	107	5	DNP		
8	10.5	107	10	pass	0.92	0.002
9	6.8	170	5	do	1.0	0.0011
10	4.4	2.8	5	do	0.19	0.0017

These results show that the kerosene can be sweetened with progressively smaller amounts of hypochlorite as excess sodium hydroxide is utilized.

From the above it is apparent that very desirable results are secured by utilizing a hypochlorite solution containing a relatively high concentration of sodium hydroxide.

EXAMPLE 2

Corrosion experiments were conducted to determine the corrosivity toward steel test panels of sweetening solutions containing variable quantities of sodium hydroxide. These experiments set forth in the table below showed that if caustic concentration was maintained above about 90 grams per liter, substantially no corrosion occurred.

Corrosion tests on steel

Composition of Sodium Hypochlorite Solution		Time on Test	Corrosion Rate, In./Yr.	Pitting
Free NaOH, g./l.	Available Chlorine, g./l.			
158	0	25	0.0001	No
129	22	25	0.0003	No
109	45	25	0.0001	No
176	109	19	0.0002	No
96	102	19	0.0002	No
83	64	25	0.0028	Yes
55	89	25	0.0097	Yes
38	84	19	0.0030	Yes

EXAMPLE 3

An uncracked kerosene secured from a West Texas crude and boiling in the range from about 350 to 530° F. which contained 99 milligrams of mercaptan sulfur per 100 milliliters was treated in various operations with the following results:

Effect of sodium hydroxide concentration in hypochlorite sweetening of West Texas kerosene in two minutes contact time

Operation	Hypochlorite Analysis		Treat, Vol. Percent	Doctor Test	Acidity, Ml.N/10 KOH/100 ml.	Chlorine, Wt. Percent
	NaOCl, g./l.	NaOH, g./l.				
1	55.7	9.0	100	Pass	20.1	0.0347
2	55.7	9.0	50	do	13.5	0.0264
3	55.7	9.0	25	do	12.1	.0527
4	55.7	9.0	15	do	11.3	.0363
5	10.6	78.0	50	do	3.3	.021

From the above data it is apparent that for a fixed NaOH concentration, as the quantity of treat increased the tendency to form undesirable sulfonic acids and sulfonyl chlorides increased prohibitively as evidenced by the increase in acidity. On the other hand, in Operation 5, wherein an excess of sodium hydroxide was employed, the acidity was appreciably lower.

EXAMPLE 4

Other operations were conducted using an uncracked kerosene, secured from an Iraq crude, and boiling in the range from 350 to 500° F. with the following results:

Operation	Hypochlorite Analysis		Treat, Vol. Percent	Doctor Test	Acidity, vol. N/10KOH	Chlorine, Wt. Percent
	NaOCl, g./l.	NaOH, g./l.				
1	10.8	156	2	DNP		
2	10.8	156	5	Pass	2.03	0.0044
3	10.5	166	2	do	0.48	0.0014
4	10.3	220	2	do	0.58	0.0014

It is apparent from this data that excellent results are secured when the amount of hypochlorite is maintained relatively low, when excess sodium hydroxide is employed, and also when a relatively low volume of treat is utilized.

EXAMPLE 4B

The same feedstock used in Example 4 was treated with a solution containing only 1.5 grams NaOCl/liter and a contact time of about two minutes, but in this example the amount of free sodium hydroxide was varied. The results tabulated below show that the volume percent treat required decreases as the caustic concentration is increased.

NaOH, g./l.	Treat, Vol. Percent	Doctor Test	Chlorine, Wt. Percent	Acidity, ml. N/10KOH	NaOCl Consumption Times Theory
96	30	DNP			
	35	Pass	0.0022	0.68	3.3
142	25	DNP			
	30	Pass	0.0014	0.58	2.9
193	20	DNP			
	25	Pass	0.0014	0.29	2.4
241	10	DNP			
	20	Pass	0.0009	0.19	1.9

It will be noted that as the concentration of caustic is increased, the weight percent of chlorine in the product is progressively reduced. By operating therefore with solutions containing significant amounts of caustic no strong caustic afterwash is required in order to obtain an acceptable product. Further, it will be observed that the ratio of actual consumption of sodium hypochlorite to theoretical is significantly reduced as the caustic concentration is increased.

EXAMPLE 5

Additional operations were conducted wherein an excess of sodium chloride was used in conjunction with an excess of sodium hydroxide. The results of these operations are as follows:

Effect of excess sodium chloride in hypochlorite sweetening of Iraq kerosene (14 mg. mercaptan sulfur/100 ml.)

Operation	Hypochlorite Composition [1]			Treat, Vol. Percent	Doctor Test	Residual Acidity	Chlorine, Wt. Percent
	NaCl, g./l.	NaOH, g./l.	NaOCl, g./l.				
1	8	1.6	10.4	50	DNP		
				75	Pass	2.30	0.0096
2	80	1.6	10.4	50	DNP		
				75	Pass	2.30	0.0096
3	8	107	10.6	5	DNP		
				10	Pass	0.92	0.002
4	80	105	10.6	5	Pass	1.06	0.0015

[1] Amounts of sodium chloride shown were weighed into the solutions; NaOH and NaOCl were determined by analysis.

From the above, it is readily apparent that when excess sodium chloride is used in conjunction with a hypochlorite solution which contains a relatively low concentration of sodium hydroxide, no marked effect is secured. However, when excess sodium chloride is used in conjunction was a hypochlorite solution which has a high concentration of sodium hydroxide, unexpected and desirable results are secured.

EXAMPLE 6

A solution containing about 2.3 grams per liter of sodium hypochlorite was heated to 210° F. After maintaining this temperature for one minute, it was found that the hypochlorite concentration had been reduced to about 0.8 gram per liter. No further hypochlorite decomposition occurred at longer heating periods.

As brought out in the preceding description, the process of this invention is a hypochlorite sweetening process in which optimum concentrations of sweetening reagents are maintained in a sweetening zone. This is accomplished by the continuous or periodical addition of makeup sweetening solution concomitant with the continuous or periodic discard of spent sweetening solution. By this means the process may readily be controlled once the flow rates are established so as to obtain optimum sweetening results with constant product quality. Discard of the spent

sweetening solution is particularly controlled in accordance with this invention so as to maintain a given concentration of sodium chloride such as 100 grams per liter in the discarded sweetening solution. The discarded sweetening solution is then decomposed by heating to a temperature above 200° F. and is diluted to provide a usable caustic solution, at least a part of which is used to pre-wash the hydrocarbons to be sweetened. As indicated, this novel treating process is particularly adapted for the treatment of hydrocarbons of the kerosene boiling range.

What is claimed is:

1. A sweetening process in which hydrocarbons are contacted in a sweetening zone with a sweetening solution having a hypochlorite content of about 1 to 12 grams per liter, a sodium hydroxide content of about 100 to 300 grams per liter, and a sodium chloride content of about 50 to 100 grams per liter, said sweetening solution being maintained to have this composition by substantially constant recirculation through the said sweetening zone, while withdrawing partially spent sweetening solution substantially constantly characterized by containing about 100 grams per liter of sodium chloride, and while introducing fresh sweetening solution substantially constantly to the said sweetening zone, said fresh sweetening solution having about 1 to 12 grams of hypochlorite per liter, a sodium hydroxide content of about 100 to 300 grams per liter, and a sodium chloride content of about 50 grams per liter.

2. The process of claim 1 in which the feed hydrocarbons are pre-washed with caustic solution.

3. The process of claim 2 in which the withdrawn sweetening solution is heated to temperatures above about 200° F., is diluted with water, and at least a portion thereof is utilized in the caustic washing steps.

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