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PROCESS OF TREATING HYDROCARBONS, INVOLVING THE REACTION BETWEEN OBJECTIONABLE SULPHUR AND MERCAPTAN CONSTITUENTS

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This invention pertains primarily to the removal of elementary sulphur and to the removal or rendering innocuous the mercaptans and substances of disagreeable odor occurring in hydrocarbon products, such as cleaners' naphthas, gasolines, kerosenes, etc., which are commonly refined to pass the "doctor" test and the copper corrosion test of the petroleum industry, described in United States Government specification for Lubricants and liquid fuels, 1927, #323 B, pages 96 and 97.

The use of plumbite solution is well known for treatment of hydrocarbons containing elementary sulphur and/or mercaptans. The chemistry of the process has been described by Wendt and Diggs in the Journal of Industrial and Engineering Chemistry, (1924), and is the process which has been generally in use.

All methods thus far found practical for sweetening sour gasoline with the aid of sulphur have consisted in bringing about the reactions between the sulphur and the mercaptans thru the agency of a compound of lead, preferably sodium plumbite, which is prepared by dissolving litharge in an aqueous caustic soda solution. The lead acts as an intermediate reagent or as a catalyst, or both, to bring about complete reaction between equivalent quantities of sulphur and mercaptans. Unless the lead compound is used, it has thus far been impossible to sweeten sour gasoline with sulphur except by adding a large excess to the gasoline over the amount necessary to react with the mercaptans, and under this condition the excess sulphur remains dissolved in the gasoline, rendering it extremely corrosive. The U. S. Bureau of Mines, Technical Paper 323–B, page 97, has rigid tests which exclude all corrosive constituents from gasoline. No reputable gasoline manufacturer will sell gasoline containing elementary sulphur.

The following two equations are representative of the process by which sodium plumbite brings about the reaction between mercaptans and sulphur in gasoline and renders the gasoline sweet and non-corrosive:

$$(1)\quad 2RSH+Na_2PbO_2=(RS)_2Pb+2NaOH$$
$$(2)\quad (RS)_2Pb+S=R-S-S-R+PbS$$

In the equations "R" represents an organic radical. The product of the reaction, the alkyl disulphide, R—S—S—R, is innocuous and remains dissolved in the gasoline. The lead sulphide, PbS, is insoluble in both the gasoline and the aqueous solution. After the sweetening, this lead sulphide usually settles from the gasoline, especially if the gasoline is washed with water; but in any case the lead sulphide carries an appreciable quantity of the gasoline as a very stable emulsion into the aqueous layer when it settles, and this emulsion entails a loss. In addition to this disadvantage of the plumbite treatment, the original litharge is expensive, and a large amount of caustic solution must be used as a vehicle to carry the sodium plumbite.

The sodium plumbite solution is remarkable in that it completely utilizes equivalent amounts of sulphur and mercaptans, leaving no traces of either in the gasoline and, moreover, if a 10 or 20% excess of sulphur is added to the gasoline over the amount actually required, the plumbite solution extracts the excess and leaves the gasoline free of sulphur. The need has long existed for an inexpensive reagent possessing the valuable properties of the plumbite solution but one which is cheaper and which will produce no troublesome by-products, such as the lead sulphide.

It has been known for some time that mercaptans in gasoline can be converted into the innocuous alkyl disulphides by dissolving free sulphur in the gasoline in large excess over the amount actually required for the reaction with the mercaptans and then agitating the gasoline with an aqueous caustic soda solution of 5 to 20% strength. This process, however, cannot be used in practice, inasmuch as the excess sulphur remains in the gasoline and renders it extremely corrosive. If less sulphur is used, the mercaptans will not be eliminated.

I have discovered that if a predetermined quantity of sulphur is added to sour gasoline (gasoline containing mercaptans), the sulphur and mercaptans can be made to react completely and almost instantly so as to leave the gasoline entirely free of elementary sulphur and mercaptans by co-mingling the gasoline bearing these ingredients with anhydrous or almost anhydrous caustic alkalies. Moreover, about 15% more sulphur than the minimum amount required to complete reaction can be added and yet all the excess is removed, thus permitting about as much margin in the proportion of sulphur added as in the plumbite treatment. All the products of the reaction which are to be removed from the gasoline are completely soluble in water and can be washed from the gasoline by means of only a little water.

Inasmuch as this new invention depends upon the mutual reaction between sulphur and mercaptans, elementary sulphur can also be instantly removed from gasoline by adding the proper proportions of mercaptans to the gasoline and then co-mingling the gasoline solution with the anhydrous caustic alkali. Thus two different samples of gasoline, one corrosive from elementary sulphur, and the other sour from mercaptans, can be properly blended and made sweet and non-corrosive with the anhydrous caustic alkali.

As illustrations of methods of applying the anhydrous or almost anhydrous alkalies to the gasoline which has already been prepared with

the proper reacting proportions of sulphur and mercaptans are the following:

(1) Finely divided anhydrous sodium or potassium hydroxide can be co-mingled with the prepared gasoline.

(2) Anhydrous caustic alkali can be dissolved in almost anhydrous alcohol, as methyl or ethyl, to make a solution containing any desired concentration, 10 or 15%, and a fraction of a per cent of this solution, about 0.1 to 0.3%, added to the prepared gasoline and agitated a few seconds.

(3) A saturated solution of sodium or potassium hydroxide in water (approximately 50% concentration or higher) can be agitated in relatively large volume (5%) for 15 minutes with the prepared gasoline.

The chemical reactions involved in oxidizing the mercaptans by means of the sulphur are more complex than indicated in the simple equations:

$$(1)\ 2RSH+2NaOH=2RSNa+H_2O$$
$$(2)\ 2RSNa+S=R-S-S-R+Na_2S,$$

inasmuch as more sulphur must be added to the gasoline than indicated in the equations. However, the amount required for any given sample of gasoline, like that required in sweetening with plumbite solution, can be varied by only a narrow margin, about 15%, as stated above. A lesser amount of sulphur will not sweeten, and a greater amount will sweeten but will leave the gasoline corrosive from the extra sulphur. The elementary sulphur added is removed as water-soluble compounds, and an analysis of the water extract shows that a sulphide is present. The yellowing color of the extract indicates the possible presence of a polysulphide, such as sodium tetrasulphide.

The greater amount of sulphur required than in the corresponding plumbite treatment is probably involved in the actual sweetening operation thru a release of energy rather than thru supplying additional sulphur for two competing reactions; one the oxidation of the mercaptans with formation of alkyl disulphides and sodium sulphide, and the other the formation of polysulphides with the sodium sulphide of the first reaction. This assumption is made from the fact that in a special test a large proportion of sodium sulphide was added to the anhydrous alcoholic-alkali solution used in sweetening, and practically no more sulphur was required than when the alcoholic-alkali solution alone was used.

That the extra sulphur is involved in supplying chemical energy for the sweetening process may also be inferred from the three facts that (1) the polysulphides are not readily formed in a dilute water solution from sulphur and sodium sulphide, (2) that a sour gasoline cannot be sweetened and made non-corrosive with sulphur and an aqueous solution of caustic alkali when the concentration is appreciably less than 50%, and (3) that sour gasoline cannot be sweetened with only sulphur and sodium sulphide in solution in water or in alcohol.

The chemistry of the polysulphides and their formation is very intricate, and I desire my claims of discovery to rest on the experimental facts rather than on the theories advanced.

A practical method of adding the necessary sulphur for sweetening is to add a determined proportion, e. g., 1 to 2%, of a like hydrocarbon which has been more or less saturated with the sulphur, which is usual in present refining practice, although the proportion of sulphur may be different. The mercaptan required for the necessary ratio to remove sulphur can be added by adding a "sour" hydrocarbon or pure mercaptan. The manner of contacting of the hydrocarbon with solid caustic alkalies needs no special discussion, and the examples given in the table show the results of the treatment.

Another practical method consists in the use of an active alkaline reagent dissolved in an organic solvent, which in turn is highly soluble in liquid hydrocarbons, such as cleaners' naphthas, gasolines, kerosenes, etc. Among such solvents are the alcohols, acetone, commercial ethyl ether, and equivalent solvents and among the alkaline reagents suitable for use are the caustic alkalies (sodium and potassium hydroxides), alkali metal alcoholates (e. g. sodium ethylate), oxides and hydroxides of the alkaline earth metals (e. g. calcium and barium). The table shows examples of these solutions as used in my laboratory experiments in treating California cracked gasoline as typical of hydrocarbons. The data do not all pertain to the same sample of gasoline, although the different samples used did not differ greatly among themselves.

The choice of solvent for the alkali will be determined mainly from its relative cost, efficiency, and ease of recovery after use. Anhydrous methyl alcohol is soluble to the extent of around 5% by volume in gasoline, while anhydrous ethyl alcohol and all the higher molecular weight monohydric alcohols of commercial importance are soluble in all proportions.

More sodium or potassium hydroxide dissolves in methyl alcohol than in the higher alcohols, but as the solubility or miscibility of the resulting solution in hydrocarbons is less than the alkali solutions of the higher alcohols, a little more agitation is required when the alkali-methyl alcohol solution is used. However, by blending the methyl alcohol solution with those of the higher alcohols, such as ethyl, the propyls, etc., a solution is obtained having a high percentage of alkali, and at the same time having characteristics of high miscibility with the hydrocarbons, and only a little agitation is required for thorough commingling. Examples 6 and 7 in the table are illustrations of such mixtures.

A mixture of the caustic alkalies in alcohol or alcohols is satisfactory and gives a little more flexibility in the proportion of sulphur or mercaptan which can be added so as to yield a product both sweet and non-corrosive.

These alkalies remove hydrogen sulphide and other acidic substances from the hydrocarbons, although hydrogen sulphide can be removed very easily by simply washing with a dilute aqueous caustic soda solution.

As stated previously, solid potassium hydroxide or solid sodium hydroxide or a concentrated solution of aqueous sodium hydroxide in relatively large quantities can be contacted with the hydrocarbon containing the proper amount of added sulphur or of added mercaptan to make the hydrocarbon sweet and non-corrosive. The excess alkali can in all cases be utilized for treating additional quantities of hydrocarbons or for other purposes in the refinery. The actual consumption of alkali in treating the hydrocarbons is the same whether the alkali is applied as solid or in solution.

To show specifically the significance of my discovery, I shall describe as a typical example the use of free sulphur and a cold saturated solution of sodium hydroxide in ethyl alcohol to

sweeten a sour cracked gasoline. A measured quantity of sulphur is added to the gasoline to be treated. This quantity is determined by control tests on a sample of the gasoline in question as is done in sweetening with plumbite solution. The ethyl alcohol solution contains about 12 to 14% by weight of the alkali. When added to the gasoline, even without agitation, the ethyl alcoholic solution immediately disperses and for an instant the whole has the appearance of complete solution. The intimate contact produced in this process is ideal for the chemical reaction, and but little agitation is required except as is needed to mix intimately any two mutually soluble liquids. The action of the propeller blades of a centrifugal pump, or that of an orifice plate, or the turbulent flow through a pipe is ample. The sweetening reaction is almost instantaneous. In a few seconds after the alcoholic alkali reagent is added, a slight whitish cloud develops which settles out completely in a few hours if no water is added, leaving the gasoline sweet and non-corrosive. The white material can be filtered out at once without waiting for the settling and the gasoline is sweet and non-corrosive. A convenient method consists in immediately washing the gasoline with a little water. All the products involved before and after the treatment are completely soluble either in the gasoline or in the water, although not in both. The amount of water used for washing can be controlled so as to remove practically all of the added alcohol. If ten to twenty times as much water is added as alcohol, the aqueous solution on separating from the gasoline has a content of approximately 5 to 10% of alcohol and not over about 0.1% of hydrocarbon. The alcohol can then be recovered from the aqueous solution by the normal processes of distillation. The water washing also leaves the gasoline sweet and non-corrosive.

In the table, the importance of the addition of sulphur is seen. In Example 3, the proper amount was added yielding a sweet and non-corrosive product. In Example 3—A, too much sulphur was added, producing a sweet, but corrosive product. In Example 3—B, too little sulphur left the product sour, and in Example 3—C, in which no sulphur at all was added, the product was left sour, even though 60 times as much alcoholic-alkali solution was used as in Example 3, which was satisfactory. The same observations maintain in Examples 2 and 2—C, inclusive, in Examples 13 and 14—B, inclusive, and in Examples 15 and 15—B, inclusive. If appreciably less alcoholic-alkali solution had been used in Examples 2 and 3, the product would have been both sour and corrosive. No harm results in using an excess of alcoholic alkaline solution except in the extra cost of the reagent. In the experiments shown in the table, the time of agitation was arbitrarily made five minutes, except in 15 and 15—B inclusive which was 15 minutes.

A hydrocarbon containing elementary sulphur or an excess of sulphur over the mercaptan content can be freed of the sulphur by the addition of the proper amount of mercaptan or of sour hydrocarbon and then treating with any of the above alkaline reagents. To verify this, the data of Example 2 were used, and a sample of otherwise sweet and non-corrosive gasoline, in which had been dissolved free sulphur in the proportion of 0.026 pound per barrel (42 gallon), was blended with an equal volume of the sour gasoline, and the whole treated with an equivalent of 0.35 pound per barrel of alcoholic-caustic soda solution. The finished product was then free of elementary sulphur and of mercaptans. A similar sample of the gasoline bearing the same proportion of elementary sulphur was rendered non-corrosive and sweet by treatment with 0.05 pound per barrel of heptyl mercaptan (Eastman Kodak Company) and 0.35 pound per barrel of the alcoholic-caustic soda solution.

For economical use of alcoholic alkali solutions, the alcohol should not be weaker than about 94%, and as a rule, the less water it contains, the better. If the alcohol contains more water, an excessive quantity of the alcoholic alkali reagent will be required. In the case of the sodium or potassium alcoholates, the alcohol must be anhydrous. The alcohols should be more or less concentrated with the alkali reagents, and the solution used while reasonably fresh. The gasoline should contain no visible water, but does not need to be anhydrous.

No. of example	Alkaline treating reagent		Sulphur added lb./bbl.	Test on treated hydrocarbon [a]	
	Lb. of reagent per bbl. of hydrocarbon	Alkaline chemical contained in treating reagent. Percent by weight		Doctor test	Copper strip test
	Stock sour gasoline			+	−
1	0.35 lb. NaOH-methyl alcohol solution	21.0	0.026	−	−
2	0.35 lb. NaOH-ethyl alcohol solution	12–14	0.026	−	−
2-A	do	12–14	0.035	−	+
2-B	do	12–14	0.020	+	−
2-C	14.00 lb. NaOH-ethyl alcohol solution	12–14	0.000	+	−
3	0.25 KOH-ethyl alcohol solution	28	0.025	−	−
3-A	do	28	0.035	−	+
3-B	do	28	0.020	+	−
3-C	15.00 KOH-ethyl alcohol solution	28	0.000	+	−
4	2.4 NaOH-iso-propyl alcohol solution	1.5	0.025	−	−
5	2.4 NaOH-butyl alcohol solution	1.5	0.025	−	−
6	0.35 NaOH in equal volumes of ethyl and methyl alcohol solution	20.00	0.025	−	−
7	0.35 NaOH in equal volumes of methyl and propyl alcohol solution	15.00	0.025	−	−
8	0.50 NaOH and KOH in ethyl alcohol solution	7% NaOH 9% KOH	0.032	−	−
9	16.00 KOH in acetone solution	0.56	0.029	−	−
10	0.28 sodium ethylate-ethyl alcohol solution (1 lb. Na in 16 lb. abs ethyl alcohol)	6.0	0.025	−	−
10-A	14.00 sodium ethylate-ethyl alcohol solution (1 lb. Na in 16 lb. abs ethyl alcohol)	6.0	0.000	+	−
11	65.00 denatured alcohol saturated with $Ca(OH)_2$	0.03	0.025	−	−
12	65.00 denatured alcohol saturated with $Ba(OH)_2$	0.30	0.025	−	−
13	2.00 powdered NaOH	100	0.028	−	−
13-A	do	100	0.023	+	−
13-B	do	100	0.031	−	+
14	2.00 powdered KOH	100	0.028	−	−
14-A	do	100	0.000	+	−
14-B	do	100	0.033	−	+
15	15.0 NaOH-water solution	50	0.025	−	−
15-A	10.0 NaOH-water solution	50	0.025	+	+
15-B	50.0 NaOH-water solution	50	0.000	+	−
16	3.0 (60% alcohol, 40% water)—NaOH	12–14	0.028	+	+
16-A	4.5 (60% alcohol, 40% water)—NaOH	12–14	0.028	−	−

[a] The minus (−) sign in the next to the last column indicates that the product is sweet, and in the last column the minus sign indicates that the product is not corrosive. The plus (+) sign in the next to the last column indicates that the product is sour, and in the last column the plus sign indicates that the product is corrosive.

The stock (cracked gasoline) used was sour, but not corrosive.

Having described my invention, I claim:

1. The process of treating hydrocarbons, involving the reaction of objectionable sulphur and mercaptan constituents in the presence of an alkali, that includes adding to a hydrocarbon deficient in one of said constituents the deficient constituent in such proportion as to react, in the presence of alkali, with substantially all of the other constituents, and adding a substantially anhydrous alkali to the hydrocarbon.

2. The process of treating hydrocarbons, involving the reaction of objectionable sulphur and mercaptan constituents in the presence of an alkali, that includes adding to a hydrocarbon deficient in one of said constituents the deficient constituent in such proportion as to react, in the presence of alkali, with substantially all of the other constituents, and adding an anhydrous solution of alkali in alcohol to the hydrocarbon.

3. The process of treating hydrocarbons, involving the reaction between objectionable sulphur and mercaptan constituents in the presence of an alkali, that includes adding to a sulphur-deficient hydrocarbon containing mercaptans, elementary sulphur in such proportions as to react, in the presence of an alkali with all the mercaptan constituents, and adding substantially anhydrous alkali to the hydrocarbon.

4. The process of treating hydrocarbons, involving the reaction between objectionable sulphur and mercaptan constituents in the presence of an alkali, that includes adding to a sulphur-deficient hydrocarbon containing mercaptans, elementary sulphur in such proportions as to react, in the presence of an alkali with substantially all of the mercaptan constituent, and adding substantially anhydrous alcoholic solution of alkali to the hydrocarbon.

5. The process of treating hydrocarbons, involving the reaction of objectionable sulphur and mercaptan constituents in the presence of an alkali, that includes adding to a hydrocarbon deficient in one of said constituents the deficient constituent in such proportion as to react, in the presence of alkali, with substantially all of the other constituents, and adding to the hydrocarbon a solution of alkali in a lower alcohol, which solution has comparatively low miscibility with the hydrocarbon, mixed with a higher alcohol having comparatively greater miscibility with the hydrocarbon.

6. The process of sweetening gasoline, involving the reaction between objectionable sulphur and mercaptan constituents in the presence of an alkali, that includes adding to the sulphur-deficient gasoline containing mercaptans, elementary sulphur in such proportion as to react, in the presence of an alkali, with substantially all of the mercaptan constituent, but with no substantial amount of elementary sulphur remaining to render the gasoline corrosive, and adding substantially anhydrous alkali to the gasoline.

7. The process of rendering gasoline non-corrosive, involving the reaction between objectionable elementary sulphur and mercaptan constituents in the presence of an alkali, that includes adding to a mercaptan-deficient gasoline containing elementary sulphur, mercaptans in such proportion as to react in the presence of an alkali with substantially all of the elementary sulphur, but with no substantial amount of the mercaptans remaining as such to render the gasoline sour, and adding substantially anhydrous alkali to the gasoline.

8. A process of sweetening gasoline comprising adding an amount of elementary sulphur sufficient to completely react with the mercaptans present in said gasoline and adding to the mixture substantially anhydrous alkali.

9. A process of sweetening gasoline comprising adding an amount of elementary sulphur sufficient to completely react with the mercaptans present in said gasoline, adding to the mixture substantially anhydrous alkali, and washing out the water soluble substances.

10. A process of eliminating the corrosiveness of gasoline containing elementary sulphur, comprising adding an amount of mercaptans to the corrosive gasoline sufficient to react completely with all of the elementary sulphur and adding to the mixture substantially anhydrous alkali.

11. A process of eliminating the corrosiveness of gasoline containing elementary sulphur, comprising adding an amount of mercaptans to the corrosive gasoline sufficient to react completely with all of the elementary sulphur, adding to the mixture substantially anhydrous alkali, and washing out the water soluble substances.

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