

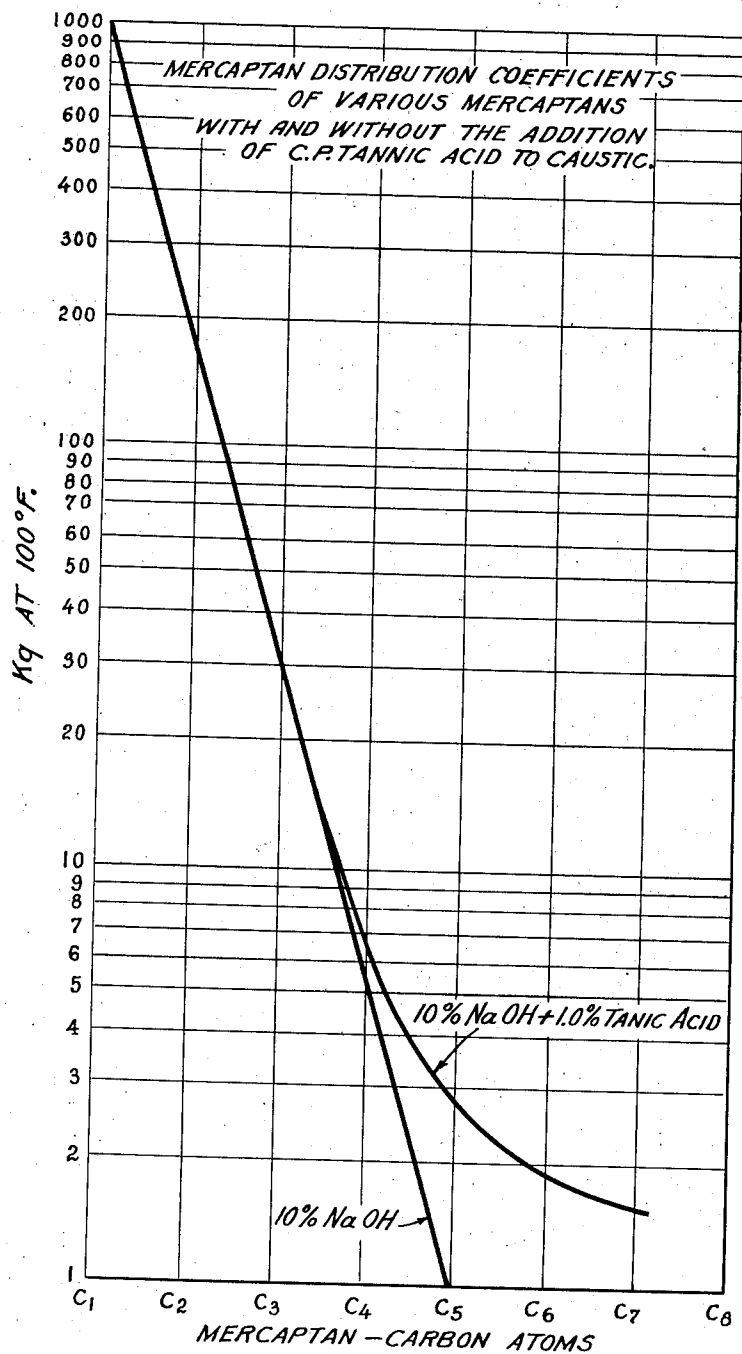
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METHOD OF TREATING OILS

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METHOD OF TREATING OILS

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8 Claims. (Cl. 196—31)

This application is a continuation in part of my prior application Ser. No. 404,835, filed July 31, 1941. The invention has to do with the reduction of the mercaptan content of hydrocarbon fractions of the nature of gasoline and the like. It has both the aspect of a process which sweetens by conversion to innocuous compounds and of a process which can reduce the mercaptan sulfur content by actual removal of the mercaptans.

In treating hydrocarbons, such as straight run gasoline, natural gasoline, cracked gasoline and the like, to render them sweet to the "doctor" test, the objective is to remove materials of the nature of dissolved sulfur, hydrogen sulphide, mercaptans or the like or to convert them to innocuous compounds. Washing with aqueous solutions of strong alkalies, such as caustic soda will remove most of the hydrogen sulphide and some, but not all, of the mercaptans. Washing with aqueous caustic to which some material has been added as a "solutizer," or solubility promoter, enables the caustic to dissolve and remove more or all of the mercaptans. Butylene glycols, butyric acids, and phenolic materials are so used. Older methods make use of sodium plumbite formed by dissolving litharge in caustic soda, the effect here being to convert mercaptans to mercaptides and later to disulphides, which are innocuous to the doctor test, by addition of free sulfur.

In general, all processes of this kind leave something to be desired, and this field, one of the oldest in petroleum refining, is still the subject of active research.

The principal object of this invention is the provision of a novel process capable of reducing mercaptan sulfur in petroleum hydrocarbons and which in one aspect of its use provides an internally regenerated treating method effective in rendering petroleum hydrocarbons sweet to the doctor test.

This invention is based upon the discovery that effective reduction of mercaptan sulfur may be effected by treatment with aqueous caustic soda solution containing tannic acid and that if, in addition to this, oxygen or an oxygen contain-

ing gas be present, during the contacting of the oil and of such reagent, a sweetening type of reaction may be accomplished.

The tannic acid when added to the usual strong caustic solution appears to be capable of exercising or of controlling two functions. In the first place, it exerts a "solutizer" type of action in enhancing the capability of the caustic soda for the solution of mercaptans of higher molecular weight. This action is quite marked for mercaptans of five carbon atoms and higher, and is apparently of little importance for mercaptans of lower molecular weight. The second function is apparently that of promoting greatly the oxidation of mercaptans to disulphides when oxygen or oxygen containing gases are present in the treating zone wherein the caustic tannin solution is contacted with the oil fraction.

The caustic alkali solution to be used may be any of the usual alkaline solutions normally used for these purposes, such as caustic soda, caustic potash, alkali metal carbonates, ammonia and basic ammonium compounds and the like. Usual preference is had for caustic soda, in aqueous solutions of from about 5° Baumé to 20° Baumé, the usual and preferred strength being around 10° Baumé.

The tannic acid used may be the usual commercial grade of the material.

I have found this tannic acid activator to be effective in quite small amounts, ranging from 5.0% downward to fractions of 1% with amounts of from about 0.3% to about 1.0%, by weight of caustic solution being the most effective.

To avoid undue consumption of reagent it is best to caustic wash the oil, prior to this treatment, as with an aqueous alkaline reagent, to remove hydrogen sulphide and the more readily removable sulfur containing materials.

The following experimental data show the effectiveness of the process herein described. To secure this data straight run and cracked gasolines were treated with various caustic alkali solutions with and without tannic acid, in various concentrations, with oxygen present, with air, and with nitrogen to show the effect of oxygen elimination.

TABLE I

Effect of tannic acid on removal of mercaptan sulfur from straight run gasoline by caustic solution

(Raw S. R. gasoline 0.005% RSH)

NaOH kind °Bé.	Tannic acid (per cent)	Temperature (°F.)	Ratio (NaOH: gaso.)	Gas atmosphere	Extractions (number of)	Mercaptan removal (percent)
Fresh 10.3.....	0.3	100	1:4	Air.....	1	72.5
Do.....	1.0	100	1:4	do.....	1	72.5
Do.....	5.0	100	1:4	do.....	1	67.5
Do.....	0.0	100	1:4	do.....	1	25.0
Do.....	1.0	82	1:4	do.....	3	75.0
Fresh 11.0.....	0.0	90	1:4	N ₂	1	29.0
Do.....	0.0	90	1:4	O ₂	1	29.0
Do.....	1.0	90	1:4	N ₂	1	31.8
Do.....	1.0	90	1:4	O ₂	1	73.4
Do.....	5.0	90	1:4	O ₂	1	62.5

TABLE II

Effect of tannic acid on removal of mercaptan sulfur from cracked gasoline by caustic solution

(Thermal cracked gasoline 0.025% RSH)

NaOH kind °Bé.	Tannic acid (per cent)	Temperature (°F.)	Ratio (NaOH: gaso.)	Gas atmosphere	Extractions (number of)	Mercaptan removal (percent)
Fresh 10.3.....	0.0	100	1:4	Air.....	1	59.0
Do.....	0.3	100	1:4	do.....	1	77.3
Do.....	1.0	100	1:4	do.....	1	81.8
Regen. 17 ¹ (approx.).....	0.0	95	1:4	do.....	1	60.2
Regen. 17 ²	1.0	95	1:4	do.....	1	70.4
Do.....	1.0	95	1:4	O ₂	1	87.1
Do.....	1.0	95	1:4	N ₂	1	58.1
Do.....	1.0	95	1:4	Air.....	3	85.3
Fresh 11.0.....	0.0	90	1:4	O ₂	1	66.6
Do.....	1.0	90	1:4	N ₂	1	67.4
Do.....	1.0	90	1:4	O ₂	1	89.0
Fresh 35.9.....	0.0	90	1:4	O ₂	1	65.3
Do.....	1.0	90	1:4	O ₂	1	83.6
Regen.....	0.0	90	1:4	N ₂	1	63.1
Do.....	1.0	90	1:4	O ₂	1	88.2
KOH						
Fresh 10.....	0.0	90	1:4	O ₂	1	68.5
Do.....	1.0	90	1:4	O ₂	1	91.8
Fresh 22.5.....	0.0	90	1:4	O ₂	1	73.2
Do.....	1.0	90	1:4	O ₂	1	91.8

¹ NaOH solu. boiled before using.

² Ditto.

The above data demonstrates the effectiveness of the reagent as a promoter of the oxidation of mercaptans under the circumstances shown. Note particularly those experiments wherein air was present in a caustic tannin solution as contrasted with those where air was present in a caustic solution treatment utilizing caustic of the same strength and free from tannin. For example, in the first four horizontal lines of Table I, the first three show caustic tannin in the presence of air and the fourth shows caustic alone in the presence of air. In the first three the mercaptan removal is around 70%, in the fourth it is around 25%. Similar contrasts occur in Table II, particularly in the first and last experiments performed with 11° Baumé caustic, the first being caustic alone in the presence of oxygen and effecting a mercaptan removal of about 67%, the last being caustic tannin in the presence of oxygen and effecting a mercaptan removal to the extent of 89%.

Another aspect of the use of caustic-tannin reagents is shown by the drawing attached hereto.

The single figure of this drawing shows the enhanced capability of caustic tannin solution for mere removal, as contrasted with oxidation, of certain mercaptans. This figure presents the distribution coefficient plotted against the number of carbon atoms contained in the mercaptans and was arrived at by treating a completely sulfur free light naphtha cut to various portions of

which known amounts of known mercaptans had been added, comparative treats being made with and without tannin present in a caustic solution of the same strength of caustic. The value plotted at the left hand in this drawing is K_d , the distribution coefficient. This distribution coefficient is a figure arrived at by dividing the concentration of the mercaptan in the treating solution by the concentration of the mercaptan remaining in the gasoline after the two have been in contact for a sufficient length of time to arrive at equilibrium. As may be seen from this drawing, there is practically no enhanced dissolving efficiency for mercaptans lighter than butyl mercaptan, the difference for that mercaptan being about 20%. However, for a five carbon atom mercaptan, the tannic acid-caustic solution is about three times as efficient and this difference increases with the heavier mercaptans. This is of particular interest, since it has always been these more difficultly removable high molecular weight mercaptans which have lowered the efficiency of attempts to remove sulfur compounds by caustic solutions.

Turning back to Table I above, wherein a cracked gasoline was treated, we find certain experiments recorded which confirm this removal. For example, considering operations with 11° Baumé caustic, we find that using caustic without tannin, the same mercaptan removal was effected whether oxygen or nitrogen

was used, namely, 29%. However, when 1% of tannin was added and nitrogen was used, the oxygen effect spoken of hereinabove not being present, the mercaptan removal was raised to 31.8%, an increase of approximately 10%.

Turning to Table II, and remembering that we have previously found that caustic solution in the absence of tannin gave about the same results, whether oxygen was present or not, we find in the first example, wherein 11° Baumé caustic was used, but tannin was not present, a mercaptan removal of 66.6%. In the line just below where 1% of tannin was used in the caustic solution, the atmosphere was nitrogen and the oxidation effect was not present, we still find an increase in mercaptan removal to 67.4%. The two increases in percentage of total mercaptan removal above, are relatively small, and in early work upon this discovery their significance was not understood. In view of later work resulting in the discovery of the effective solutizer action of tannic acid in caustic solutions, it is now realized that in these two examples, the difference between results was actually indicative of a materially increased capability of the reagent. The capability was small in the case of the cracked gasoline treated in Table II because of the rather high percentage of mercaptans present therein, practically all were necessarily low molecular weight mercaptans whose solubility in caustic was practically the same in either experiment. However, in Table I, where a straight run gasoline containing a greater amount of high molecular weight mercaptans was treated a more pronounced difference was obtained. In connection with this it must be remembered that under circumstances such as exist in the treatment of a commercial gasoline fraction containing mercaptans of a rather wide variety of molecular weights, a complete removal of a higher molecular weight mercaptan may present itself as only a slight increase in the amount of total mercaptan removal.

I claim:

1. That method of removing mercaptans of 4 or more carbon atoms from petroleum fractions comprising contacting the fraction with an aqueous alkaline reagent to which tannic acid has been added to promote the solution of mercaptans in said reagent.

2. That method of removing mercaptans of 4 or more carbon atoms from gasoline and the like comprising contacting the oil with an aqueous solution of caustic soda activated by the addition of a small amount of tannic acid to promote the solution of mercaptans in said caustic soda.

3. That method of removing mercaptans of 4 or more carbon atoms from gasoline and the like comprising contacting the oil with an aqueous solution of caustic soda activated by the addition of a small amount, less than about 5%, of tannic acid, to promote the solution of mercaptans in said caustic soda.

4. That method of removing mercaptans of 4 or more carbon atoms from gasoline and the like comprising contacting the oil with an aqueous solution of caustic soda activated by the addition of a small amount, from about 0.3% to about 1.0%, of tannic acid, to promote the solution of mercaptans in said caustic soda.

5. That method of removing mercaptan sulfur of 4 or more carbon atoms from a light petroleum fraction, which consists of contacting the fraction with an aqueous alkaline reagent to which tannic acid has been added to promote the solution of mercaptan sulfur in said reagent.

6. That method of removing mercaptan sulfur of 4 or more carbon atoms from a gasoline fraction, which consists of contacting the fraction with an aqueous solution of caustic soda activated by the addition of a small amount of tannic acid to promote the solution of mercaptan sulfur in said caustic soda.

7. That method of removing mercaptan sulfur of 4 or more carbon atoms from a gasoline fraction which consists of contacting the fraction with an aqueous solution of caustic soda activated by the addition of a small amount, less than about 5%, of tannic acid to promote the solution of mercaptan sulfur in said caustic soda.

8. That method of removing mercaptan sulfur of 4 or more carbon atoms from a gasoline fraction which consists of contacting the fraction with an aqueous solution of caustic soda activated by the addition of a small amount, from about 0.3% to about 1.0%, of tannic acid to promote the solution of mercaptan sulfur in said caustic soda.

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