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PROCESS OF REMOVING MERCAPTANS FROM HYDROCARBONS WITH ALKALI IMPREGNATED CHARCOAL

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This invention relates to the treatment of hydrocarbons to remove mecraptans therefrom. The processing of hydrocarbons, more particularly petroleum distillates such as gasoline and kerosene, in order to remove mercaptans therefrom is commonly practiced in view of the objectionable character of the mercaptans in the hydrocarbons, especially from the standpoint of odor. It has long been known that mercaptans (RSH) can be removed from hydrocarbons by treatment with an aqueous solution of an alkaline compound such as caustic soda. The extent and facility with which the mercaptans can be removed with a caustic solution depends upon a number of factors, some of which are apparent after a consideration of the following equation:

$$\underset{\text{dissolved in hydrocarbon}}{RSH} \rightleftharpoons \underset{\text{dissolved in caustic}}{RSH} \overset{+NaOH}{\rightleftharpoons} RSNa + H_2O \qquad (I)$$

One of the principal factors is the solubility of the respective compounds in the different phases and another factor is the concentration of the compounds in the different phases. The amount of the mercaptan which will be removed from the hydrocarbon phase and dissolved in the alkali phase depends in part upon the molecular weight of the mercaptan which affects solubility, and the concentration of the mercaptan in the phases. The presence of certain compounds in the caustic improve solubility of the mercaptans in it, but as the alkali is used to treat more mercaptan-containing hydrocarbon, the concentration of the mercaptan in the alkali shifts the equilibrium in the first part of the Equation I to the left. Similarly, as the concentration of the sodium mercaptide builds up in the alkali, the equilibrium in the latter part of the equation is also shifted to the left. Thus it can be seen that in treating mercaptan-containing hydrocarbons with a fresh caustic solution excellent results can be obtained initially in removing mercaptans. These results quickly diminish as additional quantities of hydrocarbons are treated with the same caustic. Because of the economics involved, it is not possible to continuously use fresh caustic solutions for treating hydrocarbons and discard the used caustic, and an attempt, therefore, has been made to treat the caustic so as to remove the mercaptan compounds and regenerate the caustic.

It will be apparent from the above Equation I that if the concentration of mercaptides dissolved in the caustic can be kept at a desirable low level, the equilibrium will be shifted to the right in each instance, and better removal of the mercaptans from the hydrocarbon will result.

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In order to accomplish this it has been proposed to regenerate the caustic solution by means of oxidation in accordance with the following general formula:

$$4NaSR + O_2 + 2H_2O \rightarrow 2R—S—S—R + 4NaOH \qquad (II)$$

This oxidation is not a simple process to operate on a commercial scale. The uncatalyzed regeneration of the spent caustic solutions by air under conditions heretofore proposed has not resulted in a sufficient regeneration unless high temperatures are used, and this causes extensive damage to operating equipment. This factor has led to the commercial practice of regeneration with the assistance of a catalyst. This, however, involves precise elements of control in order that the catalyst may be protected properly, which is often difficult to carry out in commercial practice and generally is carried out short of complete regeneration so that the caustic does not have the full mercaptan absorbing capacity when reused. A further disadvantage of such processes is occasioned by the disulfides (R—S—S—R) which are formed during the regeneration, and which are often difficult to separate from the regenerated caustic solution before it is recycled. Any disulfides present in the caustic upon recycling are absorbed in the hydrocarbons to be treated, which adds to the sulfur content of the finished product and reduces the susceptibility of the product to octane rating improvement by means of tetraethyl lead.

The need still exists for a simple method of more efficient removal of mercaptans from hydrocarbons.

In accordance with my invention I overcome the disadvantages of prior processes by treating the mercaptan-containing hydrocarbon with a solid adsorbent, during which process the mercaptans are selectively removed from the hydrocarbon by the adsorbent.

My process has the advantage over known processes in that it increases the utilization of the caustic tenfold, and is capable of producing distillates having much lower mercaptan content, as compared with conventional aqueous caustic contacting processes.

The solid adsorbent used in accordance with my invention comprises charcoal which has been treated with an aqueous solution of caustic soda. The charcoal, preferably in relatively small pieces, having a range of 4 to 80 mesh, and preferably within the range of 10 to 20 mesh, may be treated in any way and preferably saturated with an aqueous solution of caustic soda. The

concentration of the caustic soda solution used for treating the charcoal may vary, but a concentration of the order of 20% has been found desirable. Concentrations of less than 5% are so weak as not to place sufficient caustic in contact with the charcoal to justify use, and concentrations above 30% present viscosity and other similar problems. The preferable concentration is 10 to 20%.

The charcoal may be treated with the caustic at any temperature at which the caustic solution is in the liquid phase, and this is not critical. It is an advantage that room and ambient temperatures may be employed. The charcoal is kept in contact with the caustic solution for a sufficient time to become saturated, which takes place readily. The caustic solution can be drained from the charcoal and is ready for use. The caustic treated charcoal is used while the charcoal is wet with the aqueous caustic solution.

In carrying out the process, the charcoal-caustic adsorbent is contacted with the mercaptan-containing hydrocarbon in accordance with any of the known solid-liquid contact procedures. A continuous method is usually used and a simple procedure is to employ columns packed with the charcoal-caustic adsorbent through which the liquid hydrocarbon is passed at an appropriate rate. The rate depends primarily upon the extent of mercaptan removal desired, which is in turn dependent upon the amount and nature of the mercaptans in the feed stock, and the amount of mercaptans which can be present in the final product while still meeting required specifications. Preferably this is at a rate of 1 to 10 volumes of hydrocarbon per volume of charcoal-caustic adsorbent per hour (V. V. H.). The upper rate is usually limited by operating requirements, particularly the pressure drop through the bed.

If desired, caustic solution may also be present in the column in which event the process may be viewed as a liquid extraction process with the charcoal as an adsorbent in the liquid caustic phase. However, it will be apparent from the explanation hereinafter that the charcoal functions as an adsorbent for the mercaptides and this action is independent of any amount of caustic solution in addition to that which is absorbed in the charcoal itself.

The hydrocarbon treating process has the advantage of being carried out at relatively low temperatures and may be above the freezing point of the caustic solution and below the boiling point of the hydrocarbon at the pressure employed. In other words, all materials should be in the liquid phase. A temperature of 50 to 225° F. will generally be employed, and the process has the advantage of operating at temperatures of gasoline normally encountered in a refinery at the time of mercaptan removal, such as 70 to 120° F.

The following examples are indicative of results that may be obtained in accordance with the invention, but are not intended as other than illustrative.

EXAMPLE I

A commercial gasoline which has been treated in the course of manufacture to remove mercaptans, has 0.025% n-propyl mercaptan added thereto in order to evaluate the removal of a known amount of a known mercaptan. The gasoline at a temperature of 75° F. is passed at a rate of 3 V. V. H. through a bed of adsorbent 1.2 cm. in diameter, 25 cm. long. The adsorbent consisted of 40 cc. of 10 to 20 mesh charcoal pieces saturated with 20% aqueous caustic soda solution, plus 12 cc. of unabsorbed 20% aqueous caustic solution. The treated product met specifications for a doctor sweet gasoline and the product continued to be sweet until 220 volumes of hydrocarbon per volume of charcoal caustic adsorbent had been passed through the bed.

EXAMPLE II

A commercial gasoline stock which had not been treated for mercaptan removal and which contained 0.015% total mercaptan sulfur (not identified as to individual mercaptans) was treated as in Example I except that the amount of unabsorbed 20% caustic solution in the adsorbent was 1 volume per 3 volumes of charcoal. The treated gasoline had a mercaptan content of .002% and maintained this low mercaptan content until 150 volumes of hydrocarbon per volume of adsorbent had been treated, following which the mercaptan content of the finished product gradually rose upon passing additional stock through the adsorbent.

EXAMPLE III

In order to compare the charcoal-caustic adsorbent treatment with the conventional use of an aqueous solution of caustic, a hydrocarbon was prepared for comparison, consisting of iso-octane to which was added 0.05% mercaptan sulfur as propyl mercaptan.

In accordance with the invention, this stock was passed over 100 cc. of charcoal saturated with 37½ cc. of 20% aqueous caustic soda (without excess caustic solution) at a temperature of 75° F., and at a rate of 3 V. V. H. i. e., 300 cc. of the stock is passed through the 100 cc. of charcoal during 1 hour.

The aqueous caustic extraction that would be obtained in accordance with the prior art is calculated using the data of Yabroff (Industrial and Engineering Chemistry, vol. 32, page 257, 1940). The calculation is based on the use of 10% caustic solution, which is an optimum concentration for aqueous alkaline extraction, and a three-stage counter-current non-regenerative extraction, as is conventional, using one volume of caustic for 8 volumes of the hydrocarbon, which is the same as in the charcoal-caustic adsorbent. An extraction coefficient of 40 has been used, although this could be increased by the use of solutizer. The results are shown in the following table:

Table I

Volume of Feed per Volume of Adsorbent or Equivalent Aqueous Caustic	Percent Mercaptan in Finished Product	
	Adsorbent	Aqueous Caustic
3	Doctor Sweet	Doctor Sweet
6	Doctor Sweet	0.009
9	Doctor Sweet	0.016
12	Doctor Sweet	0.023
15	Doctor Sweet	0.027
21	Doctor Sweet	0.035
100	Doctor Sweet	(1)
160	Doctor Sweet	(1)
180	0.004	(1)

[1] Not run because the per cent mercaptan was so excessive at the preceding rate.

From the above table it will be seen that with the charcoal-caustic adsorbent the mercaptan content of the product was maintained uniformly low until 160 volumes of hydrocarbon

were treated, after which there was a sharp increase, showing that the caustic approached exhaustion. In contrast, the use of aqueous caustic permitted the treatment of only 3 volumes before the mercaptan content of the finished product rose above the upper permissible limit. The ten-fold improvement is readily apparent since the caustic on the charcoal is utilized to 80% as contrasted with about 9% of the aqueous caustic.

EXAMPLE IV

The process was repeated with iso-octane containing 0.25% sulfur as butyl mercaptan. This is a much greater amount of mercaptan than in the previous example and the butyl mercaptan is more difficult to extract than the propyl mercaptan. The results are as follows:

Table II

Volume of Feed per Volume of Adsorbent or Equivalent Aqueous Caustic	Per Cent Mercaptan in Finished Product	
	Adsorbent	Aqueous Caustic
2	Doctor Sweet	0.08
4	Doctor Sweet	0.20
6	Doctor Sweet	0.25

In this case the aqueous caustic only reduces the mercaptan to an amount ten times greater than an upper permissible limit, whereas the use of the charcoal-caustic adsorbent approaches the acceptable amount. The utilization of the caustic on the charcoal is 25%, and is 3% in the case of the aqueous caustic.

While the invention is not limited to any theory of operation, evidence has been obtained which supports the conclusion that the mercaptides are selectively adsorbed by the charcoal. If this explanation of the results is correct, it will be seen that the equilibrium of Equation I is shifted to the right because of the elimination of the mercaptides from the caustic through their adsorption by the charcoal. In other words, the mercaptides may be formed in situ on the charcoal. This explanation is particularly interesting since the evidence indicates that the caustic is not adsorbed and that water is adsorbed in preference to caustic. Other evidence in support of this conclusion is that charcoal not containing caustic removes far less mercaptan from gasoline than does the charcoal-caustic adsorbent. It is not believed necessary to include details of the evidence in support of this explanation since the invention is not limited to any theory.

This theory may seem inconsistent with the differences between the extent of the extraction of propyl and butyl mercaptans, especially since there has been no difference observed in this regard in a single stage equilibrium extraction of propyl and butyl mercaptan by charcoal not containing caustic. The difference by a factor of about 10 between the extraction of the propyl and butyl mercaptan by the charcoal-caustic adsorbent is about the same as the difference between their extraction coefficients between caustic and iso-octane. This suggests that the greater insolubility of butyl mercaptan in the caustic film on the charcoal is accountable for the result. In other words, the left-hand portion of the Equation I involving the equilibrium between the mercaptan in the oil phase and the aqueous phase is controlling. Since the removal of mercaptides from the caustic by the charcoal does not greatly alter the equilibrium of the left-hand portion of the equation, it is to be expected that the use of compounds to shift this equilibrium in favor of the solubility of certain mercaptans in the aqueous phase, such as solutizers, may be used in connection with the charcoal-caustic adsorbent.

It has been mentioned previously that the charcoal-caustic adsorbent may be used in conjunction with excess caustic solution, that is, more caustic solution than would be absorbed in charcoal. In order that the effect of the excess caustic may be considered, two runs were made using a commercial gasoline stock which had not been treated for mercaptan removal and which contained 0.014% mercaptan sulfur. This was treated in a column containing the charcoal-caustic adsorbent described previously, without excess caustic, and a similar column which in addition was three-quarters full of a 20% aqueous caustic solution. The results are shown in the following table:

Table III

Volume of Feed per Volume of Adsorbent	Per Cent Mercaptan in Finished Product	
	without excess caustic	with excess caustic
20	0.0005	0.0022
40	0.001	0.0024
60	0.0024	0.0026
80	0.0048	0.0038

Without the excess caustic the mercaptan removal is superior when the adsorbent is first used, but after longer periods of use the use of excess caustic is slightly superior. The difference, however, is not of great significance as would be expected if the charcoal is functioning to absorb the mercaptides from the caustic irrespective of the amount of the latter.

After the charcoal-caustic adsorbent has lost its mercaptan removing capacity, it may be discarded or it may be regenerated by any of the means known for caustic regeneration, such as blowing with steam, treatment with oxygen, etc., including the use of catalysts in this regeneration. This invention is not concerned with any particular method of regeneration but rather with the more efficient and complete removal of mercaptans in terms of the amount of caustic required, which it is believed is attributable to the selective removal of mercaptides through adsorption by the charcoal.

The charcoal used in accordance with the invention may be charcoal from any source, such as bone charcoal, wood charcoal, etc. A material found particularly suitable is "Columbia" brand carbon obtained from Carbide & Carbon Chemicals Company. Charcoal is not the equivalent of other adsorptive agents, such as adsorptive magnesia, basic ion exchange resins, spent cracking catalyst, etc.

It will be obvious that other strong alkaline materials are the equivalent of caustic soda, however, such as potassium hydroxide and the strong organic bases such as tetra methyl ammonium hydroxide.

I am aware that it has been proposed in the prior art to use carbon as a catalyst for the

vapor phase treatment of hydrocarbons with steam or water vapor at temperatures of 500 to 600° C., with a resulting hydrogenation of sulfur compounds. I am aware, also, that it has been proposed to use alkaline carbon in a similar process in which the hydrocarbons are treated in the vapor phase, such as temperatures of 572 to 875° F., in which process the mercaptans are converted to hydrogen sulfide so that the product after caustic washing is doctor sweet.

My invention is to be distinguished from these processes in that the action is not primarily one of converting mercaptans to hydrogen sulfide. It is distinguished further in that my invention has the advantage of employing ordinary temperatures in which the gasoline is in the liquid phase.

Having described the principle of my invention and the best mode of applying this principle, I particularly point out the following which I regard as my invention or discovery.

I claim:

1. The process of treating mercaptan-containing hydrocarbons to remove mercaptan sulfur therefrom, which comprises contacting said hydrocarbons in the liquid phase with charcoal impregnated with an aqueous solution of a strongly alkaline base, said mercaptans being adsorbed on said charcoal in the form of mercaptides, and separating said hydrocarbons of reduced sulfur content from the mercaptide-containing charcoal.

2. The process of treating mercaptan-containing hydrocarbons to remove mercaptan sulfur therefrom, which comprises contacting said hydrocarbons in the liquid phase with charcoal impregnated with an aqueous solution of caustic soda, said mercaptans being adsorbed in the form of mercaptides, and separating the hydrocarbons of reduced sulfur content from the mercaptide-containing charcoal.

3. The process of treating mercaptan-containing hydrocarbon distillate to remove mercaptan sulfur therefrom, which comprises contacting said distillate in the liquid phase with a solid adsorbent comprising charcoal impregnated with an aqueous solution of caustic soda on which the mercaptans are adsorbed in the form of mercaptides, and separating the hydrocarbon distillate or reduced sulfur content from the mercaptide-containing charcoal.

4. The process of treating mercaptan-containing gasoline to remove mercaptan sulfur therefrom, which comprises contacting said gasoline in the liquid phase at a temperature not over 225° F. with charcoal impregnated with an aqueous solution of caustic soda, said mercaptans being adsorbed in the form of mercaptides, and separating the gasoline of reduced sulfur content from the mercaptide-containing charcoal.

5. The process of treating mercaptan-containing gasoline to remove mercaptan sulfur therefrom, which comprises passing said gasoline in the liquid phase at a temperature of about 70 to 120° F. through a bed of charcoal impregnated with an aqueous solution of caustic soda, said mercaptans being adsorbed in the form of mercaptides, and separating the gasoline of reduced sulfur content from the mercaptide-containing charcoal.

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