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DESULFURIZING PETROLEUM FRACTIONS WITH PLATINUM

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The present invention relates to the desulfurization of petroleum distillates and in particular of petroleum fractions that serve as components in the manufacture of gasoline. The invention has application to both straight-run stocks and cracked stocks, but it has particular value in the treatment of straight-run stocks. The present invention is of special interest in the desulfurization of straight-run naphthas.

The sulfur contents of petroleum products and petroleum refining intermediates are becoming of increasing concern to the petroleum industry. Sulfur in straight-run petroleum stocks generally exists in the form of mercaptans, sulfides and disulfides. In cracked fractions it is generally present in the form of aromatic mercaptans, thiophenes, thiophanes, etc.

The sulfur compounds in both virgin and cracked stocks cause a variety of problems for the petroleum refiner. They constitute a serious corrosion problem in that the compounds themselves and products derived from them attack and corrode refinery equipment thereby causing extensive monetary losses. Sulfur compounds also act as poisons for the catalysts that are employed in various refining and chemical processes. They are also very deleterious in various refined products and especially gasoline, where they have been found to depreciate the quality of this particular product. Sulfur compounds in leaded gasoline not only have an adverse effect on the lead response of gasoline, but they also form deposits within the combustion chambers of gasoline-powered internal combustion engines, which deposits cause these engines to experience very marked octane number requirement increases during their operating lives.

Numerous processes have been employed and are presently employed by petroleum refiners in an effort to combat the various sulfur problems. These processes include treatment with chemicals such as sulphuric acid, caustic, solutizers, etc. They also include high temperature and high pressure processes such as hydrofining, hydroforming, catalytic reforming and the like which are carried out at temperatures generally in excess of 700° F. and at pressures of the order of 200 p. s. i. g. or even more. These processes are further characterized by the fact that they generally employ large amounts of hydrogen in the form of feed gas and also as recycle gas. Other processes that have been resorted to include high temperature contacting with adsorbents such as bauxite; extraction processes with a wide variety of solvents; sweetening processes; etc.

While each of the processes enumerated above has met with at least limited success, each one of them has been found to possess serious drawbacks. In many of the processes substantial amounts of the petroleum fractions treated are lost due to the severity of the reactions involved. In other processes the installation and operating costs are extremely expensive due to the need for high temperature and pressure equipment. In still other processes it is necessary to employ bulky and expensive gas-handling equipment. Furthermore, many of

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the treating agents are either non-regenerable, or they require burning operations which must be carried out at elevated temperatures. In addition, most of the processes are seriously limited as to the extent of sulfur removal. This is a particular shortcoming in the case of naphthas and other fractions that go into the manufacture of gasoline, where it has been found desirable to produce components having sulfur contents of less than 0.05 wt. percent and preferably less than 0.01 to 0.02 wt. percent. These low sulfur levels serve to circumvent the problems described above which sulfur compounds create in connection with automotive fuels and engines.

It is, therefore, an object of the present invention to provide a desulfurization process which is capable of operating at relatively low pressures and temperatures in the absence of any added hydrogen. It is a further object of the invention to provide a treating process wherein the treating agent is readily regenerable at relatively low temperatures and pressures and wherein the treating agent is capable of reducing very markedly the sulfur contents of the fractions treated. In this respect it is a particular object of the invention to make possible the manufacture of petroleum fractions that possess sulfur contents of less than about 0.05 wt. percent sulfur and preferably less than 0.02 wt. percent. It is especially preferred that the treated fractions contain less than 0.01 wt. percent sulfur.

In accordance with the present invention a petroleum distillate fraction is contacted with finely-divided platinum metal on a suitable support at temperatures and pressures such that the fraction is at least partially vaporized and desulfurized but not cracked, dehydrogenated or otherwise chemically altered to any substantial degree. Temperatures below about 500° F. and pressures below about 400 p. s. i. g. are generally suitable. The reaction is preferably carried out at temperatures within the range of about 300° to 500° F. and at pressures within the range from atmospheric up to about 100 p. s. i. g. Especially preferred operating conditions are about 350° F. and substantially atmospheric pressure.

It is preferred that the feed stocks to be desulfurized contain less than about 0.3 wt. percent sulfur and preferably in the range of about 0.4 wt. percent up to 0.2 to 0.3 wt. percent. It is particularly preferred that the feed stock contain in the order of about 0.1 wt. percent sulfur. It is further preferred that the feed stock boil in the range of about 100° F. to 450° F., and especially about 200° F. to 330° F. It is additionally preferred that the feed stock be a virgin material. The present invention is accordingly particularly attractive for the desulfurization of fractions such as light virgin naphthas that boil within the range of about 100° F. to 300° F. and that contain about 0.15 wt. percent sulfur.

The treating agent of the present invention is finely-divided platinum metal. The platinum is preferably provided on a suitable carrier such as activated alumina, charcoal, char, bauxite, silica gel or the like. Hydrous oxides that have ultramicroscopic pores are generally suitable for this purpose. Any of the platinum-impregnated catalysts that are conventionally employed in refining or chemical processes may be suitable for the purposes of the present invention. Thus, the common platinum catalysts that are employed for processes such as catalytic reforming, platinum hydroforming and the like are particularly suitable for the operation of the present process. It is of particular interest that platinum-type catalysts which are no longer catalytically effective in catalytic reforming processes are very suitable for use in the present process.

The treating agents of the present invention may be

prepared in accordance with any of the methods that are conventionally employed for preparing platinum catalysts on porous carriers. A carrier may be impregnated with an aqueous solution of chloroplatinic acid followed by slow-drying and heat-decomposition or reduction of the deposited compound.

A preferred treating agent for the present invention is 0.6 wt. percent platinum impregnated on an alumina obtained from the hydrolysis of an aluminum alcoholate solution such as aluminum amylate. This catalyst is prepared by impregnation of 1000 g. alumina, previously activated for 4 hours at 1100° F., with a solution made by dissolving 15 g. of chloroplatinic acid (40% Pt) in 1000 cc. of water. The composite is mixed well, dried for 16 hours at 250° F. The catalyst is then pilled and finally calcined for 4 hours at 1100° F. The treating agent may contain up to 2 wt. percent of platinum, but it is preferred that 0.01 to 0.6 wt. percent of platinum be used. It is particularly preferred that the treating agent contain 0.5–2.0 wt. percent platinum and especially about 0.6%.

The treating reaction may be carried out in any conventional vessel which is suitable for the purpose. The treating agent is charged to a vessel before the actual treating reaction, and the petroleum feed is then introduced within the treating zone. The feed should be at least partially vaporized and is preferably completely vaporized. Feed rates for the petroleum fraction that are suitable for the present purposes include feed rates in the range of about 0.5 to 4 w./hr./w. of feed to platinum. It is particularly preferred that feed rates of about 1 to 2 w./hr./w. be employed and especially about 1/1. The term w./hr./w. refers to the weight of feed per hour per weight of treating agent.

In the present process the sulfur compounds in the petroleum fraction combine either chemically or physically with the platinum. It has been observed that the combination takes place in a substantially quantitative manner until the treating agent contains about 2 atoms of sulfur per atom of platinum. At this point the efficiency of the treating agent falls off very appreciably, and it is desirable at such a time to regenerate the treating agent. Such regeneration of the treating agent may be carried out either directly within the treating zone, or the agent may be conveyed mechanically or otherwise to a separate zone intended solely for regeneration purposes.

When the treating agent is present as a fixed bed, a plurality of treating and regeneration zones may be employed in order to provide a substantially continuous treating process. Alternatively, the treating agent may be transferred continuously from a treating zone to a regeneration zone as is the practice in the conventional fluidized solids processes that are widely employed throughout the petroleum and chemical industries. In general it is preferred that fixed bed treating zones be used for relatively small units and fluidized beds for relatively large units. It will be noted that the operation of fixed and fluidized beds of solid treating agents is well known in the art; and it is considered to be within the knowledge of those skilled in the art to adapt the present process to either form of operation.

The spent treating agent may be regenerated by heating it at temperatures within the range of about 500° to 900° F. and at pressures of about 15 to 200 p. s. i. g. It is preferred that regeneration temperatures of 500° to 750° F. and especially about 700° F. be used. It is also preferred that the regeneration zone be maintained at substantially atmospheric pressure.

During the regeneration step, the treating agent may be purged and/or reacted with hydrogen, a hydrogen-rich gas or an oxygen-containing gas such as air. Such procedures are well known and widely employed in catalytic reforming processes for removing carbonaceous deposits and the like from platinum-type catalysts, thereby

regenerating the catalysts. In catalytic reforming, however, it has been observed that a catalyst cannot be indefinitely regenerated by this technique. Instead, the catalyst eventually loses its catalytic ability; and it then becomes necessary to recover the platinum from the carrier or to subject the spent catalyst to special rejuvenation procedures.

The treating agents of the present invention are unlike the platinum catalysts which are employed in catalytic reforming in that the former may be regenerated with oxygen and/or hydrogen substantially indefinitely without losing their affinity for sulfur. Indeed, as mentioned earlier, it is particularly contemplated to employ as treating agents those platinum-type catalysts that are no longer effective (e. g. regenerable) in catalytic reforming operations.

When a spent treating agent of the present process is regenerated with an oxygen- or hydrogen-containing gas, the sulfur on the treating agent is removed therefrom and recovered in the form of vaporous or gaseous compounds.

The treating agents of the present invention have also been successfully regenerated by merely purging them with a gas which is inert chemically toward both platinum and sulfur under the regeneration conditions described earlier. Such inert gases include steam, nitrogen, saturated paraffinic hydrocarbon gases such as methane, the rare gases, etc. When purging with nitrogen it has been observed on occasion that the sulfur on the spent treating agent has been recovered in the form of elemental sulfur. This feature renders the use of inert gases especially attractive.

Regardless of the manner of regeneration, the sulfur and/or sulfur compounds that are released by the regeneration procedure may be recovered from the stripping gas by conventional equipment located outside the regeneration zone.

Having been regenerated the treating agent may again be employed in the treating zone and/or treating phase of the process. It has been observed that the regenerated treating agent is substantially as active and efficient as the fresh treating agent.

The following example will serve to better explain the present invention and to illustrate the best mode contemplated of practicing the same. In this example a virgin naphtha boiling in the range from about 200° to 334° F. and containing 0.153 wt. percent sulfur was passed through a bed of treating agent at a temperature of about 365° F. The treating agent in this instance consisted of $\frac{3}{16}$ " x $\frac{3}{16}$ " cylindrical pills of activated alumina impregnated with 0.6 wt. percent platinum. The catalyst was prepared as discussed earlier in this description.

The feed rate of the naphtha was maintained at about 1 w./hr./w. Samples of the treated naphtha were withdrawn from the product stream at regular intervals and these samples analyzed for their sulfur contents. From these data it was possible to calculate the percentage of sulfur that was removed from the naphtha and also the amount of sulfur that combined with the platinum in the treating agent. These data are presented in the following table.

Table I

[Pt—Al₂O₃ desulfurization. 0.6% Pt on Al₂O₃; 365° F.]
FRESH TREATING AGENT

Cumulative, Wg/W.*	200–335° F. Virgin Naphtha—0.153% S		
	Sulfur in Product, Wt. Percent	Sulfur Removal, Percent	Atoms S/Atom Pt on Treating Agent
0.05	0.005	97	0.64/1
1.0	0.008	96	1.36/1
1.5	0.007	95	2/1
2.0	0.036	76	2.6/1

*Weight of naphtha per weight of reagent.

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The results in the above table clearly demonstrate that the process of the present invention is extremely effective in reducing the sulfur content of a petroleum distillate fraction. The results further demonstrate that the platinum is extremely effective in combining with sulfur up to the point where the amount of sulfur in the treating agent is sufficient to constitute about 2 atoms of sulfur per atom of platinum.

Following the desulfurization treatment described above, the spent platinum-alumina treating agent was regenerated by purging it with nitrogen at a temperature of about 750° F. The nitrogen rate was about 100 v./v./hr. and the regeneration step took about 1 hour.

Following the regeneration step, the treating agent was again employed for desulfurizing the virgin naphtha described earlier in this example. The same feed rates, operating temperatures, etc., were employed for this study as were employed in the treatment involving the fresh treating agent. Once again the treated naphtha was analyzed periodically for its sulfur content, and the degree of sulfur removal and the efficiency of the treating agent calculated from this information. These results are summarized in Table II below:

Table II

[Regenerated: Pt—Al₂O₃]

Cumulative, W ₀ /W _r	200-335° F. Virgin Naphtha		
	Sulfur in Product, Wt. Percent	Sulfur Removal, Percent	Atoms S/Atom Pt on Treating Agent
0.5.....	0.012	92	0.68/1
1.0.....	0.009	94	1.40/1
1.5.....	0.019	87	2.02/1
2.0.....	0.030	80	2.60/1

¹ Regenerated by purging with N₂ at 750° F.

From the data in Table II it is apparent that the treating agents of the present invention may be readily regenerated without any substantial loss in efficiency of the agent. These data, then, conclusively demonstrate the value of the present process.

It will be appreciated that the foregoing examples merely illustrate a portion of the scope of the present invention. It will be understood that the present process, for example, may be applied to the desulfurization of cracked naphthas, Fischer-Tropsch naphthas, etc., as well as straight-run naphthas. It may also be employed in combination with refining and chemical processes such as catalytic reforming, hydroforming, hydrogenation, dehydrogenation, isomerization, aromatization and the like. The desulfurization of the feed stocks to such operations greatly enhances the effectiveness of the operations.

It will also be noted that the feed to the desulfurizing step of the present process may be passed upflow or downflow as desired through the bed of treating agent. In the event that the feed is only partially vaporized, the downflow type of operation is more desirable than the upflow type.

What is claimed is:

1. A method of desulfurizing a petroleum fraction that

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boils within the range of 100° to 450° F. and that contains less than about 0.3 wt. percent sulfur which comprises partially vaporizing the fraction and passing the partially vaporized fraction through a bed of finely divided platinum which is impregnated on a suitable carrier, maintaining the bed at a temperature within the range of about 300° to 500° F. and a pressure within the range from about atmospheric to 100 p. s. i. g. and passing said fraction through said bed until said bed contains no more than about 2 atoms of sulfur per atom of platinum, said method being conducted in a manner that excludes the addition of hydrogen to the reaction, so that essentially the sole reactants involved in the desulfurizing reaction consist of the platinum and the sulfur compounds and hydrocarbons in the said petroleum fraction.

2. A method of desulfurizing a sulfur-containing petroleum distillate fraction which comprises at least partially vaporizing the fraction, contacting the partially vaporized fraction with a platinum-impregnated carrier at about 300° to 500° F., and about 15 to 200 p. s. i. a. until the treating agent contains about two atoms of sulfur per atom of platinum, thereafter regenerating the spent treating agent by purging it with an inert gas at about 500° to 900° F. at about 15 to 200 p. s. i., and thereafter again contacting the regenerated treating agent with said sulfur-containing distillate fraction, said method being conducted in a manner that excludes the addition of hydrogen to the reaction, so that essentially the sole reactants involved in the desulfurizing reaction consist of the platinum and the sulfur compounds and hydrocarbons in the said petroleum distillate fraction.

3. A process for desulfurizing a sulfur-containing mixture of distillate hydrocarbons which comprises at least partially vaporizing said mixture and contacting the partially vaporized mixture with finely divided metallic platinum impregnated on a porous carrier at a temperature below about 500° F. and a pressure below about 200 p. s. i. until the platinum has combined with no more than about 2 atoms of sulfur per atom of platinum, said process being conducted in a manner that excludes addition of hydrogen to the reaction, so that essentially the sole reactants entering into the desulfurizing process consist of the said platinum and the sulfur-containing materials and hydrocarbons of said hydrocarbon mixture.

4. A process as defined in claim 3 in which the temperature is within the range of about 300° to 500° F. and pressure is within the range of about atmospheric pressure up to about 100 p. s. i.

5. A process as defined in claim 3 in which the platinum is regenerated by purging it with an oxygen-containing gas at a temperature of about 500° to 900° F.

6. The process as defined in claim 3 in which the platinum is regenerated by purging it with an inert gas at about 500° to 900° F.

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