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REFINING HYDROCARBONS

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This invention relates to the refining of petroleum hydrocarbons and more particularly to the treatment of such hydrocarbons to effect the removal therefrom of sulphur compounds. Many crude petroleums contain sulphur and its compounds which are distributed more or less through the entire boiling range of the petroleums and are present in all the products obtained therefrom. These sulphur compounds have a deleterious effect on the products in which they exist as impurities. This is especially true in the case of gasoline which is used as a motor fuel and in the case of burning oil for use in lamps such as kerosene. The U. S. Bureau of Mines has seen fit to establish a limit of one-tenth per cent as a maximum allowable content of sulphur in gasoline. It has heretofore been almost impossible to attain this limit in the case of many straight run and cracked gasolines except by resorting to chemical treatment, not only costly in itself, but resulting in large losses of the products being refined.

An object of this invention is an improved desulphurizing process which is inexpensive to practice and with which there is substantially no loss of the products being refined. I have found that by vaporizing hydrocarbon fractions containing sulphur and passing the vapors into contact with fuller's earth at a high temperature, the sulphur compounds are decomposed and either retained by the earth or are transformed into other compounds which can be very readily removed and with comparatively little loss.

In carrying out this process for desulphurizing gasoline or other petroleum fractions, I have found that the best temperatures of operation are in the range between 550° F. and 850° F. Desulphurization is also effected at temperatures below and above this range, but below 550° F. the desulphurization is less substantial in amount and above 850° F. the fractions are subjected to cracking conditions and undesirable changes in the hydrocarbons are effected along with the decomposition of the sulphur compounds. Within the indicated range, I find the greatest conversion of sulphur compounds compatible with the absence of cracking or conversion of hydrocarbons. The fuller's earth may be heated to the proper temperature by pre-heating the vapors to be refined to such a temperature that they heat the fuller's earth to the required extent on contacting therewith or the fuller's earth may be heated by any other suitable means. Apparatus for carrying out the process in either of the ways above indicated will readily suggest itself to those skilled in the art.

The sulphur compounds contained in the gasoline vapors upon being contacted with fuller's earth at the temperatures indicated are decomposed from the refractory difficultly removable form in which they ordinarily exist to other sulphur compounds. Some of the latter are retained by the fuller's earth while others remain in the fraction and can be removed by a subsequent treatment, such as or similar to that hereinafter described.

After contact with the fuller's earth, the fraction is condensed and preferably is washed with a solution of caustic soda or similar treating solution. I have found that the washing operation effectively removes the converted sulphur compounds and leaves a product, such for example as gasoline having a substantially lower sulphur content than before treatment as above described. This shows that the refractory sulphur compounds originally present and which can only be removed with accompanying large losses of hydrocarbons have been converted into other sulphur compounds whereby substantial amounts of the sulphur originally present in refractory form is now present as hydrogen sulphide and light mercaptans.

The process above described enables me to effect sulphur reduction with very much smaller losses and very much more economically than by using chemical treating agents. The activity of the fuller's earth will decrease in time and it will eventually be necessary to replace the spent fuller's earth with fresh fuller's earth. However, spent fuller's earth can be revivified by roasting in the manner well-known in the art and after its revivification can be again used. As a result, the material cost is very low.

In some cases, I have found it advantageous to pass the vapors through several beds of fuller's earth or through the same bed several times, as additional desulphurization may be effected in this manner. In other cases, however, it is sufficient to pass the treated vapors through the bed a single time to effect the required desulphurization and in such cases, the re-passing of the treated vapors has no beneficial effect.

The treatment may be carried out at atmospheric or super-atmospheric pressure, so long as the temperature is maintained within the range above specified. In the treating of some distillates, I have found it to be advantageous to add steam to the same.

I am aware that desulphurizing processes have

been suggested using bauxite, copper oxide and other substances having a chemical reaction on the sulphur compounds of the vapors, but my process distinguishes from these by being merely a high temperature decomposition effected by the comparatively inert material, fuller's earth.

This process is of particular utility in the refining of gasoline obtained either by straight run distillation or by cracking. The process is, however, applicable to a refining of petroleum fractions other than gasoline.

I claim:

1. The process of refining gasoline containing as impurities sulphur compounds difficult to remove in the ordinary manner, which comprises converting the said difficultly removable sulphur compounds into easily removable sulphur compounds by subjecting said gasoline in vapor form to contact with fuller's earth at a temperature of from 550° to 850° F. removing the vapors containing said easily removable sulphur compounds and condensing them to recover the treated gasoline therefrom.

2. The process of refining gasoline containing as impurities sulphur compounds difficult to remove in the ordinary manner, which comprises converting the said difficultly removable sulphur compounds into easily removable sulphur compounds by subjecting said gasoline in vapor form to contact with fuller's earth at a temperature of from 550° to 850° F., condensing the vapors, and washing the condensate with a solution capable of removing said easily removable sulphur compounds.

3. The process of refining gasoline containing as impurities sulphur compounds difficult to remove in the ordinary manner, which comprises converting the said difficultly removable sulphur compounds into easily removable sulphur compounds by subjecting said gasoline in vapor form to contact with fuller's earth at a temperature of from 550° to 850° F., condensing the vapors and washing the condensate with an alkaline soda solution.

4. The process of refining gasoline containing as impurities sulphur compounds difficult to remove in the ordinary manner, which comprises converting the said difficultly removable sulphur compounds into easily removable sulphur compounds by subjecting said gasoline in vapor form to contact with fuller's earth at a temperature of from 550° to 850° F., removing the vapors from contact with said fuller's earth, condensing the vapors without permitting the vapors to come into contact with fuller's earth at a temperature substantially below the specified temperature range, and washing the condensate to remove said easily removable sulphur compounds.

5. The process of refining gasoline containing as impurities sulphur compounds difficult to remove in the ordinary manner, which comprises converting the said difficultly removable sulphur compounds into easily removable sulphur compounds by subjecting said gasoline in vapor form to contact with fuller's earth at a temperature of from 650° to 750° F., removing the vapors containing said easily removable sulphur compounds and condensing them to recover the treated gasoline therefrom.

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