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METHOD FOR TREATING HYDROCARBONS AND PARTICULARLY CRUDE PETROLEUM.

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To all whom it may concern:

Be it known that I, PETER VON DITMAR, subject of Russia, residing at Hamburg, Adolphstrasse 37, Germany, have invented certain new and useful Improvements in a Method for Treating Hydrocarbons and Particularly Crude Petroleum, of which the following is a specification (for which I have applied for a patent in Germany partly on September 28, 1921, partly on October 29, 1921, and partly on August 1, 1922).

The present invention relates to the treatment of hydrocarbons and more particularly to the treatment of crude petroleum wherein the hydrocarbons are heated with an addition of metallic soaps of the higher fatty acids. This method is applicable for treating sulphureous hydrocarbons as well as other hydrocarbons containing no sulphur. In both cases the method is of great advantage.

The removal of the sulphur from hydrocarbons, particularly crude petroleum, as is well known, is very difficult. Heretofore this has been done practically by introducing small pieces of ferrous sulphide into the oil and at the same time applying heat. When the necessary reaction temperature is reached, the ferrous sulphide combines with the sulphur and is turned into ferric disulphide.

This treatment, however, if carried on to a complete desulphurization, not only takes a long time and is troublesome, but is also costly inasmuch as for the recovery of the ferrous sulphide, hydrogen is required.

Moreover it is known to desulphurize petroleum distillates by driving vapors of the oil through a solution of metallic soaps. The desulphurization however in this case is very poor.

Finally it is known to add to the petroleum to be desulphurized a small quantity of metallic soaps in a cold state, dissolved in petroleum distillates, then to precipitate the metallic ingredients of the soaps by acids and to neutralize the rest of acids by alkalis. This method also gives poor results, and moreover is very complicated.

According to the present invention the desulphurization of the hydrocarbons and particularly of crude petroleum is brought about by heating them together with an addition of metallic soaps. Thus metallic sulphides are formed and precipitated and the liberated higher fatty acids can be drawn off, after accumulation of a layer has taken place. Heat may be applied during the reactions or during the fractional distillation of the petroleum.

It has been found that metallic soaps, by which not only soaps of the alkali earthy metals but also such of the heavy metals such as iron are meant, have the property that together with sulphureous hydrocarbons it is completely chemically converted at a temperature from 100 to 110° C., for instance according to the formula:

$$2C_{16}H_{31}O_2Na+H_2S=2C_{16}H_{32}O_2+Na_2S$$

The metallic sulphides, which are formed hereby, are precipitated and the fatty acids (palmitic acid, stearic acid, oleic and the like) are liberated. Generally these acids are lighter than the oil and can be removed when a layer is formed. The sulphur then will remain in the residues.

The fatty acids, it is true, would be soluble in the lighter hydrocarbons as far as they belong to the benzine group. However, since the benzine has been already distilled off at a temperature of 100 to 110° C. there is no possibility of the creation of such solution, and therefore there is no danger, that the formation of a layer be hindered.

From this it will be seen, that oils, which from the beginning or after preliminary treatment contain only heavy hydrocarbons, can be desulphurized without distillation by heating them together with soaps in a closed vessel.

In carrying out this method now and then it will be found, that when the chemical reaction has been going on for some time, the desulphurization process diminishes or under certain circumstances ceases entirely, so that even a heating of the whole mass far beyond 100 to 110° C., where the desulphurization commences, will not bring results. The reason of this is to be found in the generation of a certain state of equilibrium of the commencement of a reverse reaction. Thus when on the initial heating to 100 to 110° C. the sulphur contained in the petroleum combines with the hydrogen liberated from the hydrocarbon to form hydrogen sulphide the course of the reaction by way

of example using sodium-soap will be as follows:

$$2C_{16}H_{31}O_2Na+H_2S=2C_{16}H_{32}O_2+Na_2S$$

After some time a state of equilibrium takes place, that is to say the reaction runs evenly in all directions, so that no further precipitation of the metallic sulphides occurs.

It has been found that this state of equilibrium can be destroyed in a simple way by adding a small amount of a catalyst, for instance ½% of metallic sodium to the mass. This catalyst has the effect that hydrogen will be liberated from the hydrocarbons anew and join with the sulphur to form hydrogen sulphide, for instance according to the formula:

$$C_6H_{14}+Na+S=C_{16}H_{12}+H_2S+Na$$

Since in this manner constantly there is a surplus of hydrogen sulphide the state of equilibrium will be destroyed. Other bodies which are adapted to increase the presence of hydrogen in the total mass will have similar effects, as for instance a few drops of water may be sufficient, which at once cause the creation of foam and start the desired reaction anew. Of course the additional bodies may also be introduced at a time even when the decrease of the reaction is not yet perceptible.

In case of fractional distillation of hydrocarbons, which do not contain sulphur, the addition of metallic soaps will also afford very important advantages.

One of the many difficulties in the fractional distillation of liquid mixtures, for instance of a mixture of hydrocarbons—and such a mixture is the crude petroleum—is to be found in the fact, that, as is well known, it is difficult to obtain a complete and clean separation of the products of distillation corresponding to the various temperatures. To obtain this result is rendered still the more difficult on the one hand by the fact, that not only such parts of the mixture pass over the boiling temperature of which is equal to or surpassed by temperature attained at such stage, but also substances are carried with them that are not yet boiling and are not so volatile, and on the other hand by the fact that at every stage not all constituents of the mixture pass over which have been heated up to or beyond their boiling temperature. The consequence is that if stress is laid on a clean or complete separation, one is compelled to allow the distilling process and the increase of temperature to go on very slowly. This, however, naturally will be a bar to an economic operation.

The invention shows a way to arrive at a complete and clean separation at the highest rate of a speedy distillation. The products of distillation gained in this manner are distinguished by being devoid of foreign matter to the utmost.

The new method consists in this, that the mixtures to be distilled are given an addition of soap to the amount of about ¼ to 1½%. The soap is dissolved, when for instance crude petroleum is distilled at about 100 to 110° C. Extensive trials have proved, that by this means sharply distinguished steps of distillation are obtained, a carrying along of still liquid ingredients and foreign matter is prevented and a complete volatilization corresponding to the temperatures obtained, results. When the distilling has been brought to an end, the soap remains in the residue and when new oil is added it is dissolved in the latter, as soon as on the next following distilling operation the temperature rises to the necessary height. The same amount of soap can be used again as long as the residues do not amount to an undesirable quantity.

I claim:

A method for desulphurizing hydrocarbon oils containing sulphur comprising, heating the hydrocarbon oils with a metallic soap of the higher fatty acids in a closed vessel whereby liberated fatty acids can be drawn off when a layer of them has been formed, and adding a small percentage of metallic sodium while the chemical reaction is taking place.

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