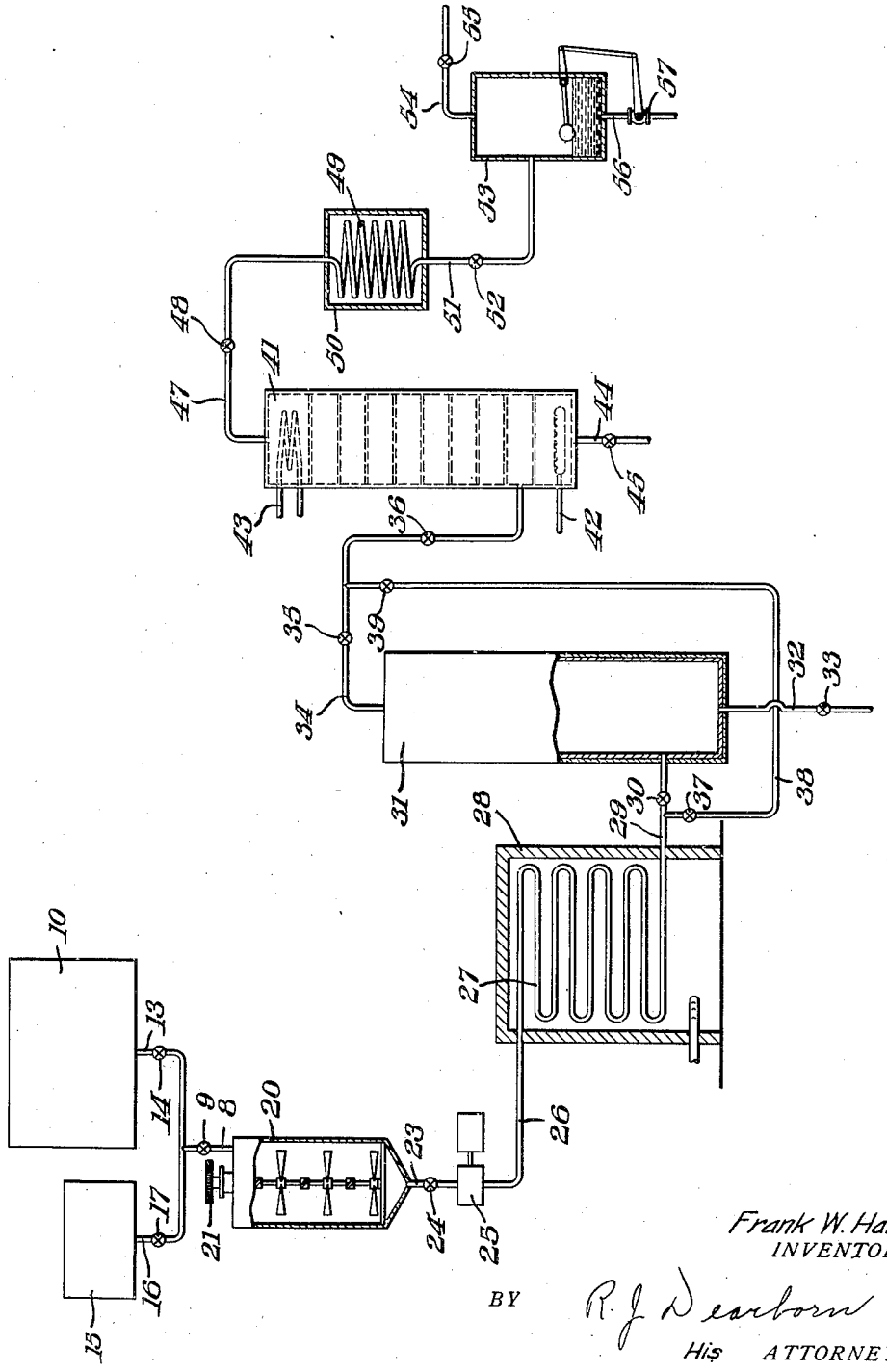
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TREATING HYDROCARBON OILS

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TREATING HYDROCARBON OILS

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This invention relates to the treatment of hydrocarbon oils and more particularly to the treatment of hydrocarbon oils containing undesirable organic sulfur compounds and dissolved elementary sulfur.

The invention contemplates a method of desulfurizing petroleum hydrocarbon oils, or distillates obtained by cracking petroleum, which contain undesirable organic sulfur compounds or dissolved elementary sulfur, which includes dissolving a heavy metal soap in the oil to be treated to form a mixture and then heating this mixture under superatmospheric pressure to an elevated temperature which may be within the range of cracking temperatures. The mixture is maintained at this temperature for a length of time sufficient to bring about the decomposition of the organic sulfur compounds and the combination of the sulfur liberated in this way, as well as the free elementary sulfur dissolved in the oil, with the heavy metal radical of the soap to form the corresponding heavy metal sulfide. The treated hydrocarbon oil is then distilled from the residue and, after a suitable fractionation, condensed to form a liquid free from elementary sulfur or corrosive organic sulfur compounds.

Many processes have been proposed for desulfurizing petroleum oils, but the original method, using sulfuric acid, is still the most extensively used. The action of sulfuric acid in desulfurizing petroleum hydrocarbons is recognized to be due in part to its solvent, and in part to its oxidizing, action. The sulfuric acid method of treatment, however, suffers from the disadvantage that when used for treating naphthas containing high percentages of desirable unsaturated compounds, the sulfuric acid brings about a polymerization of these hydrocarbons, thereby reducing the antiknock value of the finished oil. Furthermore, the quantities of hydrocarbons lost as a result of the treating reaction are undesirably high.

It has also been proposed to treat petroleum hydrocarbons with metal soaps by vaporizing the oil into a reflux tower, and then refluxing the vapors with a solution of the metal soaps dissolved in a hydrocarbon oil. This method is disclosed in U. S. Patent No. 1,740,584 to R. H. Gardner and H. G. Hodge. Experiments carried out along the lines of the method shown by this patent have indicated that it is suitable for removing the less stable sulfur compounds present in the oils. This appears to result from the fact that the temperatures used by Gardner and Hodge are only sufficiently high to bring about the distillation of the hydrocarbon oil at atmospheric pressure, which temperatures appear to be too low to bring about any appreciable decomposition of the more stable organic sulfur derivatives.

I have discovered that in order to effect a satisfactory and complete reaction between organic sulfur compounds and heavy metal soaps, it is necessary to heat the mixture to high temperatures which may be within the cracking range of temperatures. When using these temperatures, it is also necessary and desirable that the mixture be maintained in the liquid phase by the use of sufficiently high pressures. In employing this method of desulfurizing in the treatment of naphthas, it may even be desirable to carry out the reaction at such temperatures as are conducive to the reforming of the naphtha hydrocarbons into less saturated hydrocarbons. Under these conditions, it is possible to decompose substantially all of the corrosive organic sulfur compounds and to react the sulfur liberated, as well as the sulfur already dissolved in the oil, with the metal radicals of the heavy metal soaps to form the corresponding heavy metal sulfides, while simultaneously converting the naphtha hydrocarbons into hydrocarbons which have high antiknock values and which are especially suitable for use as fuels in internal combustion engines.

The invention will be fully understood from the following description taken in connection with the drawing which represents in diagrammatic sectional elevation an apparatus which may be employed for carrying out the process. The apparatus illustrated in the drawing is shown and described merely for the purpose of aiding and understanding the process, and it is to be understood that any other suitable apparatus may be substituted for that shown.

In the figure, the numeral 10 designates a storage for a supply of the hydrocarbon oil which is to undergo treatment. The numeral 15 designates a storage for the heavy metal soap reagent which may be a concentrated solution of the metal soap in a hydrocarbon oil. These storage tanks are connected respectively by the lines 13 and 16 with the line 18 which leads into the mixing chamber 20. The lines are fitted with suitable valves for controlling the rates of flow and may also be supplied with metering devices for maintaining the rates of flow within closely defined limits.

The mixing device may consist of a tank supplied with a mechanical agitating device or may be any other structure suitable for bringing about the proper agitation and solution of the metal soap in the hydrocarbon oil to be treated. The

bottom of the mixing device is connected by the line 23 controlled by the valve 24 with the intake side of the pump 25. This pump may be any type suitable for delivering oil under pressures which may be as high as 3000 pounds per square inch. The discharge side of the pump connects directly through the line 26 with the heating coil 27 which is situated within the preheater 28. The discharge side of the heating coil 27 is connected to the line 29 which discharges through the expansion valve 30 into a lower point of the flash drum 31. The bottom of the flash tower is provided with a drawoff line 32 controlled by the valve 33, while the top of the drum is provided with a vapor line 34 controlled by the valves 35 and 36 which enters a lower point of the fractionating tower 41.

In order to prevent any considerable cooling taking place in the flash drum 31, the same is desirably heavily insulated to prevent the loss of heat by radiation.

In some cases, it may be desirable to discharge the heated oil delivered from the heating coil 27 directly into the fractionating tower 41. For this purpose, the by-pass line 38, which is controlled by the valves 37 and 39, connects the line 29 with the line 34.

The fractionating tower 41 may be of any conventional type of construction. It is fitted at a lower point in its structure with the steam spray 42 and at an upper point with the reflux cooling coil 43. The bottom of the tower is provided with a liquid drawoff line 44 controlled by the valve 45 and at the top with the vapor drawoff line 47.

The vapor line 47 which is controlled by the valve 48 is connected directly with the condenser coil 49 of the condenser 50. The discharge side of the condenser coil leads to the liquid gas separator 53, the gas space of which is connected by means of the line 54 controlled by the valve 55 with a gas storage system or a gas compression plant. The liquid space, on the other hand, is connected through the line 56 controlled by the automatic valve 57 with a storage for treated hydrocarbon oil which is not shown.

In the operation of the process in connection with an apparatus such as that illustrated in the figure, a cracked naphtha distillate containing undesirable organic sulfur compounds, or dissolved elementary sulfur, or both, is drawn from the storage tank 10 and delivered to the mixing chamber 20. Simultaneously a metered amount of the metal soap is also delivered into the mixing chamber wherein it is dissolved in the hydrocarbon oil to form a solution. The solution is then delivered to the inlet side of the charge pump 25 which delivers the mixture under a pressure which may be as high as the full working pressure of the pump into the coil 27 of the preheater 28 wherein it is heated to a temperature of between 600° and 1200° F. The rate of charge through the coils of the preheater may be so controlled as to permit of the complete interaction of the organic sulfur compounds with the metal soap. In other operations, it may be desirable to heat the oil to the proper temperature at a very rapid rate and to permit the reaction to go to completion in the soaking drum 31.

The pressure maintained within the soaking drum 31 may be the same as that maintained within the coil 27 of the preheater 28 or else it may be lower. The soaking drum serves two purposes; first, it permits of maintaining the hydrocarbon oil containing the undersirable sulfur hydrocarbons, together with the metal soap at an elevated temperature for a sufficient length of time to permit of the complete decomposition of the organic sulfur compounds. Furthermore, it may serve as a reaction vessel in which the hydrocarbons are maintained at a cracking temperature in order to bring about the reforming of the same.

As a result of the interaction of the metal soap with the sulfur of the organic sulfur compounds and the sulfur which is merely physically dissolved in the hydrocarbon oil, a precipitation of the metal sulfide takes place. This material collects at the bottom of the soaking drum in the form of a sludge. There also collects at the bottom of the flash drum a residue comprising the organic radicals of the heavy metal salts and carbonaceous materials.

In certain operations of the herein disclosed process, it is found that it is not necessary to employ the flash drum. In these particular cases it is therefore of advantage to draw off the hot reaction mixture from the preheater coil and to flash it directly into the fractionating tower 41. This is accomplished by suitably manipulating the valves which are shown in the figure.

The oil vapors, which are free from any corrosive sulfur compounds and elementary sulfur, are delivered into a lower point of the fractionating tower 41. The vapors rise through the tower in countercurrent to the descending reflux liquid and are in this way fractionated. In some cases, it may be desirable to inject steam into the bottom of the tower in order to bring about a more effective stripping of the desirable vapors from the residual oils which collect at the bottom of the tower. The residual oils which collect in this way are drawn off through the line 44 and delivered to a suitable storage facility.

The overhead vapors, which are drawn off from the top of the fractionating tower, are delivered to the condenser coil 49 where the normally liquid hydrocarbons are substantially condensed. The hydrocarbons which leave the condenser coil 49 consist of a mixture of liquid and gaseous hydrocarbons, which mixture is conducted into the liquid gas separator 53 where a separation of the two phases is brought about. The gases are drawn off and delivered to a suitable storage system or a gas compression plant while the liquid hydrocarbons are conducted to tankage.

Petroleum hydrocarbon oils which have been treated in accordance with the method which forms the basis of this invention are found to be free not only from mercaptan compounds and elementary sulfur which may have been dissolved in the oils, but also substantially free from those organic sulfur compounds which cause the oil in which they are present to be corrosive. The process is suitable, not only for treating straight run naphthas and naphtha distillates produced by cracking operations, but also for desulfurizing kerosine distillates and gas oils. In treating oils of the kerosine type, it is usually undesirable to carry out the desulfurizing operation at temperatures above the normal range of cracking temperatures unless the treating operation is followed by an after-treatment such as extraction with a selective solvent such as furfural or solvents having comparatively the same solvent characteristics in order to remove any unsaturated compounds formed as a result of the submission of the oil to cracking temperatures.

The choice of the heavy metal soap for use in this method of desulfurizing is dependent upon

the fact that copper naphthenate is apparently the most economical and the most reactive. However, any one of the fatty acid salts of metals which yield insoluble sufides with sulfur may be used. These include the lead, bismuth, mercury, cadmium, arsenic, antimony, tin, nickel, cobalt, manganese, and zinc salts of acids such as oleic, naphthenic, stearic, rosin, and the like.

The quantities of the heavy metal soap necessary cannot be set forth specifically since these vary with the temperatures and pressures used in carrying out the reaction, as well as upon the constitution and quantities of the organic sulfur compounds which it is desired to remove. For most efficient operation of the process, the quantity of heavy metal soap should be such as to insure an excess of from 10 to 20% of the heavy metal over the quantity equivalent to the sulfur content of the petroleum hydrocarbon oil. The use of such an excess is necessary to insure rapid and complete interaction between the heavy metal soap and the sulfur which is available for reaction.

The process herein described may be followed by either a liquid phase or vapor phase treating step in which the desulfurized hydrocarbon oil is contacted with a polymerization catalyst such as fuller's earth, bauxite or one of the acid-treated clays of the montmorillonite type. By using the desulfurization process in conjunction with such a treating process, it is possible to produce a final product which is sweet, free from undesirable sulfur compounds which has a high anti-knock value and which is color and gum stable.

Obviously many modifications and variations of the invention as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The method of treating naphtha distillates which comprises dissolving an oil-soluble heavy metal soap in a naphtha distillate containing relatively stable corrosive organic sulfur compounds, said soap being used in an amount necessary to react with the sulfur content of the distillate, heating the mixture to a reforming temperature of between 800 and 1200° F. under superatmospheric pressure such as to maintain a substantial amount of the distillate in liquid phase whereby the sulfur compounds are decomposed and metal sulfides are formed, and then distilling the purified and reformed distillate from the residue to obtain a non-corrosive product.

2. The method according to claim 1 in which the soap is copper naphthenate.

3. The method of treating naphtha distillates which comprises dissolving an oil-soluble heavy metal soap in a naphtha distillate containing relatively stable corrosive organic sulfur compounds, said soap being used in an amount necessary to react with the sulfur content of the distillate, continuously passing the mixture through a heating coil and heating the same therein to a temperature of between 800 and 1200° F. under superatmospheric pressure such as to maintain a substantial amount of the distillate in liquid phase, whereby the sulfur compounds are decomposed and metal sulfides are formed, and then distilling the purified and heat-treated distillate from the residue to obtain a non-corrosive product.

4. The method according to claim 3 in which the soap is copper naphthenate.

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