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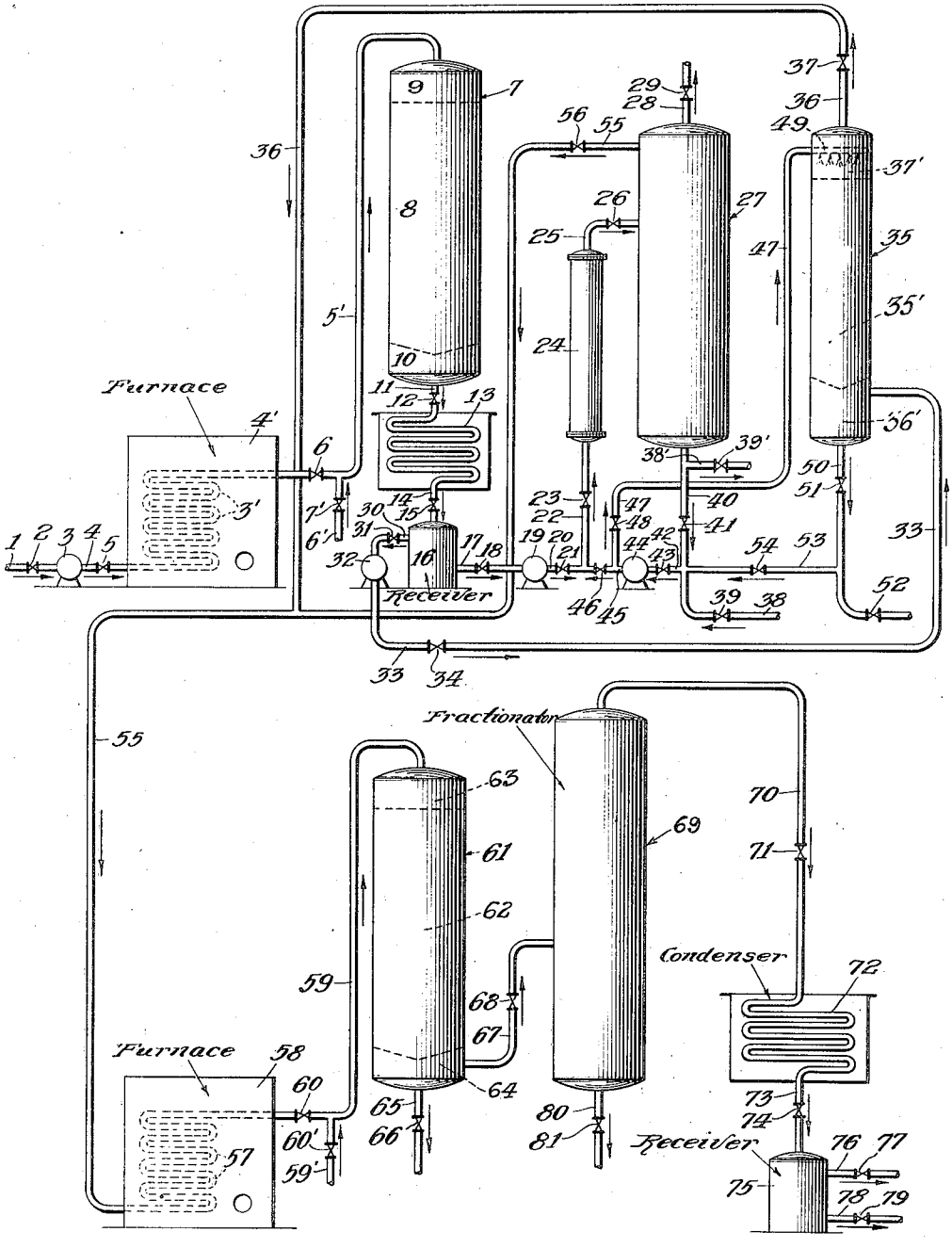

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TREATMENT OF HYDROCARBON OIL

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5 Claims. (Cl. 196—24)

This invention relates more particularly to the treatment of the light gasoline boiling range fractions produced in the cracking of heavy petroleum oils, although it may also be effectively applied to corresponding straight run gasoline and naphtha fractions.

In a more specific sense the invention is concerned with a process for more efficiently desulfurizing gasoline-containing naphthas, although in the operation of the process upon such stocks other refining effects of a positive and beneficial character are produced.

Practically all of the naphthas produced in cracking the heavy portions of petroleum and other heavy hydrocarbon mixtures require special chemical treatment before they can be utilized as fuel in the modern automobile engine. In contrast to straight run gasoline, which usually contains very low percentages of olefins of any character, the cracked distillates may contain as high as 50% of hydrocarbons of an unsaturated character depending upon the intensity of the conditions under which they were produced. The unsaturated hyrocarbons comprise both mono olefins which are desirable constituents of gasoline on account of their high anti-knock characteristics and their complete stability under storage conditions, even in light, and olefins of a more highly unsaturated character such as di and tri olefins whose presence is undesirable on account of their pronounced tendency to polymerize and form gummy and resinous materials which gradually choke up gasoline feed lines and cause valve sticking. The selective removal of this last named class of compounds is one of the primary objects of the chemical processes employed in treating cracked distillates.

The other main group of undesirable constituents of cracked distillates from a motor fuel standpoint are the sulfur compounds which comprise besides dissolved hydrogen sulfide, low boiling mercaptans, sulfur ethers, alkyl disulfides, and apparently certain heterocyclic sulfur compounds related to thiophene. The hydrogen sulfide is readily removable by alkali washing and the mercaptans may be converted without difficulty into dialkyl disulfides by sweetening agents such as sodium plumbite and hypochlorite solutions. The removal of the sulfur ethers and the cyclic sulfur compounds to bring the total sulfur content of a given gasoline down to a permissible percentage, usually around 0.10% without concurrently extracting, polymerizing or saturating too great a percentage of the desirable olefins in the hydrocarbon mixture is one of the major problems of the oil refining industry and it is with improvements in processes for selectively desulfurizing low boiling cracked distillates that the present invention is concerned. While the process to be disclosed is more directly applicable to the treatment of sulfur-containing cracked distillates, it may also be applied to advantage in desulfurizing some high sulfur straight run naphthas such as those produced in distilling the sulfur containing petroleums of California, Texas and other localities.

In one specific embodiment the present invention comprises treating the vapors of cracked distillates with hydrogen in the presence of suitable catalysts in several stages with intermediate removal of hydrogen sulfide between stages. The hydrogen sulfide may be removed either by treatment of the vapors with selective reagents for combining with the hydrogen sulfide or the gas-vapor mixtures may be condensed and revaporized between stages with removal of hydrogen sulfide in the fixed gases.

The principal object of the present process is to increase the efficiency of desulfurizing by limited hydrogenation by periodically removing hydrogen sulfide as one of the products of the hydrogenating reactions so that desulfurization proceeds further owing to the removal of the principal reaction product. While hydrogen sulfide is usually the main product of the desulfurizing reactions, the term is used in the present connection to include other types of more or less readily removable sulfur compounds such as some low boiling mercaptans and other reactive sulfur compounds.

Hydrogen sulfide may be removed from the vapors by the use of such alternative materials as caustic alkalies either as solids or in concentrated solution, by the use of solid mixes containing lime and other materials for reacting with hydrogen sulfide, by metals, or metal oxide mixtures, etc. The use of any particular reagent for removing the hydrogen sulfide will be dictated by the amount encountered in the vapors after each stage.

While the process may be conducted in various types of plant setup, it will be of advantage in disclosing the exact character of the invention to describe a particular operation in which the hydrogen sulfide is removed by bleeding off the fixed gases remaining on condensation of the vapors between stages. The invention is not, however, limited to this particular type of operation nor to the specific details given in connection with its description. To assist in describing the opera-

tions the attached drawing has been provided which shows diagrammatically in side elevation an arrangement of interconnected elements designated by conventional figures in which operations characteristic of the present invention may be conducted. For the sake of simplicity the plant shown has been limited to a two-stage operation, although any number of stages may be employed. For the same reason multiple treaters have not been shown although these may be employed at any point to insure the continuity of the operations. For example, each stage may comprise two or more catalytic treaters so that active catalyst may be in service while spent material is being removed and the treaters refilled.

Referring to the drawing and assuming the distillates to be treated to be in originally liquid phase, they are introduced to a charging pump 3 by way of a line 1, containing control valve 2, and discharged through line 4, containing control valve 5, through a heating element 3' suitably disposed to receive heat from a furnace 4'. This preliminary vaporizing step is advantageous for two reasons. In the first place it permits the use of mild preliminary treatment to remove the more readily reactive sulfur compounds and if desired the gum-forming constituents. In the second place the operating pressure in the desulfurizing treaters may be as high as several hundred pounds per square inch, and higher than the pressure upon the receivers of the ordinary cracking plant. In some cases it may be possible, however, to dispense with the preliminary vaporizing step and introduce the low boiling cracking plant vapors directly to the plant under their own pressure. The temperature to which the distillate vapors are brought by the primary heating and vaporizing furnace will depend upon several factors such as their volatility, their percentage of sulfur and the character of the sulfur compounds which they contain, the type of catalyst employed in the hydrogenating treater, et cetera, so that consequently only very general ranges can be given. Pressures may be employed from about 200 to 1,000 pounds per square inch or higher and temperatures of from 500 to 800° F. Good results have been obtained on high sulfur cracked distillates (as will be shown in later examples) when employing pressures of 300 pounds per square inch and temperatures of approximately 700° F. in the primary treating step. Hydrogen may be introduced at any point in the line of flow of the vapors such as, for example, into line 5' by way of line 6', containing control valve 7', at the exit of the heating element. As hydrogen is consumed in the reactions of treatment more may be added as desired or found necessary for best results.

The distillate vapors mixed with hydrogen pass through line 5', containing control valve 6, and enter a primary hydrogenating treater 7 which contains a stationary body of catalyst indicated in space 8 dividing the treater into upper and lower vapor spaces 9 and 10, respectively. The catalysts which may be employed constitute no special feature of the process which may use any of the well known effective hydrogenating catalysts such as, for example, the oxides or sulfides of chromium, molybdenum and tungsten which are of known value in the art. In the case of oxides they will be gradually converted to sulfides with some loss in efficiency but with a corresponding extension of their active life. Catalysts of different types and varying degrees of activity may be employed in the successive stages, as the distillate becomes partly desulfurized, though this will be principally a matter of choice or convenience.

The total products of the primary stage reactions are then drawn through line 11, containing control valve 12, through a cooler and condenser 13, the condensed liquids and fixed gases passing together through line 14, containing control valve 15, to a receiver 16 from which liquids and gases are separately withdrawn and subjected to treatment for the removal of hydrogen sulfide. A simple and generally utilizable method of accomplishing this object consists in employing caustic soda solutions on both the distillate and the gases, and this method will be described in essential detail. However, the invention is not limited to the use of caustic soda for this purpose nor even to aqueous solutions of other alkalies but may employ any type of absorbing solids or liquid reagents found to be effective and economical in effecting the desired removal of hydrogen sulfide.

To remove hydrogen sulfide from the distillate it may be passed through line 17, containing control valve 18, to a pump 19 which discharges through line 20, containing control valve 21, to join with a line 45 supplying a solution of caustic soda, the lines joining to form line 22, containing control valve 23, which conducts the distillate and alkali to some type of mixing device 24 indicated in the drawing as a pipe of moderate diameter which may contain filling or baffling material to produce turbulence and insure thorough mixing of the distillate and the treating reagent. Silica or porcelain fragments may be conveniently used as filler or the mixer may contain a succession of perforated plates or metal baffles.

The distillate and alkali are then discharged by way of line 25, containing control valve 26 to a settler 27 which has a release line 28, containing control valve 29, which permits the removal of any fixed gas accumulations and a caustic recirculating line 40, containing control valve 41, which joins with line 38, containing control valve 39 to form line 42, containing control valve 43, and leading to recirculating pump 44. When the absorptive capacity of the alkali solution has been reduced to an uneconomical point it may be discharged from the system by way of line 38', containing valve 39'. The passage of the recirculated alkali through line 45, containing control valve 46, has already been described. Fresh alkali solution may be introduced to the suction side of pump 44 by way of line 38, containing control valve 39.

The gases accumulating in receiver 16 may be released through line 30, containing control valve 31, to a gas pump or compressor 32 which discharges through line 33, containing control valve 34, into the bottom vapor space 36' of a gas washing tower 35 which contains filling material in space 35' consisting generally of the same type of substances utilizable in mixer 24. The ascending gas stream meets descending streams of alkali solution which gradually absorbs hydrogen sulfide so that the gas accumulating in upper space 37' and leaving the tower by way of line 36, containing control valve 37, is substantially free from hydrogen sulfide.

The alkali solution necessary for the desulfurizing may be obtained by way of line 47 branching from line 45 and containing control valve 48, the line ending in a spray device 49 for effecting subdivision of the solution and more intimate contact of the gases therewith.

Spent or partly spent caustic from tower 35 may be withdrawn through line 50, containing control valves 51 and 52, and either wasted through valve 52 or utilized for further absorption. In the latter case the solution passes through line 53, containing control valve 54, to the suction side of pump 44 which thus functions as a circulating pump for both the liquid and gas washing operations.

The distillate and gases thus freed from hydrogen sulfide are now recombined and brought up to a suitable temperature for further desulfurizing action, gas line 36 joining with line 55, containing control valve 56, from the top of treater 27 and the mixture of liquids and gases passing through heating element 57 positioned in furnace 58. If found necessary or desirable more hydrogen may be introduced either before or after the passage of the mixture through this furnace, for example, by way of line 59', containing control valve 60'. The mixture of oil vapors and hydrogenating gases then follows a course comparable in all respects to the hydrogenating treatment of the first stage although conditions may be modified in respect to temperature, pressure and catalytic activity. Thus, the mixture of oil vapors and hydrogenating gases follows line 59, containing control valve 60, and enters secondary treater 61, containing a mass of solid catalytic material 62 which divides the inside of the treater into upper and lower vapor spaces 63 and 64, respectively. Since the present description is limited to a two-stage operation a draw line 65, containing control valve 66, is shown for the removal of heavy reflux material which may accumulate at this point and line 67, containing control valve 68, is shown for conducting the vapors to a final fractionator 69 of proper design and capacity for producing overhead vapors of gasoline boiling range and separating heavier refluxes, which are withdrawn through line 80, containing control valve 81. The vapors and fixed gases from the tower pass through line 70, containing control valve 71, and enter a condenser 72 in which the liquefiable constituents are condensed, passing along with the uncondensed gases through line 73, containing control valve 74, to a receiver 75 which has a fixed gas release line 76, containing a control valve 77, and a liquid draw line 78, containing control valve 79, for finished product.

The liquid refluxes withdrawn through lines 65 and 80, respectively may be returned to the cracking plant which produced the distillates for treatment or utilized for fuel for the process as the exigencies of the case may dictate. The gases withdrawn through line 76 from the final receiver may be treated for the removal of hydrogen sulfide and recycled insofar as they contain enough hydrogen to render such a step economical. The gasoline withdrawn through line 78, containing control valve 79, may be washed with caustic soda to remove dissolved hydrogen sulfide and other soluble sulfur compounds or subjected to any other type of treatment to render it saleable.

The following example will give an idea as to the type of results which are obtained in practice when utilizing the process of the invention to desulfurize cracked distillates. While the example is characteristic and illustrative, the data given are not to be construed as imposing corresponding limitations upon the scope of the invention.

The stock treated was a cracked naphtha from California charging oil which contained 92% of 415° F. end point gasoline. The naphtha was vaporized, the vapors mixed with hydrogen and passed twice over a hydrogenating catalyst mixture with intermediate alkali washing of the distillate and removal of hydrogen sulfide from the gases. The same catalyst was used in both stages and had the following composition:

	Per cent
Molybdic acid	37.8
Nickelous oxide	50.1
Sodium aluminate	12.1

A pressure of 300 pounds or thereabouts was maintained on the hydrogenating treaters and the average temperature was 650° F. in the first stage and 700° F. in the second. The following table shows the properties of the gasoline produced by fractionating the naphtha without treatment of any character, the corresponding properties of the gasoline produced after the first hydrogenating stage and the properties of the gasoline produced after a second hydrogenating stage with intermediate removal of hydrogen sulfide:

Properties of untreated and treated 415° end point gasolines

	I	II	III
A. P. I. gravity	51.7	52.7	56.6
Mg. of gum by copper dish	154	19	25
Mg. of gum with inhibitor*	116	11	20
Total sulfur content, percent	0.60	0.24	0.16
Octane number	65	64	64

*0.025 percent of wood tar fraction.

It will be seen from the above data that there was a sulfur reduction of 73.5% with a loss of but one octane number. This reduction in sulfur with the corresponding small loss in anti-knock value is not possible in a single stage treatment. Furthermore, the consumption of hydrogen was considerably lower than that used up when a corresponding desulfurization was effected in a single stage treatment.

The foregoing specification and the numerical data presented to show the utility of the invention are sufficient for their respective purposes but neither is to be construed as imposing exactly corresponding restrictions upon the scope of the invention.

I claim as my invention:

1. A process for refining sulphurous hydrocarbon oils which comprises treating the oil with hydrogen and reacting a portion of the latter with a part of the sulphur content of the oil thereby forming hydrogen sulphide in admixture with the unused hydrogen, separating the hydrogen sulphide from the unused hydrogen and isolating the same from the process, and then further treating the oil with the unused hydrogen to effect further desulphurization of the oil.

2. In the desulphurization of hydrocarbon oils by treatment thereof with hydrogen, the method which comprises treating the oil with hydrogen in successive stages and in each stage converting a part of the sulphur content of the oil into hydrogen sulphide by reacting the same with hydrogen, isolating the hydrogen sulphide thus formed between the successive stages of treatment, and passing unreacted hydrogen, freed of hydrogen sulphide, from stage to stage.

3. A process for improving sulphurous hydrocarbon oils which comprises treating the oil with

a hydrogen-containing gas and reacting a portion of the hydrogen with sulphur compounds contained in the oil, thereby forming hydrogen sulphide, separating the latter from the oil and from the gas, and then again treating the oil with the gas thus freed of hydrogen sulphide.

4. A process for improving sulphurous hydrocarbon oils which comprises treating the oil with a hydrogen-containing gas and reacting a portion of the hydrogen with a part of the sulphur content of the oil, separating resultant hydrogen sulphide from the oil and from the gas, and then further treating the oil with the gas and reacting additional hydrogen contained in the latter with another part of the sulphur content of the oil.

5. A process for refining sulphurous hydrocarbon oils which comprises treating the oil in vapor phase with a hydrogen-containing gas in the presence of a hydrogenating catalyst, reacting a portion of the hydrogen with a portion of the sulphur content of the oil, thereby forming hydrogen sulphide, cooling the resultant products to separate the partially desulphurized hydrocarbons as condensate from the admixture hydrogen sulphide and unconsumed hydrogen, separating the hydrogen sulphide from the unconsumed hydrogen and isolating the former from the process, and treating said partially desulphurized hydrocarbons with the unconsumed hydrogen thus freed of hydrogen sulphide to remove additional sulphur therefrom.

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