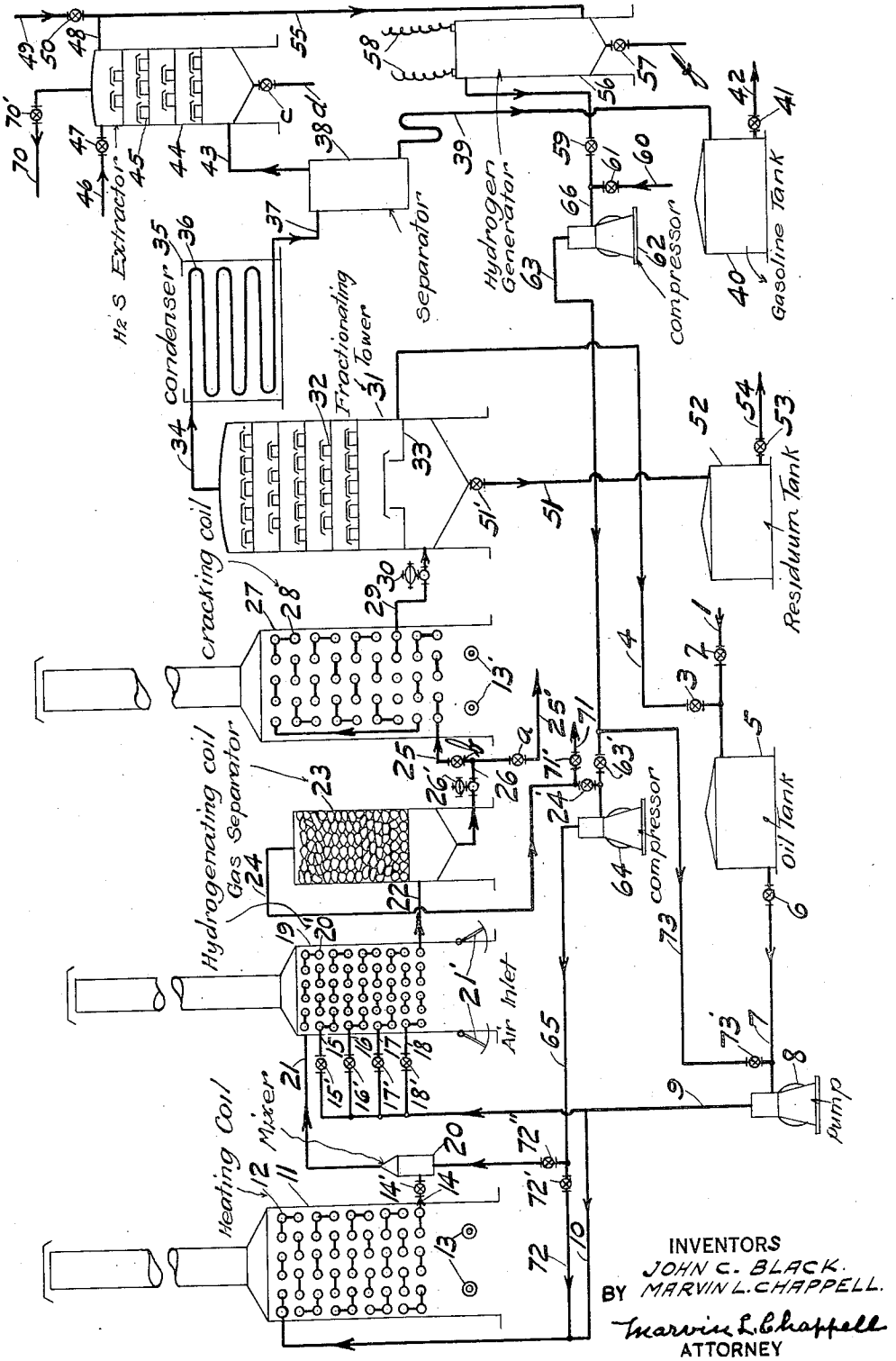
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METHOD OF PROCESSING OILS

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METHOD OF PROCESSING OILS

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This invention relates to a process for hydrogenating oils containing unsaturated hydrocarbons for the manufacture of gasoline stocks, motor fuels, lamp oils, lubricating oils, or other hydrocarbon products, in which the addition of hydrogen is effected to produce more desirable products for various uses. This application is in part a continuation of our pending application, Serial Number 230,114, filed October 31, 1927, for process for producing gasoline from high boiling hydrocarbon oils which discloses a process for the production of motor fuel by cracking higher boiling petroleum oils, introducing hydrogen gas and hydrogenating the cracked products under pressure, at a hydrogenating temperature of approximately 700 to 750 degrees F., maintained by extracting the exothermic heat produced by the hydrogenating reaction, then separately separating, by fractionation, gaseous products, a motor fuel and a higher boiling hydrogenated distillate from a residual oil, and returning the higher boiling hydrogenated distillate to the cracking system to be again processed in like manner as before for the further production of motor fuel.

Now, we have discovered additional improvements thereto, consisting in the use of a catalyst, and maintaining a receding temperature by the introduction of a cooler oil during the hydrogenation operation, in which temperatures ranging from approximately 750 to 550 degrees F. may be employed to hydrogenate petroleum oils; that a receding temperature ranging from approximately 800 to 600 degrees F. is best suited when a catalyst is not employed to hydrogenate petroleum oil to be subsequently cracked for the production of motor fuel; that a receding temperature ranging from approximately 750 to 550 degrees F. is best suited to hydrogenate lubricating oil stocks with or without the aid of a catalyst; that a receding temperature ranging from approximately 550 to 375 degrees F. is best suited to hydrogenate animal or vegetable oils with or without the aid of a catalyst; and also that cracked petroleum distillates and other sulphur bearing hydrocarbons may be desulphurized to a high extent by hydrogenating at a receding temperature ranging from approximately 800 to 600 degrees F.

In general, this invention comprises a continuous method for hydrogenating the unsaturated hydrocarbon products contained in mineral oils, mineral oil products, animal or vegetable oils, or animal or vegetable oil products, to form saturated hydrocarbons, or to add hydrogen to the required degree, such for example as the conversion of acetylene or diolefine hydrocarbons into olefines and paraffines or hydrocarbons of the series C_nH_{2n} and C_nH_{2n+2}, or to cause the addition of hydrogen to any hydrocarbon mixture to convert unstable unsaturated hydrocarbons into stable hydrocarbons which will not materially change in chemical composition, boiling point ranges or color when stored in tanks for a period of time and exposed to light and atmospheric conditions.

This invention is also applicable for hydrogenating unsaturated hydrocarbons of the carbocyclic series with or without side chains into the corresponding saturated or partly saturated hydrocarbons; for example, benzol, toluol or xylol may be converted into the corresponding hexahydro-benzol, hexahydro-toluol or hexahydro-xylol.

This invention also includes the use of any of the known catalytic agents to assist in the hydrogenation operation, such for example as the metal, oxide or salts or nickel, cobalt, copper, iron, aluminum, zinc, etc. We are aware that sulphur, hydrogen sulphide, mercaptans and other like active or corrosive sulphur compounds if present in an oil in appreciable amounts, may render a metal or metal compound catalyst partly inactive, if excessive amounts of the catalyst are not employed. For example, if an oil to be hydrogenated by our invention contains .02% by weight of sulphur in an active or corrosive form, and 1% by weight of nickel oxide catalyst would be required if the sulphur were not present, then 1.25% by weight of nickel oxide would be used, the .25% by weight excess amount of nickel oxide being sufficient to overcome the deleterious action of the sulphur.

If an oil contains a high percentage of active or corrosive sulphur which would poison or decrease the catalytic efficiency of the metallic agent or compound used to assist in the hydrogenation of an oil by our invention, such corrosive sulphur may be removed or converted into noncorrosive compounds by methods known in the art before the hydrogenation operation.

More specifically, our process consists in continuously passing the oil to be hydrogenated in stream flow through a heating coil or other heating means, at a pressure of more than 500 pounds absolute, where the oil is heated to a suitable hydrogenating temperature ranging from approximately 600 to 800 degrees F., the actual degree in temperature to which the oil is heated depending upon the variety and character of oil to be hydrogenated, the time of contact between the oil and the hydrogen gas, and the extent of hydrogenation desired. From the heating coil the oil stream without decrease in pressure and at the required hydrogenating temperature is continuously commingled with hydrogen gas or a hydrogen bearing gas, and the commingled mixture passed through a second pipe coil provided with cooling means to extract the exothermic heat as produced by the hydrogenating reaction, and to provide a receding temperature of the oil stream mixed with the hydrogen gas by continuously extracting a portion of the retained heat as the oil and hydrogen mixture passes through the coil.

To obtain a high degree of hydrogenation, the oil and hydrogen gas mixture enters the hydrogenating coil at a pressure of approximately 1500 to 3000 pounds maintained by pump 8, and at a temperature of approximately 800 degrees F., and leaves the hydrogenating coil at approximately 600 degrees F., although other temperature and pressure ranges may be employed depending upon the character of the oil and the extent of hydrogenation desired. If catalytic agents are used lower temperature ranges are employed, such for example as 750 to 550 degrees F. for mineral oil products, and a still lower temperature range of approximately 550 to 375 degrees F. if animal or vegetable oil or products of the same are to be hydrogenated, such as olein or oleic acid to form stearine or stearic acid.

The cooling means employed to extract the exothermic heat produced by the hydrogenating reaction and to cause a decreasing temperature may be any exterior cooling fluid such as air, which may be caused to flow through the passageway of the compartment containing the hydrogenating coil either concurrent or countercurrent to the flow of the mixed hydrogen gas and oil flowing through the coil; or a cooler oil may be introduced into each row or alternate row of pipe lengths of the hydrogenating coil to absorb or extract the exothermic heat produced by the hydrogenating reaction and further produce the required decreasing or receding temperature.

The hydrogen gas employed for hydrogenating the oil containing unsaturated hydrocarbons may be from any source of manufacture known, such, for example, as the hydrogen produced by electrolysis of water, the thermo-decomposition of hydrocarbon oils or gases, or by the decomposition of steam with highly heated carbon. We prefer, however, to obtain hydrogen by the thermo-decomposition of hydrocarbon gases, either obtained from an accompanying cracking operation or from natural gases which contain a high percentage of methane, by passing such gases through an electric furnace or an intermittent blast coke furnace. When the hydrogen gas is obtained by the decomposition of steam with highly heated coke or coal, known as water gas, which consists of equal volumes of CO and H, such gas is preferably used only once through the system for hydrogenation purposes, and may thereafter be used as a fuel. In general, the hydrogen gas employed to hydrogenate oils by our process may be any hydrogen containing gas, such as water gas and hydrogen gas containing other hydrocarbon gases such as methane, ethane, propane, butane, ethylene, propylene, etc., which may or may not be recycled for further use.

With the foregoing preliminary explanation, the preferred embodiment of our invention will now be more fully explained by reference to the accompanying drawing, which is a diagrammatical representation of an apparatus in which the invention may be carried out in various ways, as follows:

Example #1.—For the manufacture of motor fuel or gasoline stock.

Example #2.—For stabilizing gasoline or naphtha stocks, or other hydrocarbons containing unstable hydrocarbons.

Example #3.—For stabilizing and hydrogenating lamp oil stocks.

Example #4.—For stabilizing and hydrogenating lubricating oil stocks.

Example #5.—For hydrogenating oil with a catalyst.

Example #6.—For hydrogenating animal or vegetable oils or derivatives therefrom.

Example #7.—For desulphurizing cracked petroleum distillates and other sulphur bearing hydrocarbons.

In the drawing, 5 represents generally a tank for holding the oil or oil product to be processed, which may be filled by opening valve 2 in pipe 1. Pipe 1 leads to a source of the oil or oil product to be processed. In case a catalytic agent is employed, the oil charged into tank 5 through pipe 1 will contain the agent in the required amount. Cata-

lytic agents may not be used in hydrogenating mineral oil, but it is found advantageous to use a catalytic agent in hydrogenating animal or vegetable oils or products derived therefrom, such as for the conversion of olein or oleic acid into stearine or stearic acid, in which case one of the well known catalytic agents, nickel, nickel oxide or nickel salt is preferably used.

For the manufacture of gasoline or motor fuel, tank 5 is filled with mineral oil distillate, residuum or crude petroleum oil by opening valve 2 in pipe 1. Pipe 1 leads to a source of the oil or distillate to be processed. Valve 6 in pipe 7 is opened to the required degree, which permits a regulated stream of oil to flow from tank 5 through pipe 7 and into the suction side of pump 8. 8 is preferably a multiple stage compression pump so that the oil may be discharged at a pressure as high as 3000 pounds per square inch if desired. Pump 8 discharges the oil at a pressure ranging from approximately 1500 pounds or lower to as high as 3000 pounds through pipe 9, pipe 10, and then through heating coil 12 which is stationed in furnace 11. Furnace 11 is provided with burners 13, by means of which the oil passing through heating coil 12 is heated to the required hydrogenation temperature, which may range from 600 to 800 degrees F. to as low a range as 375 to 550 degrees F. in case animal or vegetable oil products are to be hydrogenated with a catalyzer.

From heating coil 12 the oil at the required hydrogenating temperature and pressure passes out through pipe 14, controlled by valve 14', and into mixing chamber 20, wherein the heated oil is continuously mixed with hydrogen gas or a hydrogen containing gas in excess of the amount necessary to hydrogenate the oil under treatment, preferably two or three times the quantity of hydrogen gas necessary to complete the hydrogenation reaction. For example, an oil having 30% by weight unsaturated hydrocarbons having an average molecular weight of 260, and requiring the addition of two hydrogen atoms to produce the desired degree of hydrogenation, will require approximately 0.5 to 0.7% by weight hydrogen gas, and 1 to 1.4% by weight hydrogen gas in case the addition of four hydrogen atoms is to be effected, the excess hydrogen being continuously returned to the system in case a substantially pure hydrogen gas is used. The ratio of hydrogen to the oil is not critical and may range from approximately 6 cubic feet to as much as 40 cubic feet or more (calculated to 0 degrees C. and 760 mm. pressure) per gallon of oil under treatment.

The hydrogen gas is introduced into mixing chamber 20 through pipe 65 and valve 72'', valve 72' being closed, under the same pressure and preferably at the same temperature as the oil entering mixing chamber 20. If desired, the hydrogen gas may be introduced into the oil through pipe 72 by opening valve 72' and closing valve 72''. It may be desired to introduce the hydrogen or hydrogen bearing gas into the suction side of pump 8 through pipe 73 controlled by valve 73'. In this manner it is possible to introduce hydrogen gas into the oil going to heating coil 12, so as to obtain the benefit of the longer time of contact between the hydrogen and the oil passing through the coils, and also making it possible to pass hydrogen gas commingled with the temperature regulating oil which is injected into hydrogenating coil 20' through pipes 15, 16, 17 and 18.

From mixing chamber 20 the commingled oil and hydrogen gas, at a pressure greater than 500 pounds, preferably approximately 1500 to 3000 pounds absolute maintained by pump 8, and at a temperature of approximately 750 to 800 degrees F. in case mineral or petroleum oils are to be hydrogenated as completely as possible, pass through pipe 21 and then through hydrogenating coil 20', which is stationed in container 19. A temperature as low as 600 degrees F. may be employed for hydrogenating hydrocarbons containing hydrocarbons of the diolefine or acetylene group to form the more stable unsaturated hydrocarbons of the olefine type.

Container 19 is provided with doors 21', through which cool air may be introduced in quantities sufficient to extract all the exothermic heat produced as the hydrogenation reaction proceeds, as well as to gradually extract retained heat from the oil in order to produce a graduated receding temperature, so that the oil and excess hydrogen leaving coil 20' will be at a temperature of approximately 600 degrees F. We have found that extracting the heat produced by the hydrogenating reaction and causing a receding temperature from approximately 800 to 600 degrees F. produces the greatest degree of hydrogenation. The velocity of the hydrogenation reaction is greatest at the higher temperature, but must be followed by a receding temperature to obtain the maximum degree of hydrogenation and prevent a counter reaction of dehydrogenation.

We have discovered that the exothermic heat of the hydrogenation reaction, and a graduated reduction in temperature of the oil and hydrogen gas from approximately 800 to 600 degrees F., may also be carried out by introduction of regulated quantities of a cooler oil into hydrogenating coil 20' through branch pipes 15, 16, 17 and 18, by regulated opening of valves 15', 16', 17' and 18', which may or may not be carried out in conjunction with the introduction of a cooling fluid through doors 21'.

The hydrogenated oil and excess hydrogen

gas pass from coil 20′ through pipe 22 and into gas separator tank 23, wherein the excess hydrogen gas is separated from the hydrogenated oil. The separated hydrogen gas passes from the top of separator tank 23 through pipe 24 and valve 24′, and then into pipe 63, controlled by valve 63′, where it is mixed with other hydrogen gas for further use, or if a hydrogen bearing gas containing CO is employed, it may be passed out of the system and into a storage tank not shown by opening valve 71′ in pipe 71 and closing valve 24′. The hydrogenated oil separated from the excess hydrogen gas passes out from the bottom of separator 23 through pipe 26, pressure regulating and reducing valve 26′, and into pipe 25 controlled by valves *a* and *b*. If the hydrogenated oil is sufficiently processed for the purpose desired, such as previously stated for Examples No. 2, 3, 4, 5, 6 and 7, valve *a* is kept open and valve *b* closed, and the hydrogenated oil is conducted by pipe 25′ through a cooler and then into a storage not shown.

The hydrogenation operation thus described is used for any of the examples given, except that different pressures and temperatures or different decreasing temperature ranges may be employed to suit the oil treated to obtain the product desired, and it is to be understood that any suitable metal, metal oxide or metal salt catalyst may be employed in the operation, as previously stated.

The following are preferred temperature ranges, at pressures greater than 500 pounds, for the hydrogenation operations of the examples given:

Example #1.—Temperature range 800 to 600 degrees F. without a catalyst, and 750 to 550 degrees F. with a catalyst such as a nickel compound or the like.

Example #2.—Temperature range 800 to 600 degrees F., or other temperature ranges less than 800 to 600 degrees F., with or without a catalyst, depending upon the character of the stock treated and time of contact.

Example #3.—Temperature range 800 to 600 degrees F. without a catalyst, and 750 to 550 degrees F. with a catalyst.

Example #4.—Temperature range approximately 750 to 550 degrees F. with or without a catalyst.

Example #5.—Temperature range 750 degrees F. to 550 degrees F. or lower.

Example #6.—Temperature range 550 degrees F. to 375 degrees F. or lower.

Example #7.—Temperature range from approximately 800 to 600 degrees F.

In the manufacture of gasoline stock or motor fuel, the hydrogenated mineral oil or mineral oil distillate, mixed with the hydrogenated return cracked distillate from fractionating tower 31, passes from separator tank 23 through pipe 26, pressure regulating and reducing valve 26′, and into pipe 25, wherein the pressure is preferably reduced to approximately 1000 pounds absolute. From pipe 25 the hydrogenated oil passes through valve *b* in pipe 25 and then through cracking coil 28, which is stationed in the upper section of furnace 27. In this mode of operation valve *a* is closed.

Furnace 27 is provided with burners 13′, stationed in the lower section of furnace 27, which provide sufficient heat to heat and maintain the hydrogenated oil stream at a cracking temperature for a period of time sufficient to crack the oil to the required degree to produce a maximum yield of gasoline stock or motor fuel without carbon deposition. Any cracking coil or commercial cracking equipment may be employed, wherein the oil is cracked to the required degree. Also the hydrogenated oil may be cracked by pipe coils arranged in any other manner than the arrangement shown in furnace 27, in which the oil may flow through the cracking coil either concurrent, countercurrent, or alternately concurrent and then countercurrent with the flow of combustion gases.

The temperature and pressure maintained during the cracking operation may be also varied to suit the hydrogenated oil being cracked, which may range from approximately 750 degrees to as high as 950 degrees F., or higher in case a high percentage of benzol hydrocarbons is desired, and the pressure maintained is preferably above 500 pounds absolute, although lower pressures may be employed.

From cracking coil 28 the cracked oil in stream flow passes through pipe 29, pressure release valve 30, and then into the lower section of fractionating tower 31, wherein the lower boiling portion of the cracked oil is vaporized, and the gasoline stock separated by fractionation from a higher boiling distillate and a residual oil. Fractionating tower 31 is provided with bubble trays 32 and a separator plate 33. The residual oil which collects below separator plate 33 passes into pipe 51, the rate of flow being controlled by valve 51′. From pipe 51 the separated residual oil passes into storage tank 52. Tank 52 is provided with outlet pipe 54, controlled by valve 53, by means of which the residual oil which collects in tank 52 may be conveyed to other storage not shown and used as a fuel oil or for other purposes.

The higher boiling distillate which collects above separator plate 33 passes through pipe 4, controlled by valve 3, pipe 1, and then into tank 5, and is continuously again processed as produced along with the oil contained in tank 5 for the further production of gasoline stock or motor fuel. The gasoline stock and gaseous products separated in fractionating tower 31 pass out through pipe 34 and into condenser coil 36. Condenser coil 36 is sta-

tioned in condenser box 35, and is provided with cooling means not shown, wherein the gasoline stock is condensed and passes through pipe 37 along with the gaseous hydrocarbon products into separator 38. In separator 38 the gaseous products separate from the condensed gasoline stock, pass out of separator 38 through pipe 43 and then into wash tower 44.

The condensed gasoline stock, separated from gaseous products, passes from separator 38 through pipe 39 and into gasoline storage tank 40. Gasoline storage tank 40 is provided with a pipe connection 42, controlled by valve 41, by means of which the gasoline stock as produced may be conducted to other storage not shown, and may be purified thereafter, if necessary, by methods known in the art, such as treatments with sulphuric acid, caustic soda, etc.

The hydrocarbon gases generated by the cracking operation, which, as previously stated, are separated in separator 38 and then passed into wash tower 44 through pipe 43, usually contain small percentages of hydrogen sulphide, which are removed by washing the said gases with a water solution of an alkali such as caustic soda. Wash tower 44, employed for separating the H_2S from the gaseous products, is provided with bubble trays 45. Pipe 46, controlled by valve 47, leads to a source of supply of caustic soda not shown. The gases entering wash tower 44 pass up and through the bubble tray wash system in countercurrent flow to the water solution of caustic soda, which is introduced into wash tower 44 at the top by a regulated opening of valve 47. The caustic soda solution passes down through the series of bubble trays, combines with substantially all the H_2S contained in the upcoming gas, and then passes out of tower 44 through pipe *d* to a storage or recovery plant not shown, the flow being controlled by operation of valve *c*.

The purified hydrocarbon gases may be conducted to a storage not shown by means of pipe 70 controlled by valve 70′, or the said purified gases may be used for the production of hydrogen, in which case the said gases, free from H_2S, pass out of tower 44 through pipe 48 and into pipe 55. By means of pipe 49, controlled by valve 50, hydrocarbon gases from a source not shown may be introduced into pipe 55, along with the hydrocarbon gases generated in the cracking operation. The flow of hydrocarbon gases introduced into pipe 55 passes through electric furnace 56, or other like heating devices or other hydrogen generating apparatus, in which a temperature may be produced sufficient to decompose the major portion of these hydrocarbon gases into hydrogen and carbon, such operations being known in the art. Electric furnace 56 is provided with electric connections 58 and means for separating the carbon produced by the decomposition from the hydrogen gas, and the carbon is continuously or intermittently removed from furnace 56 through pipe *f*, controlled by valve 57, to a storage not shown.

The hydrogen gas generated by the decomposition of the hydrocarbon gases, substantially free from carbon, passes from furnace 56 through pipe 66, controlled by valve 59, into the suction side of compressor 62. A branch pipe 60, controlled by valve 61, leads to a source of hydrogen gas or water gas not shown, which may be employed instead of producing hydrogen gas by decomposition of the hydrocarbon gases produced by the cracking operation, or other introduced hydrocarbon gases previously described. Compressor 62 discharges the hydrogen gas, or hydrogen gas mixed with other gases, such as CO in case water gas is employed, at a pressure greater than 500 pounds absolute, through pipe 63 and into the suction side of compressor 64. Compressor 64 discharges the hydrogen gas, or hydrogen gas mixed with other gases, together with the excess hydrogen gas separated from the hydrogenation operation previously described, at a pressure greater than 500 pounds absolute, preferably at pressures ranging from 1500 to 3000 pounds absolute, into pipe 65, and the operation is continued in the cycle as described.

The heating coil 12, the hydrogenating coil 20′ and the cracking coil 28 are preferably constructed of chrome-nickel-steel, chrome steel, or nickel steel alloy pipe lengths connected by welded return bends or cross overs of such thickness and diameter as will withstand working pressures up to 3000 pounds per square inch, well known in the art.

It is to be understood that the terms "catalyzing agent" or "catalytic agent", as used in the specification and claims, is to mean only any metal, metal oxide or metal salt known in the art to assist in hydrogenating operations.

While the process herein described is well adapted for carrying out the object of the present invention, various modified forms of apparatus and methods of operation may be made without departing from the spirit of the invention, and the invention includes all such modifications and changes as appear within the scope of the appended claims.

What we claim is:

1. A process of hydrogenating mineral oil, comprising, heating the oil to a temperature of approximately 800° F., and without allowing time for substantial cracking reactions, commingling the heated oil with hydrogen gas and passing the commingled mixture through an elongated passageway, at a pressure greater than 500 pounds absolute, for a period of time sufficient to hydrogenate the

oil, and continuously reducing the temperature of the commingled mixture to approximately 600° F. during the passage of the oil and hydrogen gas through the elongated passageway.

2. A process of hydrogenating mineral oil, comprising, heating the oil containing an added catalyst to a temperature of approximately 750° F., and without allowing time for substantial cracking reactions, commingling the heated oil containing the added catalyst with hydrogen gas, and passing the commingled mixture through an elongated passageway at a pressure greater than 500 pounds absolute, for a period of time sufficient to hydrogenate the oil, and continuously reducing the temperature of the commingled mixture to approximately 550° F. during the passage of the oil containing the added catalyst and hydrogen gas through the elongated passageway.

3. A process of hydrogenating mineral oil, comprising, mixing the oil with hydrogen gas and heating the mixture to a temperature of approximately 800° F., then, without allowing time for substantial cracking reactions, passing the heated mixture through an elongated passageway at a pressure greater than 500 pounds absolute, for a period of time sufficient to hydrogenate the oil, and continuously reducing the temperature of the mixture to approximately 600° F. during the passage of the oil and the hydrogen gas through the elongated passageway.

4. A process of hydrogenating mineral oil, comprising, mixing the oil containing an added catalyst with hydrogen gas and heating the mixture to a temperature of approximately 750° F., then, without allowing time for substantial cracking reactions, passing the heated mixture through an elongated passageway at a pressure greater than 500 pounds absolute, for a period of time sufficient to hydrogenate the oil, and continuously reducing the temperature of the mixture to approximately 550° F. during the passage of the oil containing the catalyzing agent and the hydrogen gas through the elongated passageway.

5. A process of hydrogenating mineral oil, comprising, heating the oil to a temperature of approximately 800° F., and without allowing time for substantial cracking reactions, commingling the heated oil with hydrogen gas and passing the commingled mixture through an elongated passageway at a pressure greater than 500 pounds absolute, for a period of time sufficient to hydrogenate the oil, and continuously reducing the temperature of the commingled mixture to approximately 600° F. with a flowing cooling fluid surrounding the passageway, during the passage of the oil and the hydrogen gas through the elongated passageway.

6. The process of hydrogenating mineral oil, comprising, heating the oil containing an added catalyst to a temperature of approximately 750° F., and without allowing time for substantial cracking reactions, commingling the heated oil containing the added catalyst with hydrogen gas and passing the commingled mixture through an elongated passageway, at a pressure greater than 500 pounds absolute, for a period of time sufficient to hydrogenate the oil, and continuously reducing the temperature of the commingled mixture to approximately 550° F. with a flowing cooling fluid surrounding the passageway, during the passage of the oil containing the added catalyzing agent and hydrogen gas through the elongated passageway.

7. The process of hydrogenating mineral oil, comprising, heating the oil to a temperature of approximately 800° F., and without allowing time for substantial cracking reactions, commingling the heated oil with hydrogen gas and passing the commingled mixture through an elongated passageway, at a pressure greater than 500 pounds absolute, for a period of time sufficient to hydrogenate the oil, and continuously reducing the temperature of the commingled mixture to approximately 600° F. by regulated introduction of a cooler oil into the elongated passageway during the passage of the oil and hydrogen gas through the elongated passageway.

8. A process of hydrogenating mineral oil, comprising, heating the oil containing an added catalyst to a temperature of approximately 750° F., and without allowing time for substantial cracking reactions, commingling the heated oil containing the added catalyst with hydrogen gas and passing the commingled mixture through an elongated passageway, at a pressure greater than 500 pounds absolute, for a period of time sufficient to hydrogenate the oil, and continuously reducing the temperature of the commingled mixture to approximately 550° F. by regulated introduction of a cooler oil into the elongated passageway, during the passage of the oil containing the catalyst and hydrogen gas through the elongated passageway.

9. A process of hydrogenating mineral oil, comprising, heating the oil to a temperature of approximately 800° F., and without allowing time for substantial cracking reactions, commingling the heated oil with hydrogen gas and passing the commingled mixture through a hydrogenating zone, at a pressure greater than 500 pounds absolute, for a period of time sufficient to hydrogenate the oil, and continuously reducing the temperature of the commingled mixture to a temperature of approximately 600° F. by a regulated flow of atmospheric air through a passageway surrounding the hydrogenating zone, during the passage of the oil and the hydrogen gas through the hydrogenating zone.

10. A process of hydrogenating mineral oil, comprising, heating the oil containing an added catalyzing agent to a temperature of approximately 750° F., and without allowing time for substantial cracking reactions, commingling the heated oil containing the added catalyst with hydrogen gas and passing the commingled mixture through an elongated passageway at a pressure greater than 500 pounds absolute, for a period of time sufficient to hydrogenate the oil, continuously reducing the temperature of the commingled mixture to approximately 550° F. by a regulated flow of atmospheric air through a passageway surrounding the elongated passageway, during the passage of the oil and hydrogen gas through the elongated passageway.

11. A process of hydrogenating petroleum oil, comprising, mixing the oil with hydrogen gas and heating the mixture to a temperature of approximately 800° F., then, without allowing time for substantial cracking reactions, passing the mixture through a hydrogenating zone at a pressure greater than 500 pounds absolute, for a period of time sufficient to hydrogenate the oil, and continuously reducing the temperature of the mixture to approximately 600° F. by regulated introduction of cooler oil into the hydrogenating zone at intervals during the passage of the oil and hydrogen gas through the hydrogenating zone.

12. A process of hydrogenating mineral oil and cracking the hydrogenated oil to produce gasoline stock, comprising, heating the oil, mixed with cracked oil distillate subsequently produced in the process, to a temperature of approximately 800° F., and without allowing time for substantial cracking reactions, commingling the heated oil mixture with hydrogen gas and passing the commingled mixture through an elongated passageway, at a pressure greater than 500 pounds absolute, for a period of time sufficient to hydrogenate the oil; continuously reducing the temperature of the commingled mixture to approximately 600° F. during its passage through the elongated passageway, then separating excess hydrogen gas from hydrogenated oil; cracking the hydrogenated oil to produce cracked oil products containing gasoline stock; separately separating by vaporization and fractionation gaseous products, gasoline stock, higher boiling distillate and residual oil from the cracked oil products, and continuously returning the higher boiling distillate to the process to be again hydrogenated and cracked along with other mineral oil for the further continuous production of gasoline stock.

13. A process of hydrogenating petroleum oils and continuously cracking the hydrogenated oil to produce gasoline stock and residual oil, comprising, passing petroleum oil and hydrogen gas through a heating zone and heating the oil mixed with the hydrogen gas to a temperature of approximately 800° F., and without allowing time for substantial cracking reactions, passing the heated mixture of oil and hydrogen gas, maintained at a pressure of approximately 1500 to 3000 pounds absolute, through an elongated passageway stationed in a container, for a period of time sufficient to hydrogenate the oil; continuously reducing the temperature of the oil and hydrogen gas stream to approximately 600° F. by a regulated flow of a cooling fluid through the container and in contact with the elongated passageway, then separating the excess hydrogen gas from hydrogenated oil; reducing the pressure of the hydrogenated oil stream to approximately 1000 pounds absolute; heating and cracking the hydrogenated oil at cracking temperatures to produce cracked oil products containing gasoline, and separately separating by vaporization and fractionation gaseous products, gasoline stock and a higher boiling distillate from residual oil, and continuously returning the higher boiling distillate to the process to be hydrogenated and cracked along with other petroleum oil for the further continuous production of gasoline and residual oil.

14. A process of hydrogenating petroleum oils and cracking the hydrogenated oil to produce gasoline stock and residual oil, comprising, passing petroleum oil and hydrogen gas through a heating zone and heating the oil mixed with the hydrogen gas to a temperature of approximately 800° F., and without allowing time for substantial cracking reactions, passing the heated mixture, maintained at a pressure of 1500 to 3000 pounds absolute, through a hydrogenating zone for a period of time sufficient to hydrogenate the oil; continuously reducing the temperature of the oil and hydrogen gas mixture to approximately 600° F. by a regulated introduction of a cooling fluid into the stream of oil and hydrogen gas while passing through the hydrogenating zone, then separating the excess hydrogen gas from hydrogenated oil; reducing the pressure of the hydrogenated oil stream to approximately 1000 pounds absolute; heating and cracking the hydrogenated oil at cracking temperatures to produce cracked oil products containing gasoline, and separately separating by vaporization and fractionation gaseous products, gasoline stock and a higher boiling distillate from residual oil, and continuously returning the higher boiling distillate to the process to be hydrogenated and cracked along with other petroleum oil for the further continuous production of gasoline and residual oil.

15. A process of hydrogenating mineral oil containing unsaturated hydrocarbons, comprising, heating and commingling the oil with hydrogen gas at a temperature of approximately 800° F., and before substantial

thermomolecular decomposition can begin, passing the commingled mixture through an elongated passageway under superatmospheric pressure greater than 500 pounds absolute, for a period of time sufficient to hydrogenate the oil, and continuously reducing the temperature of the commingled mixture at a rate sufficient to prevent thermomolecular decomposition thereof during the passage of the oil and hydrogen gas through the elongated passageway.

In testimony whereof we affix our signatures.

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