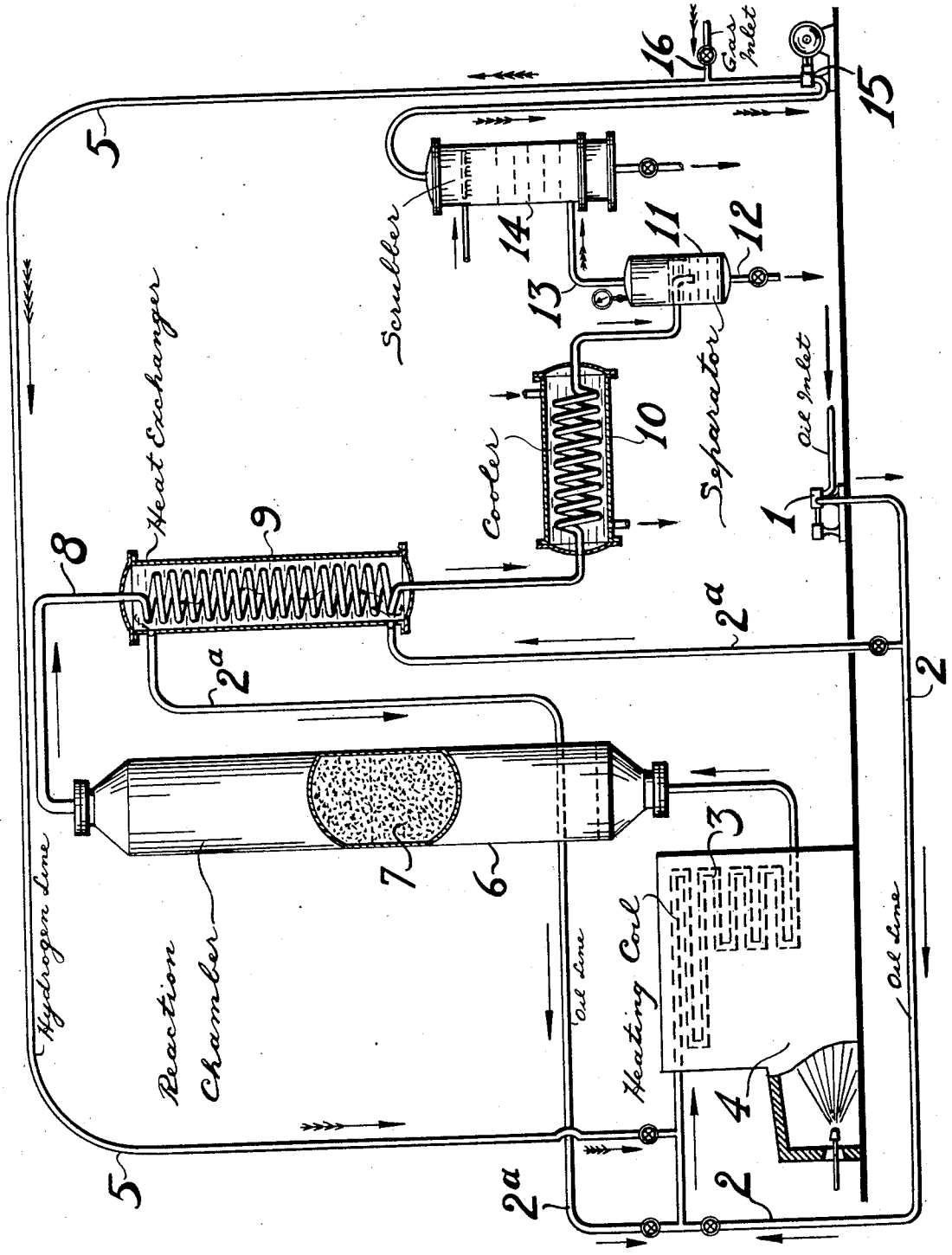
June 19, 1934. R. P. RUSSELL 1,963,385

PROCESS FOR PRODUCING LUBRICANTS BY HYDROGENATION OF HYDROCARBON OILS

Filed Jan. 8, 1930



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Patented June 19, 1934 1,963,385

UNITED STATES PATENT OFFICE

1,963,385

PROCESS FOR PRODUCING LUBRICANTS BY HYDROGENATION OF HYDROCARBON OILS

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Application January 8, 1930, Serial No. 419,472

6 Claims. (Cl. 196—78)

The present invention relates to the art of producing refined viscous hydrocarbons from unrefined heavy hydrocarbons by the action of hydrogen under extremely high pressures. The invention will be fully understood from the following description.

The drawing is a semi-diagrammatic representation of the type of apparatus in which the present process may be conducted.

Petroleum oils have been hydrogenated under high pressures in excess of 20 atmospheres for the production of lubricants and the pressures ordinarily employed have been from 100 to 200 atmospheres or slightly higher. This process for producing and improving lubricating oils by hydrogenation is described in co-pending applications Serial No. 363,984, filed May 17, 1929 by the applicant and G. H. B. Davis, Serial No. 385,762, filed August 14, 1929 by J. M. Jennings, Serial No. 379,086, filed July 18, 1929, and Serial No. 397,732, filed October 5, 1929 by E. M. Clark. In this process the hydrogen treatment of heavy hydrocarbon oils is preferably carried out under conditions permitting not more than a limited decomposition of the oils to lighter oils. Generally this is accomplished by operating with a short time of reaction so that not more than about 20% of light oil boiling below about 400° F. is produced with light feed stocks such as for example, light lubricating oil. This production of oil boiling below 400° F. will be relatively larger than is produced from a heavier feed stock such as cylinder oil or the like. For example, with a heavy cylinder oil the production of light oil boiling below about 400° F. is below 15% and may be as low as 10 or even 5%. In the process catalysts are generally used and it has been found that the hydrogenated oil is markedly superior when catalysts such as oxides and sulphides of chromium, molybdenum, tungsten and similar metals are used, either alone or in combination with other oxides or sulphides, such as those of the alkali, alkaline earth, rare earth metals as well as alumina, zinc and the like. It is desirable to keep the reactants and the catalyst in violent agitation but even so it has been observed that there is a gradual loss of catalytic activity. This loss is not due to sulphur or similar catalyst poisons since it occurs with substantially sulphur-free as well as high sulphur oils but appears to be due to incomplete mixing and local absence of hydrogen. In absence of hydrogen the oil decomposes to form tars or tarry or gummy substances of unknown constitution which are not only detrimental to the oil, making further treatment necessary with consequently higher losses, but where catalysts are used, the decomposition products adhere to the solid surfaces, preventing the catalyst from functioning in the proper manner.

Attempts have been made with only partial success to increase the agitation rate and to use finely ground catalysts but mechanical difficulties make it desirable to attack the problem from another angle.

It is impossible under the usual pressure conditions to dissolve sufficient hydrogen initially to react completely with the oil and as a consequence a great excess is forced into the oven or retort to dissolve during the reaction. In the present invention pressures far in excess of those now used are employed, greatly increasing hydrogen solubility and substantially preventing local absence of hydrogen. It has been found that the solubility of hydrogen in hydrocarbon oils increases greatly with temperature and the present invention comprises use of a combination of pressure and temperature conditions within the retort, so that substantially the entire quantity of hydrogen required for reaction is dissolved in the oil and the reaction is therefore substantially completely carried out in the liquid phase. In this way the local absence of hydrogen with its undesirable consequences is substantially avoided. Mechanical stirring can be eliminated, greatly simplifying the operation of the retort. This also results in a considerable saving in hydrogen as it is unnecessary to recirculate such large volumes as is now the practice. Packed catalysts can be used with great advantage and the loss of activity is almost completely eliminated.

In the operation of the present process heavy oil such as petroleum, or heavy distillates or residues thereof are forced together with a controlled quantity of free hydrogen or a gas containing the same in substantial amount under high pressure through a heating coil or other equivalent means and into a high pressure drum or retort. The drum is preferably packed with suitable catalytic material. The retort is also heat insulated and constructed to withstand both temperature and pressure as well as the corrosive effect of the reactants. The drum temperature is preferably in excess of 650° F. and ordinarily within the limits of 700 to 870° F. The quantity of hydrogen is so regulated that it is not greatly in excess of that required to fully react with the oil and may be from 500 to 2500 cu. ft. measured at standard conditions per barrel of oil fed. Pressure is selected so that under the temperature conditions

the requisite quantity of hydrogen is dissolved and it is preferable that a suitable excess also be dissolved. The gas is dissolved during the heating period and the pressure will vary from 400 or 500 atmospheres as a minimum to 800 to 1200 atmospheres or higher where the quantity of hydrogen used is larger than ordinarily required. The preferable pressures are from 500 to 1000 atmospheres. The reaction within the drum is substantially entirely in one phase and the oil is preferably continually withdrawn and cooled. Pressure is then reduced and the oil is distilled and cut to suitable specifications. It has been found that by operating in this manner catalytic activity is greatly prolonged, almost indefinitely.

The requirements of different oils in respect to the hydrogen differ quite widely but in general oils of low gravity in proportion to their viscosities at, say 100° F., require more hydrogen than oils of relatively higher gravities. In other words, oils which approach the Pennsylvania type in their gravity-viscosity characteristics, require less hydrogen than, say Colombian or Texas coastal oils which have low gravities for a given viscosity at 100° F. The hydrogen solubility in some particular oil may be estimated by ordinary physico-chemical methods at pressure of, say 10,000 to 35,000 pounds per square inch, and at temperatures of, say 600 and 400° F. where there is no noticeable reaction and then the increase in solubility may be estimated for the higher temperature, assuming that the logarithm of the solubility increases linearly with the reciprocal of the absolute temperature.

The following relation has been found generally satisfactory under most circumstances but it is only an approximate method of estimating solubility:

$$\text{Log}_{10} S = K - \frac{450}{T}$$

$$K = \text{Log}_{10}(10.0 + .026P)$$

Where S=volumes of hydrogen at atmospheric conditions/volume of oil
T=° F. Abs.=° F.+460° F.
P=pounds per square inch.

In the above manner the hydrogen requirement may be estimated and an excess of, say 20 to 50% may be added which excess is not large in comparison with the excess volumes now used. The pressure is then set to insure solubility of substantially the full hydrogen requirement within the drum and insuring that the reaction proceeds substantially in the liquid phase and that the drum is filled completely.

I am aware that it has been suggested to use extremely high pressures, say 4,000 to 10,000 atmospheres in the production of low boiling oil suitable for motor fuel from coal but the present process is clearly distinguished therefrom, in that high grade lubricants are produced and such pressures as the above are not required for this purpose.

Any convenient form of apparatus of sufficient strength to withstand the severe conditions may be used in carrying out the present process and the following description is given to illustrate a form of apparatus considered satisfactory. Oil is forced by pump 1 through a pipe 2 into a heating coil 3 which is mounted in a furnace setting 4. Hydrogen under superelevated pressure is admitted to the heating coil by a branch pipe 5. In passing through the tubes the mixture is raised to reaction temperature and under the superelevated pressure which is calculated as indicated above, the entire volume of hydrogen required for reaction is dissolved in the oil, including also a suitable excess. The agitation caused by the flow is ordinarily sufficient to bring about a complete solution but if desired baffles, not shown, may be placed within the heating pipes to increase the agitation rate.

The heated mixture, at substantially reaction temperature, passes into a reaction chamber 6 packed with a suitable catalyst 7 in lump or pellet form. The oil with its dissolved hydrogen then flows through the packed chamber and finds exit through pipe 8 which conducts it to a heat exchanger 9. The fresh feed or part of it may be conducted through the heat exchanger by a branch pipe 2a and thus be suitably preheated.

The oil is further reduced in temperature in the cooler 10 and is discharged therefrom into a separator 11 from which it is taken by pipe 12 to storage or for further treatment. Gas is taken from the separator by pipe 13 and is purified by scrubber 14 which is adapted to remove hydrocarbons and hydrogen sulfide. The purified gas is then recompressed by booster pump 15 and is returned for recirculation through the apparatus by means of pipe 5. Fresh hydrogen is introduced by pipe 16.

The present invention is not to be limited by any theory of the mechanism of the process nor to any details given for illustrative purposes but only to the following claims in which it is desired to claim all novelty inherent in the invention.

I claim:

1. In a process for manufacturing improved lubricating oils from petroleum lubricating fractions by destructive hydrogenation in the presence of solid catalyst wherein an appreciable but limited quantity of low boiling fractions is produced, the improvement which consists in conducting the reaction under superelevated hydrogen pressure sufficient to insure complete solubility in the oil of the volume of hydrogen required for reaction.

2. In a process for manufacturing improved lubricating oils from petroleum lubricating fractions by destructive hydrogenation in the presence of a solid catalyst wherein an appreciable but limited quantity of low boiling fractions is produced, the improvement consisting in conducting the reaction at a temperature between 650 and 870° F. under a hydrogen pressure in excess of 400 atmospheres and adapted to insure solubility in the oil of the entire volume of hydrogen required for the reaction.

3. In a process for manufacturing improved lubricating oils from heavy fractions of petroleum by destructive hydrogenation wherein an appreciable but limited quantity of naphtha is formed, the improvement which consists in conducting the reaction under temperature between about 700 and 870° F. while in the presence of a solid catalyst comprising a compound of a metal of the VI Group of the Periodic system and under hydrogen pressure in excess of 400 atmospheres adapted to insure complete solubility in the oil of the volume of hydrogen required for the reaction.

4. In a process for the manufacture of lubricating oils by destructive hydrogenation wherein an appreciable but limited amount of naphtha is formed, the improvement comprising subjecting a lubricating fraction of petroleum derived from an asphaltic base crude to reaction at temperatures from 650 to 870° F. in the presence

of a solid catalyst while under superelevated hydrogen pressure sufficient to insure complete solubility of the volume of hydrogen required for reaction.

5. In a process for the manufacture of improved lubricating oils by destructive hydrogenation wherein an appreciable but limited amount of light oil is formed, the improvement comprising passing a lubricating fraction derived from an asphaltic base crude through a reaction zone packed with a solid catalyst comprising a compound of a metal of the VI Group of the Periodic system while maintained at a temperature between about 700 and 870° F. and under superelevated hydrogen pressure sufficient to insure solubility of the entire volume of hydrogen required for reaction.

6. In a process for the manufacture of improved lubricating oils by destructive hydrogenation wherein an appreciable but limited amount of naphtha is formed, the improvement comprising passing a lubricating fraction derived from an asphaltic base crude through a reaction zone packed with a solid catalyst comprising a compound of a metal of the VI Group of the Periodic system while maintained at a temperature between about 700 and 870° F. and under superelevated hydrogen pressure in excess of 400 atmospheres.

ROBERT P. RUSSELL.