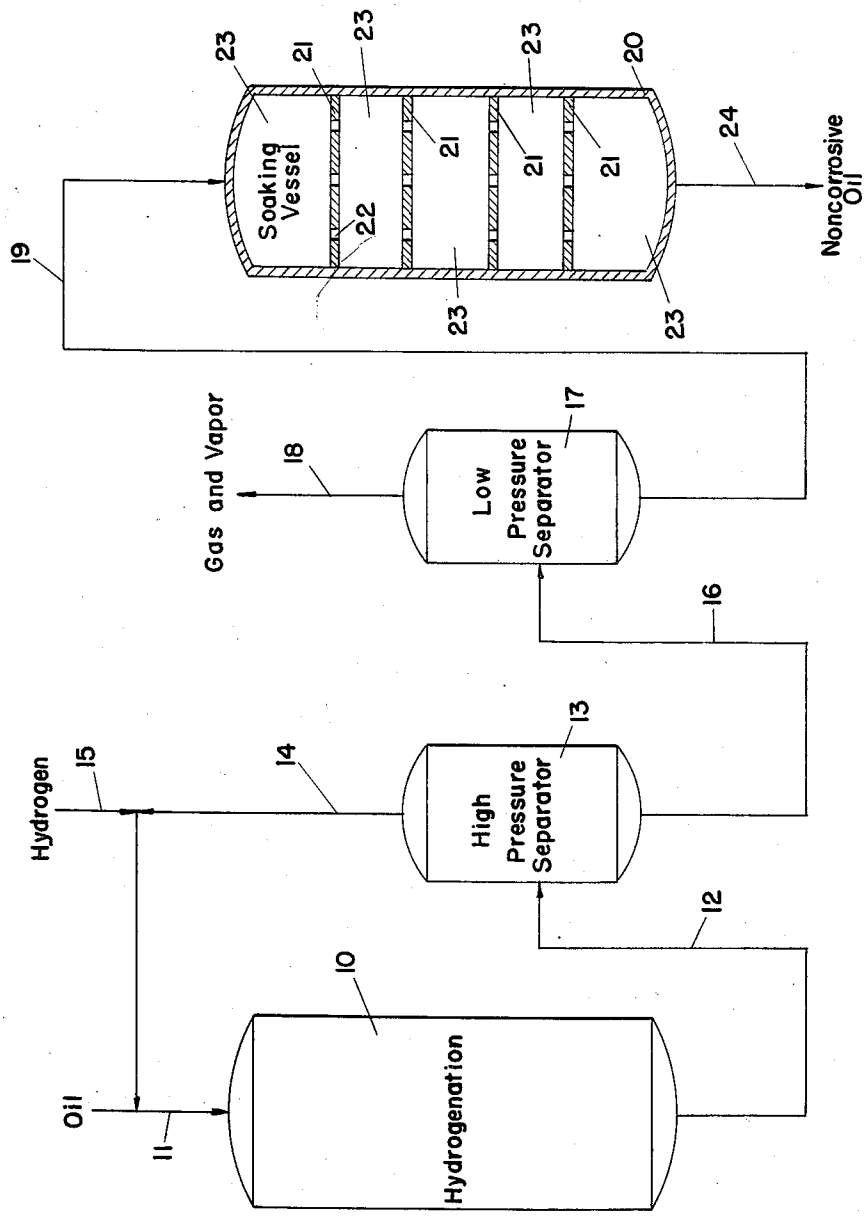
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HYDROFINING FOLLOWED BY HEAT STABILIZING

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HYDROFINING FOLLOWED BY HEAT STABILIZING

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This invention relates to refining petroleum by hydrogenation.

The invention provides a novel manner of producing refined petroleum products by catalytic hydrogenation. The products obtained according to the process of the invention have highly satisfactory properties for various uses, for example as transformer oils, cable oils, refrigerator oils, waxes, etc.

The process of the invention involves, first, catalytic hydrogenation under conditions providing conversion of nonhydrocarbon constituents of the petroleum charge stock, and producing a product having improved oxidation stability and other properties. Under the conditions employed to obtain these results, relatively nonvolatile corrosive sulfur-containing material is also produced, apparently by conversion of sulfur compounds in the charge stock. This sulfur-containing material is thought to be elemental sulfur, though the invention is not to be limited by any theory.

The process of the invention further involves subjecting the hydrogenation products to a heat treatment in the absence of hydrogenation catalyst. The purpose of the heat treatment is to convert the corrosive sulfur-containing material into noncorrosive sulfur compounds. The latter compounds are not only noncorrosive but also generally exhibit advantageous oxidation inhibiting properties.

In the heat treatment, the liquid hydrogenation products are passed continuously through a soaking system containing obstructions to the flow of the liquid hydrogenation products. The obstructions cause the liquid products to undergo sufficient pressure drop that thermal currents are avoided. The obstructions in the soaking system are essential, since in continuous passage through an ordinary unobstructed soaking vessel, thermal currents in the flowing liquid cause nonuniform residence time of liquid in the soaking system. Portions of the liquid therefore frequently do not remain in the soaking system sufficiently long to undergo complete removal of corrosive sulfur. This invention solves the problem, since the liquid does not flow backward past the obstructions, and thermal currents are limited to small portions of the soaking system.

The heat treatment according to the invention is carried out in continuous fashion. Such operation provides better control of the process conditions, and a generally superior product as a result of better control of the residence time.

The temperature of the oil during passage through the soaking system is within the approximate range from 450° F. to 650° F. Lower temperatures generally do not provide satisfactory conversion of sulfur-containing material. Higher temperatures generally result in thermal degradation and discoloration of the hydrogenation products.

The total residence time of hydrogenation products in the soaking system must be long enough to provide satisfactory conversion of sulfur-containing material, but not

so long as to result in excessive thermal degradation and discoloration of the hydrogenation products. The exact limits of residence time to provide these results vary with many factors including the temperature in the soaking system, the nature of the hydrocarbons treated and the desired properties of the ultimate product. In some instances, particularly where relatively high temperatures are used in the soaking system, the residence time must be controlled within close limits in order to obtain the optimum combination of conversion of sulfur and avoidance of thermal degradation. In any event, it is important that the difference between the residence time of the portions which remain in the soaking system the longest time and the residence time of the portions which remain the shortest time, i.e. the difference between the maximum and minimum residence times, should be as small as possible, in order to give the optimum combination of corrosive sulfur elimination and avoidance of degradation.

The average residence time in the soaking system will usually be within the approximate range from 5 to 150 minutes. Preferably the time does not exceed about 30 minutes. Generally, relatively short residence times are employed in conjunction with relatively high temperatures and vice versa.

The soaking system through which the hydrogenated oil is passed in the process according to the invention contains obstructions which provide, in at least one intermediate location in the soaking system, a free space for travel of hydrogenated oil which has cross-sectional area not more than 0.75 times, and preferably not more than 0.5 times, the cross-sectional area which would be available at that level in the absence of the obstruction. Any suitable lesser proportion which does not result in excessive pressure drop can be employed.

In a preferred embodiment of the invention, the soaking system comprises a plurality of soaking zones in series, each adjacent pair of soaking zones being connected by a relatively constricted passageway. In this embodiment, the flowing liquid, in passing from a relatively expanded soaking zone into a relatively constricted connecting passageway, encounters the obstruction which provides the benefits of the invention. In this embodiment, the number of soaking zones in the soaking system can be two or more. Generally, greater numbers of zones provide greater uniformity in residence time. Since the liquid undergoes substantial pressure drop in passing through the constricted passageways between the soaking zones, greater numbers of the latter generally result in greater total pressure drop. Since the smallest pressure drop which gives sufficiently uniform residence time is preferred, the number of zones is preferably not greater than 10.

Preferred apparatus for use according to this embodiment of the invention comprises a vertically elongated vessel having therein one or more horizontal perforated plates. The perforations constitute the constricted passageways separating the soaking zones above and below the plate. Preferably, the total perforation area constitutes not more than 50 percent of the cross-sectional area of the vessel at the level of the plate, so that the available cross-sectional area for passage of liquid through the plate is not more than 50 percent of the available area for such passage in the soaking zones. The total perforation area may constitute any desirable lesser proportion than 50 percent of the cross-sectional area, any lesser proportion, e.g. down to 0.5 percent or less, that does not give excessive pressure drop being generally satisfactory.

Other means for providing constricted passageways between soaking zones can be employed in place of the

perforated plates previously described. Thus, for example, a series of vessels constituting the soaking zones, with connecting pipes constituting the constricted passageways, can be employed. This arrangement corresponds generally to a vessel containing a perforated plate having only one perforation therein. Perforated plates containing a plurality of perforations, e.g. 10 to 100, are preferred in that they provide generally superior results.

Other means of providing obstructions in the soaking system can be employed. Thus, for example, transverse baffles extending across a portion of the cross section of a soaking vessel can be employed. A plurality of such baffles arranged in such manner that the flowing liquid is obliged to follow a tortuous path can be employed if desired.

It is also within the scope of the invention to employ a soaking vessel containing a nonadsorbent packing material, the packing material providing the obstructions and eliminating thermal currents. The packing should be nonadsorbent in order to avoid undesirable adsorption of the sulfur compounds formed in the heating. Any nonadsorbent packing material as known in the art, e.g. Raschig rings, etc., can be employed.

The use of a plurality of soaking zones such as cylindrical vessels or portions thereof, interconnected by constricted passageways, is generally preferred to the use of a packed vessel, since in the latter case a larger vessel is required for a given throughput.

The passage of liquid through the soaking system is preferably in a substantially vertical direction, though other directions of flow, such as horizontal, are within the scope of the invention.

The charge stock for the process according to the invention is preferably a distillate petroleum fraction having A.P.I. gravity of from 20 to 40 and boiling range at least as high as that of gas oil. Gas oil, lubricating oil, and wax distillates are examples of the preferred charge stocks according to the invention. Crude petroleum or residues can also be treated according to the invention.

Preferred conditions for use in the hydrogenation step according to the invention are temperatures in the approximate range from 500° F. to 800° F., more preferably 650° to F. to 750° F., and pressures in the approximate range from 100 to 2000 p.s.i.g., more preferably 1000 to 2000 p.s.i.g. However, any conditions which result in a product containing corrosive sulfur-containing material may be involved in the first step. The invention is generally applicable to those situations wherein the desired hydrogenation conditions for general purposes result in the specific concurrent result of forming corrosive sulfur-containing material.

A typical manner of performing the hydrogenation is by passing the charge through a stationary bed of solid hydrogenation catalyst in the presence of hydrogen, the space velocity being 0.25 to 5 volumes of charge per volume of catalyst bed per hour, and the hydrogen consumption 20 to 500 standard cubic feet per barrel of charge. Other known manners of performing the hydrogenation can be employed. Typical catalysts are various metals or oxides or sulfides thereof, such metals being for example cobalt, iron, nickel, manganese, chromium, molybdenum, magnesium, platinum, copper, zinc, vanadium, etc. Typically, the catalyst is associated with a suitable base or support, e.g. bauxite, alumina, silica gel, clay, silica-alumina composites, kieselguhr, pumice, charcoal, activated carbon, aluminum silicates, etc. The well known hydrogenation catalysts for mineral oils are suitable as a class for use according to the invention.

The following example illustrates the invention. The example will be described with reference to the attached drawing which illustrates one embodiment of the invention.

A petroleum distillate, e.g. a naphthenic lubricating oil distillate having A.P.I. gravity of 25, is hydrogenated in zone **10** at a temperature of about 675° F. and pressure of about 1500 p.s.i.g., by passing the oil downwardly through a stationary bed of solid hydrogenation catalyst comprising about 20 percent molybdenum sulfide on an alumina base, the liquid hourly space velocity being about 0.5 volume of oil per volume of catalyst bed per hour.

Oil is introduced through line **11** into zone **10**, and hydrogenated oil is withdrawn through line **12** into high pressure separator **13**, which may suitably operate at approximately the same pressure as the hydrogenation vessel. Gaseous and vaporous material including unreacted hydrogen is recycled, after suitable treatment for H_2S removal and light hydrocarbon removal if desired, through line **14** to zone **10**. Makeup hydrogen is supplied through line **15** as needed. Liquid hydrogenation products are introduced through line **16** into low pressure separator **17**, which may suitably operate at atmospheric pressure. Gaseous and vaporous material is withdrawn through line **18**. Liquid products are withdrawn through line **19**, cooled by suitable means not shown to a temperature of 550° F. for example, and passed downwardly through soaking vessel **20**. Vessel **20**, which constitutes the soaking system, contains a plurality of plates **21** having perforations such as the perforation indicated by the numeral **22**.

The space velocity of the liquid oil in passing through vessel **20** is 6 volumes of oil per volume of vessel per hour, thus providing an average residence time of 10 minutes in vessel **20**, or an average residence time in each of the soaking zones **23** of 2 minutes. The necessary minimum residence time in vessel **20** is for example about 9 minutes, in order to obtain freedom from corrosiveness to copper. The lowest residence time of any portion of the liquid in vessel **20** is greater than 9 minutes. However, if the vessel **20** did not contain the plates **21**, the lowest residence time would, because of the thermal currents and resulting inequalities of residence time, be less than 9 minutes, though the average residence time would still be 10 minutes. Thus, operation under generally similar conditions except that the perforated plates **21** are omitted from vessel **20** results in a corrosive oil, indicating incomplete conversion of sulfur-containing material.

The oil removed through line **24** is cooled to room temperature by suitable means not shown. If desired, the cooling of this oil and of the oil in line **19** can be effected by indirect heat exchange with the charge oil in line **11**. The product oil is steam stripped by means not shown to remove dissolved hydrogen sulfide.

The stripped product oil is free from corrosivity towards copper, as determined for example by immersing a copper strip, polished to A.S.T.M. standards, in the oil at 212° F. for 3 hours, and then examining the strip for stain. The oil also has improved oxidation stability, as a result of the hydrogenation and also of the production of oxidation inhibiting sulfur compounds.

The corrosive sulfur-containing material which is formed in the hydrogenation is, because of its low volatility, not strippable from the hydrogenation products. Therefore, stripping of hydrogen sulfide from the hydrogenation products, without previous passage through the soaking system, produces a corrosive oil. In the soaking system, the corrosive sulfur-containing material is thought to be converted in part to hydrogen sulfide and in part to organic sulfur compounds, though the invention is not to be limited by any theory. The hydrogen sulfide can be removed by subsequent stripping to obtain a noncorrosive oil, the remaining organic sulfur compounds being noncorrosive and often having oxidation-inhibiting properties.

The soaking operation according to the invention can be performed if desired at elevated pressure, for example by introducing the effluent **16** from the separator **13** di-

rectly into vessel 20, the effluent 24 being introduced into separator 17.

The overall ratio of length to major dimension of the relatively expanded, or soaking zone portions, of the soaking system according to the invention is preferably within the approximate range from 1:1 to 50:1 for the overall soaking system. Thus, the ratio of length to diameter of the vessel 20 in the drawing is preferably within the indicated range.

The invention claimed is:

1. Process for producing improved petroleum products which comprises: catalytically hydrogenating a petroleum charge stock to produce a refined product containing relatively nonvolatile corrosive sulfur-containing material; separating the refined product from the hydrogenation catalyst; and passing a stream of the separated refined product in liquid phase at 450° F. to 650° F. continuously through a soaking zone, distributing said liquid stream in an expanded area in said soaking zone, then subdividing said stream into a plurality of streams having a total cross-sectional area not more than 0.75 times the otherwise unconstricted cross-sectional area of the stream,

whereby thermal currents in the stream are reduced and backward flow is prevented, the residence time of said stream in said soaking zone being at least about 5 minutes and insufficient to produce excessive thermal degradation and discoloration of the product, thereby to produce a refined product having improved oxidation stability and freedom from corrosiveness to copper.

2. Process according to claim 1, wherein the liquid stream is passed alternately into an expanded zone and then subdivided into a plurality of subdivided streams.

3. Process according to claim 2, wherein the cross-sectional area of the subdivided streams ranges from 0.5 to 50 percent of the unrestricted cross-sectional area of the stream.

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