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MANUFACTURE OF WHITE OILS

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This invention relates to improvements in the manufacture of high boiling, viscous petroleum products, characterized by relative freedom from coloration, taste, and odor. The invention has particular reference to "white oils". These include liquid petrolatum U. S. P. and specially refined technical oils of less purity. The improved method comprises two principal operations: (1) saturating, stabilizing, and purifying the stock by treatment with hydrogen at high pressure and temperature, and (2) further refining of the stock by chemical and/or physical means.

The following example is illustrative of my preferred method: The stock to be treated, for instance a Peruvian or Pennsylvania crude oil, or a heavy fraction of these or similar crudes, is first subjected at a temperature of 750 to 850° F. or thereabouts to a pressure of 50 to 200 atmospheres of hydrogen gas. The reaction is best conducted in a pressure resistant reactor having non-reactive alloy steel surfaces in contact with the oil, which may be supplied as a single charge or continuously.

Preferably the oil under treatment is agitated by continuous injection of hydrogen, but mechanical agitation may be adopted. Catalysts such as a mixture of finely divided metal oxids, especially a mixture of about 90% chromium oxid and 10% molybdenum oxid, should be kept in suspension in the oil for accelerating the action of the hydrogen. Under the conditions stated, destructive hydrogenation occurs and sulfur compounds present in the oil are attacked. The sulfur comes off mainly as hydrogen sulfid. The cracked and hydrogenated product distills over in admixture with hydrogen, from which it is separated by any suitable condensation, with or without rectification, and the hydrogen is recirculated for further action on the oil in the reactor.

The particular object of the treatment as carried out for the purpose of the present invention is to secure a substantial proportion of stable, saturated, low-sulfur or sulfur-free distillate of high boiling point and of the required viscosity—that is, from 50 to 600 seconds Saybolt at 100° F.

Considerable amounts of lighter hydrocarbons are always formed when working at the temperatures stated. These amounts are controllable within limits by proper adjustment of the treating temperature with reference to the hydrogenation effect and the rate of distillation. The hydrogenation effect is fixed by the partial pressure of the hydrogen and the proportion and activity of the catalysts present. The distillation is controllable by the rate of passage of hydrogen through the reactor and condensing equipment. The factors mentioned are variables depending upon the nature of the stock being treated and the product sought. By operating in accordance with well known principles, a satisfactory yield of high boiling products of the desired characteristics may be obtained.

The heavier portions of the distillate produced, as described, are excellently suited for the manufacture of white oils, both for the technical grades of low viscosity, for example 50 to 80 seconds Saybolt at 100° F., and medicinal oils having high viscosity, for example around 400 seconds Saybolt.

To produce a finished oil from the stable, saturated, sulfur-free distillate, the latter is treated to remove substantially all the remaining impurities or undesired constituents, leaving an oil which appears to be composed almost exclusively of paraffin and naphthene hydrocarbons. This treatment is best carried out by reacting upon the oil with sulfuric acid of not less than 98% strength and preferably with fuming acid, at low temperature, and with active mechanical agitation. The acid should be introduced in successive stages, the separation of the acid and products dissolved in the same being carried out between stages. The total amount of acid employed will depend upon the character of the oil to be produced, but may be from 10 to 50% by volume with reference to the oil treated.

Following the acid treatment, the oil is washed with caustic soda solution, blown dry and filtered through fuller's earth. For the production of especially good oil, the treatments above referred to may be repeat-

ed, or other purification methods may be used.

In some cases, especially when working with oils containing large amounts of unsaturated compounds, either initially present or produced by cracking, the hydrogenation may advantageously be carried on at temperatures below the cracking range, for example about 650° F. at a pressure of 100 atmospheres of hydrogen gas. The oil is, in this way, hydrogenated only in preparation for the further chemical treatment. Generally, however, destructive hydrogenation is recommended.

The present invention resides broadly in the combination of hydrogenation and subsequent treating, whereby there is effected a substantial economy in the overall cost of manufacture, as compared with present methods, and the quality of the finished product is also improved, as compared with the product now obtained. The undesired constituents of the oil are in part removed by the destructive hydrogenation, and in part placed in better form for reaction with the treating agents in the subsequent operations. Low grade stocks, hitherto considered unsuitable for white oil manufacture, can be used with the present process.

The invention is not to be limited to the specific details given, which are merely illustrative. The hydrogenation may be carried out in any desired way and the subsequent treating may take any suitable form. Various changes may be made within the scope of the appended claims, in which it is my intention to claim all novelty inherent in the invention as broadly as the prior art permits.

I claim:

1. Process of making a highly purified petroleum oil product, comprising preliminarily heating a petroleum oil of substantially higher boiling point than the desired product with hydrogen at high pressure and temperature, collecting a hydrogenated product having a viscosity in the range suitable for medicinal oils, and further treating this oil for the removal of remaining impurities to produce an oil product substantially free from coloration, taste, and odor.

2. Process of making a highly purified petroleum oil product, comprising heating a petroleum fraction of higher boiling range than the desired product to a temperature above about 750° F. under a pressure of 50 to 200 atmospheres of hydrogen gas, taking off a distillate having a viscosity between about 50 and 600 seconds Saybolt at 100° F., treating the distillate with sulfuric acid of not less than 98% strength to remove substantially all undesired constituents of the oil, and separating the purified oil from the acid reaction products and residual acid, to produce an oil substantially free from coloration, taste, and odor.

3. Process of making a highly purified substantially sulfur-free, odorless, colorless and tasteless white oil from a heavy sulfur-containing petroleum fraction unsuited for the direct preparation of white oil, which comprises subjecting said heavy petroleum fraction to the action of hydrogen under pressure in excess of 20 atmospheres at a temperature between about 750 and 850° F., and in the presence of a catalytic material, separating from the hydrogenated product a distillate having a viscosity between about 50 and 600 secs. Saybolt at 100° F., treating this distillate with sulfuric acid of not less than 98% strength, and separating the purified distillate from the excess acid and acid extraction products.

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