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MANUFACTURE OF LUBRICATING OIL

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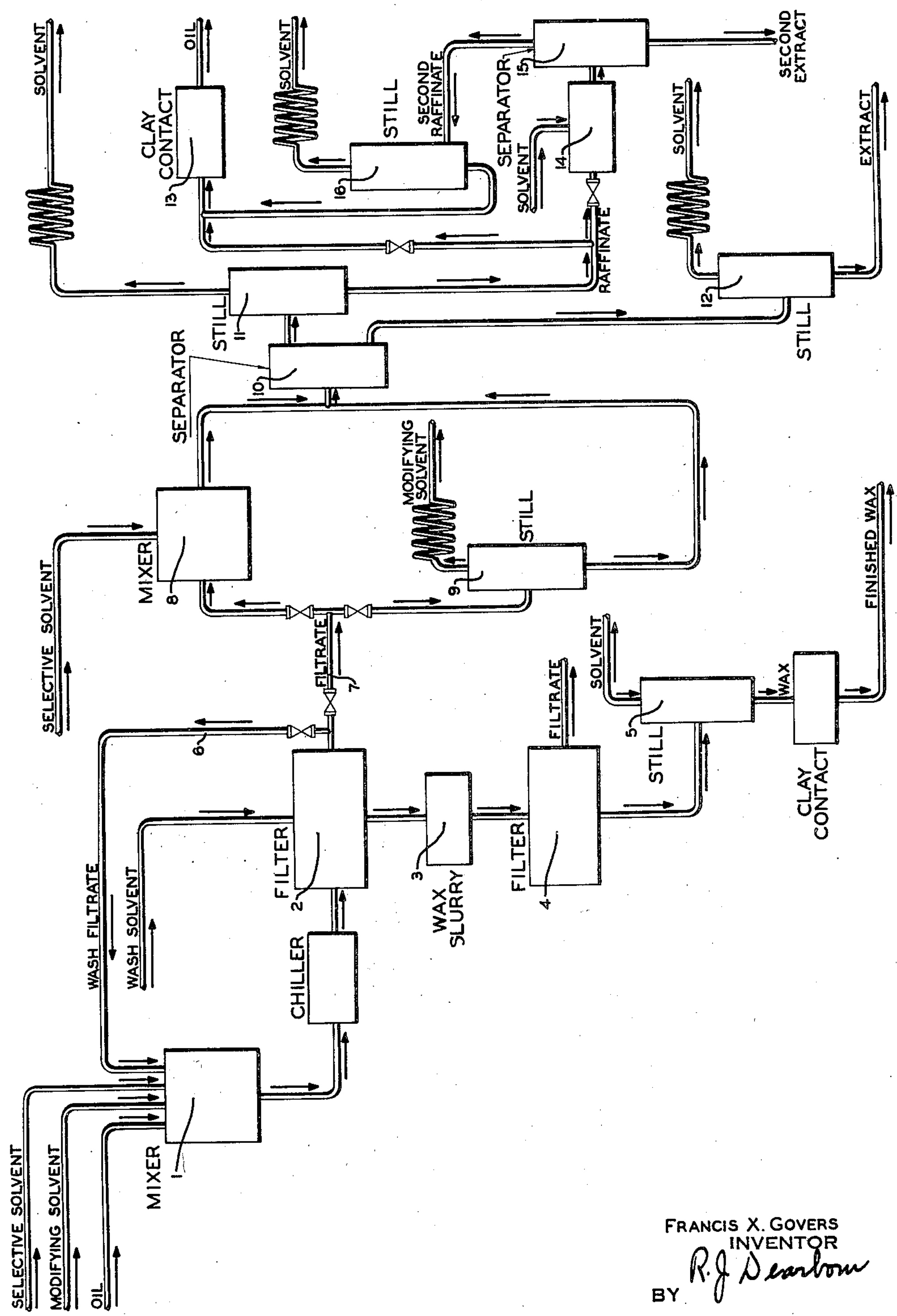

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MANUFACTURE OF LUBRICATING OIL

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2 Claims. (Cl. 196—19)

This invention relates to the manufacture of lubricating oil from hydrocarbon oils, and more particularly to the manufacture of high viscosity index, low pour test lubricating oil from wax-bearing mineral oils.

This application is a continuation in part of my co-pending application, Serial Number 601,-888, filed March 29, 1932, for Improvements in manufacture of lubricating oil.

In its broadest aspect, as disclosed in Serial No. 601,888, and also in Serial No. 711,735, a divisional application thereof, filed on February 17, 1934, the invention contemplates an improved process of treating hydrocarbon oils, particularly paraffin-bearing lubricating fractions of petroleum with solvents to selectively produce therefrom low pour test lubricating oils characterized by having a desired viscosity temperature relationship and improved lubricating qualities. The invention contemplates a process of manufacturing lubricating oils having a low pour and cloud test, low sulphur content, low Conradson carbon content, a relatively high viscosity index and free from bodies of little or no lubricating value.

Low pour test in a lubricating oil denotes an oil, as used in internal combustion engines, possessing the characteristics of easy starting in cold weather and readiness of flow sufficient to respond to methods of circulation so as to immediately reach all parts necessary to be lubricated.

The presence of sulphur or sulphur-containing bodies in lubricating oil is objectionable on account of the corrosive effect of sulphur upon bearing surfaces and other metal portions of the engine. Efforts to reduce the sulphur content of lubricating fractions to a desirable degree by methods ordinarily employed have resulted in an over-refined oil with impaired lubricating value.

Lubricating oil having a low Conradson carbon content is desirable since such oil has little tendency to carbonize in the motor, and such carbon as may be deposited is of a flocculent nature, having little or no tendency to adhere to the piston head or cylinder walls. High Conradson carbon content is characteristic, for example, of residual oils, or oils not redistilled under low absolute pressure, and is characteristic of oils having desired high viscosity index, as ordinarily produced heretofore.

The viscosity index of a given oil is readily determined by resorting to the method of Dean and Davis, published on pages 618–619 of the 1929 issue of Chemical and Metallurgical Engineering. Lubricating oils of high viscosity index are characterized by having a relatively narrow increase in viscosity with respect to temperature. Such oils have the property of possessing the desired viscosity at elevated temperature with no great loss of mobility at very low temperature.

Lubricating oils, as ordinarily made from naphthene-base crudes, have a low pour and cloud test, low Conradson carbon content, but have a low viscosity index and fairly high sulphur content. On the other hand, lubricating oils, as ordinarily made from paraffin-base crudes of the Pennsylvania type, have a high pour and cloud test, high Conradson carbon content and a fairly high sulphur content, depending on the particular crude source. Oils derived from mixed base crudes may fall somewhere between these limits although usually high in sulphur content. Oils of the Pennsylvania type, as well as those derived from mixed base crude sources, are difficult to refine without undue loss and impairment of their lubricative value. In any case, it is difficult, by methods now employed, to reduce the sulphur content of lubricating oil fractions to the desired point, regardless of their crude source.

The generally accepted method, as used in the art of refining petroleum lubricants for the removal of sulphur as well as other undesired constituents, is by the use of sulphuric acid. Much stress has recently been put on the danger of over-refining due to the use of this method of refining with its consequent impairment of lubricating value due to over-refinement. Sulphur dioxide has been proposed as a substitute in the refining art but the use of this solvent by itself in refining in viscous fractions, particularly of the paraffin type, has not been successful from the standpoint of producing a product having the desired high viscosity index, low pour test and other characteristics.

I have discovered that by the use of the methods herein disclosed lubricating oils of any desired viscosity index and scale of purification, coupled with low pour test and low cloud test, can be made from mixed-base or paraffin-base crudes, and the oils so produced are characterized further by low Conradson carbon and low sulphur content. The obtaining of oils having these desired qualities does not depend on methods involving redistillation or acid treatment.

More specifically the invention comprises mixing with a wax-bearing fraction of a mineral oil a solvent mixture comrising two or more solvent liquids of different solvent properties which, in certain ratios of one solvent liquid to other solvent liquids, has substantially complete solvent action on the oil at temperatures of around 100°

F., and at temperatures of around 0° F. substantially complete solvent action on the liquid hydrocarbons therein but substantially no solvent action on the solid hydrocarbons therein and of such a nature that upon cooling a solution of the mineral oil fraction in such solvent mixture to 0° F. and removing the solid hydrocarbons so precipitated and the solvent liquid the resulting oil has a cold test of substantially 0° F. or below but which solvent mixture in certain other ratios of one solvent liquid to the other solvent liquids has, at temperatures of 32° F. and below, a selective solubility as between differing viscosity index constituents of the liquid hydrocarbon content.

The mixture is then chilled to form a precipitate of solid or semi-solid material comprising suspended wax or solid hydrocarbons which are insoluble in, and immiscible with, the solvent mixture. The mother liquor is separated from the cold mixture advantageously by filtration. The separated mass of solid hydrocarbons is then washed free of mother liquor containing dissolved oil by additional quantities of chilled solvent liquid of approximately the same composition as used in the original mix.

A certain portion of the filtrate from this washing operation may be added to the original filtrate, the amount of liquid so added depending on the amount of dissolved oil contained therein. To the original filtrate or mixture of original filtrate and first wash liquor is then added an additional amount of one of the component solvents of the solvent liquid mixture to alter the percentage composition of the components of the solvent mixture in an amount sufficient to affect the solvent capacity of the solvent mixture and cause a separation between soluble and insoluble constituents of the hydrocarbons. This mixture is chilled to effect a sharp and rapid separation into two layers, the upper layer containing oils characterized by relatively high viscosity index, and the lower layer containing oils characterized by relatively low viscosity index. The amount and character of the separation is influenced by the amount of alteration in the percentage composition of the components comprising the solvent liquid mixture.

I have found that a suitable solvent liquid mixture may comprise a mixture of liquid sulphur dioxide and an organic solvent liquid such as benzol or one of its homologs, or a derivative thereof such as monochlorobenzol. Other solvent liquids may also be employed in conjunction with the sulphur dioxide, as for example, propylene dichloride. The selective solvent action of a mixture of these solvents upon the various constituents of a hydrocarbon oil fraction is readily altered by varying the proportion of the solvent components of the mixture.

Instead of sulphur dioxide other compounds having a selective solvent action as between relatively low and relatively high viscosity index constituents of the oil may be used. Such solvent compounds comprise aniline, benzaldehyde, dichlorethyl ether for example. These compounds may be used with any of the auxiliary solvents mentioned, or with other suitable auxiliary solvents of somewhat similar character, such as ethyl ether and isopropyl ether for example.

As an example in carrying out the above invention: 200 gallons of untreated vacuum distilled wax distillate having a viscosity of 70 Saybolt Universal seconds at 210° F. with a pour test of 80° F. and a sulphur content of about .4%, derived from a semi-paraffin base crude, is mixed with 600 gallons of a solvent liquid comprising 30% sulphur dioxide and 70% monochlorobenzol, the mixture is chilled to −15° F. to precipitate the wax-like or solid hydrocarbons and introduced to filtering means described in my application, Serial No. 585,844, now matured into United States Patent No. 2,003,664, for "Method of and apparatus for filtration," filed January 11, 1932, wherein the solid hydrocarbons are separated from the liquid to produce a filter cake.

A wash solvent liquid comprising 30% sulphur dioxide and 70% monochlorobenzol and chilled to −15° F. is introduced to the press to wash out of the filter cake the adhering mother liquor. The first portion of the filtrate resulting from this washing, which may contain a substantial quantity of dissolved oil may be mixed with the original filtrate, while the remaining portion may be used to mix with and dissolve fresh untreated wax distillate to be treated in the same manner as the original material as above described.

The slurry remaining in the filter press is then removed and the bulk of the adhering solvent filtered off advantageously by filtering this slurry in a filter means, such, for example, as described in my application, Serial No. 588,586, now matured into United States Patent No. 1,920,126, for "Filtration," filed January 25, 1932. The solvent retained in the resulting filter cake is evaporated from the wax and the wax contacted with clay or finished up in the usual manner.

The wax in the above example will amount to approximately seven and one-half per cent of the original wax distillate and after removal of the solvent by evaporation and decolorizing will be white and have a melting point, without sweating, of about 136° F.

To the mixture of original filtrate and initial portion of wash liquor is added liquid sulphur dioxide chilled to a temperature of −10° F. This additional sulphur dioxide should bring the ratio of sulphur dioxide to monochlorobenzol up to about equal volumes of each.

The mixture is well stirred and allowed to settle and stratify. The top layer will comprise low gravity, relatively high viscosity index oils, while the lower layer comprises high gravity, low viscosity index oils. The oil in the top layer after removal of the solvent will have a gravity of approximately 27.5 A. P. I., a viscosity of 66 Saybolt Universal seconds at 210° F. and a viscosity index of approximately 87. The oil in the bottom layer, after removal of the solvent, will have a gravity of approximately 13 A. P. I., a viscosity of approximately 118 Saybolt Universal seconds at 210° F. and a viscosity index below −30.

The fraction of relatively high viscosity oil may be contacted with clay and filtered, and is then ready for use as a so-called wide cut, or it may be fractionated by vacuum distillation to produce cuts of narrower distillation range.

On the other hand, this relatively high viscosity material may be still further improved or refined by dissolving in monochlorobenzol, cooling the mixture to 0° F. and adding chilled liquid sulphur dioxide in about the same proportion as the monochlorobenzol. The mixture is well stirred, chilled to −10° F. and allowed to settle. The oil in the top layer, after removal of the solvent, contacting and steaming in the presence of clay and contact filtering, will have the following approximate characteristics: Gravity 30.6, viscosity of 64 Saybolt Universal seconds at 210°

F., viscosity index 95, Conradson carbon .015, and sulphur .1, with a pour test of —5° F.

As an additional example in carrying out the above invention:

Untreated vacuum distilled wax distillate, similar to that used in the preceding example, is also similarly mixed with sulphur dioxide and monochlorobenzol in the proportion of about 200 gallons of oil to 600 gallons of solvent mixture, and chilled to —15° F. to precipitate the wax-like or solid hydrocarbons. The mixture is filtered and the resulting filter cake washed with the same fresh solvent in the same manner, the initial portion of the wash filtrate being mixed with the original filtrate.

To this mixture of original filtrate and wash liquor is added chilled sulphur dioxide sufficient to give a solvent mixture of 60% sulphur dioxide and 40% monochlorobenzol. The mixture is stirred well, chilled to —10° F. and allowed to settle and stratify.

The separated bottom layer is drawn off, the solvent evaporated and the oil recovered. There will be recovered an oil having a gravity of approximately 12.4 A. P. I. and a viscosity index of approximately —32.

The separated top layer is mixed with a chilled mixture of monochlorobenzol and sulphur dioxide comprising about 40% sulphur dioxide and 60% monochlorobenzol, well stirred, chilled to —10° F. and allowed to separate. The bottom layer is drawn off, the solvent evaporated and the contained oil contacted at 500° F. with 20 pounds of clay to the barrel. This contacting may be carried out in the presence of steam. The oil and clay mixture is cooled to 350° F. and filtered. The filtered oil will amount to about 73 gallons and have the following approximate characteristics: Gravity 27.5 A. P. I., viscosity 67 Saybolt Universal seconds at 210° F., viscosity index 79½, with a pour test of —10° F.

The solvent is evaporated from the separated top layer and the contained oil contacted at 500° F. with 20 pounds of clay to the barrel while steaming. The oil and clay mixture is cooled to 350° F. and filtered. The filtered oil will have the following approximate characteristics: Gravity 31.1 A. P. I., viscosity 63 Saybolt Universal seconds at 210° F., viscosity index 102, pour test —5° F., Conradson carbon .012, sulphur .09.

When using propylene dichloride as one of the solvent components, the procedure is substantially similar to that outlined in the foregoing examples except that the proportions of propylene dichloride and sulphur dioxide to each other and to the oil undergoing treatment may differ considerably. Thus, in the initial treating step for the removal of wax constituents, the wax-bearing oil may be mixed with straight propylene dichloride alone or with a solvent mixture comprising this solvent liquid and not in excess of about 7½% by volume of sulphur dioxide. The resulting cold solution of liquid hydrocarbons in solvent liquid is then mixed with fresh cold sulphur dioxide in an amount, for example, which may be equal to or greater than the propylene dichloride content but usually in excess of about 20% of the solvent mix. This mixture is then chilled to —5° F. or below and settled to form two layers from which the oil is recovered and finished up as has already been described.

The solvent is advantageously removed from the separated oil by evaporation and, in the case of the high-boiling solvent component, under diminished pressure. The evaporation may be carried out in the presence of steam and the clay-contacting material may be added to or commingled with the oil during the latter stage of the solvent removal. I have found that when the clay contacting is carried out in the presence of a small amount of sulphur dioxide, the final product is improved in color.

When using propylene dichloride and sulphur dioxide, as above described, products are obtained having the following characteristics:

	High viscosity index oil	Low viscosity index oil
Gravity, A. P. I.	28.5	12.2
Saybolt Universal viscosity at 210° F.	65	120
Pour	—10	
Viscosity index	88	Below —30

The invention is not limited to the production of final products having the particular characteristics of those described above. Products of differing characteristics, as desired, may be prepared by varying the proportions of the solvent liquids and also the temperatures at which the treating steps are carried out.

Furthermore, the invention is not limited to the treatment of wax distillate such as given in the examples herein but is adapted to the treatment of other paraffin-containing fractions, precipitates or materials somewhat similar in nature derived in various ways from mineral oils.

Thus my invention is applicable to the treatment of hydrogenation products resulting from the hydrogenation of carbonaceous materials, or mineral oils including liquid or solid hydrocarbon fractions derived from mineral oils. Hydrogenation products may contain substantial quantities of waxy or paraffin material as well as other constituents of relatively low lubricating value. By treating such products in accordance with my invention, final products of desired characteristics can be obtained.

The invention is not restricted to any particular operating conditions such as that of temperature, or the composition of the solvent mixtures employed since these conditions may advantageously be varied, depending upon the nature of the fraction undergoing treatment as well as upon the particular characteristics desired in the final products.

In this connection reference may be made to my U. S. Patent No. 2,158,361 (Serial No. 633,461) and also to my U. S. Patent No. 2,137,218 (Serial No. 648,988), disclosing solvent mixtures which may be employed in the process.

Where the solvent mixtures used comprise a selective solvent such as benzaldehyde or dichlorethyl ether, for example, and a relatively less volatile auxiliary solvent such as benzol, toluol, ethyl ether or light petroleum hydrocarbon, for example, the composition of the solvent mixture, following the removal of the wax, can be altered by vaporizing a portion of the auxiliary solvent. For example, one part wax bearing oil is mixed with four parts of a solvent mixture consisting of 40% dichlorethyl ether and 60% ethyl ether. After chilling to 0° F. and removing the solidified wax, substantially all the ethyl ether is vaporized from the dewaxed solution. The remaining mixture of oil and solvent is then cooled and allowed to settle, for example, at a temperature of around 40° F., whereupon the mixture separates into layers.

The accompanying drawing illustrates the carrying out of the process of the invention as above described.

Wax-bearing oil, from a source not shown, is introduced to a mixer 1. In this mixer the oil is mixed with a selective solvent, such as sulphur dioxide or benzaldehyde, and a modifying solvent, such as benzol or an aliphatic ether. The oil and solvents are mixed in proportion such that the mixture has the required solvent action as between wax and oil at a temperature of around 0° F. and below.

This mixture is then passed through a chiller wherein it is chilled to the desired waxing temperature, for example, about −15° F.

The chilled mixture is then conducted to a filter 2 wherein the solid hydrocarbons are deposited in the form of a filter cake. The filter cake is washed with a wash solvent, as already described, and the resulting washed cake is withdrawn from the filter to a wax slurry tank 3.

As previously described, the wax slurry may be subjected to filtration in another filter 4 for the purpose of removing additional liquid as filtrate.

The remaining wax cake is then drawn off to a still 5 for the recovery therefrom of the retained solvent.

The wax from which the solvent has been removed is withdrawn from the still and is, advantageously, subjected to clay-contacting or other treatment to produce a finished wax.

The filtrate drawn off from the filter 2 comprises the main body of dewaxed oil and may contain some of the wash filtrate—that is, that portion of the wash filtrate which contains substantial amounts of oil.

The remainder of the wash filtrate lean in oil is returned through a pipe 6 to the mixer 1 for mixing with fresh charge.

The main body of filtrate is conducted through a pipe 7 to either a mixer 8 or a still 9, depending upon the nature of the solvent mixture. Thus, if the modifying solvent is less volatile than the selective solvent component and it is therefore necessary to add additional quantities of the slective solvent in order to alter the solvent composition, the filtrate is passed to the mixer 8. In such case the amount of selective solvent component which is added is sufficient to cause the solvent mixture to exert selective action as between naphthenic and paraffinic constituents, so that the mixture separates into two liquid phases upon standing. The mixture thus formed in the mixer 8 is drawn off to a separator 10 wherein separation into two liquid phases occurs.

On the other hand, if the modifying solvent is more volatile than the selective solvent component, the solvent composition of the mixture may be altered merely by evaporating a sufficient portion of the modifying solvent from the mixture. In this case the filtrate is conducted to the still 9, as previously indicated, and wherein a portion of the modifying solvent is removed by evaporation.

The unvaporized portion is then withdrawn and conducted to the separator 10 for separation into two liquid phases.

The upper phase comprises a raffinate phase rich is high viscosity index constituents and is withdrawn from the top of the separator 10 to a still 11.

The extract phase rich in low viscosity index constituents is drawn off from the bottom of the separator 10 to a still 12. In the stills 11 and 12 the solvent liquid is removed from the oil.

The raffinate oil from the still 11 may be passed directly to a clay-contact plant 13 wherein the oil is treated with clay and steam to produce a finished product.

On the other hand, the raffinate oil may be subjected to further solvent fractionation, in which case it is mixed with further solvent in a vessel 14 and from there conducted to a separator 15 for separation into secondary raffinate and extract phases. The secondary raffinate phase is conducted to a still 16 for removal of its solvent content and the resulting raffinate is then conducted to the aforementioned clay-contact plant 13 for final treatment.

It is also contemplated, in many instances, that it may be of advantage to carry on the filtration step in the presence of a comminuted solid filter-aid material. Such material may be admixed with the chilled mixture of oil and solvent liquid prior to introduction to the filtering means.

In some instances it may be desirable to remove the low viscosity index constituents or a portion thereof, before dewaxing. In that case it is only necessary to mix the wax-bearing fraction with the mixture of selective and auxiliary solvent in a proportion such that the mixture has selective action as between the low viscosity index constituents and the high viscosity index constituents, including paraffin wax. The dissolved phase containing the low viscosity index constituents is removed and the ratio of the solvent liquids in the undissolved phase is altered so as to provide a solvent mixture having selective action as between the high viscosity index oil and solid wax at temperatures of 0° F. and below. Upon chilling and filtering to remove the solidified wax, oil of desired pour test and of high viscosity index is obtained.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The process of manufacturing high viscosity index lubricating oil having a low pour test from wax-bearing mineral oil which comprises mixing with the oil a solvent liquid mixture composed of a selective solvent and a modifying solvent liquid having substantially no selective action as between constituents of the oil of differing viscosity indices, and mixed with each other and with the oil in proportions such that at temperatures of around 0° F. the mixture has substantially complete solvent action on the oil, and substantially no solvent action on the wax, chilling the mixture to precipitate wax constituents of the oil, removing the wax thus precipitated, removing from the resulting dewaxed mixture a suitable portion of the modifying solvent to thereby render the remaining solvent liquid selective as between constituents of the oil of differing viscosity indices, and separating from the remaining mixture a fraction of desired viscosity index and low pour test.

2. The process of manufacturing high viscosity index lubricating oil having a low pour test from wax-bearing mineral oil which comprises mixing with the oil a solvent liquid mixture composed of a selective solvent and a relatively more volatile modifying solvent liquid having substantially no selective action as between constituents of the oil of differing viscosity indices, and mixed with each other and with the oil in pro-

portions such that at temperatures of around 0° F. the mixture has substantially complete solvent action on the oil, and substantially no solvent action on the wax, chilling the mixture to precipitate wax constituents of the oil, removing the wax thus precipitated, vaporizing from the resulting dewaxed mixture a suitable portion of the modifying solvent to thereby render the remaining solvent liquid selective as between constituents of the oil of differing viscosity indices, and separating from the remaining mixture a fraction of desired viscosity index and low pour test.

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