March 15, 1960 J. L. JEZL 2,928,788

VISCOSITY INDEX AND OXIDATION STABILITY OF LUBRICATING OIL

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Fig. 1

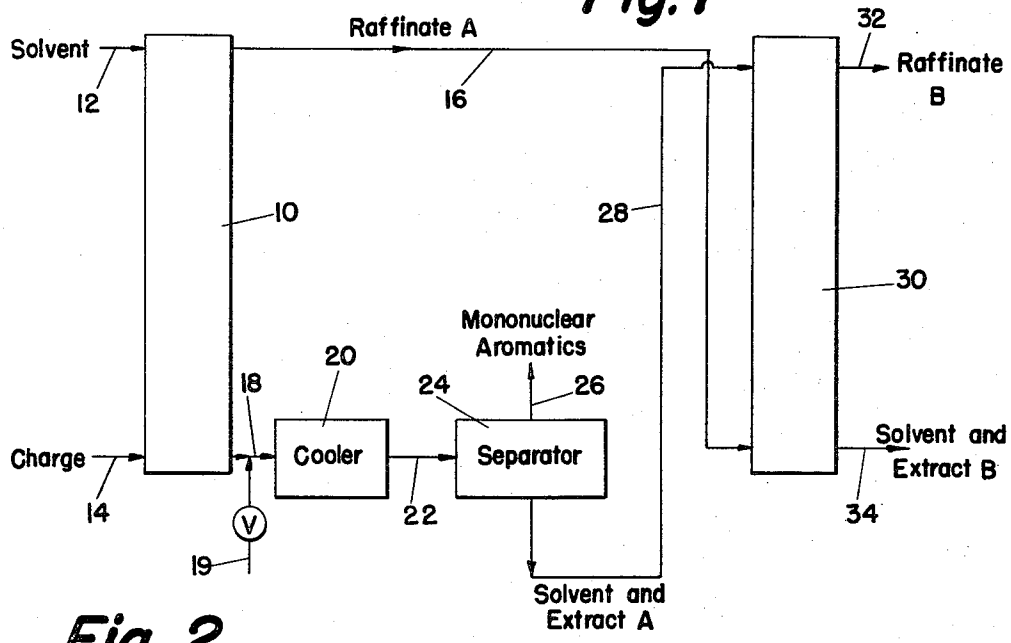
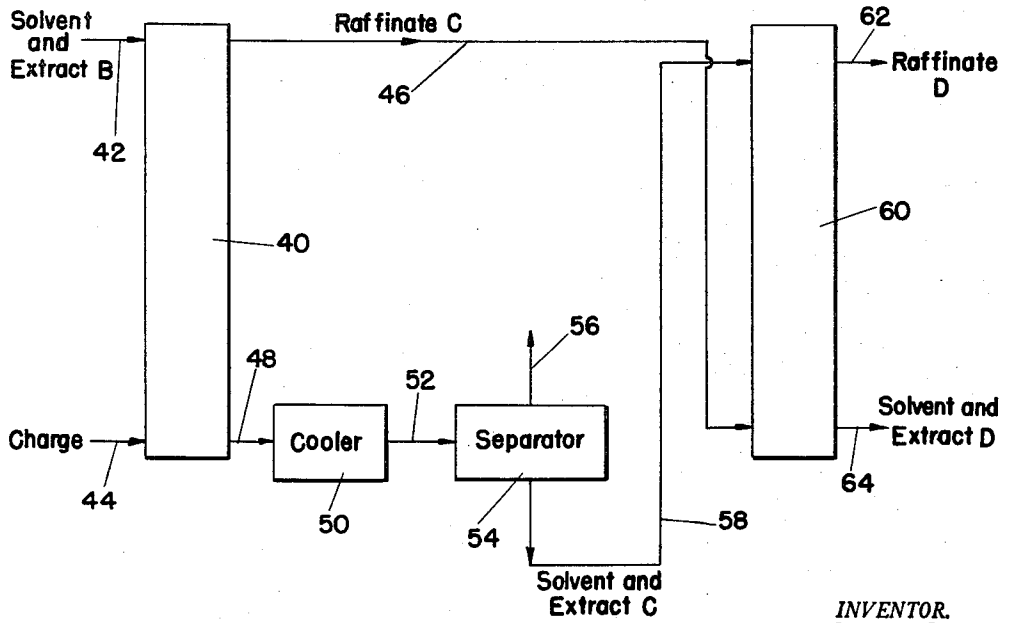


Fig. 2



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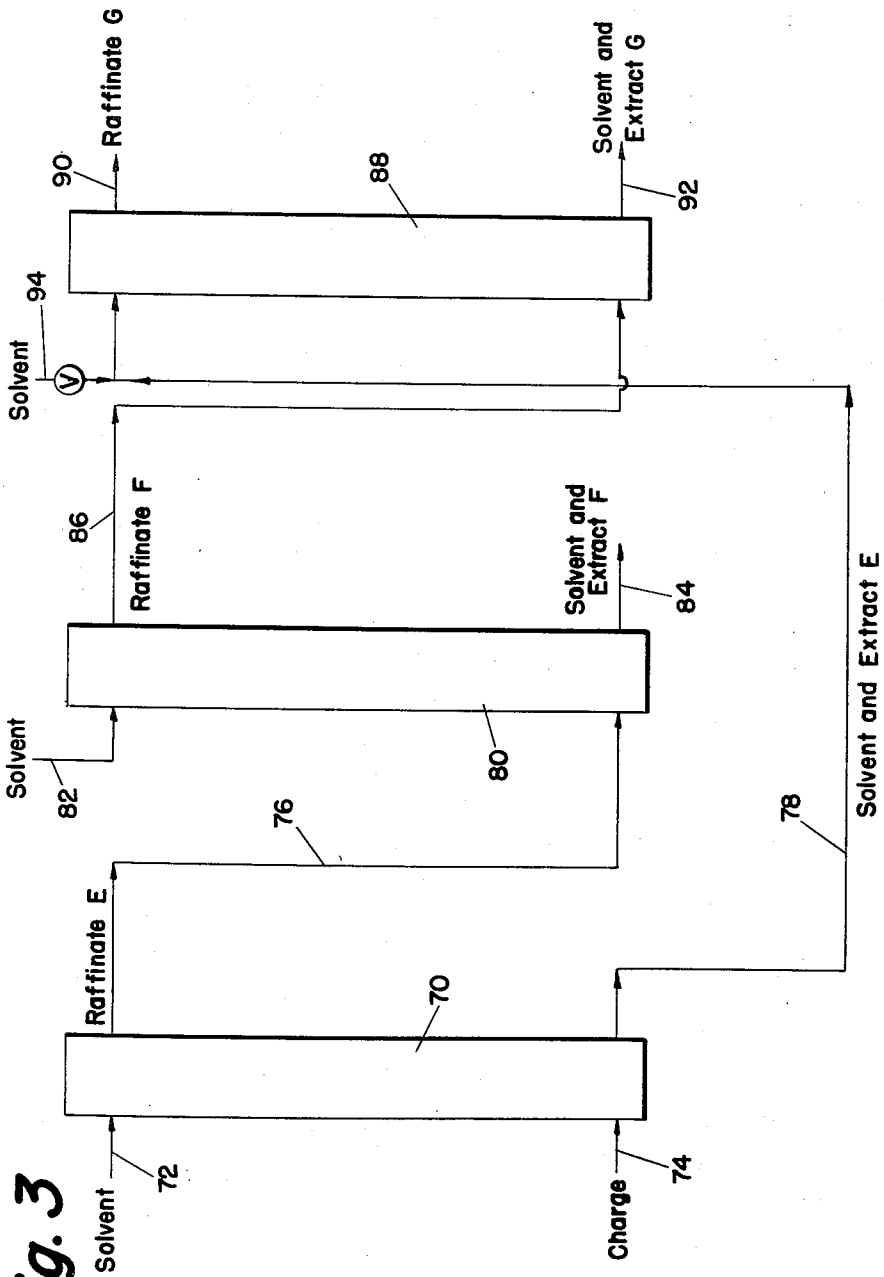


Fig. 3

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VISCOSITY INDEX AND OXIDATION STABILITY OF LUBRICATING OIL

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5 Claims. (Cl. 208—314)

This invention relates to the extraction of low viscosity index components from petroleum lubricating oil, and more particularly to a manner of improving the oxidation stability of the high viscosity index oils produced thereby.

It is known in the art to extract aromatic hydrocarbons having generally low viscosity index from petroleum lubricating oils, e.g. by solvent extraction to produce a raffinate having high viscosity index. In such extractions, however, the raffinate produced often has unsatisfactorily poor oxidation stability because of the removal of natural inhibitors from the oil during the extraction. The natural inhibitors are in part polynuclear aromatic hydrocarbons which exhibit good stability to oxidation as contrasted with the mononuclear hydrocarbons which are less satisfactory in this respect.

According to the present invention, a novel refining procedure is provided which enables high viscosity index raffinates to be obtained, which contain greater proportions of polynuclear hydrocarbons to mononuclear hydrocarbons than those obtained in conventional solvent extraction processes, and which have superior oxidation stability to the conventional raffinates.

According to the present invention, this result is obtained by contacting lubricating oil, from which mononuclear and polynuclear aromatic hydrocarbons have been extracted, with a selective solvent such as furfural, this solvent containing aromatic hydrocarbons having a higher ratio of polynuclear aromatics to mononuclear aromatics than the total hydrocarbons previously extracted from the oil. The result of such contacting is in one embodiment to transfer polynuclear aromatics to the lubricating oil and also to transfer mononuclear aromatics remaining in the oil to the solvent phase, thereby increasing the ratio of polynuclear to mononuclear aromatics in the lubricating oil.

According to one embodiment of the invention, a lubricating oil charge stock is initially contacted with furfural to extract both mononuclear and polynuclear aromatics, and the resulting solvent phase is treated in such manner as to selectively remove mononuclear aromatics therefrom, thereby to obtain a solvent phase having a higher ratio of polynuclear to mononuclear aromatics than the solvent phase as originally obtained in the extraction. The solvent phase containing the higher ratio of polynuclear to mononuclear aromatics is then contacted with the raffinate from the original extraction. In the latter step, lubricating oil, from which mononuclear and polynuclear aromatics have been extracted, is contacted with a solvent containing a higher ratio of polynuclear to mononuclear aromatics than the total hydrocarbons extracted from the oil.

The following examples, which illustrate the invention, will be described with reference to the attached drawing wherein Figure 1 is a schematic flowsheet of one embodiment of the invention, Figure 2 is a schematic flowsheet of a further operation which in one embodiment is performed subsequent to the operation illustrated in Figure 1, and Figure 3 is a schematic flowsheet of another embodiment of the invention.

Referring to Figure 1, a charge stock, e.g. a lubricating oil having Saybolt Universal viscosity at 210° F. of about 40 seconds and viscosity index of about 65, is introduced through line 14 into countercurrent solvent extraction zone 10. Furfural is introduced through line 12 at a rate to provide a furfural:oil ratio of 3:1. The average temperature in the extraction zone is 200° F. A raffinate A is removed through line 16 in 75% yield based on charge. The extract phase comprising furfural containing mononuclear and polynuclear aromatics in a ratio of about 1:2 is removed through line 18.

The extract phase is cooled to about 100° F. in cooler 20 and introduced through line 22 into separator 24, wherein stratification of phases is performed at about 100° F. Mononuclear aromatics are precipitated from the solvent by the lowering of the temperature and withdrawn through line 26. It is to be understood that this material will also contain polynuclear hydrocarbons, but it is considerably more concentrated in mononuclear hydrocarbons than the total hydrocarbon in the extract removed through line 18.

The solvent phase containing residual aromatic hydrocarbons, the ratio of mononuclear to polynuclear hydrocarbons being about 1:3, is withdrawn through line 28 and introduced into countercurrent contacting zone 30 at a rate to provide a ratio of solvent and extract A to raffinate A of about 4:1. Raffinate A prior to introduction into zone 30 is cooled by suitable means not shown to a temperature of about 100° F., and the contacting in zone 30 is carried out at an average temperature of about 100° F. Raffinate B having viscosity index of about 85 is withdrawn through line 32 to suitable means not shown for stripping solvent therefrom. Solvent containing extract B is withdrawn through line 34 and can either be treated to remove solvent therefrom by conventional means, or further employed as described subsequently with regard to Figure 2.

The ratio of mononuclear to polynuclear hydrocarbons in raffinate B is substantially lower than the ratio in raffinate A. This results from a transfer of polynuclear hydrocarbons from extract A to raffinate B during the contacting in zone 30, and also from a transfer of mononuclear aromatics from raffinate A to the solvent phase during that contacting. The oxidation stability of raffinate B is superior to that of raffinate A as a result of the higher ratio of polynuclear to mononuclear aromatics in raffinate B.

As an alternative to the operation described above, the solvent containing extracted hydrocarbons which is introduced into cooler 20 can be supplied from line 19 in place of or in addition to the solvent containing extract which is removed from zone 10. The material introduced through line 19 is a solvent phase obtained in another solvent extraction performed in a similar manner to that performed in zone 10 upon a similar or different charge stock. Thus the raffinate A can be further treated in zone 30 either with solvent containing material extracted from the same charge stock from which raffinate A was obtained or from a different charge stock.

Referring now to Figure 2, the solvent containing extract B which was removed through line 34 in Figure 1 is introduced through line 42 into countercurrent solvent extraction zone 40. Charge stock, e.g. another portion of the oil extracted in Figure 1, is introduced through line 44 into zone 40 at a rate to provide a ratio of solvent and extract B to charge of 4:1. The average temperature in zone 40 is 200° F. Raffinate C is removed in about 80% yield through line 46. This raffinate has a lesser ratio of mononuclear to polynuclear hydrocarbons than raffinate A of Figure 1. Solvent containing

dissolved extract is removed through line 48 into cooler 50. In cooler 50, the liquid is cooled to about 100° F., and the cooled liquid is introduced through line 52 into separator 54. The precipitated mononuclear hydrocarbons are withdrawn through line 56, and solvent containing extract C is withdrawn through line 58.

In countercurrent contacting zone 60, raffinate C and the solvent containing extract C are contacted at a ratio of 1:3 and an average temperature of 100° F. Raffinate D removed through line 62 has a higher ratio of polynuclear to mononuclear aromatics than raffinate C. Solvent containing extract D is removed through line 64.

The material withdrawn through line 64 can be stripped of solvent in conventional manner. Alternatively it can be employed to contact an additional portion of fresh charge stock in a manner generally similar to that disclosed in Figure 2 with regard to the solvent containing extract B. Thus the solvent can be re-used a plurality of times without separation from the hydrocarbons contained therein, other than the separation of a mononuclear hydrocarbon concentrate which takes place in zone 54. In each re-use of the solvent to contact a raffinate such as the raffinate C, polynuclear hydrocarbons are transferred from the solvent to such raffinate and mononuclear hydrocarbons are transferred from the raffinate to the solvent phase. The raffinates obtained in each stage of the operation corresponding to raffinate D have satisfactorily high viscosity index and good oxidation stability as a result of the increased ratio of polynuclear to mononuclear aromatics. When the hydrocarbon content of the solvent phase becomes excessive, solvent can be recovered therefrom by known means and re-used as in zone 10.

Referring now to Figure 3, fresh charge stock, which may for example be an additional portion of the same charge employed in Figures 1 and 2, is introduced through line 74 into countercurrent solvent extraction zone 70. Furfural is introduced through line 72 to provide a furfural:oil ratio of 1:1. The average temperature in zone 70 is 200° F. Raffinate is removed through line 76 and introduced without intermediate cooling into countercurrent solvent extraction zone 80. Solvent phase containing dissolved extract E is withdrawn through line 78.

Fresh furfural is introduced through line 82 into zone 80 to provide a ratio of solvent to raffinate E of 2:1. The average temperature in zone 80 is 200° F. Solvent phase containing dissolved extract F is removed through line 84 to conventional means not shown for stripping solvent. Raffinate is removed through line 86, cooled and introduced into countercurrent contacting zone 88. The solvent phase containing extract E is introduced through line 78 into zone 88. If desired additional fresh solvent can also be introduced into zone 88 through line 94. The ratio of solvent and dissolved extract E to raffinate F in zone 88 is 2:1, and the average temperature is 100° F.

Raffinate G is removed through line 90. This raffinate has a ratio of polynuclear to mononuclear aromatics which is greater than that of raffinate F, as a result of transfer of polynuclear hydrocarbons from extract E to raffinate F and of mononuclear hydrocarbons from raffinate F to extract E during the contacting in zone 88.

Extract E contains a relatively high ratio of polynuclear to mononuclear aromatics, whereas extract F contains a relatively low ratio of polynuclear to mononuclear aromatics. Consequently extract E contains a higher ratio of polynuclear to mononuclear aromatics than the total material extracted to produce raffinate F. Upon contacting extract E with raffinate F in zone 88, the equilibrium between the phases is such that polynuclear aromatics are transferred from the solvent phase to the raffinate phase while mononuclear aromatics are transferred from the raffinate phase to the solvent phase.

Because of its higher ratio of polynuclear to mononuclear aromatic hydrocarbons, raffinate G has superior oxidation stability to that of raffinate F.

Solvent phase containing extract G is removed through line 92. This material can be treated according to conventional procedure to recover solvent therefrom. Alternatively it can be re-used to contact additional charge in a manner generally similar to that disclosed with regard to the fresh solvent introduced through line 72. That is, the solvent containing extract G can be re-used in a further operation bearing the same general relationship to the Figure 3 operation as the Figure 2 operation does to the Figure 1 operation.

The operation described in connection with Figures 1 and 2 has important advantages with regard to simplicity and efficiency of operation as compared with the operation illustrated in Figure 3, and is therefore preferred to the latter operation.

In the operation illustrated in Figures 1 and 2, a mononuclear hydrocarbon concentrate is separated from the solvent phase containing dissolved aromatics by cooling the solvent phase. Alternatively any other suitable manner of selectively removing mononuclear hydrocarbons from the solvent phase can be employed. Thus for example the mononuclear hydrocarbons can be selectively extracted from the solvent phase by contact with paraffinic hydrocarbons such as n-pentane, petroleum naphtha, etc. Such means of selectively extracting mononuclear hydrocarbons from solvent phases obtained in extraction processes are well known in the art. Alternatively water can be added to the solvent phase to precipitate mononuclear hydrocarbons, this manner of separation also being well known in the art. Any other suitable means for selectively removing mononuclear hydrocarbons can be employed.

In the preceding description, furfural has been referred to as the selective solvent for removal of aromatics from lubricating oils. It is to be understood however that any of the known selective solvents for removing aromatics can be employed, e.g. phenol, dichloroethyl ether, nitrobenzene, dimethyl formamide, diethylene glycol, liquid sulfur dioxide, etc. Selective solvents for extraction of aromatic hydrocarbons constitute a recognized class of materials and any suitable member of the class can be employed. Mixtures of solvents as well known in the art can also be employed.

The conditions which are employed in the extraction steps according to the invention can be any suitable known conditions for solvent extraction. Thus for example in the initial contacting of fresh charge stock with solvent, the temperature will generally be within the approximate range from 100° F. to 300° F. In the subsequent contacting of the raffinate, e.g. as in zone 30 of Figure 1, the temperature may be lower than in the original extraction, e.g. within the approximate range from atmospheric temperature to 200° F. However, it is within the scope of the invention to perform this contacting at the same temperature as or a higher temperature than the original solvent extraction. The most desirable temperatures to be used will depend to some extent on the nature of the solvent. In the original extraction, the conditions conventionally employed with any given solvent can advantageously be employed according to the invention.

With regard to ratios of solvent or of solvent plus extract to charge or to raffinate, these proportions can be those which are conventionally employed in solvent extraction. In zone 30, the ratio is preferably that which is inherently provided by contacting solvent containing extract A for example with raffinate A in the amounts in which they are produced in the preceding operations. However, any other suitable ratio as conventionally employed in solvent extraction can be used.

Although continuous countercurrent extraction has been disclosed in connection with the drawings, it is to be

understood that any suitable contacting method can be employed in the respective extraction stages.

Raffinates B, D, G, etc. can if desired be subjected to a finishing operation for color improvement, e.g. acid and clay treating or light solvent extraction, etc.

The process according to the invention involves contacting, with solvent containing polynuclear aromatics, an oil from which hydrocarbons comprising mononuclear and polynuclear aromatics have previously been extracted. Preferably, the total material extracted prior to such contacting constitutes at least 10 weight percent of the charge to the extraction. Usually, the amount will not exceed 50 weight percent. Preferred amounts are those within the range from 20 to 40 weight percent. The extent of extraction is one which is sufficient to remove significant amounts of mononuclear aromatics, which are on the average less readily extracted than polynuclear aromatics. Preferably, the ratio of mononuclear to polynuclear aromatics in the total aromatics removed prior to the contacting according to the invention is at least 1:5 and more preferably at least 1:2.5, though lower ratios are within the scope of the invention. Usually, the ratio will not be greater than 1:1, though higher ratios are within the scope of the invention. In the light of the present specification, a person skilled in the art can select proper conditions to obtain the desired ratio.

The oil product obtained in the contacting according to the invention usually contains a greater ratio of polynuclear aromatics to mononuclear aromatics than the charge oil to the contacting, though this is not necessarily the case. In any event, the oil product contains a greater ratio of polynuclear aromatics to mononuclear aromatics than an oil having the same aromatic content as produced by conventional solvent extraction.

Mononuclear aromatics, as the term is used herein, are compounds which contain one aromatic ring and which may or may not contain a nonaromatic ring or rings. Polynuclear aromatics are compounds which contain more than one aromatic ring and may or may not contain a nonaromatic ring or rings.

The invention claimed is:

1. Method for preparing lubricating oils having high viscosity index and good oxidation stability which comprises extracting mononuclear and polynuclear aromatic hydrocarbons from a petroleum lubricating oil charge stock: contacting the resulting lubricating oil, from which mononuclear and polynuclear aromatic hydrocarbons have been extracted, with a selective solvent for aromatic hydrocarbons, said solvent containing aromatic hydrocarbons more concentrated in polynuclear aromatic hydrocarbons than the total hydrocarbons previously extracted from the oil; and separating solvent from lubricating oil.

2. Method according to claim 1 wherein the aromatic hydrocarbons in said solvent were obtained by separating a solvent extract from said oil into a mononuclear hydrocarbon concentrate and a polynuclear hydrocarbon concentrate, the latter constituting the aromatic hydrocarbons in said solvent.

3. Method according to claim 2 wherein said solvent containing aromatic hydrocarbons was previously obtained by cooling solvent containing mononuclear and polynuclear hydrocarbons extracted from said oil, thereby to precipitate from the solvent a mononuclear hydrocarbon concentrate, separating solvent from the latter concentrate, the separated solvent constituting said solvent containing aromatic hydrocarbons.

4. Method according to claim 1 wherein said solvent containing aromatic hydrocarbons was previously obtained by extracting polynuclear hydrocarbons from a charge oil to obtain an extract and a first raffinate, and wherein said lubricating oil is a second raffinate obtained in further extraction of said first raffinate to remove mononuclear hydrocarbons.

5. Method according to claim 1 wherein the separated solvent is contacted with additional lubricating oil charge stock.

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