

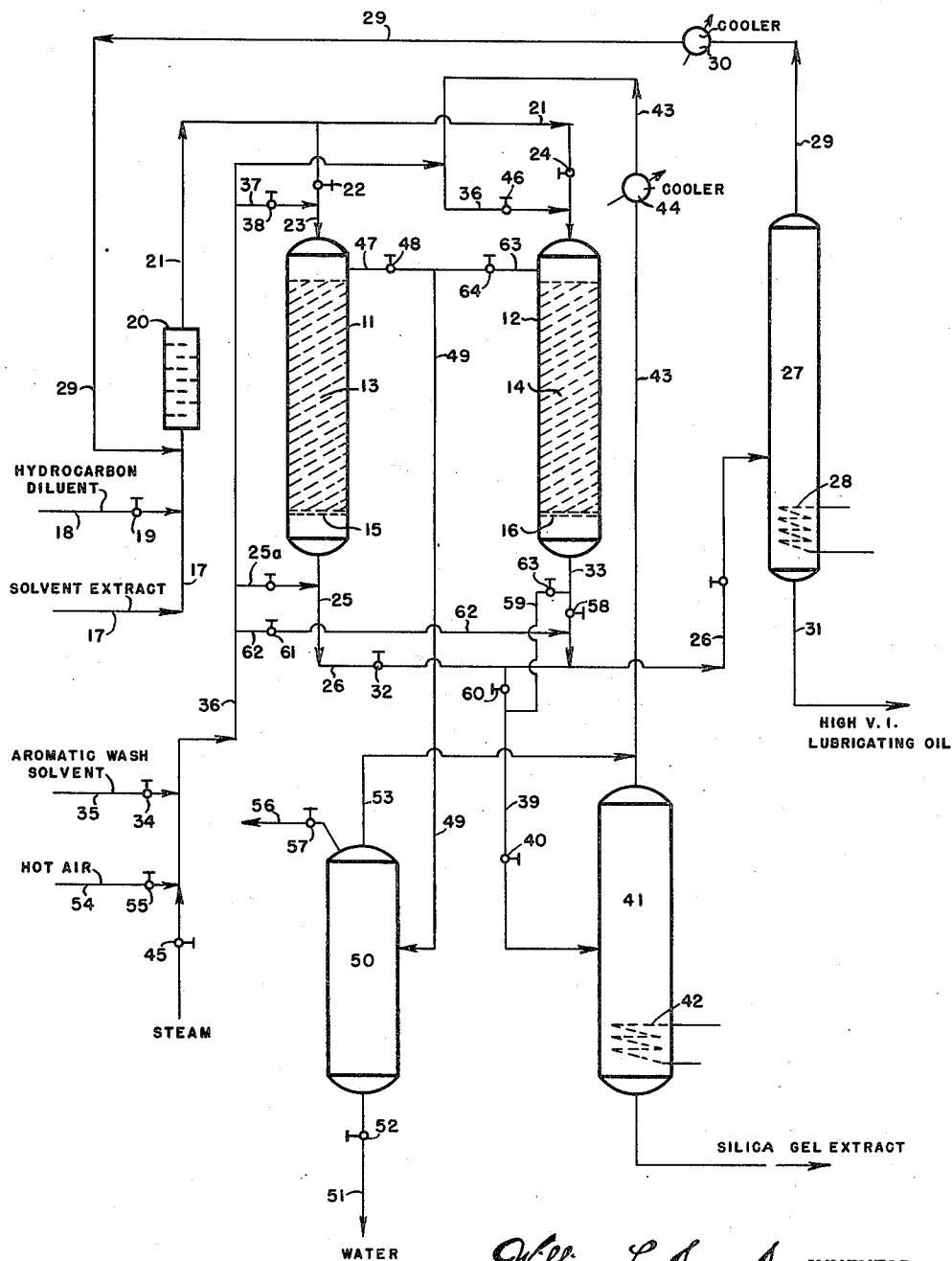
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RECOVERY OF LUBRICATING OIL FROM SOLVENT EXTRACTS

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RECOVERY OF LUBRICATING OIL FROM
SOLVENT EXTRACTS

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The present invention is directed to an improved method for producing lubricating oils. More particularly, it is directed to a method for recovering lubricating oils having high viscosity indexes from lubricating oil solvent extracts. In a more specific aspect, the invention has to do with the treatment of lubricating oil solvent extracts with a solid adsorbent.

Prior to the present invention, it has been known to extract lubricating oil fractions with solvents having the ability to concentrate the more aromatic constituents as opposed to the more paraffinic constituents, the latter being the more desirable as a lubricating oil fraction. It has also been proposed by the prior art workers to re-extract solvent extracts with solvents such as those employed in the preliminary solvent extraction to recover therefrom material having lubricating oil qualities approaching the quality of the solvent raffinate. The prior art teachings have shown that while a lubricating oil may be recovered from solvent extracts by re-extraction, the quality of the oil recovered is not as good as that obtained in the primary extraction.

It has also been known to contact hydrocarbons with porous adsorbents such as silica gel, which is incompletely dehydrated silicic acid containing water in an amount from about 3 to 7%. Silica gel has been used to remove aromatics from hydrocarbons boiling in the gasoline and kerosene boiling ranges. It has also been known to employ silica gel to remove sulfur compounds from fractions boiling through the kerosene boiling range. However, this work has not resulted in commercial success.

The demands imposed by the last great war have resulted in unprecedented consumption of crude petroleum. The premium crude oils, which contain appreciable quantities of high quality lubricating oil, are being consumed more rapidly than new sources of them can be found. Therefore, it is important that the supplies of the high quality lubricating oils be augmented by more efficient utilization of what is available or by provision of new sources for these high quality materials.

Therefore, it is the main object of the present invention to provide a process in which solvent extracts of lubricating oils are contacted with silica gel to obtain high quality lubricating oil fractions.

Another object of the present invention is to recover from lubricating oil solvent extracts high quality lubricating oil fractions which heretofore were lost.

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It has now been found that the lubricating oil solvent extracts, such as those obtained by solvent extraction of lubricating oil fractions with phenol, furfural, mixtures of sulfur dioxide and aromatic hydrocarbons boiling in the gasoline boiling range, nitrobenzene, cresolic mixtures, aniline, and the like, may be treated with silica gel to obtain therefrom a high viscosity index lubricating oil approximating or exceeding the quality of the oil obtained in the solvent extraction.

In accordance with the present invention, a solvent extract of a lubricating oil fraction, after freeing of solvent, is admixed with a hydrocarbon diluent, such as a paraffinic hydrocarbon boiling in the gasoline boiling range, and contacted with an excess of silica gel, which is incompletely dehydrated silicic acid containing from about 3 to 7% water. The silica gel preferentially adsorbs the non-paraffinic constituents from the mixture of light hydrocarbon diluent and solvent extract, allowing high quality lubricating oil fractions, which heretofore were unrecoverable, to be obtained. Following the adsorption of the undesirable components from the solvent extract, these materials are removed from the adsorbent, silica gel, by contacting the material containing the adsorbed matter with an aromatic hydrocarbon solvent or other suitable solvent which effectively desorbs the adsorbed material and allows the recovery of the latter and makes the silica gel suitable for regeneration for reuse in the process. Regeneration may be accomplished by steaming followed by a drying cycle with hot air or other heated gases.

The silica gel employed in the practice of the present invention is available on the market, the commercial grades having particle sizes sufficient to be retained by 28 mesh up to 200 mesh being eminently suitable in the practice of the present invention. However, silica gel having particle sizes up to 350 mesh may be used. The amount of silica gel employed should be in excess of the amount of oil which is contacted with it. For example, in a single pass operation, a range from about 2 to 1 to about 30 to 1 of silica gel to oil ratios gives satisfactory results. A ratio of about 4 to 1 of silica gel to aromatic constituents contained in the oil is preferred.

In order to obtain throughput at a satisfactory rate, it may be necessary to contact a bed of silica gel with the oil at an elevated pressure. For example, a pressure slightly above atmospheric to about 300 pounds per square inch gauge

may be used with a preferred range of about 35 to 135 pounds per square inch gauge.

Temperatures to be employed in the practice of the present invention may be substantially atmospheric, but higher temperatures may be used. For example, a temperature of about 60° to about 200° F. may be satisfactory. However, the temperature will depend on the viscosity of the oil used and the amount of dilution with the paraffinic diluent. Ordinarily, when diluting the oil with equal volumes of paraffinic diluent, a temperature in the range from about 80° to 100° F. will be satisfactory.

The paraffinic diluent employed in the practice of the present invention should be substantially aromatic free. A suitable fraction to employ will boil from about 100° F. to about 175° F. provided no aromatics are contained therein. It is also within the scope of my invention to employ substantially pure hydrocarbon fractions such as normal hexane, normal heptane, the octanes, and even the higher members of the same homologous series such as the nonanes and the like. As a general rule, the boiling range of the paraffinic diluent should be sufficiently different from the boiling range of the solvent extract being treated to allow easy separation by distillation.

The aromatic wash solvent employed to remove the adsorbed material from the silica gel may be any one of the lower boiling aromatic hydrocarbons or mixtures thereof boiling in the gasoline boiling range. For example, benzene, toluene, xylenes, and also the alkylated derivatives of benzene and toluene such as ethylbenzene, propylbenzene, and the butylbenzenes, and the like. Any one of these aromatic hydrocarbons or mixtures thereof may be used as a desorbent to remove the adsorbed material from the silica gel.

The invention will be further illustrated by reference to the drawing in which the sole figure presents a flow diagram of one mode of practicing the invention.

Referring now to the drawing, numerals 11 and 12, respectively, designate contacting zones containing beds 13 and 14 of silica gel which is indicated by the shaded portion. These beds are supported on suitable grills 15 and 16.

A solvent extract such as a phenol extract of a lubricating oil fraction is introduced into the system by line 17 and is admixed with a hydrocarbon diluent introduced thereto by line 18 controlled by valve 19. The hydrocarbon diluent ordinarily will be a paraffinic hydrocarbon such as normal heptane. The mixture flows through line 19 into an incorporator or other mixing device 20 where intimate contacting between the paraffinic diluent and solvent extract occurs. The admixture then discharges from incorporator 20 by line 21 from whence it may be routed to either contacting zone 11 or 12. For purposes of illustration, it is assumed that the admixture is directed to contacting zone 11, valve 22 in line 23 being in the open position while valve 24 in line 21 is in the closed position. The admixture of paraffinic diluent and solvent extract flows downwardly through bed 13 in contacting zone 11 which effectively removes from the solvent extract the hydrocarbons and other organic compounds having ring structure, leaving the paraffinic and the more nearly paraffinic-like hydrocarbons substantially unadsorbed. The unadsorbed material issues from contacting zone 11 by line 25 and is discharged by line 26 into a

stripping zone 27 which may be a distillation tower or a series of distillation towers provided with suitable internal baffle equipment such as bell cap trays and packing to allow intimate contact between liquids and vapors. In this particular instance, stripping zone 27 is shown as a single distillation tower equipped with a heating means illustrated by coil 28 by way of which temperatures and pressures in zone 27 are adjusted. The conditions are maintained in zone 27 to obtain as an overhead fraction the hydrocarbon diluent injected into the system by line 18. This overhead fraction is removed from zone 27 by line 29, is cooled and condensed in cooler 30 and then returned to be used for admixture with additional quantities of solvent extract introduced by line 18. Withdrawn from the bottom of stripping zone 28 is a fraction including high viscosity index lubricating oil constituents which are removed by line 31. This material, without further treatment, is suitable for use as a high grade lubricating oil having a viscosity index above 100.

After a period of operation, the bed 13 of silica gel in contact zone 11 loses its ability to remove undesirable components from the solvent extract. When these conditions obtain, valve 22 in line 23 is closed and valve 24 in line 21 is opened. Valve 32 in line 26 is also closed. Thus, it will be seen that contacting zone 11 will be removed from the system and contacting zone 12 placed on the operating stream with the mixture of hydrocarbon diluent and solvent extract flowing through line 21 and valve 24 into contacting zone 12 whence it contacts bed 14 and has its undesirable constituents removed therefrom by adsorption. The unadsorbed material discharges from zone 12 by line 33 into line 26 and thence into stripping zone 27 where it follows the cycle as has been described.

It now becomes necessary to remove the adsorbed materials from bed 13. This may be accomplished by introducing an aromatic wash solvent of the type illustrated into the system by opening valve 34 in line 35 and allowing it to flow by lines 36 and 37 controlled by valve 38 into line 23 and downwardly through bed 13 in contacting zone 11. The material adsorbed on the silica gel is desorbed by the washing action of the aromatic solvent and discharges from zone 13 by line 25 into line 26 controlled by valve 32 and thence into line 39 controlled by valve 40 into a second stripping zone 41 which, similar to stripping zone 27, may be a series of distillation towers, but for convenience is illustrated as a single tower provided with a heating means illustrated by a coil 42. It will be understood, of course, that stripping zone 41 will be provided with all necessary equipment for suitable contact between vapors and liquids. In stripping zone 41 temperatures and pressures are adjusted to remove overhead by line 43 the aromatic wash solvent introduced into the system by line 35. This material is cooled and condensed in cooler 44 and admixed with the wash solvent in line 36 to wash additional quantities of material from the bed undergoing the washing cycle.

After substantially all of the adsorbed material has been removed from the bed 13, it is then subjected to a steaming operation, the flow of aromatic solvent being terminated by closing valve 34. Steam is introduced into line 36 from a source not shown by opening valve 45, valve 38 in line 37 being closed and valve 46 in line 36 also being in the closed position. Valve 32 in line 26 is also in the closed position. Steam is then

routed by lines 36 and 25a upwardly through bed 13 in contacting zone 11 and effectively removes the remainder of adsorbed material and wash solvent. These materials flow outwardly from zone 11 by line 47 controlled by valve 48 and thence into line 49 where it is introduced into a separation zone 50 to allow the separation of hydrocarbons from the condensed steam. Water is withdrawn from separator 50 by line 51 controlled by valve 52 while the hydrocarbons are withdrawn by line 53 which discharges them into line 43 for recycling with the wash solvent removed from stripper 41 as has been described. The bed 13 in zone 11 is now in condition to be dried and this is accomplished by introducing heated air or other gases by line 54 controlled by valve 55. The heated air or gas follows substantially the flow of steam with the gases being vented from the top of separator 50 by line 56 controlled by valve 57.

When the bed 14 in contacting zone 12 loses its ability to remove undesirable constituents from the solvent extract, it may be subjected to a similar cycle of washing, steaming, and drying with a heated gas as has been described with reference to the bed 13. When contacting zone 12 is taken out of the operating system, valve 24 in line 21 is closed and valve 58 in line 33 is closed. Aromatic wash solvent is introduced by way of line 35 into line 36 and flows thereby into line 21 by opening valve 46. The aromatic hydrocarbon flows downwardly through zone 12 and washes bed 14 of adsorbed material. The washed material flows from zone 12 by lines 33 and 59 into line 39 controlled by valve 40 which discharges it into stripping zone 41 where the aromatic hydrocarbons are recovered and recycled as has been described. It will be understood, of course, that valve 60 will be closed, preventing admixture of the unadsorbed material flowing in line 26 with the desorbed material flowing through line 59. Following the washing operation the bed 14 is then steamed by introduction of steam by opening valve 45 in line 36 and opening valve 61 in line 62 allowing the steam to flow by lines 36, 62, and 33 upwardly through bed 14 and outwardly therefrom by line 63 controlled by valve 64 and thence into line 49 and settler 50 where water is separated therefrom and the hydrocarbons are routed by lines 53 and 43 back into the washing cycle. After introduction of steam has been terminated, the bed 14 may then be dried by introducing hot air or heated gas by opening valve 55 in line 54. The heated gas follows the flow of the steam and may be vented from settler 50 by line 56 controlled by valve 57. After the regeneration has been completed the bed 12 may be placed back on the operating cycle by closing valve 61, valve 55, valve 64, and opening valves 24 and 58, line 59 having been isolated by closing valve 63.

It will be seen from the foregoing description taken with the drawing that a continuous process has been provided whereby a plurality of beds on operation and regeneration cycles may be used to remove valuable hydrocarbons from solvent extracts by contacting with silica gel.

In order to illustrate the invention further, reference will now be had to an example in which a motor oil fraction from Panhandle crude was extracted with phenol to obtain a raffinate corresponding to 80% by volume of the charge to the phenol extraction. This raffinate had a viscosity index of 102. The extract, after freeing of solvent, was tested and found to have a vis-

cosity index of -5. This material was unsuitable for use as a lubricating oil stock, and prior to the present invention, had been segregated for employment as a feed to a thermal cracking unit. As illustrative of the magnitude of this material, one commercial plant has accumulated over an operating period of 5 days some 4300 barrels of this -5 viscosity index solvent extract.

A portion of this material was then percolated, after dilution with an equal volume of normal heptane, downwardly through a 52 foot column containing silica gel of 28 to 200 mesh. The percolation was conducted with a silica gel to oil ratio of 4 to 1, a pressure in the range between 35 to 135 pounds per square inch, and a temperature ranging from 81° to 96° F. The percolate was collected in fractions and blended. A lubricating oil fraction amounting to the first 23.2% of the material charged was freed of solvent by stripping and on testing was found to have a viscosity index of 108.6. This recovered lubricating oil of the high viscosity index mentioned was water white in color and is suitable for use as a lubricating oil.

It is believed that the solvent extraction of lubricating oils removes natural inhibitors and concentrates them in the extract. It is believed that the silica gel does not remove the natural inhibitors from a solvent extract and that they remain in the percolates that are made available in the present invention as high quality lubricating oil material.

As illustrative of the magnitude of the savings possible in the practice of the present invention, lubricating oil having a viscosity index of 108.6 has a value of about \$10 per barrel. It will thus be seen that even though the percentage of the lubricating oil recoverable by the practice of the present invention is of the nature of 25%, the magnitude of the savings is relatively large.

The invention has been described and illustrated by examples in which solvent extracts of lubricating oil fractions are contacted with beds of silica gel. It will be understood by the skilled workman that it will be possible to practice the present invention by forming a mixture of the solvent extract with the paraffinic diluent and then forming a slurry of the silica gel in the admixture and allowing the silica gel to remain in contact with the admixture until the undesirable constituents are adsorbed thereon. The silica gel containing adsorbed components of the extract mixture may then be separated by gravity settling, filtration, or other settling methods well known to the art.

In the several examples, reference has been made to contacting the mixture of solvent extract and paraffinic diluent with a bed of silica gel. It will be understood that a plurality of beds may be employed. For example, it may be desirable to use two or more beds in the practice of the present invention so the operation may be conducted on a continuous basis with several of the beds adsorbing undesirable components from the feed mixture while one or more of them are undergoing the regeneration cycle.

The nature and objects of the present invention having been fully described and illustrated, what I wish to claim as new and useful and to secure by Letters Patent is:

1. A method for recovering high viscosity index lubricating oil fractions from low viscosity index solvent extracts of lubricating oils which comprises forming a mixture of a low viscosity in-

dex solvent extract of a lubricating oil and a light paraffinic hydrocarbon, said solvent extract containing high viscosity index components forming a bed of silica gel having a particle size in the range between 28 and 350 mesh, contacting the mixture with the bed of silica gel at a temperature in the range between 60° F. and 200° F. with said silica gel being in excess of said extract to cause selective adsorption by the silica gel of low viscosity index constituents in said mixture, removing unadsorbed mixture from contact with said bed, and recovering from said unadsorbed mixture by distillation high viscosity index lubricating oil fractions.

2. A method in accordance with claim 1 in which the light paraffinic hydrocarbon is normal heptane and the solvent extract is a phenol extract.

3. A method in accordance with claim 1 in which the temperature is in the range between 80° F. and 100° F.

4. A method for recovering high viscosity index lubricating oil fractions from a low viscosity index solvent extract of a lubricating oil which comprises admixing a low viscosity index phenol extract of a lubricating oil fraction in equal volumes with normal heptane, said phenol extract containing high viscosity index components forming a bed of silica gel having a particle size in the range between 28 and 200 mesh, contacting the admixture with said bed at a temperature in the range between 80° F. and 100° F., maintaining a ratio of silica gel to oil in the range between 2 to 1 and 30 to 1 to cause selective adsorption by the silica gel of low viscosity index constituents in said admixture, removing unadsorbed admixture from contact with said bed, and distilling said unadsorbed admixture to recover normal heptane and high viscosity index lubricating oil fractions.

5. A method for recovering high viscosity index lubricating oil fractions from a low viscosity index solvent extract of a lubricating oil which comprises admixing said extract with a light paraffinic hydrocarbon, said solvent extract containing high viscosity index components forming a plurality of beds of silica gel having a particle size in the range between 28 and 200 mesh, contacting the admixture with at least a first of said plurality of beds at a temperature in the range between 60° F. and 200° F. with said silica gel being in excess of said extract to cause selective adsorption of low viscosity index constituents in said admixture until said first bed has substantially lost its ability to remove low viscosity index constituents from said admixture, terminating contact of said admixture with said first bed, contacting said admixture with at least a second of said plurality of beds at a temperature in the range between 60° F. and 200° F. said silica gel being in excess of said extract to cause selective adsorption of low viscosity index constituents in said admixture, recovering unadsorbed admixture from contact with said beds, distilling said unad-

sorbed mixture to recover high viscosity index components, regenerating said first bed, and returning it to contact additional quantities of said admixture.

6. A method in accordance with claim 5 in which the light paraffinic hydrocarbon is normal heptane and the solvent extract is a phenol extract.

7. A method in accordance with claim 5 in which the temperature is in the range between 80° F. and 100° F.

8. A method for recovering high viscosity index lubricating oil fractions from solvent extracts of lubricating oils which comprises forming a mixture of a low viscosity index solvent extract of a lubricating oil and a light paraffinic hydrocarbon, said solvent extract containing high viscosity index components forming a bed of silica gel having a particle size in the range between 28 and 200 mesh, contacting the mixture with the bed of silica gel at a temperature in the range between 60° F. and 200° F. with said silica gel being in excess of said extract to cause selective adsorption by the silica gel of low viscosity index constituents in said mixture, removing unadsorbed mixture from contact with said bed, regenerating said bed by contacting it with a low boiling aromatic hydrocarbon, and recovering from said unadsorbed mixture by distillation high viscosity index lubricating oil fractions.

9. A method in accordance with claim 8 in which the low boiling aromatic hydrocarbon boils in the gasoline boiling range.

10. A method for recovering high viscosity index lubricating oil fractions from a low viscosity index solvent extract of a lubricating oil which comprises admixing said extract with a light paraffinic hydrocarbon, said solvent extract containing high viscosity index components, forming a slurry of silica gel having a particle size in the range between 28 and 200 mesh in the admixture at a temperature in the range from 60° F. to 200° F. with said silica gel being in excess of said extract to cause selective adsorption by the silica gel of low viscosity index constituents in said admixture, removing silica gel containing adsorbed low viscosity index constituents from the slurry, and recovering high viscosity index lubricating oil fractions from the unadsorbed admixture by distilling same.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,106,767	Smith	Feb. 1, 1938
2,117,602	Bulkley	May 17, 1938
2,441,572	Hirschler et al.	May 18, 1948
2,487,805	Hermanson	Nov. 15, 1949