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REFINES LUBRICATING OIL WITH SULFUR TRIOXIDE AND ALKALI

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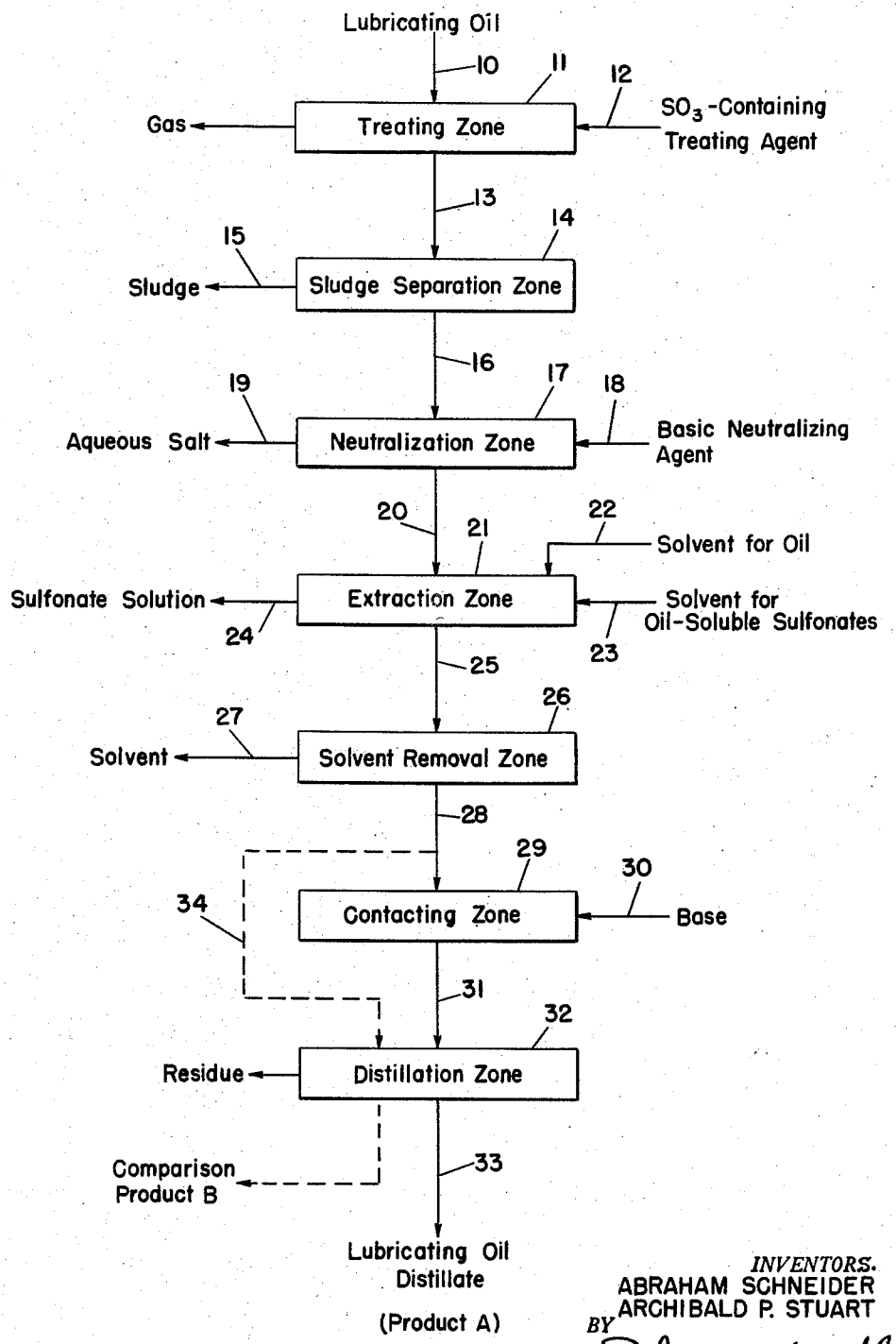

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REFINES LUBRICATING OIL WITH SULFUR TRIOXIDE AND ALKALI

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This invention relates to the refining of mineral lubricating oil, and more particularly to the production of lubricating oils having exceptionally good oxidation stability and other properties.

Oxidation stability is a highly important property of lubricating oils, and in many uses of lubricating oils, it is difficult or impossible by ordinary refining methods to obtain sufficiently good oxidation stability to meet the requirements of such uses.

The present invention provides a method of refining mineral lubricating oils to obtain a product having excellent oxidation stability. Other properties of the oil are also benefited by the treatment according to the invention. For example, in the manufacture of refrigerator oils, a product is obtained by the process of the invention which product has considerably improved resistance to copper transfer, an objectionable characteristic to which refrigerator oils are susceptible during use in refrigeration systems.

According to the present invention, mineral lubricating oil is treated with an SO_3-containing treating agent and sludge is separated; then the oil is neutralized, e.g. with caustic soda, and salt is separated; then oil-soluble sulfonates are extracted from the oil by means of an oil-immiscible solvent; and then the remaining oil is distilled in the presence of free alkali metal or alkaline earth metal oxide or hydroxide.

Mineral lubricating oils generally are advantageously treated according to the invention. The charge stock may or may not have previously been subjected to solvent refining, e.g. with furfural or other well-known solvent refining agents. Naphthenic or paraffinic lubricating oils, specialty oil stocks such as electrical oil stocks, transformer oil stocks, refrigerator oil stocks, etc. can be treated according to the invention.

Any suitable SO_3-containing treating agent can be employed in the SO_3-treating step, e.g. anhydrous SO_3, oleum, etc. Concentrated sulfuric acid, chlorosulfonic acid, and other sulfonating agents are to be considered as SO_3-containing treating agents for the purpose of the present invention. Highly suitable treating agents are those containing a major proportion of a carrier gas, e.g. air, nitrogen, etc. and a minor proportion of substantially anhydrous SO_3.

The conditions employed in the SO_3-treating step are such as to provide formation of substantial amounts of mahogany sulfonic acids. Preferably, the formation of green sulfonic acids is as small as can be obtained with formation of the desired amounts of mahogany sulfonic acids. Preferred sulfonation conditions are the following: temperature of oil upon removal from sulfonation zone 70° C. to 115° C.; pounds of SO_3 per barrel of oil 3 to 50.

Any suitable basic neutralizing agent can be used to convert the mahogany sulfonic acids in the product oil into sulfonates. Various neutralizing agents are well-known in the art for this purpose. Alkali metal basic

materials, such as sodium and potassium hydroxide and carbonates are particularly suitable.

Any suitable solvent can be employed for extraction of mahogany sulfonates from the oil. Various solvents are well-known in the art for this purpose. Aqueous alcohols, such as ethanol and isopropanol, are highly suitable. The extraction conditions can be selected, in the light of the present specification, by a person skilled in the art. Preferably, the extraction of sulfonates is complete or substantially complete.

A diluent for the lubricating oil, e.g. petroleum naphtha, can be employed if desired in various steps of the operation, e.g. the SO_3 treatment, sludge separation, extraction, etc.

The basic material which is used in the contacting and distilling steps following the solvent extraction is an alkali metal or alkaline earth metal oxide or hydroxide, e.g. sodium hydroxide, potassium hydroxide, lithium hydroxide, calcium oxide, magnesium hydroxide, etc. Other bases having similar basic strengths can be used. Preferably, 0.01 to 10 parts by weight of the base, on the water-free basis, are employed per 100 parts by weight of oil; more preferably the ratio is 0.1 to 5 parts per 100. The base may be employed either in anhydrous condition or in aqueous solution; the latter is preferred because it facilitates obtaining good contact between caustic and oil.

Prior to the distillation with basic material, the oil and base are preferably contacted at a temperature above room temperature, e.g. 50° C. to 300° C., more preferably 150° C. to 250° C., for a substantial period of time, e.g. 15 minutes to 5 hours. Such contacting improves the results obtained upon subsequent distillation.

The process of the present invention has been unexpectedly found to require a distillation over strong base after mahogany sulfonates have been extracted. Previously, it would not have been expected that a distillation over strong base would produce any beneficial effect beyond that which was obtained by removal of mahogany sulfonates. It is not definitely known why the distillation over strong base produces additional benefits, but it is believed that under the conditions of preheating, if any, and of distillation, the strong base causes chemical reaction of certain undesirable constituents which were not removed with the sulfonates, such reaction resulting in the formation of nonvolatile products, whereas the constituents in question would have entered the distillate if the distillation had been conducted in the absence of strong base. As examples of the constituents in question, pyrroles may be mentioned. Also, it is believed that the oil may contain aldehyde materials formed by oxidation side reactions during the sulfonation; these aldehydes may undergo an aldol condensation during the distillation over strong base.

The invention will be further described with reference to the attached drawing which illustrates the invention. Mineral lubricating oil is introduced through line **10** into treating zone **11**, wherein it is contacted with an SO_3-containing treating agent, e.g. a gaseous mixture of anhydrous SO_3 and a carrier gas such as air, introduced through line **12**. The SO_3 reacts with at least a portion of the aromatic compounds in the oil to produce oil-soluble "mahogany" sulfonic acids and oil-insoluble "green" sulfonic acids. The liquid products are introduced through line **13** into sludge separation zone **14**. Removal of sludge containing green sulfonic acids is indicated schematically by line **15**, and removal of the supernatant oil is indicated schematically by line **16**. The oil is neutralized in neutralization zone **17** by basic neutralizing agent, e.g. caustic soda, introduced through line **18**. Removal of the aqueous salt layer and of the super-

natant oil layer is indicated schematically by lines 19 and 20 respectively. The oil, containing mahogany sulfonates in solution, is introduced into extraction zone 21, wherein it is contacted with a solvent for oil, e.g. petroleum naphtha, and a solvent for mahogany sulfonates, e.g. 66% aqueous isopropanol solution, introduced through lines 22 and 23 respectively. The sulfonate layer is separated from the supernatant oil layer and removed through line 24. Mahogany sulfonates can be recovered from this layer, which is a solution of sulfonates in solvent, by known means. The oil layer, a solution of oil in solvent, is introduced through line 25 into solvent removal zone 26, wherein solvent is stripped off through line 27. The solvent-free oil is then introduced through line 28 into contacting zone 29, wherein it is contacted, e.g. at 200° C. for about half an hour, with a base, e.g. caustic soda, introduced through line 30. The oil is then introduced through line 31 into distillation zone 32. The oil is distilled to obtain a distillate, e.g. a 0–98% distillate, which is schematically represented as being removed through line 33. This distillate product (A) has exceptionally good oxidation stability. If desired, this product may be further refined, e.g. by clay treating, by means not shown.

For purposes of comparison, the production of lubricating oils by a process other than the process of the invention is also illustrated in the figure. Thus, a comparison product B is produced by the same operation as product A, except that the contact with base in zone 30 is omitted, the solvent treated oil being bypassed from line 28 through line 34 into zone 32, and the distillation in zone 32 is performed in the absence of free strong base.

The following example illustrates the invention:

The preparation of the product A of the figure was as follows: naphthenic base crude oil was topped, and the topped crude was saponified to neutralize naphthenic acids. The saponified oil was vacuum distilled to recover a lubricating oil distillate having viscosity at 100° F. of 9.37 centistokes and viscosity at 210° F. of 2.26 centistokes and containing 35 weight percent of compounds containing at least one aromatic ring. This distillate was treated with an anhydrous SO_3-air mixture containing 15 mole percent SO_3 in amount to provide 24.5 pounds of SO_3 per barrel of oil. Liquid products were removed from the treating zone at a temperature of about 200° F. Sludge was separated from the liquid products, and the supernatant oil was neutralized with 50° Bé. caustic soda and aqueous salt was separated. 100 parts by volume of the oil were then dissolved in 100 parts by volume of naphtha and extracted with 30–60 parts by volume of a 66% solution of isopropanol in water. The aqueous alcoholic sulfonate layer was separated from the naphtha-oil layer. Three extractions of the latter with 5–10 parts of 66% isopropanol in each followed. Naphtha was stripped from the naphtha-oil layer product of the last extraction, 1 part by weight of 50° Bé. caustic soda was added to 100 parts by weight of the naphtha-free oil, and the oil and caustic were maintained at about 200° C. for about half an hour to obtain good contact of the oil and caustic. The oil and caustic were then introduced into distillation apparatus, and a 0–98% distillate fraction of the oil was recovered.

In another distillation of oil and caustic obtained in the same manner as described, a 0–79% distillate fraction of the oil was recovered.

The preparation of product B was essentially the same as the preparation of product A except that the naphtha-free oil obtained as product of the solvent extraction was directly introduced into distillation apparatus, and a 0–98% distillate was recovered therefrom.

Products A and B were each tested for oxidation stability according to ASTM Test D670–42T, method B. The following table shows the results obtained:

Product	Treatment	Percent Sludge Formed in Test
A	According to invention; 0-79% distillate	0.027
A	According to invention; 0-98% distillate	0.035
B	Distillation to 98% without caustic	0.175

This table shows that the treatment according to the invention produces a much more stable oil than the other treatment. Comparison of products A with product B shows that the use of excess base in the distillation is essential to obtaining the improved results according to the invention.

The invention claimed is:

1. Method for refining mineral lubricating oil which comprises: contacting such oil with a sulfonating agent under sulfonating conditions, thereby to form oil-soluble sulfonic acids; extracting the oil-soluble sulfonic materials from the product oil; and distilling the product oil in the presence of an inorganic base having cation selected from the group consisting of alkali metal and alkaline earth metal cations and having anion selected from the group consisting of oxide and hydroxide anions.

2. The method according to claim 1 wherein said base is aqueous sodium hydroxide.

3. Method for refining mineral lubricating oil which comprises: contacting such oil with anhydrous gaseous SO_3 under sulfonating conditions, thereby to form oil-soluble sulfonic acids; neutralizing the latter with caustic soda; extracting the oil-soluble sodium sulfonates from the product oil by means of aqueous isopropanol as solvent; adding an aqueous solution of 0.01 to 10 parts by weight of sodium hydroxide to 100 parts by weight of the raffinate produced in said extracting; contacting the raffinate and sodium hydroxide at 50–300° C. for 0.25 to 5 hours; and distilling the raffinate in the presence of the sodium hydroxide to obtain a refined distillate product.

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