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PROCESS FOR THE PRODUCTION OF A HIGH QUALITY LUBE OIL

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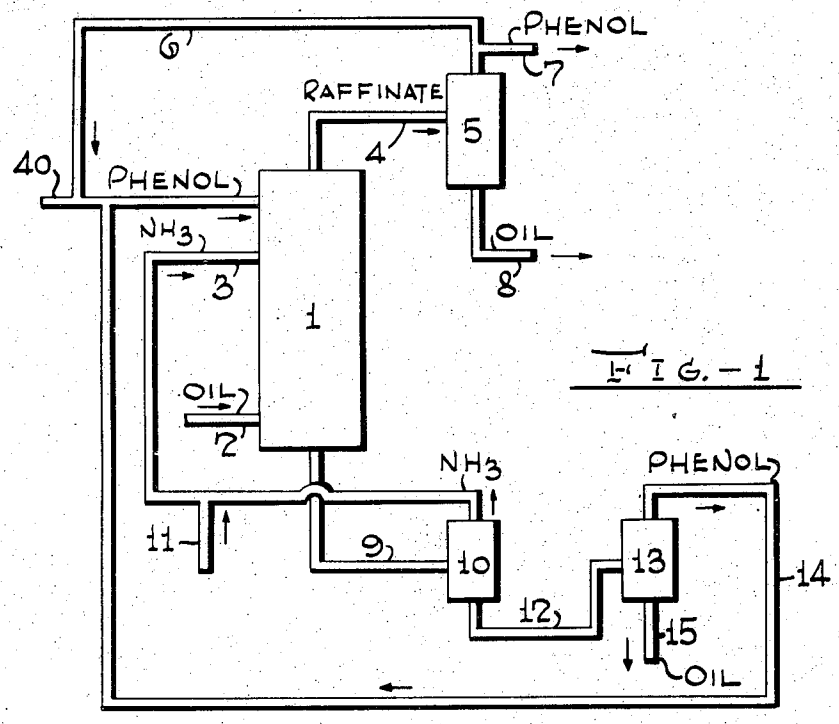


FIG. - 1

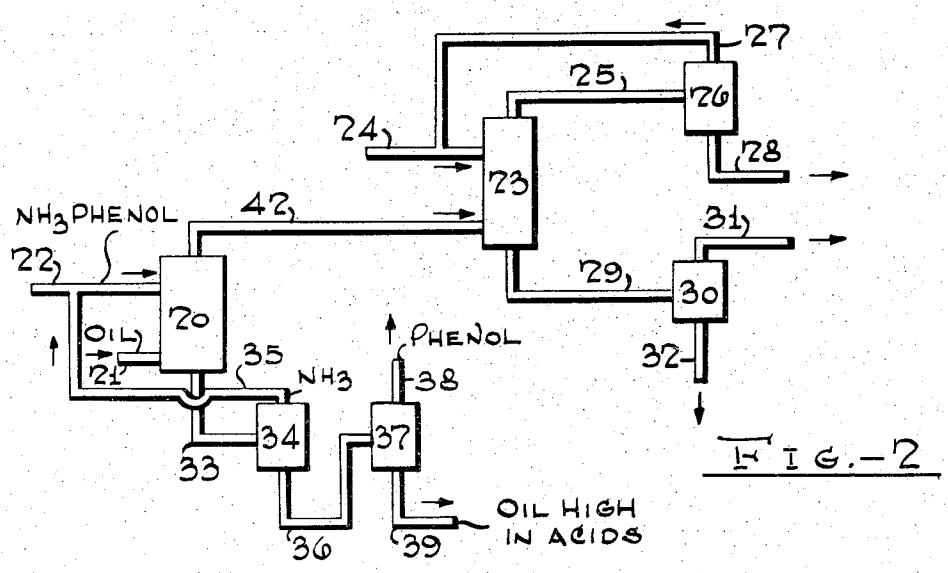


FIG. - 2

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PROCESS FOR THE PRODUCTION OF A HIGH QUALITY LUBE OIL

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8 Claims. (Cl. 196—14.12)

The present invention is concerned with an improved process for the production of high quality lubricating oils. The invention is more particularly directed toward an improved liquid-liquid contacting process wherein solvents having a preferential selectivity for the more aromatic type constituents are utilized for the treatment of lubricating oil fractions. In accordance with the present invention, solvents of this character, as for example phenol, are utilized in conjunction with a relatively small amount of ammonia whereby lubricating oils having a very low acidic content are produced.

It is well known in the art to contact hydrocarbon fractions with solvents having a preferential selectivity for the more aromatic type of hydrocarbon constituents as compared to the more paraffinic type hydrocarbon constituents. Solvents of this character are for example, phenols, furfural, sulfur dioxide, nitrobenzene, aniline, cresols, chlorex, dimethylformamide, dipropionitriles, ammonia, amines, etc. It is also known in the art to use in conjunction with these aromatic type solvents, solvent-modifying agents as for example, water, alcohols, esters and the like. Temperatures usually employed in the treating operation are in the range from —40° F. to 250° F., while the solvent to oil ratios are in the range from about 0.4 to 10 volume of solvent per volume of oil. These operations have been carried out either in batch or in countercurrent treating zone processes.

While the solvent treating operations, as described and known in the art, have been entirely satisfactory for improving the viscosity index and other critical factors of most lubricating oil fractions by the removal of aromatic type constituents, certain difficulties have been encountered when the feed oil has a relatively high neutralization number. Phenol, for example, will not produce a satisfactory treated oil with a satisfactory neutralization number unless an excessive amount of the solvent be employed. This results in lower yields of treated oil having excessively good quality in all properties other than neutralization number. Normally, it is considered that a satisfactory lubricating oil should have a neutralization number not in excess of about 0.1 (acidity as measured in mg. KOH per gr. oil).

The neutralization number is an indication of the quantity of acidic materials present, usually naphthenic acids and related compounds. The naphthenic acids are very undesirable in a lubricating oil since under operating conditions of high temperatures and pressures they tend to cause excessive corrosion and sludging in the engine. Manufacturing experience has shown that a satisfactory viscosity index is about 60. However, when extracting distillate fractions (secured from Coastal crudes) boiling in the lubricating oil boiling range with phenol to this viscosity index, the neutralization number is about .2. This is not a satisfactory lubricating oil product for the reasons given. The lubricating feed oils from these sources have neutralization numbers of about .7 and above.

In accordance with the present invention, lubricating oil fractions, having a neutralization number above about 0.5 particularly above about 0.7, are contacted with an aromatic type solvent preferably phenol. In accordance with the present invention there is used in conjunction with the phenol or equivalent solvent, an amount of ammonia below about 1%, preferably below about 0.5% based upon the oil. The preferred range of concentration of ammonia is 0.1 to 0.4% by volume based upon the oil. In accordance with the present invention, the ammonia and phenol are handled in a distinct way to secure an efficient operation producing a high quality product.

The process of the present invention may be readily

understood by reference to the attached drawing illustrating embodiments of the same. Figure 1 illustrates a single tower operation, while Figure 2 illustrates an embodiment of the invention wherein a pretreat of the oil is carried out using a small amount of an ammonia-phenol solvent.

Referring specifically to Figure 1, a lubricating oil fraction having a neutralization number above about 0.5 is introduced into the bottom of countercurrent treating zone 1 by means of line 2. An aromatic acid type solvent, preferably a phenol, is introduced into the top of countercurrent treating zone 1 by means of line 40, In accordance with a preferred adaptation of the invention, ammonia is introduced into treating zone 1 at a point below the point of introduction of phenol by means of line 3. The quantity of phenol used for purposes of illustration is in the range from about 0.4 to 1 volume of phenol per volume of oil. The amount of ammonia used is below about 1% by volume, preferably below about 0.5% based upon the volume of oil feed, and most preferably in the range of from 0.1% to 0.4% based upon the volume of oil feed. It is to be understood that the ammonia may be added as ammonium hydroxide. Temperature conditions in the countercurrent treating tower are in the range from about 110° F. to 250° F. It is preferred that the top temperature be in the range from about 130° F. to 250° F., while the temperature at the bottom of the tower be in the range from about 110° F. to 210° F. A raffinate phase comprising phenol and paraffinic type constituents is removed overhead from zone 1 by means of line 4 and passed to a distillation zone 5. Temperature and pressure conditions in distillation zone 5 are adapted to remove overhead by means of line 6 phenol which is preferably recycled to line 40. A high quality lubricating oil product of a satisfactory neutralization number is removed from the bottom of distillation zone 5 by means of line 8.

A solvent extract phase is removed from the bottom of extraction zone 1 by means of line 9 and passed to an initial distillation zone 10. Temperature and pressure conditions in zone 10 are adapted to remove overhead by means of line 3 ammonia which is recycled to zone 1 as hereinbefore described. Fresh ammonia may be added to the system by means of line 11.

A solvent extract phase free of ammonia is removed from the bottom of distillation zone 10 by means of line 12 and introduced into a second distillation zone 13. Temperature and pressure conditions in zone 13 are adapted to remove overhead by means of line 14 the phenol which is preferably recycled to the system by means of line 40. A solvent free extract oil is removed by means of line 15 and handled or further refined as desired. It is to be understood that zones 1, 5, 10 and 13 may comprise any suitable number and arrangement of stages.

Referring specifically to Figure 2, a feed oil similar to that utilized with respect to the description of Figure 1 is introduced into solvent treating zone 20 by means of line 21. The oil flows upwardly in zone 20 and countercurrently contacts a downflowing solvent mixture comprising ammonia and phenol which is introduced into the top of zone 20 by means of line 22. When utilizing this pretreatment, the amount of solvent mixture utilized per volume of oil is in the range from about 0.2 to 1, preferably in the range from about 0.4 to 0.6. The solvent mixture per se preferably comprises from 0.2 to 0.4% ammonia based upon the volume of oil. Temperature conditions are preferably in the range from about 110 F. to 150° F. at atmospheric pressure to 20 p. s. i. g.

The treated raffinate phase comprising phenol and oil, and free of naphthenic and related acidic materials is removed overhead from zone 20 by means of line 42. This raffinate phase is introduced into the bottom of a second treating zone 23. In zone 23 the oil flows upwardly and countercurrently contacts additional downflowing phenol which is introduced into the top of zone 23 by means of line 24. Treating conditions in zone 23 are the same as in zone 1 of Figure 1 without further addition of ammonia.

The raffinate phase is removed overhead from zone 23

by means of line 25 and passed to distillation zone 26. Temperature and pressure conditions in zone 26 are adapted to remove overhead by means of line 27 phenol which is preferably recycled to zone 23 by means of line 24. A high quality lubricating oil fraction of a satisfactory neutralization number is removed from the bottom of distillation zone 26 by means of line 28. A solvent extract phase is removed from the bottom of zone 23 by means of line 29 and passed to distillation zone 30. Temperature and pressure conditions in zone 30 are adapted to remove overhead by means of line 31 phenol which is preferably recycled to zone 23. An extract phase free of solvent is removed from the bottom of zone 30 by means of line 32 and may be further refined or handled as desired.

The solvent extract phase comprising naphthenic or equivalent salts, phenol and ammonia, is removed from the bottom of zone 20 by means of line 33 and passed to distillation zone 34. Temperature and pressure conditions in zone 34 are adapted to remove overhead by means of line 35 ammonia which is preferably recycled to zone 20 by means of line 22. An extract phase comprising naphthenic acid salts is removed from the bottom of zone 34 by means of line 36 and passed to distillation zone 37 wherein temperature and pressure conditions are adapted to remove overhead by means of line 38 phenol which is preferably recycled to zone 20 by means of line 22. An oil phase comprising a high concentration of naphthenic acids and their salts is removed from the bottom of zone 37 by means of line 39. This stream is rich in naphthenic and equivalent acids and may be processed and handled as desired to segregate the same.

The present invention is broadly concerned with the treatment of lubricating oil feed fractions, particularly those lubricating oil feed fractions having a high acidic content with an aromatic type solvent and using in conjunction therewith a relatively low concentration of ammonia. The invention is particularly applicable to the treatment of feed oils (Coastal and Colombian type distillates) having a neutralization number in excess of 0.5, preferably above about .7 in the range of 1.0 to 3.0 to make high yields of treated oil, e. g., greater than 70% of feed. As pointed out heretofore, the amount of ammonia utilized should be below about 1% by volume, preferably below about 0.5% by volume in the range of about .1% to .4% based upon the oil.

The process of the present invention may be more fully understood by the following examples illustrating the same.

Example 1

A lubricating oil fraction of the following specifications:

	Feed stock
Refractive index (R. I.) at 20° C	1.5022
Aniline point, ° F	180
Spec. gravity at 60° F	0.9144
Vis. at 100° F. SUS	285
Vis. at 210° F. SUS	47.0
Pour, ° F	−30
Neut. No., —mgs. KOH/gm. oil	1.44

was contacted with phenol containing 1% water and with phenol containing 0.9 weight per cent of ammonia in single stage batch treats.

The results of these operations are as follows:

Solvent	Phenol (1.0% Water)	Phenol (0.9 Vol. Percent Ammonia)
Temperature, ° F	130	130
Solvent Treat, Vol. Percent on Oil	100	100
Raffinate Yield, Vol. Percent by R. I.	77	77
Solubility of oil in Extract Phase, Vol. Percent	21	21
Solubility of Solvent in Raff. Phase, Vol. Percent	13	13
Raffinate Quality:		
R. I. at 20° C	1.4940	1.4942
Aniline Point, ° F	191	193
Spec. Gravity at 60° F	0.9019	0.9011
Vis. at 100° F. SUS	242	
Vis. at 210° F. SUS	46.0	
Pour, ° F	−30	
Neut. No., mgs. KOH/gm	0.70	0.25
Extract Quality:		
R. I. at 20° C	1.5292	1.5289
Spec. Gravity at 60° F	0.9581	0.9566

From the above it is apparent that in a single stage the ammonia produced a treated oil of appreciably lower neutralization number.

Example 2

A feed oil having the following inspections:

	Feed inspections
Gravity at 60° F., ° API	21.4
R. I. at 20° C	1.5121
Neut. No., mgs. KOH/gm	2.70
Color, T. R	3/4
Vis. at 100° F., SSU	463
Vis. at 210° F., SSU	53.6
Viscosity index	35

was contacted countercurrently with a phenol solvent with and without ammonia using the same number of stages in both cases. The results of these operations are as follows:

Stages	19	19
Treat, Vol. Percent on Oil	89	87
Water, Percent on Phenol	9.8	9.8+0.2 Wt. Percent NH_3.
Water inj., Percent on Phenol	2.1	1.6
Yield, Vol. Percent (Grav.)	82.9	80.1
Raffinate Inspections:		
Gravity at 60° F., ° API	24.9	25.0
R. I. at 20° C	1.4982	1.4979
Neut. No., mgs. KOH/gm	.13	0.03
Color, T. R	1½	1½
Vis. at 100° F., SSU	354	374
Vis. at 210° F., SSU	51.6	52.2
Viscosity Index	63	61
Extract Inspections:		
Gravity at 60° F., ° API	6.4	8.4
R. I. at 20° C	1.5754	1.5681

From the above it is apparent that the 0.03 neutralization number represents an excellent quality oil and meets the requirements of 0.1 maximum, whereas the run without ammonia does not meet the desired requirement.

Example 3

A feed oil having the following inspections:

	Feed inspections
Gravity at 60° F., °API	21.6
R. I. at 20° C	1.5079
Neut. No., mgs. KOH/gm	1.15
Color, T. R	1
Vis. at 210° F., SSU	971
Viscosity index	28

was countercurrently phenol extracted with and without ammonia and then clay contacted. The results of these operations are as follows:

Processing Method	Phenol Extraction+ Clay Contacting	
	Without NH_3	0.1% NH_3 in Solvent
Extraction data:		
Treat, Vol. Percent	81	91
Raff. Yield, Vol. Percent	88	86
Color, T. R	2¾	3¾
Neut. No., mgs. KOH/gm	0.23	0.11
Super Filtrol Used, #/gal	0.3	0.3
Finished Oil Yield, Vol. Percent	85	83
Finished Oil Quality:		
Neut. No., mgs. KOH/gm	0.10	0.03
Sligh No., SD	37	43
Indiana Life, Hrs	40	36
Color, T. R	10½	11¼
Color Hold (16 Hrs. at 210° F.) TR 10	9	10

From the above it is apparent that a feed oil having a neutralization number of 1.15 was satisfactorily solvent treated in accordance with the present invention to secure a satisfactory product having a neutralization number of 0.11.

What is claimed is:

1. Process for the production of a high quality lubricating oil product having a low neutralization number from a feed oil having a relatively high neutralization number which comprises contacting said feed oil with a solvent having a preferential selectivity for the more aromatic type constituents as compared to the more paraffinic type con-

stituents and using in conjunction with said solvent from about 0.2 to 0.4 volume % of ammonia based upon the amount of feed oil, separating a raffinate phase and recovering said high quality lubricating oil product therefrom.

2. Process as defined by claim 1 wherein said solvent comprises a phenol.

3. Process as defined by claim 1 wherein said feed oil has a neutralization number above about .5.

4. Process as defined by claim 1 wherein said feed oil has a neutralization number in the range from about 1 to 3.

5. Process for the production of a high quality lubricating oil product having a low neutralization number from a feed oil having a relatively high neutralization number which comprises introducing said feed oil into the bottom of a countercurrent treating zone, introducing a solvent having a preferential selectivity for the more aromatic type constituents as compared to the more paraffinic type constituents into the top of said countercurrent treating zone, introducing into said zone at a point intermediate the point of introduction of said oil and said solvent from about 0.2 to 0.4 volume % of ammonia based upon the amount of feed oil, removing from the top of said zone a raffinate phase comprising oil and solvent, separating from said raffinate phase the solvent to secure a high quality lubricating oil having a relatively low neutralization number.

6. Process as defined by claim 5 wherein the feed oil is characterized by having a neutralization number in the range from about 1 to 3.

7. Process for the production of a high quality lubricating oil of a low neutralization number which comprises contacting a feed oil having a relatively high neutralization number in an initial solvent treating zone with a relatively small quantity of a solvent mixture comprising a solvent having a preferential selectivity for the more aromatic type constituents as compared to the more paraffinic type constituents and from about 0.2 to 0.4 volume % of ammonia based upon the amount of feed oil, separating a raffinate phase free of ammonia from said initial zone and contacting the same in a secondary treating zone with additional quantities of a solvent having a preferential selectivity for the more aromatic type constituents as compared to the more paraffinic type constituents, separating a raffinate phase from said secondary treating zone and removing the solvent therefrom to produce a lubricating oil fraction of a low neutralization number.

8. Process as defined by claim 7 wherein the neutralization number of the feed oil to said initial stage is above about .5%.

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