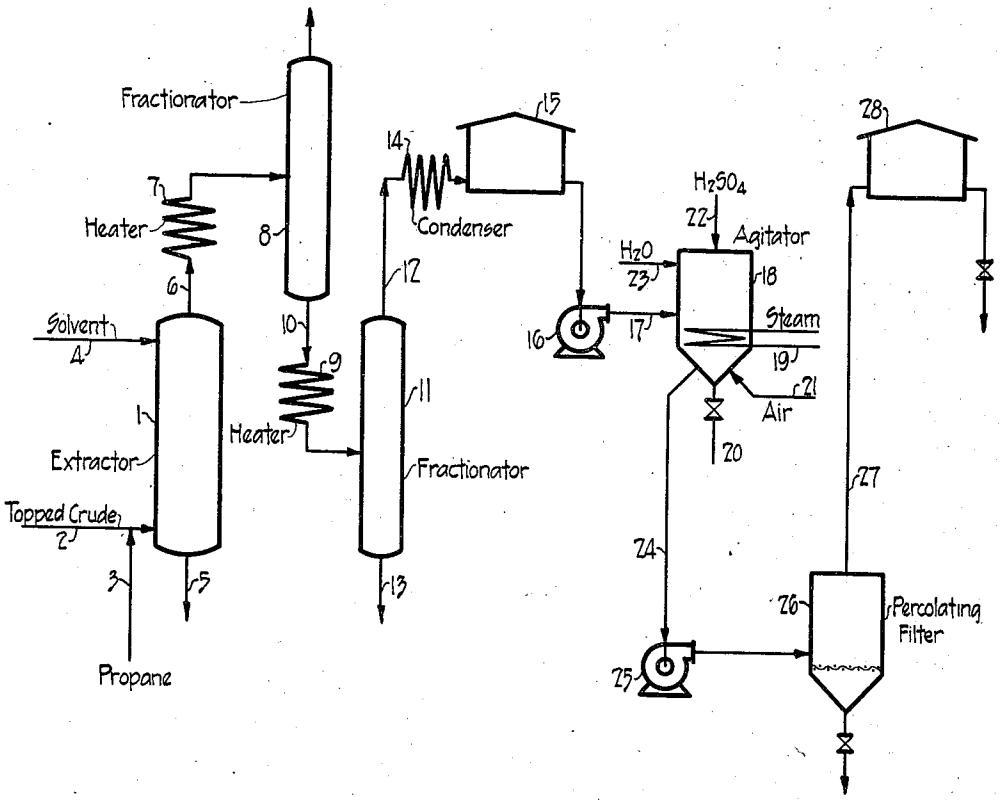
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MANUFACTURE OF TURBINE OILS

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MANUFACTURE OF TURBINE OILS

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10 Claims. (Cl. 196—40)

This invention deals with a method for producing hydrocarbon oils, such as light lubricating oils, and which are highly resistant to sludge formation, and more particularly is concerned with the manufacture of turbine oils by a method involving known steps and requiring nothing more than conventional petroleum refining equipment, whereby satisfactory turbine oils may be produced from stocks heretofore considered more or less unsuitable for this purpose.

It is a purpose of my invention to produce stable oils suitable as turbine oils, transformer oils, spray oils, medicinal oils, etc. It is another purpose to produce such oils by steps requiring conventional treating equipment. It is another purpose to treat hydrocarbon oils with sulfuric acid and neutralize them without the use of caustic alkali or contact clays or both; and it is a further purpose to produce acid treated oils free from objectionable sulfuric acid reaction products which are frequently left in the oil by the conventional methods of neutralization.

It is well known that turbine oils must be more resistant to sludge formation by the action of air and water in the presence of the metals with which they come in contact during use than any other type of lubricating oils. Sludge interferes with the proper lubrication and the expense of interrupting operation of large, high-speed turbines and cleaning them out is so great that high resistance to sludge formation is one of the essential requirements of turbine oils.

Heretofore, so-called Mid-Continent oils have in general yielded more or less unsatisfactory turbine oils unless they were produced by exceedingly severe treatment. Solvent extracting these oils with so-called naphthenic solvents produced oils with very bad emulsion properties after aging, and, in fact, it was believed by many that solvent extraction was more harmful than useful in this matter. Now, however, I have discovered that by subjecting a solvent raffinate of proper viscosity range obtained by extraction with a naphthenic solvent from a Mid-Continent lubricating distillate oil to a series of simple treatments, highly satisfactory turbine oils can be obtained. While my method of treating appears to be particularly useful when applied to Mid-Continent raffinates, it is, however, not limited thereto, but is applicable as well to raffinates from other sources as, for example, from Pennsylvania, Gulf Coast, California, Rumania, Colombia, etc., oils.

The solvent extraction should preferably be accompanied by a treatment capable of removing asphaltenes, resins and the like from the oil. This treatment may comprise or consist of distillation, propane precipitation, Pilat treatment, etc. It may precede or follow, or, as in the case of the Duosol process, may be carried out simultaneously with the solvent extraction. If necessary, the oil may also be dewaxed at one stage or another, as convenience may direct.

The raffinate which is substantially free from asphaltenes and preferably free from wax, and having a preferred Saybolt Universal viscosity at 100° F. of about 100 to 200 seconds is treated at a normal temperature, i. e., at about 50° to 140° F. with concentrated sulfuric acid.

About 5 to 20 pounds per barrel of sulfuric acid having a concentration of 93% to 100%, and preferably 95% to 99%, is used advantageously. This treatment may be carried out in batch or continuously, and any conventional means for mixing, such as air blowing or mechanical mixing, are applicable. The oil so treated is allowed to settle, and insoluble sludge is removed as completely as possible. A small amount of water, e. g., about ⅛ to 2 per cent may be added to the sour oil to hydrolize the soluble sludge and to effect precipitation of suspended pepper sludge. Additional sludge, which is thereby settled, is removed.

Instead of removing soluble sludge by hydrolysis with water, it may be extracted with suitable solvents such as methyl or ethyl alcohol, acetone, etc. In the course of this treatment, whether it be hydrolysis or extraction, the color of the oil is materially improved.

The sludge-free oil which still contains dissolved SO_2 is blown with air or other convenient gas which is substantially chemically inert under the conditions of this blowing, such as CO_2, flue gas, nitrogen, hydrogen, etc., at an elevated temperature below 200° F., e. g., preferably between about 150°–190° F. to drive off the dissolved SO_2. The SO_2 should be removed substantially completely, and this blowing treatment should be continued until a sample of the oil tested shows a negative reaction for SO_2. SO_2, if allowed to remain in the oil at this stage, will promote side reactions in the next following step and induce the formation of oxidized substances, which may have a detrimental effect on the qualities of the finished turbine oil. It is further of importance that in the SO_2 removal step the temperature be kept below about 200° F. because at higher temperatures undesirable side reactions may and frequently do take place.

After the last traces of SO_2 have been eliminated, the temperature of the oil is raised to 220°–300° F. and preferably 250°–270° F., while a small stream of air is blown through the oil. In the course of this operation, the oil turns dark purple and solids begin to form, some of which may settle out upon standing. The time required to form these solids, which I believe to be polymerization products of unstable components in the oil, may vary from about one to two hours at 300° F. to two to three days at 220°

F. At 250°–270° F., normally between about 8 to 20 hours of air blowing are required. At temperatures below 220° F., the polymerization normally remains incomplete, no matter how long blowing is continued, and at temperatures above 300° F. undesirable oxidation reactions make themselves felt.

Instead of air, other oxygen-containing gases, such as pure oxygen, or non-oxidizing gases, may be used. However, if non-oxidizing gases are used, the polymerization proceeds very slowly and often remains incomplete.

The suspended solids in the blown oil are so finely divided that they cannot be removed completely by settling. Moreover, frequently colored substances are formed in the high temperature blowing which are soluble in the oil and which must be removed by means other than settling. I have found that both the suspended and dissolved harmful impurities contained in the oil after this stage may be removed by simple percolation, preferably at a temperature below about 100° F., of the oil through a suitable, active, preferably naturally active, percolation clay such as Florida clay, Attapulgas clay, fuller's earth, etc. I prefer to use a 30/60 mesh clay for this operation, although coarser or finer clay may be used if desired. The oil resulting from the percolation has a light color and has the stability which is required of turbine oils. If desired, activated clays may be used, although I prefer naturally active clays.

The chemistry involved in the air blowing at the temperatures between 220°–300° F. is not well understood. In particular, it is difficult to explain why unextracted mineral oils such as ordinary Mid-Continent distillates normally yield relatively dark oils of poor stability when treated as above, and that treatment with excessive amounts of clay does not substantially improve their stability. Further, I have found that elimination of all the insoluble acid sludge prior to the high temperature air blowing at 220°–300° F., as well as at least a major portion of the soluble sludge together with dissolved SO_2 is essential. It is, however, relatively immaterial by what means this is accomplished. For example, I may treat the acid treated acidic oil, which has been freed from insoluble sludge but which contains small amounts of dissolved sludge, with liquid water at a temperature above 212° F. and under superatmospheric pressure, if desired, in the presence of an amount of a base such as caustic soda, lime, aqueous ammonia, etc. However, I do prefer the method hereinbefore described, of hydrolyzing with water at normal pressure, settling additional sludge formed thereby and eliminating SO_2 by blowing at temperatures below 200° F. This method is simple, effective, inexpensive and consumes no chemicals other than air and water.

My invention will be more fully understood from the accompanying drawing which represents a flow diagram of a preferred form of my process. Topped mineral crude oil containing lubricating fractions substantially free from gas-oil and lighter components enters extractor 1 near its bottom through line 2 from a source not shown. Propane is simultaneously injected through line 3. A naphthenic solvent, such as liquid SO_2, furfural, phenol, cresylic acid, beta-beta-dichlorethyl ether, etc., is introduced into the top of the extractor 1 through line 4. The propane solution and naphthenic solvent flow countercurrently through the extractor 1, extract comprising the naphthenic solvent emerging at the bottom of the extractor through line 5, and raffinate-propane solution flowing through line 6 to heater 7 and column 8 where propane containing traces of naphthenic solvent is flashed off. Raffinate free of solvent is conducted through heater 9 in line 10 to fractionating column 11 where a light lubricating distillate having preferably a Saybolt Universal viscosity at 100° F. of 150 to 160 seconds is taken overhead through line 12, residue being withdrawn through bottom line 13. The distillate vapors in line 12 are condensed in condenser 14 and condensate is stored in tank 15.

Lubricating distillate is conveyed from tank 15 by pump 16 in line 17 to agitator 18, which is equipped with steam heating coil 19, sludge line 20, air line 21 and lines 22 and 23 for introducing concentrated sulfuric acid and water, respectively. When the agitator has been filled with raffinate distillate oil to the desired level and the temperature has been adjusted to between 50 and 140° F., the proper amount of sulfuric acid is dumped into it. Air is then admitted through line 21 to provide the necessary agitation, and after sludge has been formed, the air current is turned off and sludge is allowed to settle and is withdrawn through line 20. A small amount of water is now introduced into the oil through line 23 and is agitated with the oil to effect removal of the suspended pepper sludge and hydrolysis of the dissolved sludge. The secondary sludge so formed is settled and drawn through line 20. The oil which is now substantially sludge-free but contains dissolved SO_2 is heated by means of coil 19 to a temperature preferably between 150° and 190° F. At this temperature, air is blown through the oil to remove the dissolved SO_2. When this has been accomplished, the temperature of the charge in the agitator is further raised to about 250°–270° F., while air blowing is continued for about 8–20 hours. During this period, the oil turns dark purple. Without allowing coloring material to settle, the dark oil is cooled, is withdrawn from the agitator through line 24 and is conveyed by pump 25, preferably at a temperature below about 100° F. through percolation filter 26 which is filled with a suitable active bleaching clay such as fuller's earth. The percolated oil, which is very bright and of light color, goes through line 27 to storage tank 28.

The clay, which has been spent by contact with the oil treated as described, can be revivified by burning in the conventional manner.

While in the above I have described a simplified flow diagram of my process, it is understood that many modifications within the scope of my invention are possible. For example, the different treatments carried out in the single agitator as shown may be carried out in different agitators. This may often be desirable because it may be difficult to remove all the acid sludge from the vessel used in carrying out the sulfuric acid treating step. Again, the oil polymerized by air blowing may be cooled by passing it through a conventional cooler. Moreover, the installation of pumps wherever required is considered within the skill of the designer for refinery requipment.

The following example further serves to illustrate my process:

A lead lined agitator was charged with 743 barrels of a lubricating oil raffinate distillate having a Saybolt Universal viscosity at 100° F. of 155 seconds, obtained from a Mid-Continent crude by extraction by the Duosol process. The charge

was treated at 80° F. with 10.1 pounds per barrel 98% sulfuric acid. The resulting mixture was air agitated for 50 minutes and the sludge was allowed to settle and was drawn off. 0.75% water was then added to the sour oil and the agitation was resumed for 30 minutes at 80° F. to effect hydrolysis of dissolved sludge. The hydrolyzed oil was settled and an asphaltic sludge was drawn off. The oil was then passed through a heat exchanger into another lead lined agitator. The temperature of the oil after transferring was 150° F., and at this temperature the oil was blown with air free of SO_2.

After the removal of the SO_2, the oil was circulated through the heat exchanger until the temperature reached 240° F. During the heating, a small amount of air was blown through the oil to remove the excess moisture and to insure mixing. When the temperature reached 240° F. the air was increased until violent agitation was attained. The polymerization of unstable constituents was effected by blowing for 14 hours with air between the temperatures of 250° and 270° F. The polymerized oil was then allowed to cool and was percolated through fuller's earth at a temperature slightly below 100° F. The following data were obtained:

	Barrels	Percent
Oil charged to agitator	743	100
Oil lost in acid treatment	24	3.23
Acid sludge removed	35	
Polymerized oil yield	719	96.77
Filtration loss	64	
Clay yield, gallons of oil/pound of clay=1.72		

Some of the more important properties of the treated oil in comparison with the properties of a turbine oil produced by conventional sulfuric acid treatment followed by contact neutralization with clay were as follows:

Oil properties	New turbine oil	Conventional turbine oil
Gravity, °A. P. I.	31.6	31.2.
Color	19 Say	1½+NPA.
Demulsification at 130° F.	1620	1620.
Emulsion test—NaOH at 130° F.	1 minute	4 minutes.
Steam emulsion number	30	60.
RL emulsion test [1]:		
Initial emulsion	No emulsion	900.
Emulsion after 1 hour's aging	1000	280.
Emulsion after 6 hours' aging	276	180.
Original interfacial tension, dynes/centimeter.	38.9	37.7.
Interfacial tension after 1 hour's aging.	27.8	24.8.
Interfacial tension after 6 hours' aging.	20.4	19.0.
Swiss turbine oil aging test [2]:		
Steam jet test	550	95.
RL emulsion after aging	210	190.
Interfacial tension after aging	17.5	14.9.
Sludge mg./200 cc	6	8.3.
Acid number	.1	.20.
Saponification number	1.1	2.7.

[1] For description of the RL emulsion test, see the "Institute of Mechanical Engineers—General Discussion on Lubrication and Lubricants Group IV Properties and Testing," October 1937, pps. 6–12.

[2] The Swiss turbine oil test is described in "Schweizerischer Verband für die Materialprüfungen der Technik" SVMT 17, July 12, 1928.

If desired, oxidation or corrosion inhibitors such as phenyl alpha naphthylamine, aromatic sulfur compounds, etc., may be added to the oils treated by my process further to increase their resistance against the sludge inducing influence of metals.

I claim as my invention:

1. In the process of producing stable hydrocarbon oils suitable for lubrication, the steps comprising treating a lubricating raffinate obtained by extracting a hydrocarbon oil with a naphthenic solvent which is substantially free of asphalt and resins with an amount of concentrated sulfuric acid sufficient to produce sludge and SO_2, separating the sludge to produce a substantially sludge-free oil containing SO_2, blowing the resulting sour oil with a gas which is substantially chemically inert under the conditions of the blowing to remove SO_2, further blowing the resulting SO_2-free oil with an oxygen containing gas at a temperature between 220° and 300° F. for a time sufficient only to substantially effect polymerization of unstable components of the lubricating oil, whereby the color of the oil is materially darkened, and contacting the darkened oil with an active bleaching clay to decolorize the oil.

2. In the process of producing turbine oils, the steps comprising treating a lubricating raffinate obtained by extracting a hydrocarbon oil with a naphthenic solvent which is substantially free of asphalt and resins and has a viscosity suitable for turbine oils with an amount of concentrated sulfuric acid sufficient to produce sludge and SO_2, separating the sludge to produce a substantially sludge-free oil containing SO_2, blowing the resulting sour oil with a gas which is substantially chemically inert under the conditions of the blowing to remove SO_2, further blowing the resulting SO_2-free oil with an oxygen containing gas at a temperature between 220° and 300° F. for a time sufficient only to substantially effect polymerization of unstable components of the lubricating oil, whereby the color of the oil is materially darkened, and contacting the darkened oil with an active bleaching clay to decolorize the oil.

3. The process of claim 1 in which the oil is a distillate oil.

4. The process of claim 2 in which the oil has a Saybolt Universal viscosity at 100° F. of 100–200 seconds.

5. In the process of producing a turbine oil, the steps comprising treating a lubricating raffinate distillate obtained by extracting a hydrocarbon oil with a naphthenic solvent having a viscosity suitable for turbine oils with 5 to 20 pounds concentrated sulfuric acid at a temperature between 50°–140° F., thereby producing soluble and insoluble sludge and SO_2, separating the insoluble sludge, treating the resulting sour oil containing dissolved sludge and SO_2 with a small amount of liquid water to hydrolyze soluble sludge, thereby precipitating same, separating the hydrolyzed sludge, blowing the sludge-free oil containing dissolved SO_2 with air at a temperature below 200° F. to remove SO_2, further blowing the SO_2-free oil with air at a temperature between 220°–300° F. for a time only sufficient to substantially polymerize unstable components of the oil whereby the color of the oil is darkened, and contacting the darkened oil with an active clay at a temperature below 100° F.

6. The process of claim 5 in which the sulfuric acid has a concentration of 95–100%.

7. The process of claim 5 in which the amount of water is ⅛% to 2% of the oil.

8. The process of claim 5 in which the temperature of blowing the SO_2-free oil is between 250°–270° F.

9. The process of claim 5 in which the time and temperature of blowing the SO_2-free oil is 8 to 20 hours at 250–270° F.

10. The process of claim 5 in which the clay is a naturally active percolation clay.

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