

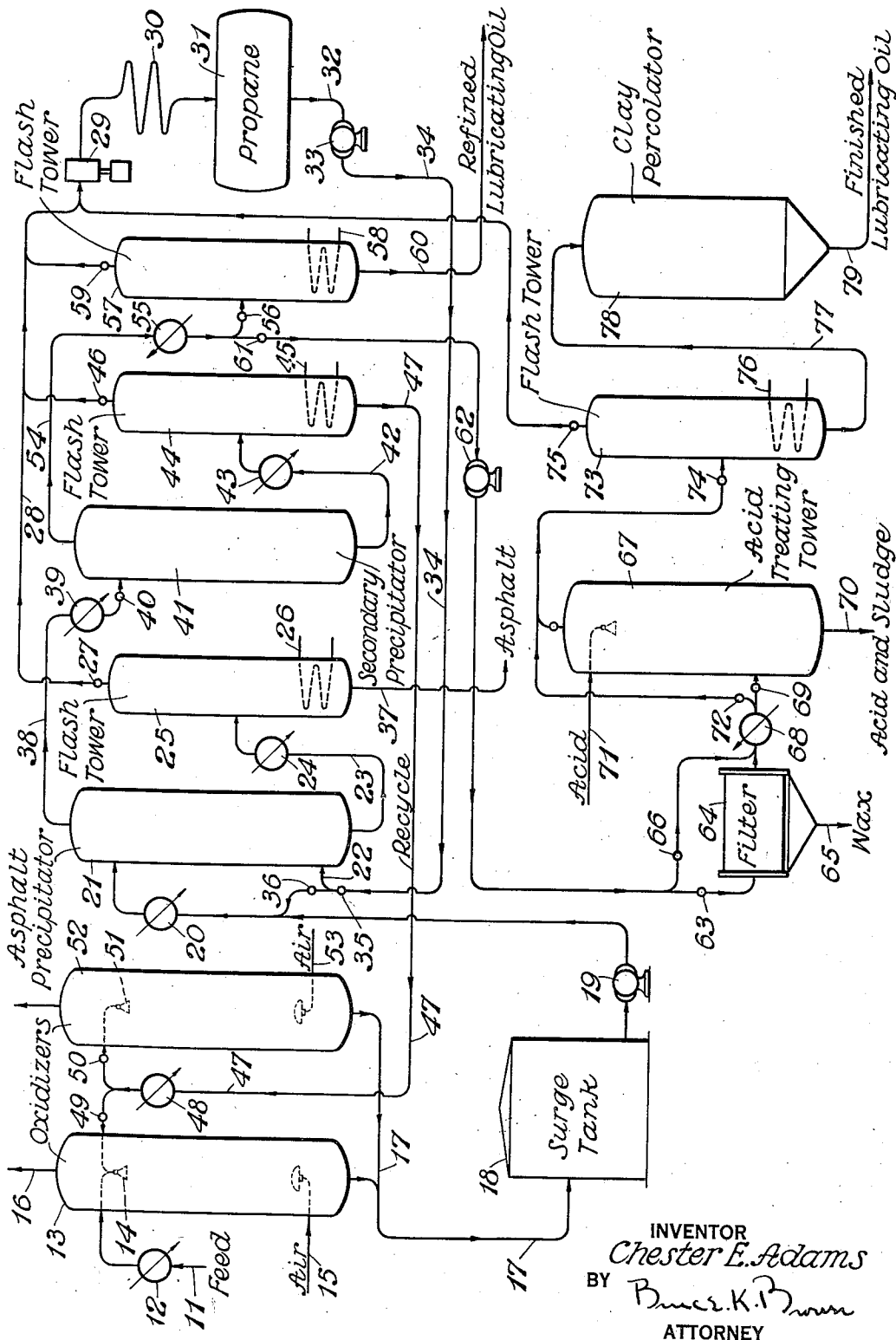
Feb. 16, 1937.

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2,070,567

LUBRICATING OIL REFINING

Filed May 10, 1935



UNITED STATES PATENT OFFICE

2,070,567

LUBRICATING OIL REFINING

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Application May 10, 1935, Serial No. 20,878

14 Claims. (Cl. 196—42)

This invention relates to the refining of lubricating oils and more specifically to the refining of lubricating oil stocks by oxidizing some of the constituents and then removing the oxidation products by treatment with a normally gaseous hydrocarbon such as propane preferably at a temperature in the vicinity of the critical temperature of the normally gaseous hydrocarbon. It also relates to the production of asphalt.

It is an object of my invention to provide an efficient and economical process for the production of lubricating oils having improved qualities with respect to temperature coefficient of viscosity, volatility, color, sludge stability, etc. It is also an object of my invention to provide an improved process for the manufacture of asphalt. Other and more detailed objects of my invention will become apparent as the description thereof proceeds.

It has found that when a lubricating oil stock is drastically oxidized many or most of its less desirable constituents are converted into oxidation products, while most of its more valuable constituents remain unoxidized. The oxidation method is therefore a valuable method of refining lubricating oil stocks provided only that efficient means can be found for the removal of the oxidation products. I have found that these oxidation products can be removed from the unoxidized hydrocarbons more completely and more efficiently by precipitation with propane or similar normally gaseous hydrocarbon at relatively high temperatures, i. e. at temperatures in the vicinity of the critical temperature of the normally gaseous hydrocarbon, than in any other known manner.

As compared for example with removal of the oxidation products with propane at relatively low temperatures, high temperature propane treatment gives an oil having a lower temperature coefficient of viscosity, a higher volatility, a lower carbon-forming tendency, and a better color.

My invention is applicable to any type of hydrocarbon lubricating oil stock since all such stocks are composed of various constituents which differ materially in the ease with which they can be oxidized and since in general the more readily oxidizable constituents are the less desirable constituents from the lubricating oil standpoint. Furthermore the oxidized products are quite uniformly less soluble in propane and similar normally gaseous hydrocarbons at high temperatures than the unoxidized hydrocarbons. My invention is, however, particularly applicable to

Mid-Continent and other mixed base lubricating oil stocks which contain large quantities of difficulty oxidizable relatively paraffinic hydrocarbons and which also contain considerable quantities of the less desirable and relatively readily oxidizable hydrocarbons of a relatively non-paraffinic nature.

In the oxidation step of my process I can use any oxidizing agent which will give selective oxidation of the relatively non-paraffinic hydrocarbons but I prefer to use air or other oxygen-containing gas. The temperature of the oxidation is subject to wide variation. In general, the desired oxidation can be accomplished at temperatures as low as 200° F., but I prefer to use temperatures at least as high as 250° F. and still more preferably, temperatures in the approximate range 300° F. to 400° F. in order to secure more rapid and efficient oxidation. Oxidation temperatures as high as 500° F. or even higher can be used but the oxidation obtained at these temperatures is somewhat less selective than that obtained by the use of lower temperatures. In any event the oxidation temperature should be below that at which substantial cracking occurs.

Various catalysts can also be used to expedite the oxidation reaction and to render it more selective. Ferric chloride is my preferred catalyst and it is particularly useful at temperatures of 250°–350° F. Quantities of catalyst of the order of magnitude of 1% of the weight of the lubricating oil stock are suitable. However, amounts of from 0.1% to 10% or more may be used.

The time of oxidation will depend upon the character of the stock, the character of the product desired, the oxidizing agent chosen, the presence or absence of a catalyst, the degree of intimacy with which the oxidizing agent is contacted with the stock and particularly the temperature of the material undergoing oxidation. Using air as the oxidizing agent in the absence of a catalyst and with intimate contact between the oxidizing agent and the stock being oxidized, the oxidation time at a temperature of between 300° F. and 400° F. may suitably be from 30 to 200 hours. At lower temperatures longer times will be required to obtain the same degree of oxidation, while at higher temperatures the time of contact need not be as long. In any event, the oxidation step of my process should produce drastic oxidation for the purpose of removing a substantial portion of the undesired constituents of low temperature coefficient of viscosity

and not merely superficial oxidation for color removal, improvement in sludge stability, removal of volatile materials, etc. I prefer, in general, that the oxidation be sufficiently drastic to convert a substantial amount of the constituents of low temperature coefficient of viscosity into oxidation products.

Defining temperature coefficient of viscosity in terms of the Dean and Davis viscosity index (Dean and Davis, Chemical and Metallurgical Engineering, volume 36, 1929, page 618) it may be said that the lubricating oil produced by the oxidation and propane (or other normally gaseous hydrocarbon) treatment steps of my process should have a viscosity index at least 10 and preferably at least 15 Dean and Davis units higher than that of the stock charged to my process.

The degree of oxidation to be effected in any case will depend somewhat on the nature of the stock used as well as on the characteristics of the product desired. For Pennsylvania lubricating oil stocks, the oxidation may suitably convert about 5% to about 10% or more of the soluble material in the stock into materials insoluble in propane or similar material under the conditions of my process. The degree of oxidation, similarly defined, for a Mid-Continent lubricating oil stock may suitably be from about 15% to about 30% or higher and for a Coastal lubricating oil stock from about 20% to about 40% or higher.

Following the oxidation step, the oxidized products together with the unoxidized portion of the stock is agitated or otherwise contacted with a normally gaseous hydrocarbon. I prefer to use propane in most cases. However, the use of ethane is sometimes advantageous, particularly when it is desired to produce a relatively volatile and nonviscous lubricating oil. Isobutane and normal butane can also be used, particularly in the manufacture of heavy lubricating oils. It is also possible to use the olefinic hydrocarbons corresponding to the foregoing paraffinic hydrocarbons but they are not as efficient. Mixtures of these various hydrocarbons can be used but I prefer to use a single relatively pure hydrocarbon. The quantity of normally gaseous hydrocarbon used may suitably range from 2 volumes of normally gaseous hydrocarbon per volume of material undergoing treatment up to 10 volumes or even more normally gaseous hydrocarbon per volume of material undergoing treatment. I prefer, however, to use from about 4 to 8 volumes of normally gaseous hydrocarbon per volume of material undergoing treatment.

The temperature used in the case of propane should be at least 125° F. and preferably at least 150° F. For other normally gaseous hydrocarbons, the temperature should have a similar relation to the critical temperature of the normally gaseous hydrocarbon and, in general, the minimum temperature of the normally gaseous hydrocarbon treatment should be about 80° F. below and preferably about 50° F. below the critical temperature of the light hydrocarbon used.

As to the upper limit of the temperature useful in this step of my process, I prefer to operate at a temperature at least 10° F. below the critical temperature of the normally gaseous hydrocarbon used. It is possible, however, to operate at the critical temperature or even considerably above the critical temperature. The critical temperature in the case of propane is approximately 204° F.

The pressure used in the normally gaseous hydrocarbon treatment step of my process should

preferably be sufficient to maintain the bulk of the propane or other normally gaseous hydrocarbon in the liquid state. In operating at temperatures above the critical temperature this is obviously impossible and in these cases the pressure should be sufficiently high to give a density of the order of magnitude of that which the same system would have in the liquid state in the vicinity of the critical conditions. Normally gaseous hydrocarbons when in the liquid state or when in the high pressure, high density condition referred to in the last sentence are referred to in the appended claims as "condensed".

Following the precipitation of oxidation products by the use of normally gaseous hydrocarbon and removal of the normally gaseous hydrocarbon from the unoxidized oil, other refining steps may and usually should be used. These subsequent refining steps are particularly useful in order to enhance the sludge stability and color of the finished lubricating oil. Acid treating, clay treating, solvent extraction and dewaxing are among the finishing steps which may suitably be used, individually or in combination. I prefer in general that these steps follow the normally gaseous hydrocarbon treatment but it is to be understood that some of them may precede the oxidation step and/or be interposed between the oxidation and normally gaseous hydrocarbon treatment steps without departing from the spirit of my invention.

I prefer to finish the oxidized and normally gaseous hydrocarbon treated oil by dewaxing, if necessary, followed by low temperature sulfuric acid treating, preferably in light hydrocarbon solution and/or clay contacting.

One particularly advantageous sequence of steps is to chill the solution of processed oil discharged from the high temperature separation step to a dewaxing temperature, for instance -40° F., remove the wax, and then treat with sulfuric acid preferably at a relatively low temperature, for instance 20° F., while still in normally gaseous hydrocarbon solution. This low temperature acid treating in normally gaseous hydrocarbon solution gives a finished oil of particularly good color.

Certain specific embodiments of my invention will be described in the following examples:

Example 1.—A Mid-Continent distillate having a viscosity of 107 seconds at 210° F. and a viscosity index of 69 was placed in a still and blown with air for 144 hours at 300° F. in the presence of 1% of its weight of hydrated ferric chloride. The material from the oxidation still was then placed in a bomb together with 5.7 times its volume of liquid propane. The temperature was raised to 160° F. The bomb, which was mounted on trunnions and equipped with side-draws, was rotated for a short time and then allowed to stand still whereupon the insoluble oxidation products settled to the bottom, the supernatant solution of unoxidized processed oil was drawn off through the appropriate side-draws and propane was flashed off. The processed oil was found to have a viscosity of 86.4 seconds Saybolt at 210° F. and a color of 2¼ (15% oil in 85% water white kerosene—Tag-Robinson method). The yield up to this point was 53%. This oil was then dewaxed, yielding an oil having a viscosity of 92.6 seconds Saybolt at 210° F. and a viscosity index of 83.4 (14.4 units higher than that of the stock). After treating with one-

half pound of 98% sulfuric acid per gallon of oil in hexane solution at 20° F., the finished oil had a viscosity of 82.2 seconds Saybolt at 210° F. and a viscosity index of 89.1.

5 *Examples II and III.*—A Mid-Continent distillate having a viscosity of 124 seconds Saybolt at 210° F. and a viscosity index of 65 was placed in a still and blown with air for 26 hours at 450–475° F. without a catalyst. The material from
10 the oxidation still was divided into two portions, each of which was treated with 5.7 times its volume of propane in the manner described above. The temperature of the propane treatment varied in the two cases and the results were as follows:

	Example II	Example III
Temperature of propane treatment.....	109° F.	187° F.
Characteristics of oil recovered following propane treatment:		
Viscosity at 210° F.....	100 sec.	85 sec.
Viscosity index.....	77	80
Color (15% oil in 85% water white kerosene—Tag-Robinson method).....	Black	3½ R.
Yield.....	67.7%	43.3%

25 It will be noted that although the treatment at the higher temperature (Example III) gave a somewhat lower yield, it gave an oil markedly superior to that produced by the lower temperature treatment (Example II). This superiority
30 included viscosity index, color and viscosity. The lower viscosity in Example III indicates a more volatile oil having lower carbon-forming tendencies.

35 Each of these oils was dewaxed and then percolated through clay without acid treatment. Both oils were percolated to a finished oil color of 3½–4 N. P. A. The oil of Example II gave a percolation yield of 75 gallons of oil per ton of clay while under identical conditions with the
40 same clay the oil of Example III gave a yield of 154 gallons per ton. This is another indication of the superiority of the higher temperature treatment.

45 This superiority is much more marked when compared with propane treatment at atmospheric or sub-atmospheric temperatures.

I will now proceed to outline a preferred method of operating my process. This method will be
50 described in conjunction with the accompanying drawing in the form of a flow diagram which forms a part of this specification and which shows conventionalized apparatus for carrying out my process.

55 Referring now more particularly to the drawing, the feed stock, which may for instance be the lubricating oil stock of any of the preceding examples, is introduced through line 11, heated to the desired temperature in heat exchanger 12 and then introduced into oxidizer 13 through a
60 downwardly directed spray 14. Oxidizer 13 may be of any desired type. In the form shown it is a counter-current tower which may suitably be provided with baffles not shown. Air, oxygen or other oxidizing agent is introduced into this tower through line 15 and ultimately passes out through
65 vent 16. This counter-current oxidation is preferred but it will be understood that a simple batch process can be used. Furthermore, a battery of these oxidizers 13 can be used in series in
70 order to increase the oxidation time.

The material from the oxidation step passes out of oxidizer 13 through line 17 into surge tank 18 from which it is pumped by pump 19 through
75 heater or cooler 20 into asphalt precipitator 21.

In precipitator 21 the material from the oxidation step is passed counter-current to propane or similar normally gaseous hydrocarbon which is introduced through line 22 in a manner hereafter to be described. The propane passes up
5 ward and dissolves the unoxidized constituents from the oxidation step. It may also dissolve some of the oxidized constituents. The insoluble material which passes out of precipitator 21 through
10 line 23 constitutes a superior asphalt (even though the original stock was completely asphalt free) and the characteristics of this asphalt can be closely controlled by controlling the degree of precipitation in precipitator 21. This in turn is
15 a function of the temperature and pressure existing in precipitator 21 and of the ratio of propane or other normally gaseous hydrocarbon to the material being treated. When operating in my preferred temperature and pressure range immediately below the critical conditions of the propane or other normally gaseous hydrocarbon the
20 amount of precipitation will vary directly with the temperature and indirectly with the pressure. When operating at atmospheric or sub-atmospheric temperatures, however, the amount of
25 precipitation will vary indirectly with the temperature and the pressure will have little effect on the degree of precipitation so long as it is sufficient to maintain liquid phase conditions.

At low temperatures the asphalt withdrawn
30 from the bottom of extractor 21 may be a plastic solid and require the use of a conveyor in the place of conduit 23.

By simple control of the aforementioned variables in precipitator 21 an asphalt of any desired specifications can be obtained. A batch precipitator or a multi-stage counter-current precipitator can, of course, be used.

The asphalt from the precipitator passes through a heater 24 (which may in many cases
40 be omitted) into a flash tower 25 which may if necessary be heated at its base by coil 26. Propane or other normally gaseous hydrocarbon passes overhead from the flash tower through
45 valve 27, line 28, compressor 29 and condenser 30 into storage tank 31 from which it may suitably be withdrawn for reuse through line 32, pump 33, line 34, valve 35 and line 22. A portion of this propane may also if desired be passed through
50 valve 36 and thereby introduced into precipitator 21 along with the material from the oxidation step in order to reduce the viscosity of that material.

The bottoms from flash tower 25 are withdrawn through line 37 and constitute the desired asphalt.

The soluble material from precipitator 21 passes
55 out from the precipitator at the top thereof through line 38 and heater or cooler 39 and (if desired) reduction valve 40 into a secondary precipitator 41. This secondary precipitator is operated under such conditions as to precipitate
60 any residual oxidized material or other undesirable material which was retained in solution in precipitator 21. Since precipitator 21 is operated to produce the desired type of asphalt it is impossible to remove all the constituents undesirable in a lubricating oil stock. If all these constituents were removed the asphalt would have
65 a high penetration and other undesirable properties. Thus, it is preferred to operate precipitator 21 under conditions adjusted with a view to producing the best possible asphalt and then to
70 operate secondary precipitator 41 under such conditions as to remove a further quantity of insoluble matter in order to produce a lubricating oil of the desired specifications. Further precipita-
75

tion in secondary precipitator 41 is obtained by control of the temperature, pressure and concentration variables as aforementioned. Thus when operating at temperatures immediately below the critical temperature, further precipitation can be obtained by raising the temperature or lowering the pressure. When operating at low temperatures on the other hand further precipitation can be obtained by lowering the temperature. These conditions can be obtained by control of heater or cooler 39 and/or reduction valve 40 and the degree of precipitation to be obtained in precipitator 41 is that necessary to produce a lubricating oil of the desired specifications.

The insoluble material from precipitator 41 passes out of the base thereof through line 42 and (if necessary) heater 43 into a flash tower 44 which may be heated at its base by heating coil 45. The propane or other normally gaseous hydrocarbon vapors pass overhead through valve 46 to the vapor recovery system hereinbefore described.

The material from the base of this tower is in general neither a good asphalt nor a good lubricating oil and it is preferred to recycle this material to the process for further oxidation whereby the bulk of it is converted into asphalt and any small amounts of desirable lubricating oil constituents contained in it will be returned to the process and ultimately find their way into the finished lubricating oil. The material from the base of flash tower 44 may be returned through line 47, heater 48 (which may often be omitted) and valve 49 into the original oxidizer 13. However, it is sometimes the case that this recycled stock will need rather different oxidation conditions than does the original feed and in this case the recycled stock may be introduced through valve 50 and spray 51 into a second oxidizer 52 supplied with air or other oxidizing agent near its base through line 53. In either case the material from the oxidation step finds its way into surge tank 18 and is returned to the process.

The soluble material from secondary precipitator 41, passes out of the top of the precipitator through line 54, is heated if required in heater 55 and passes through valve 56 into flash tower 57 which may suitably be heated at its base by heating coil 58. The propane or other normally gaseous hydrocarbon vapors from flash tower 57 pass overhead through valve 59 into the recovery system hereinbefore described and the refined lubricating oil passes out of the base of the tower through line 60. As previously mentioned this refined lubricating oil may be subjected to further refining steps such as dewaxing, acid treating, clay treating, etc.

I prefer, however, to conduct these further treating steps in the presence of the propane or other normally gaseous hydrocarbon. When operating in this manner valve 56 is closed and valve 61 is open. Heater 55 is replaced by a cooler or by a flash chamber wherein self-refrigeration is secured by evaporating a portion of the propane. The propane solution is then pumped by pump 62 through valve 63 and filter press 64. This filter press may be of any conventional type, either batch or continuous. Wax is removed through line 65. In general the temperature of the dewaxing step should be from -20°F. to -60°F. and this temperature may suitably be obtained by flashing off a portion but not all of the propane or other normally gaseous hydrocarbon.

If the oil used in the process does not contain wax, filter 64 may be by-passed by closing valve 63 and opening valve 66.

In either case the next step may suitably be an acid treating step which is shown as conducted in counter-current treating tower 67. The temperature of this acid treatment may suitably be as low as the dewaxing temperature or as high as 50°F. , but I find that highly superior results can be obtained by the use of relatively low temperatures (under about 50°F.) and by conducting the acid treating in solution in propane or other light hydrocarbon. The presence of the light hydrocarbon greatly improves the ease with which sludge can be withdrawn. The material from filter 64 or by-pass valve 66 may be heated if desired in heater 68 and then introduced into acid treating tower 67 through valve 69. The acid and sludge are removed through line 70 and may be recycled to the acid introduction line 71 or purified and recycled, but these steps are conventional and are therefore not shown. If acid treating is not required valve 69 can be closed and valve 72 opened. In either case the next step may suitably be the removal of propane or other normally gaseous hydrocarbon which may be accomplished in flash tower 73 provided with reduction valve 74, valve 75 (leading into the vapor recovery system) and heating coil 76. The oil from the base of flash tower 73 may then suitably be introduced through line 77 into clay percolator 78 from the base of which the finished lubricating oil is removed through line 79. Clay contacting may suitably be used in place of clay percolation and either step may be conducted in the presence of the propane or other normally gaseous hydrocarbon rather than subsequent to its removal.

While I have described my invention in connection with certain specific embodiments thereof it is to be understood that numerous variations will occur to those skilled in the art and I do not intend to be limited to my specific embodiments but only to the broadest valid scope of the appended claims in which I have defined the novel features of my invention.

I claim:

1. A method of refining a hydrocarbon lubricating oil stock containing constituents of relatively high viscosity index and constituents of relatively low viscosity index, which comprises contacting said stock with a gas containing free oxygen under conditions corresponding in effect to an oxidation temperature of about 300°F. to about 400°F. and an oxidation time of about 30 hours to about 200 hours whereby a substantial portion of said constituents of relatively low viscosity index are converted into oxidation products insoluble in a light hydrocarbon of the class hereinafter defined and under the conditions hereinafter defined, whereby said constituents of relatively high viscosity index are not converted into oxidation products and whereby the materials resulting from said oxidation step which are soluble in a light hydrocarbon of the class hereinafter defined under the conditions hereinafter defined have a viscosity index at least about 10 Dean and Davis units higher than the viscosity index of said stock, contacting the material from the aforementioned oxidation step with from about two to about ten times its own volume of a liquefied light hydrocarbon of the class consisting of ethane, propane, isobutane and butane at a temperature below the critical temperature of said light hydrocarbon and within about 80°F.

of the critical temperature of said light hydrocarbon whereby said unoxidized constituents are dissolved and said oxidized constituents are precipitated, and removing said oxidized constituents.

2. A method according to claim 1 in which said liquefied light hydrocarbon is propane.

3. A method according to claim 1 in which the step of contacting said stock with a gas containing free oxygen is carried out in the presence of ferric chloride.

4. A method according to claim 1 in which the contacting step for precipitating oxidized constituents is conducted at a temperature below, but not more than about 50° F. below, the critical temperature of said liquefied light gaseous hydrocarbon.

5. A method for the refining of a lubricating oil stock containing constituents of relatively high viscosity index and constituents of relatively low viscosity index which comprises contacting said stock with a gas containing free oxygen at an elevated temperature in the presence of ferric chloride for a period of time sufficient to convert a substantial quantity of said constituents of relatively low viscosity index into oxidation products without converting said constituents of relatively high viscosity index into oxidation products, the oxidation being sufficiently drastic to raise the viscosity index of the unconverted part of the stock at least ten Dean and Davis units above the viscosity index of the stock, contacting the material from the aforesaid oxidation step with from about two to about ten times its own volume of a liquefied hydrocarbon selected from the group consisting of ethane, propane, isobutane, normal butane and the corresponding olefinic hydrocarbons at a temperature between the critical temperature of said hydrocarbon and a temperature about 100° F. below the critical temperature of said hydrocarbon whereby said oxidized constituents are precipitated, and removing said oxidized constituents.

6. A method according to claim 5 in which the oxidation temperature is about 250° F. to about 350° F.

7. A method for the refining of a lubricating oil stock and for the production of asphalt from non-asphaltic constituents of said stock, comprising drastically oxidizing said stock, contacting the material from the oxidation step with a condensed normally gaseous hydrocarbon to precipitate an asphalt and to dissolve the remaining constituents of said material, removing said precipitated asphalt, precipitating a further quantity of material from the solution of said remain-

ing constituents without precipitating the desired lubricating oil constituents, removing the material thus precipitated, re-oxidizing said last-mentioned material, recycling the products of the re-oxidation step to said contacting step, and removing the residual normally gaseous hydrocarbon from said desired lubricating oil constituents.

8. A method according to claim 7 in which at least one of said precipitation steps is conducted at a temperature within about 80° F. of the critical temperature of said normally gaseous hydrocarbon.

9. A method according to claim 7 in which at least one of said precipitation steps is conducted at a temperature at least about 10° F. below, and not more than about 80° F. below, the critical temperature of said normally gaseous hydrocarbon.

10. A method according to claim 7 in which the second precipitation step is conducted at a temperature below, but not more than about 50° F. below, the critical temperature of said normally gaseous hydrocarbon.

11. A method for the refining of a lubricating oil stock and for the production of asphalt from non-asphaltic constituents of said stock, comprising drastically oxidizing said stock, contacting the material from the oxidation step with a condensed normally gaseous hydrocarbon to precipitate an asphalt and to dissolve the remaining constituents of said material, removing said precipitated asphalt, precipitating a further quantity of material from the solution of said remaining constituents without precipitating the desired lubricating oil constituents, removing the material thus precipitated, recycling said last-mentioned material to said drastic oxidation step, and removing the residual normally gaseous hydrocarbon from said desired lubricating oil constituents.

12. A method according to claim 11 in which at least one of said precipitation steps is conducted at a temperature within about 80° F. of the critical temperature of said normally gaseous hydrocarbon.

13. A method according to claim 11 in which at least one of said precipitation steps is conducted at a temperature at least about 10° F. below, and not more than about 80° F. below, the critical temperature of said normally gaseous hydrocarbon.

14. A method according to claim 11 in which the second precipitation step is conducted at a temperature below, but not more than about 50° F. below, the critical temperature of said normally gaseous hydrocarbon.

CHESTER E. ADAMS.

CERTIFICATE OF CORRECTION.

Patent No. 2,070,567.

February 16, 1937

CHESTER E. ADAMS

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 20, after the word "has" insert been; and second column, line 2-3, for "difficulty" read difficultly; page 4, first column, line 10, for "condtions" read conditions; and second column, line 40, for "cetrain" read certain; page 5, first column, line 16, claim 4, strike out "gaseous"; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 30th day of March, A. D. 1937.

(Seal)

Henry Van Arsdale
Acting Commissioner of Patents.