Patented May 24, 1932

1,859,514

UNITED STATES PATENT OFFICE

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MANUFACTURING OF LUBRICATING OIL

No Drawing. Application filed June 6, 1927. Serial No. 197,011.

This invention relates to improvements in the manufacturing and refining of lubricating oil. The invention relates more particularly to an improved method of treating inferior grades of lubricating oil or petroleum oil fractions from which lubricating oils are to be obtained for the production of an improved lubricating oil product therefrom. This application is in part a continuation of application 709,682 filed April 28, 1924.

According to the present invention lubricating oils of inferior grade and low viscosity or petroleum oil fractions from which lubricating oils are to be obtained are subjected to a digesting treatment at elevated temperatures and pressures to produce an improved lubricating oil of higher viscosity and good lubricating properties.

In the refining of petroleum oil for the production of lubricating oil therefrom, the oil is commonly subjected to distillation with steam or under a reduced vapor pressure, subatmospheric, in order to avoid any possibility of cracking of the lubricating oil constituents, and it is generally accepted that a lubricating oil or a distillate from which a lubricating oil is to be produced should not be subjected to cracking temperatures and pressures, if a lubricating oil of good lubricating properties is to be obtained.

In some cases the oils from which the lubricating oils are to be obtained are subjected to a treatment to facilitate the removal of wax, but hitherto such treatment has been confined to such treatment of the wax as would convert it to a so-called crystalline form and the use of temperatures and pressures that might produce cracking of the lubricating oil constituents has been carefully avoided.

As distinguished from such commonly practiced refining methods, the process of the present invention involves the digestion of the lubricating oil constituents at high temperatures and pressures. The reaction is apparently a cracking of the heavy oils and a recombining of the condensates of unsaturated constituents to form heavier hydrocarbons and a very small proportion of lighter hydrocarbons.

The lubricating oil or distillate may be subjected to the digesting treatment prior to removal of wax therefrom or the wax may be first removed in the crystalline form by pressing or in the amorphous form by centrifuging or cold settling, and the wax free oil subsequently subjected to the digestion treatment. Where the digestion treatment is carried out prior to the removal of wax substantially no conversion of the crystalline wax into lubricating oil character constituents occurs, though a considerable increase in the viscous bodies formed by the conversion of the remainder of the oil may be noted. It is accordingly preferable to remove the wax prior to the digestion treatment because of the tendency of these constituents to undergo cracking with the formation of low viscosity and low boiling point constituents at the temperatures employed and the greater difficulty encountered in the separation of the unconverted wax from the more viscous oil formed during the digestion treatment. Following the digestion treatment the treated oil may be reduced by fractional distillation with or without steam or at reduced pressure to give a product having the viscosity and flash point of the desired lubricating oil product and to remove the small quantity of lighter constituents formed during the digesting operation.

The temperature to which the oil is heated, as well as the length of time during which the temperature and pressure are maintained, will vary somewhat with different oils and with the characteristics of the product it is desired to produce. In general, the higher the temperature and the greater the length of time, within certain limits, the greater the proportion of viscous bodies formed.

The oil which has been subjected to the di-

gesting operation may advantageously be given a suitable chemical treatment, for example, agitation with sulphuric acid, settling and withdrawing the sludge formed followed by neutralization with lye or treatment with an absorbent or filtering material, to remove the more unstable, unsaturated constituents and heavy asphaltic constituents contained in the oil treated or formed during the digesting operation. In the treatment of an oil containing a large percentage of asphaltic constituents the digesting operation may be preceded by treatment with sulphuric acid. When the desired lubricating oil fraction which has been subjected to the digesting operation is to be obtained as an overhead distillate from a subsequent fractional distillation, such subsequent distillation may advantageously be carried out over lye, the asphaltic bodies being held with the lye and a clean oil resulting.

According to one method of carrying out the process of the invention an oil containing constituents suitable as components of a lubricating fraction, for example, pressed distillate from which the crystalline wax has been removed, raw wax distillate, reduced crude, or a practically finished low viscosity lubricating oil is placed in an autoclave and gradually heated to a temperature of about 640 to 790 degrees F. and maintained at that temperature for the requisite period. The pressure may advantageously be maintained at from 125 lbs. to 200 lbs. per square inch. The pressure in any event is maintained sufficiently high to prevent substantial vaporization.

When the oil to be treated contains a small percentage of lighter constituents the use of excessive pressures may be avoided by taking off these lighter constituents as drips while the autoclave is being brought to the desired temperature. Similarly, the pressure may be prevented from increasing excessively during the digesting operation, due to the formation of a small quantity of low boiling constituents, by taking off drips at intervals during the digesting operation.

The time during which the temperature and pressure conditions necessary for the conversion of the lighter constituents to heavier and more viscous oils may be maintained will vary with the oil treated, the degree of conversion desired and with the temperatures employed, a longer time being required to secure the same amount of conversion at a lower temperature. From 4 to 12 hours has been found to give very satisfactory results though a slight amount of additional conversion may be obtained by continuing the digesting operation for a somewhat longer period. Tests in which the digesting treatment was continued for 24 hours indicated a slight increase in the yield of extremely viscous bodies but a decrease in the yield of lubricating distillates of slightly lower viscosity as compared to the yields obtained in a similar treatment of 12 hours' duration.

Subsequent to the digesting operation the oil may be given suitable chemical treatment and redistilled or reduced, the final product being used alone or blended with other finished lubricating oils, or the product from the digesting operation may be blended with other unfinished lubricating oil stocks and the mixture subsequently treated as required.

The apparatus that can be used in carrying out the process of the invention varies. An ordinary shell still can be used, provided it is suitably heated so that over-heating of the charge or any part thereof is avoided. A tube still such as is employed in commercial cracking operations for the production of gasoline or pressure distillate from heavy hydrocarbon oils in which oil is circulated through heating tubes, preferably by mechanical circulation so that danger of local overheating of the oil passing through the tubes is positively avoided, may also be advantageously employed.

The process of the invention will be further described in connection with the following specific examples which are given to illustrate the effect of varying temperatures, pressures, character of oil treated and duration of run, but it is intended and will be understood that the process of the invention is merely illustrated thereby and not limited thereto. The viscosities in the following examples are the values as determined by the Saybolt universal viscosimeter:

Example 1.—Pressed distillate from a mid-continent crude having a gravity of 28.8 degrees Baumé and viscosity of 66 at 100 degrees F. was charged to an autoclave and gradually heated to a temperature of 700 degrees. During the preliminary heating 5% of the charge was taken off as drips. The autoclave was maintained at a pressure of 180 pounds per square inch for 4 hours during which time the temperature varied from 680 to 790 degrees F. The autoclaved stock was then treated with 10 pounds per barrel of 66 degree Baumé sulphuric acid, the sludge settled and withdrawn and the settled oil neutralized with lye. The treated oil was then distilled over lye, the distillate being separated in 4% cuts from which various test distillates were made by blending. The fractional distillation was carried down to 5% lye bottoms.

The various test distillates were made by blending fractions from the above distillation, starting with the heaviest cut or fraction and adding successively lighter cuts or fractions until an oil of the desired viscosity was obtained. In obtaining a 100 viscosity at 100 degrees F. fraction, however, 7½% of the heaviest distillate was omitted. The

test distillates were blown with steam to remove the odor and then blown bright with air.

Raw pressed distillate was similarly fractionated and corresponding test distillates made by blending the fractions obtained.

Results of tests of the samples obtained from the autoclaved stock and from the raw pressed oil are tabulated below in the columns marked "A" and "B" respectively:

Grade	100 vis.		180 vis.		235 vis.		285 vis.		500 vis.
	A	B	A	B	A	B	A	B	A
% stock	37.1	−59.0	32.7	−24.0	26.5	−16.0	22.0	−11.0	13.2
Gravity °B	24.0	−25.7	22.0	−23.9	20.8	−23.3	19.8	−22.9	19.3
Flash °F	360	−360	375	−400	395	−405	400	−410	425
Fire °F	415	−420	455	−480	465	−490	480	−500	510
Vis./100° F	109	−108	186	−190	238	−235	284	−275	499
Vis./210° F	40	−40	45	−45	47	−47	49	−28.5	57
Pour °F	20	−20	15	−20	15	−20	15	−20	20
Carbon res	.037	−.016	.187	−.034	.185	−.045	.190	−.086	.45%
Sulphur	.043	−.44	.49	−.51	.53	−.54	.55	−.56	.57%

No fraction comparable to the 500 viscosity distillate was obtained from the raw pressed oil.

The effect of increasing the length of the digesting period and of decreasing pressure are illustrated by the following example:

Example 2.—A pressed oil from a mid-continent crude having a gravity of 28.6 degrees Baumé and viscosity of 66 at 100 degrees F. was treated in an autoclave at 125 lbs. pressure for a period of 12 hours during which time the temperature varied between 715 and 750 degrees F., 5% of the charge was taken off as drips during the initial heating period. The autoclaved stock was then treated with 10 lbs. per barrel of 66 degrees Baumé sulphuric acid, the sludge settled and withdrawn and the settled oil neutralized with lye. The autoclaved and acid treated oil was then fractionally distilled over lye and portions of the cuts obtained thereby blended to give the following test distillates which were steamed to remove the odor and then blown bright with air:

	100 vis.	180 vis.	235 vis.	285 vis.	500 vis.
% stock	39.2	36.7	29.1	25.0	15.2
Gravity	34.1	21.8	20.9	20.3	18.5
Vis./100° F	108	186	236	284	509
Vis./210° F	40.0	45.0	47.0	49.0	58

Comparison of the test distillates obtained in Examples 1 and 2 indicate that a slightly higher yield of viscous constituents was obtained as a result of the longer period of digestion even though at somewhat reduced temperatures and pressures.

Comparison of Examples 3 and 4 which follow illustrates the effect of excessively prolonging the digestion period.

Example 3.—A light lubricating oil distillate from a mid-continent crude having a gravity of 26.7 degrees B. and a viscosity of 89 at 100 degrees F. was charged to an autoclave and maintained at a pressure of 125 pounds per square inch for 12 hours during which time the temperature varied from 755 degrees F. at the start to 640 degrees F. at the close. 5% of the charge was taken off as drips at the start of the run.

The autoclaved oil was then treated with 10 pounds per barrel of 66 degree B. sulphuric acid, the sludge allowed to settle and withdrawn and the settled oil neutralized with lye.

The autoclaved and acid treated stock was fractionally distilled leaving 5% bottoms. The distillate was separated into 5% cuts and these cuts or fractions blended to obtain the desired test distillates. The test distillates were given a fine earth treatment to bring them to type colors. A portion of the blank stock was reduced to obtain a 100 viscosity oil. Results of tests on the reduced blank stock and the autoclaved test distillates are given below:

	100 vis., blank	100 vis., autoclaved	180 vis., autoclaved
% stock	60	69.5	29.0
Gravity	26.3	25.4	23.2
Vis./100° F	102	104	191
Vis./210° F	40	40	45.5

Fractional distillation of the treated and autoclaved stock and of the original lubricating oil distillate were both continued until 5% of the charge remained as still bottoms. The viscosities of the heaviest fraction obtained as distillate in each case comprising 5% of the charge were found to be 564 at 100 degrees F. in the distillate from the autoclaved stock as against 181 at 100 degrees F. in the distillate from the blank stock.

Example 4.—A light lubricating oil distillate from a mid-continent crude having a gravity of 28.9 degrees B. and viscosity of 62.5 at 100 degrees F. was charged to an autoclave and maintained at a pressure of 125 pounds per square inch for a period of 24 hours during which time the temperature varied between 632 and 795 degrees F. 2½% drips were taken off at the end of 6, 12 and 18 hours to prevent excessive rise in pressure.

The autoclaved oil was then treated with 10 pounds per barrel of 66 degree Baumé sulphuric acid. The autoclaved and treated oil was then fractionally distilled over lye and the various cuts obtained blended to give test distillates of the desired viscosity. The quantity of the original distillate was reduced to give an oil of approximately 75 viscosity at 100 degrees F. Results of tests on the reduced blank stock and the autoclaved distillates are given below:

	75 vis., reduced oil-blank	75 vis., autoclaved	100 vis., autoclaved	180 vis., autoclaved	235 vis., autoclaved
% stock	60.0	57.0	35.0	17.1	10.7
Gravity	28.0	35.4	23.5	21.0	20.0
Vis./100° F	74.0	75.0	104.5	185	235
Vis./210° F	38.0	38.0	40.0	45	48

The heaviest fraction of the autoclaved oil comprising 5% of the still charge was found to have a viscosity of 653 at 100 degrees F. while the same fraction from the untreated distillate had a viscosity of only 127 at 100 degrees F. Comparison of the results obtained in Examples 3 and 4 indicates that the longer period of digestion causes the conversion of a small quantity of the original distillate to a higher viscosity oil than that obtained in a digesting operation of shorter duration, but yields a smaller quantity of lubricating oil distillates having but slightly lower viscosities.

The following example illustrates the effect of increased pressure in the treatment of reduced crudes in accordance with the process of the invention and also the effect of acid treating the charging stock prior to the digesting operation.

Example 5.—The charging stock was prepared by reducing a mid-continent crude 53% being taken off as an overhead distillate. The bottoms comprising 46% and having a gravity of 30.3 degrees Bé. was used as charging stock, 1% being lost as fixed gas.

A. A portion of the reduced crude was charged to an autoclave and maintained at a pressure of 125 pounds for a period of twelve hours during which time the temperature varied from 660 to 710 degrees F. 8½% of the charge was taken off as drips at the start of the run. The autoclaved stock was then treated with 20 pounds per barrel of 66 degree B. sulphuric acid, the sludge settled and withdrawn and the settled oil neutralized with lye. The autoclaved and acid treated oil was fractionally distilled 76.7% of the still charge being taken off as an overhead distillate. The bottoms comprising 17.6% of the original autoclave charge had a viscosity of 154 at 210 degrees F. and a gravity of 22.0 degrees B. This highly viscous oil was of a very dark green color and gave a carbon residue of 6.14% as determined by the Conradson method.

B. A portion of the same charging stock was treated in an autoclave at 200 pounds pressure for 12 hours during which time the temperature was maintained between 640 and 750 degrees F. No drips were removed. The autoclaved oil was treated with 20 pounds per barrel of 66 degree B. sulphuric acid, the sludge settled and withdrawn and the settled oil neutralized with lye. The autoclaved and acid treated stock was reduced by fractional distillation 73% being taken off as overhead distillate. The reduced oil comprising 22.6% of the autoclave charge was of a very dark green color and had a viscosity of 160 at 120 degrees F. and a gravity of 23.6 degrees B. An appreciable increase in the yield of highly viscous oil being obtained as a result of the higher pressure employed during the digesting operation.

C. A quantity of the reduced crude similar to the original autoclave charge in the two preceding examples was treated with 10 pounds per barrel of 66 degree B. sulphuric acid, the sludge settled and withdrawn and the settled oil neutralized with lye. The acid treated oil was then charged to an autoclave and heated for 12 hours at a pressure of 125 pounds per square inch during which time the temperature varied between 640 and 710 degrees F. No drips were taken off. The autoclaved stock was then treated with 15 pounds per barrel of 66 degree B. sulphuric acid and the treated and autoclaved stock reduced by fractional distillation, 77% of the still charge being removed as an overhead distillate. The still bottoms, comprising 19.8% of the original reduced crude charging stock was of a very dark green color having a gravity of 23.9 degrees B. and a viscosity of 146 at 210 degrees F. and showed a carbon residue of 4.128% as determined by the Conradson method. An appreciable decrease in carbon residue will be noted where the preliminary acid treatment was given prior to the digesting operation.

Example 6.—A lubricating oil distillate prepared from a Gulf Coast or asphalt base crude was treated in an autoclave at a pressure varying between 180 and 200 pounds per square inch for a period of 4 hours during which the temperature varied from 690 to 750 degrees F. No drips were taken off. Samples of the autoclaved and raw stocks were treated with 15 pounds per barrel of 66 degree B. sulphuric acid and the treated stock fractionally distilled to remove the lighter constituents and obtain a lubricating oil fraction of 235 viscosity at 100 degrees F. These distillates were then filtered through half their volumes of tempered Olmstead earth of 16/30 mesh. Comparative tests of the

finished lubricating oil distillates from the blank and autoclaved stocks are given below:

	Blank distillate	Autoclaved distillate
% of original lubricating distillate	57.6	47.4
Gravity °Baumé	19.9	17.8
Vis. at 100° F	246	240

The autoclaved stock from the above treatment, as well as that in each of the previous examples, was characterized by a bright green bloom whereas a similar oil finished in the regular way has a blue bloom. The yield of viscous bodies, however, is apparently not increased by the autoclave treatment of purely asphalt base oils.

Example 7.—A pressed oil distillate from a mid-continent crude having a gravity of 28.4 degrees Baumé and viscosity of 72 at 100 degrees F. was treated in an autoclave at a pressure of 150 to 170 pounds per square inch for a period of 4 hours during which the temperature varied between 650 and 735 degrees F. The autoclaved stock was treated with 10 pounds per barrel of 66 degree Baumé sulphuric acid, the sludge settled and withdrawn and the settled oil neutralized with lye. The autoclaved and acid treated stock and a sample of the original pressed distillate were reduced to obtain lubricating oil fractions of the desired viscosity. Results of tests on the reduced autoclaved stock and on the corresponding fractions from the original pressed distillate are tabulated below in columns "A" and "B", respectively:

	235 vis.		275 vis.		500 vis.
	A	B	A	B	A
% stock	41.3	26.8	39.0	23.5	22.7
Gravity	21.7	23.5	21.4	23.2	20.7
Viscosity	267	270	294	300	565

No oils, corresponding to the 500 viscosity fraction were obtained by reduction of the original pressed distillate.

Example 8.—To produce a red lubricating oil similar to that known to the trade as "Queen's Red", the properties of a representative sample of which are given below, by the improved process of the invention a pressed oil from a mid-continent crude was charged to an autoclave and heated for 12 hours at a temperature varying between 710 and 720 degrees F., and at a pressure of 125 pounds per square inch. 5% of the charge was taken off as drips at the opening of the run to establish constant pressure conditions. The autoclaved stock was then treated with 10 pounds per barrel of 66 degree B. sulphuric acid, and the sludge settled and withdrawn. The autoclaved and acid treated stock was redistilled over lye, 3% of the charge being added as 30 degrees Baumé lye. 6.5% of the charge was separately collected as gas oil and 88.5 as red oil stock, 5% remaining in the still as lye bottoms. The red oil stock was then reduced, 74.9% being removed as an overhead distillate suitable as a light lubricating oil stock and the bottoms comprising 19.2% of the original autoclaved charge, bleached by digestion with 2% by weight of fine fuller's earth of 200 mesh and up. Comparative results of tests on the finished autoclaved oil and on the typical example of "Queen's Red" oil are given below:

	Queen's red	Autoclaved red oil
Gravity °B	24.0	21.3
Flash	430	420
Fire	500	505
Vis./100° F	379	384
Vis./210° F	54	55
Pour	50	20
Color	Dark red.	Dark red.

Example 9.—A raw wax distillate having a gravity of 30.3 B. and pour of 70 degrees F. was treated in an autoclave for 12 hours at a pressure of 125 pounds and at temperatures varying from 640 to 740 degrees F. 10% of the charge was removed as drips during the fore part of the run to establish constant pressure conditions. The autoclaved product was treated with 12 pounds per barrel of 66 degree B. sulphuric acid, the sludge settled and withdrawn and the settled oil neutralized with lye. The autoclaved and acid treated stock was fractionally distilled over lye, the distillate being separately collected in 5% cuts. The viscosities and pour tests of the various fractions are given below:

Cut	Gravity	Vis. at 100° F.	Pour
1	43.0		0
2	38.8		0
3	35.8		5
4	33.6	40	15
5	32.3	44.5	25
6	31.2	49.5	35
7	30.4	56	45
8	29.7	61	50
9	29.2	68	55
10	28.6	76.5	60
11	28.1	88	65
12	27.4	109	70
13	27.0	129	75
14	26.2	162	80
15	25.4	201	80
16	24.4	273	85
17	23.3	55.5 at 210	90
18	22.5	67	95
19	19.0	107	95

The high pour tests of the heavier fractions show that practically no conversion of the crystalline wax into high viscosity lubricating oils was caused by the autoclave treatment. A substantial increase in viscous bodies was, however, produced by conversion of the lighter constituents in the raw distillate as a result of the autoclave treatment.

The improved high viscosity lubricating oils produced by the practice of the invention are characterized by the relatively higher specific gravity (lower Baumé gravity) for an oil of a given viscosity. The degree of saturation as indicated by the iodine number is less for the heavier fractions of the autoclave treated stock than for the lighter fractions. This characteristic is the exact reverse of the conditions obtained with pressure treatment where the products of reaction are released as fast as formed. Lubricating oils produced by the improved process of the present invention are also more stable and less readily decomposed at the temperatures encountered in the lubrication of internal combustion engines.

The invention is capable of numerous modifications as will be apparent from the variety of the foregoing examples which have been given to illustrate certain preferred applications, but the scope of the invention is set forth in the following claims:

I claim:

1. The improvement in the manufacturing and refining of lubricating oils which comprises subjecting a petroleum oil containing a lubricating oil fraction to a digestion treatment at a temperature of from 640 to 790 degrees F. from 4 to 12 hours at the pressure necessary to prevent substantial vaporization of the lubricating oil constituents.

2. The improvement in the manufacturing and refining of lubricating oil which comprises digesting a petroleum oil containing members of the paraffine series suitable as components of lubricating oil at a temperature of 640 to 790 degrees F. for from 4 to 12 hours, and maintaining on the oil during the digesting operation the pressure necessary to prevent substantial vaporization of the lubricating oil constituents to increase the yield of high viscosity lubricating oil constituents.

3. The method of treating petroleum oil containing lubricating oil constituents to increase their viscosity comprising digesting the oil from 4 to 12 hours at temperatures between 640 and 790 degrees F. and at pressures upward of about 125 pounds per square inch and sufficient to prevent substantial vaporization of the lubrication oil constituents, treating the digested oil with sulphuric acid to remove the more unstable, unsaturated hydrocarbons and subsequently fractionally distilling the treated oils to obtain the desired lubricating oil fraction.

4. The method of treating petroleum oils containing lubricating oil constituents to increase their viscosity comprising heating a charge of the oil in an autoclave to a temperature in excess of 640 degrees F. removing the lighter constituents vaporized during the preliminary operation to establish constant pressure conditions and maintaining a temperature between 640 to 790 degrees F. and the pressure necessary to prevent substantial vaporization of the lubricating oil constituents at the temperature employed for a period of 4 to 12 hours on the remainder of the charge and subsequently treating the digested oil to remove therefrom the lighter oils and the more unstable unsaturated constituents formed during the digesting operation.

5. The improvement in the manufacturing and refining of lubricating oils which comprises subjecting a petroleum oil containing a lubricating oil fraction to a digestion treatment for from 4 to 24 hours at a temperature of from 640 to 790° F. and a pressure upwards of about 125 pounds and sufficient to prevent substantial vaporization of the lubricating oil fraction.

6. The improvement in the manufacturing and refining of lubricating oils which comprises treating a petroleum oil containing constituents suitable as components of a lubricating oil fraction to remove the wax contained therein and subsequently digesting the wax-free oil from 4 to 24 hours at temperatures between 640 to 790° F. under the pressure necessary to prevent substantial vaporization of the lubricating oil constituents to increase their viscosity.

7. The improvement in the manufacturing and refining of lubricating oils which comprises subjecting a petroleum oil containing a lubricating oil fraction to a digestion treatment for from 4 to 24 hours at a temperature of from 640 to 790° F. at the pressure necessary to prevent substantial vaporization of the lubricating oil constituents, treating the digested oil with sulphuric acid and subsequently distilling the treated oil over lye.

8. The improvement in the manufacturing and refining of lubricating oils which comprises treating an oil containing lubricating oil constituents with sulphuric acid and subsequently digesting the treated oil for from 4 to 24 hours at a temperature of 640 to 790° F. at the pressure necessary to prevent substantial vaporization of the lubricating oil constituents.

In witness whereof, I have subscribed my name.

EDWARD W. ISOM.

CERTIFICATE OF CORRECTION.

Patent No. 1,859,514. May 24, 1932.

EDWARD W. ISOM.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, line 82, for the numeral "120" read 210; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 12th day of July, A. D. 1932.

(Seal)

M. J. Moore,
Acting Commissioner of Patents.