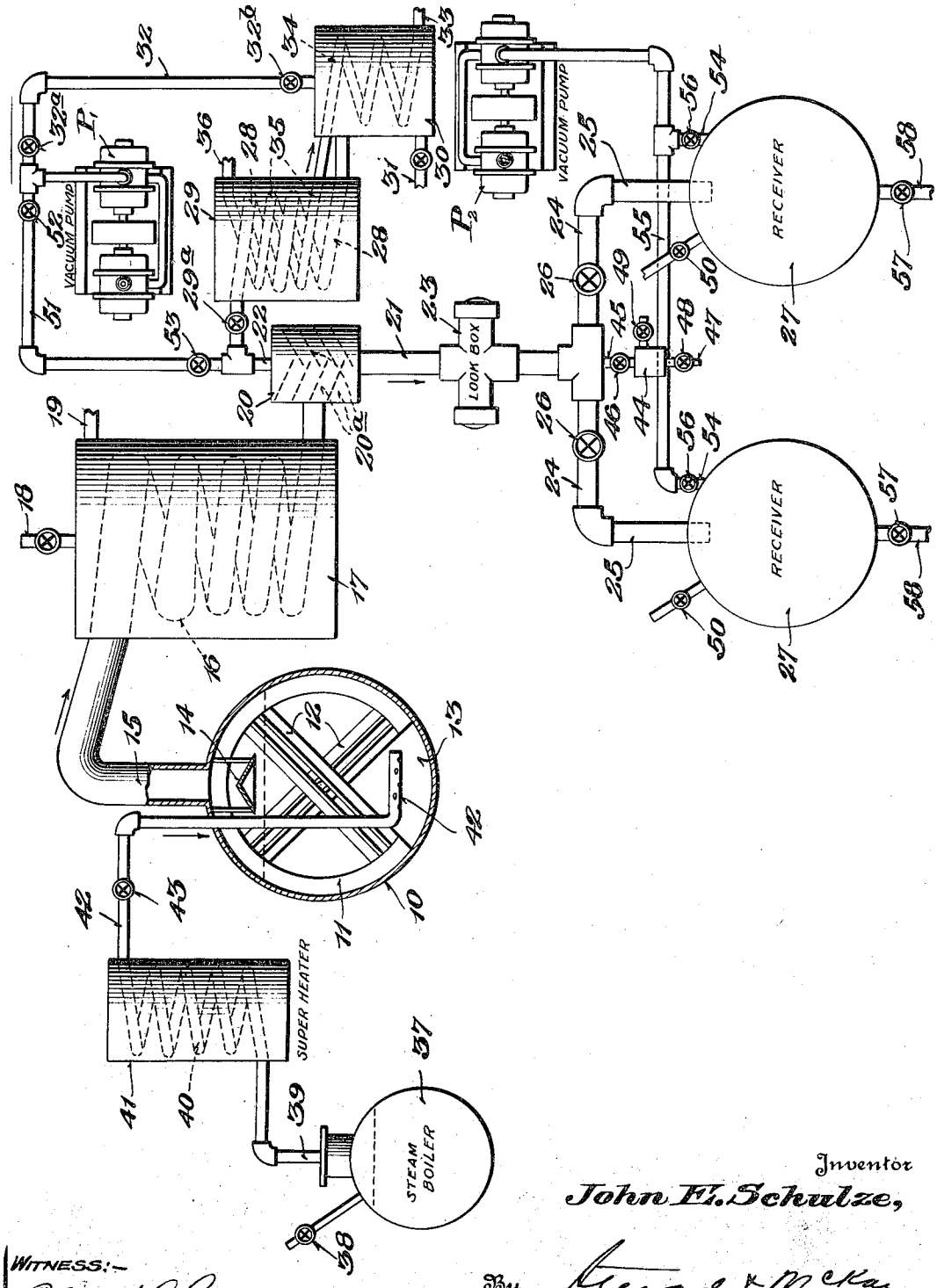
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ART OF OIL DISTILLATION

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UNITED STATES PATENT OFFICE.

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ART OF OIL DISTILLATION.

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To all whom it may concern:

Be it known that I, JOHN E. SCHULZE, a citizen of the United States, residing at Chicago, county of Cook, State of Illinois, have invented certain new and useful Improvements in the Art of Oil Distillation; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to art of oil distillation; and it relates more particularly to distillation of mineral oils, such as petroleum, shale oil, distillates, residua, and the like, under conditions so controlled that valuable products are obtainable having novel characteristics that render said products superior to those of comparable types heretofore known in the art. In general, the process of the invention is characterized by distillation under reduced pressure, and particularly under an absolute pressure not exceeding about 25 millimeters of mercury as an upper limit; while distillation at very much lower pressures, say not to exceed 5 millimeters of mercury and most desirably still lower, offers advantages that are particularly noteworthy and remarkable and is a feature of my novel process in some of its best embodiments. The novel process as practiced to greatest advantage also includes, as an important factor, control of the distillation and determination of the successive lubricating cuts or fractions by observation of one or more physical characteristics of real significance, such as viscosity, flash point, and fire point, rather than by observation of gravity as has heretofore been the practice. It is to be understood that the invention also includes the novel commercial products resulting from the process and definitely distinguishable from products heretofore obtainable; as well as novel apparatus in which the process may be carried out.

Petroleum is a mixture of a great variety of hydrocarbons with widely varying boiling points, viscosities and other characteristics. In refining petroleum, for the production of illuminating oils, fuels and lubricants, the problem is to separate out certain groups of hydrocarbons by distillation, such a group being known as a "cut," or "fraction." In the ordinary or usual distillation methods of refining, the narrowness of a cut, as shown for example by the range of boiling points observed upon re-distilling a sample of the cut in question, is limited in part by the mechanical carrying over of portions of the oil as spray, with the vapor or "overhead" before such portions have reached their boiling point. Narrowness of cuts in the case of lubricants particularly is desirable because the narrower the cut, the higher the boiling point of the most volatile constituent of an oil of given average boiling point or viscosity, viscosity rather than boiling point being the property upon which specifications for lubricants are ordinarily based. The volatile portion, or "light ends," of a cut as obtained in prior manufacturing practice are objectionable in a lubricant, both on account of their causing greater losses by evaporation in use and because it is the light ends which cause oxidation and deteriorate. On the other hand, the extremely heavy ends cause gumming and carbon deposition when the oil is used in an internal combustion engine.

In the usual method of refining there is considerable decomposition or "cracking" as it is called due to overheating, and this occurs throughout practically the entire distillation. By cracking is meant a chemical decomposition and degradation, as distinct from the physical separation of fractions of different boiling points, which latter is the desired object of distillation. Cracking produces both light and heavy products. The light products pass over and are condensed with each of the successive cuts or fractions, thus increasing the range of viscosity, boiling points, etc. of each cut. Moreover some of the cracked products give the oil a dark color and bad odor, and on this account it is necessary to get rid of them by expensive and time-consuming treatment with sulphuric acid, neutralization, washing and filtration. Steam is often used as an aid in refining by distillation, but it does not eliminate cracking and causes much trouble with emulsifying.

An object of the present invention is to prevent, or at least to greatly reduce, the mechanical carrying over of the oil with the vapor, as above described, and, by avoid-

ing cracking, to obviate the necessity of acid treatment, neutralization, washing and filtration, thus not only saving time and expense but also conserving the oil usually wasted in these operations.

Another object of the invention is to produce by straight overhead distillation lubricating oils of viscosities attainable in lubricating oils heretofore only by blending cylinder stock still bottoms with lighter fractions of low viscosity and low flash and fire test.

Still another object of the invention is to produce what can be termed narrow cut oils, particularly, lubricating oils, which are distinguishable, respectively, from comparable oils heretofore known by their relatively small range of viscosity, boiling points, and flash and fire tests, as determined by examination of initial and final fractions obtained by distilling samples under conditions precluding cracking or decomposition.

Other important objects and advantages of the invention will appear more fully hereinafter.

According to distillation methods heretofore in general use in the practical art, it has been customary to distil the starting material, whether it be crude petroleum, or a distillate to be re-run, either with or without the aid of steam, in such manner and under such conditions that the various cuts or fractions obtained each consist of constituents whose physical characteristics vary widely, the physical characteristics of each cut or fraction as a whole being merely an average or resultant of those characterizing the widely varying extremes. That is to say, given a lubricating oil cut, for example, obtained by straight run overhead distillation as commonly practiced, that cut consists of constituents having very low specific gravity (high Baumé) low viscosity, and low flash and fire test on the one hand, and also, on the other, of constituents having very high specific gravity, high viscosity, and high flash and fire test. Mechanical entrainment of liquid oil particles by the vapors leaving the still has already been mentioned as one of the causes of this trouble. In other words, such a product is merely the equivalent of a blend produced by mixing various oils having the various physical constants mentioned; and in fact blends of this kind are of course extensively produced as a regular practice by manufacturers in order to comply with the ordinary average specifications called for by oil users. Such products, and these are in fact the only type of products that have been commercially available heretofore in the art, are inherently faulty because of the above mentioned wide variation in the significant physical constants of the various constituents or fractions of which each is always composed. However obtained, lubricating oils heretofore available all contain on the one hand, a certain substantial proportion of oil having low viscosity, and low flash and fire test; and, on the other hand, varying proportions of oil having high viscosity and high flash and fire test, the proportion depending upon the grade of the particular oil under discussion. As a consequence, such oils show excessive consumption when used in internal combustion engines, for example, and are otherwise objectionable.

As before stated, the process of the invention is characterized essentially by the employment of low absolute pressure in the distilling apparatus. It is also characterized by the fact that in obtaining even the heaviest lubricating oil overhead cuts hereinafter described, the temperature does not usually exceed about 620° or 630° F. as a maximum. The present process enables lubricating oils having a viscosity of greater than 100 seconds as measured on the Saybolt universal viscosimeter at 212° F., to be produced by overhead distillation, something heretofore unknown in the art; and the new products are characterized by high standards of color, clearness and purity heretofore unattained in lubricating oils of comparable viscosity.

The process of the invention may be applied to various mineral oil starting materials. For example, it is applicable on the one hand to topped or stripped crudes of any character and is effective to produce therefrom a series of oil products markedly superior to those obtainable by the usual distillation methods. On the other hand the process can be employed with great success to treat residua that are now practically waste materials, such as still bottoms, remaining after distillation of all fractions (including lubricants) that can now be obtained by the usual distillation methods, providing the particular method by which the residuum was obtained was not such as decomposed or cracked the constituents of the residuum too extensively. Such still bottoms ordinarily have heretofore had no use except as fuel oil or as starting material in certain cracking processes for the production of gasolene. By applying the present novel method to such residua, as much as 80 to 95 per cent of the volume thereof may be obtained in the form of valuable oil products, including a series of the heavier lubricating oils which are of excellent color and each of which may have a relatively narrow range of viscosity as well as high flash and fire test. The foregoing starting materials are mentioned merely by way of example as indicating certain common hydrocarbon materials to which the present process is applicable; but it is to be understood that reference to these

typical starting materials is merely illustrative and is not intended to be restrictive.

In carrying out the process of the invention, it is important that the still and associated apparatus employed therewith be of such character that the whole system can be kept under the desired low pressure clear through to and including the receiving tanks. This requires that the apparatus be so constructed that all leaks are avoided. It is also important that the vapor offtake means leading from the distilling apparatus to the condensing system be of such ample cross sectional area, and that it be so designed and constructed that the vapors arising from the body of oil undergoing distillation can pass freely out of the still to the condensers in the minimum amount of time and with the minimum obstruction. Care should be taken particularly to avoid as far as is practicable the refluxing of any condensed vapors back into the still. In other words, cracking in the ordinary sense of the word, whether by refluxing or otherwise, is to be avoided as far as possible in carrying out the novel process. In some embodiments of my invention I employ steam to assist the distillation, and in that case the apparatus used should include provision for supplying steam under such control as nevertheless to permit operation at the desired low pressure.

One practical form of apparatus in which the novel process may be carried out is shown in the accompanying drawing which illustrates, more or less diagrammatically, a complete working system in elevation, parts being in section for clearness of illustration. This system is adapted for distillation either with or without the use of steam.

At 10 is a horizontal cylindrical still internally strengthened in any suitable manner to prevent collapse, as by means of peripheral ribs 11 and diametral braces 12; the peripheral ribs 11 being apertured or interrupted at the bottom of the still, as indicated at 13, in order not to obstruct free movement of liquid material along the bottom. Vapors from the still 10, after passing the baffle 14 guarding the vapor outlet of the still, go through large vapor offtake pipe 15 to a condenser coil 16 contained in a condenser box 17, which is provided with a pipe 18 for admission of steam or other fluid heating agent to warm the coil 16 where desirable, and with an overflow pipe 19. Said baffle 14 should be positioned far enough below the vapor outlet to avoid materially restricting the outflow of vapors or causing refluxing to the still. The condenser coil 16 discharges into a closed baffle box or separator 20 at a point below the top thereof, said box or separator containing a series of baffles indicated at 20^a, and having a liquid discharge pipe 21 leading from the lower part thereof, and a vapor offtake pipe 22 leading from the upper part thereof. The liquid discharge pipe 21 goes through a look box 23, and thence into a manifold or header 24 which communicates by branches 25, through valves 26, with receivers 27.

Vapor offtake pipe 22 goes to a condenser coil 28 immersed in a cooling liquid contained in box 29, said coil 28 discharging into the receiving tank 30, having a valved draw-off pipe 31 and a pipe connection 32 leading from the upper part of the tank to the main vacuum pump P_1, which should be capable of maintaining a diminished pressure of as low as 1.0 or 1.5 mm. of mercury in the entire system. Means are provided to cool the condenser 28 and receiver 30, when these are employed, such means taking the form in this instance of a refrigerating system in which cooling brine is supplied from a suitable brine pump (not shown) through pipe 33 to coil 34 in the receiver, and thence to coil 35 in the condenser box 29, the brine returning to the brine tank (not shown) through pipe 36. When steam or water vapor is to be used in the distillation, this is furnished by a boiler 37 provided with a bleeder valve 38, and with a vapor exit pipe 39 leading to a coil 40 arranged in a superheater 41, said coil 40 discharging through pipe 42 past valve 43 into the still 10. Said discharge pipe 42 extends well toward the bottom of the still and has its lower part 42^a perforated for delivery of the superheated steam or water vapor in jets into the still contents.

In order to permit rapidly withdrawing samples of the oil distillate for test as the distillation progresses, without admitting any substantial quantity of air into the system, a sampling device is provided comprising a small closed container or chamber 44 connected to header 24 by an inflow pipe connection 45 valved at 46, and having a discharge 47 valved at 48. Said chamber is also provided with a bleeder valve 49, opening to atmosphere. With valve 46 open and valves 48, 49 closed, distillate flows into and fills container 44. Upon closing valve 46 and opening valves 48, 49, the distillate in the container is discharged under atmospheric pressure. The valves are then restored to their first mentioned positions. The sampling container is of such small size as compared to the rest of the apparatus, that the quantity of air admitted into the container at each sampling is negligible as regards its effect on the system or on the oil therein. It is to be noted that admission of any substantial quantity of air into the system is to be guarded against, not only because of the consequent difficulty of maintaining the desired high degree of vacuum,

but also because of the oxidizing effect on the oil. Substantial oxidation would seriously impair effective operation of the process or even defeat it altogether.

Assuming the distillation of oil under high vacuum and with the use of water vapor introduced into the still, the still 10 is charged with oil, such as topped crude or residuum, up to approximately the level indicated in dotted lines, and the vacuum pump P_1 connected with pipe 32 is started, valves 29^a, 32^a and 32^b being open, and valves 52, 53 being closed. Heat is applied to still 10 and superheater 41. If the atmospheric temperature is sufficiently low to require it, heat is also applied at the same time to water boiler 37 to generate water vapor. Valve 43, which has been closed up to this time, is now opened slightly and the brine pump is started to supply brine through pipe 33 to the refrigerating coils 30 and 35 for cooling the condenser 28—29 and receiving tank 30. Steam may be run into condenser box 17 through pipe 18 in order to keep the condenser 16—17 warm enough to prevent condensation of moisture and yet to ensure condensation of the oil vapors coming over from the still 10. Water resulting from the condensation of steam in 18 overflows at 19. The admission of steam is so controlled by valve 43 as to permit the vacuum pump P_1 to maintain an absolute pressure of not more than 5 mm. mercury in the system.

When the condensed oil and uncondensed water vapor reach the baffle box or separator 20, they separate, the water vapor passing out through the offtake 22 and thence into the cold condenser 28—29 where it condenses, the resultant water collecting in receiving tank 30. The water vapor is accompanied by volatile matter which if not separated from the condensed oil would be absorbed by the latter upon cooling and would contaminate the same. The condensed oil, on the other hand, flows down by gravity through the separator 20 and passes to the sight box 23, going thence into whichever one of the receivers 27 is at that time open to the header 24. Thus the water and oil are collected entirely separately and the formation of emulsions is prevented.

When the distillation is completed, valve 43 is closed and bleeder valve 38 opened to establish atmospheric pressure in the boiler. This prevents the oil or residue siphoning back from still 10 into boiler 37. The main vacuum pump P_1 is then shut down, and the bleeder valve 50 of the connected receiver 27 is opened to bring the system back to atmospheric pressure. Steam is cut off from condenser box 17 and the brine pump is shut down. Water is then drained from receiving box 30 through drain pipe 31. The liquid residue in still 10 may be run off through a suitable drain pipe (not shown), the entire residue being easily removed because of the entire absence of coke. The operation is thus completed and the apparatus is ready for another run.

In employing the described apparatus for carrying out the process of the invention where water vapor is not used in conjunction with the high vacuum, the baffle box 20 and the parts in series therewith through vapor outlet pipe 33 are not required, and the intake of main vacuum pump P_1 is connected directly to vapor outlet 22 through pipe 51 by opening valves 52, 53, while valves 29^a and 32 are now closed. It is of course also unnecessary to employ the steam generating system, and valve 43 therefore remains closed when employing dry distillation. Ordinarily it is also unnecessary to admit steam to the condenser tank 17; and where desirable, a cooling fluid may even be admitted thereto through pipe 18.

Pipes 54, connected with an auxiliary vacuum pump P_2 through header 55, enable restoration of low pressure in either receiver 27, after withdrawal of the condenser distillate therefrom, without disturbing the pressure in the system or admitting air thereinto. When a receiver 27 is filled, its admission valve 26 is closed, air is admitted through bleeder valve 50, valve 57 of discharge pipe 58 is opened, and the distillate is pumped to storage tanks (not shown). When the receiving tank is empty, valves 57 and 50 are closed, the auxiliary vacuum pump P_2 connected to pipe 54 is started, and valve 56 in pipe 54 is opened; and when the desired reduction in pressure has been reached, valve 56 is closed and valve 26 is opened, the main vacuum pump P_1 thereafter acting to maintain the desired degree of vacuum in the receiver as well as in the other parts of the system.

Having outlined above the general procedure that may be followed in employing the described apparatus for treating oils in accordance with the invention, typical examples of the novel process as applied to distillation of different hydrocarbon materials available as starting materials will now be set forth in greater detail.

Assume that the novel process is to be applied to the manufacture of valuable hydrocarbon lubricants from crude petroleum of naphthenic or asphaltic base origin. So far as concerns the removal of the lighter fractions from the crude, that is to say, removal of fractions lighter than lubricating oils, this may be effected by any suitable topping method, and as such methods are in themselves well known, generally speaking, no detailed description thereof is necessary here. For best results, however, the stripping or topping should be conducted in such manner as to avoid cracking any of the

heavier hydrocarbons. The crude having been topped to a point where the first lubricating cut or fraction is about to come over, or a crude topped to this extent having been obtained, the remainder of the distillation may be substantially as follows: The still is charged with the topped crude, and by means of the main vacuum pump the pressure in the entire system, including the still, condenser and the particular receiver connected therewith, is reduced to below 5 millimeters mercury absolute pressure, and most desirably is reduced to from 1 to 1.5 millimeters. As low a pressure as this is attainable in practicing the invention where the oil is substantially free of moisture; and operation at 2 to 4 millimeters is practically always feasible. This assumes, of course, the employment of an absolutely tight apparatus system. The still is then fired with fuel oil or other suitable heating medium to bring the temperature up gradually to the initial distillation temperature which, in the case of a topped oil like that assumed, is usually around 300° to 350° F. Care is taken that the firing flame does not come in contact with the bottom of the still, thus avoiding localized overheating and consequent cracking of the oil; and the heating of the still is therefore accomplished by radiation, proper provision being made to keep the flame away from actual contact with the still itself while conveying the necessary heat units thereto. Various arrangements for this purpose are available in the art and unnecessary to describe here. If the oil to be treated contains water, the still should be gradually heated up before being placed under high vacuum.

Unless it is desired to obtain products of exceptionally fine color and sweet odor, as for example in the manufacture of white medicinal oils, it is not necessary to introduce steam into the still; and it will be assumed in this example, therefore, that steam is not employed. The temperature of the oil in the still is under observation at all times by means of a pyrometer which may be so located that the thermo-couple is within a half an inch or so of the bottom of the still at a central point therein. The temperature of the oil in the still may be closely controlled by regulation of the firing flame. As soon as distillate begins to come over, a sample is taken, and its viscosity, and optionally also its flash and fire points, are accurately determined. The distillation is continued, samples being taken at suitable intervals until the increase in viscosity indicates the necessity or desirability of cutting the distillate into a second receiver. For example, if it is desired to make spindle oils, the first cut can be made when the distillate shows a viscosity of 100 seconds Saybolt universal (at 100° F.). The pressure in the first receiver may then be released and the first cut, spindle oil, may be pumped to storage.

The procedure is substantially the same as described for the remainder of the distillation, the pressure being maintained at around 1 to 1.5 mm., or at any rate below 5 mm. for best results, and the distillate being cut for the desired fractions in accordance with the increase in viscosity as determined by the testing of samples at frequent intervals. Proceeding in this way, products aggregating from 80 to 95 per cent of the volume of the topped crude originally charged into the still may be obtained as straight overhead distillates. The residue in the still is known to the trade as a flux oil, usually having a gravity of around 12° to 14° Baumé. The final distillation temperature should not ordinarily be allowed to exceed 620° to 630° F. as a maximum. Under these conditions, cracking or decomposition, and formation of coky products, are entirely avoided. The radical differences between the present method and those heretofore customary in the art, become especially apparent when it is borne in mind that in the usual methods of obtaining lubricating oils up to viscosities of only 750 seconds (at 100° F.), distillation temperatures of 750° to 800° F. and higher are employed, which of course causes extensive cracking and gives dark colored oils which must be acid-treated to render them fit for use. In the present process, on the other hand, lubricating oils of viscosities as high as 150 seconds (at 212° F.) may be distilled over at around 575° to 600° F., and as high as 170 seconds (at 212° F.) at around 600° to 620° F., this latter being approximately the end-point of the kerosene cut in ordinary distillation at atmospheric pressure.

The various distillation products may correspond in a general way to products known under the usual grades in the trade, that is, light, medium, heavy, etc., but they differ markedly in very important respects from the products heretofore known under those grades. Taking these new products just as they distil over in the present process and without acid treatment or filtration, they are all superior in color to oils of corresponding grades heretofore available commercially. Furthermore, as already pointed out, they are of much narrower viscosity range, and also of better flash and fire test. It is especially emphasized again that the novel products just referred to have not been treated with acid or filtered, notwithstanding the fact that they show the before-mentioned points of superiority over the corresponding grades of oil now commonly known in the trade, which latter invariably have been treated with acid and filtered. By subjecting the products obtained in my process to

treatment with acid and filtration, a still further superiority in color is attainable. It is to be understood, of course, that the acid treatment, if employed, is restricted from a commercially profitable standpoint to the lighter lubricating oils obtained up to a critical viscosity beyond which acid treatment is not feasible without dilution.

The products obtained in the described distillation range from the light and medium lubricating oils up through heavy and extra heavy motor oils, and far beyond these up to viscosities as high as 170 seconds Saybolt universal (at 212° F.) In this connection it is to be especially noted that lubricating oils of above 100 seconds (at 212° F.) viscosity, obtained by overhead distillation, have been heretofore unknown and unobtainable in the art. The present process therefore makes possible, among other things, the production of a series of heavy lubricating oils that are novel in character and of the very highest utility for certain purposes where extremely heavy lubricants are required. Heretofore lubricating oils having a viscosity greater than 100 seconds (at 212° F.) have been produced solely by filtration of still bottoms after the lighter lubricating fractions have been distilled off. These still bottoms or cylinder stocks invariably contain a substantial portion of cracked products and asphaltic constituents and are very dark in color. The heavy lubricating oils having a viscosity from 100 to 170 (at 212° F.) obtained by the present process are, on the other hand, free from cracked products and asphaltic constituents, and the color of the darkest is better than the color of the best filtered cylinder stock now obtainable which is known to the trade as FFF color.

In the foregoing specific example of one way of carrying out the distillation of a topped crude oil, it was assumed that the various desired final products were obtained directly in one distillation by cutting at the necessary intervals indicated by viscosity tests throughout the entire range of products. Another mode of procedure and one which has some practical advantages, consists in making only two cuts in a first distillation of the starting material, the first cut being made when the distillate has attained a viscosity of about 750 seconds (at 100° F.), and then cutting the remainder of the distillate into a separate receiver. The first cut therefore includes all the lubricants up to and through the heavy motor oils; while the second cut includes the extra heavy motor oils and the heaviest lubricating oils up to a viscosity of as high as 170 seconds (at 212° F.). Sufficient quantities of these two cuts are accumulated to enable redistillation or re-running of the cuts separately in re-run stills provided for this purpose. In re-running the cuts, narrower cuts are made corresponding to the various commercial grades it is desirous to make. This method of re-running has the advantage of giving products of even better color than those obtained by method of distillation first described, and the viscosity ranges of the various products obtained are respectively somewhat narrower.

The process of the invention is especially applicable to the treatment of still bottoms obtained from the ordinary distillation of naphthenic base crudes. Where such still bottoms are used, the method of distillation is substantially as hereinabove described, but the initial distillate is usually of a viscosity of about 70 seconds (at 212° F.). Succeeding cuts increase in viscosity up to about 170 seconds (at 212° F.), as before described. At least 85 to 95 per cent of the still bottoms, which material has heretofore been practically waste material in the art, is thus obtainable as overhead distillates in the form of high grade heavy lubricating oils of narrow range high viscosities, high flash and fire tests, free from tarry or asphaltic matter and of exceedingly good color. The darkest of these oils is ordinarily not darker than 6 N. P. A. (National Petroleum Association), the N. P. A. color standard being that commonly employed in measuring color. As before stated, these high viscosity overhead distillates are novel products in the art.

My novel process is also applicable to the treatment of topped or stripped crudes and still bottoms of paraffinic base origin, but in order to treat such starting materials commercially it is necessary to make special provision for the removal of the paraffin wax content which comes over during the entire distillation. One method of removing paraffin from the distillates is by centrifuging although it is to be understood that other methods can be employed for this purpose.

In handling paraffin base crudes, the prevailing refinery practice is to distil overhead with steam up to a critical temperature at which decomposition takes place. The distillates thus obtained are freed from their paraffin content, re-distilled, acid-treated, and filtered, to produce commercial products commonly known to the trade as "200 Pennsylvania neutral". The still bottoms (cylinder stock) remaining are freed from amorphous waxy content and filtered to desired color, known as "FFF". In contrast to this practice, the novel process herein described makes it possible to treat the still bottoms or cylinder stock from paraffin base crudes by distilling overhead without decomposition and obtaining 60 per cent of the material in distillates ranging in viscosity from 400 to 900 seconds Saybolt (at 100° F.), the color ranging

from 2 to 5 N. P. A. which is remarkably good color. These products are also of exceptionally high flash and fire test and are free of tarry matter. This series of products is unknown to the trade at the present time. Moreover, the residuum or still bottoms resulting from the described distillation according to my novel process is an extremely heavy cylinder stock of a viscosity as high as 250 seconds Saybolt (at 212° F.), 630° F. flash test and 700° F. fire test, and is also a novel product. This is an example of how the new process may be applied to the manufacture, from paraffin-base oils, of high viscosity lubricants by straight overhead distillation, and of a novel cylinder stock.

In order to afford a definite comparison between typical novel products obtainable in accordance with the invention, on the one hand, and products of approximately corresponding commercial grades of oils heretofore available on the other, a table is given below in which the principal test characteristics of light, medium and heavy motor oils produced from a naphthene base crude in accordance with the present invention are compared with those of the corresponding three commercial grades of well known paraffin base and naphthene base motor oils, the prior oils selected for this comparison representing the best quality obtainable on the market. The figures given are the results of actual laboratory tests.

	Prior oils.		Schulze narrow cut naphthene base.
	Paraffin base.	Naphthene base.	
Light oil.			
Gravity Baumé	30.0	21.0	21.0
Flash (° F.)	405	320	360
Flash range (° F.)	290 to 550	250 to 460	340 to 380
Viscosity at 100° F. Saybolt universal (sec.)	190	200	200
Viscosity range (sec.)	60 to 600	60 to 2,000	100 to 300
Color N. P. A.	2½	2½	1½
Pour test (A. S. T. M.) (° F.)	30	Below zero.	Below zero.
Initial boiling point at 1.5 mm. (° F.)	374	320	400
Per cent distilled over up to 450° F. (1.5 mm.)	10%	60%	98%
Medium oil.			
Gravity Baumé	29.0	20.5	20.5
Flash (° F.)	425	330	380
Flash range (° F.)	300 to 550	255 to 480	370 to 430
Viscosity at 100° F. Saybolt universal (sec.)	260	300	300
Viscosity range (sec.)	70 to 1,400	60 to 2,200	300 to 450
Color N. P. A.	3½	3	2
Pour test (A. S. T. M.) (° F.)	35	Below zero.	Below zero.
Initial boiling point at 1.5 mm. (° F.)	410	350	435
Per cent distilled over up to 475° F. (1.5 mm.)	22%	46%	98%
Heavy oil.			
Gravity Baumé	28.5	19.5	19.5
Flash (° F.)	435	360	400
Flash range (° F.)	305 to 550	260 to 510	385 to 450
Viscosity at 100° F. Saybolt universal (sec.)	365	500	500
Viscosity range (sec.)	75 to 1,600	70 to 2,400	400 to 700
Color N. P. A.	5	3½	2½
Pour test (A. S. T. M.) (° F.)	35	Below zero.	Below zero.
Initial boiling point at 1.5 mm. (° F.)	437	390	440
Per cent distilled over up to 500° F. (1.5 mm.)	35%	56%	98%

The foregoing table is self-explanatory; but it may be noted in connection with the figures given for the per cent of sample distilled over up to the maximum distillation temperature mentioned, that the figure of 98% for the new oils signifies that substantially the entire sample distilled over, the deficit of 2% representing the unavoidable mechanical loss of oil in handling the sample in conducting the test. It is also to be understood that the figures for "flash range" and "viscosity range" represent the flash points and viscosities of the first and last 10% fractions, respectively, obtained by distilling a sample of the oil at a pressure of 1.5 mm. mercury absolute.

As further examples of the novel type of lubricating oils obtainable in the practice of the invention, identifying characteristcs of five typical heavy narrow cut lubricating oils are also given below, all distillation data having been obtained in operation in a commercial still at 1.5 mm. mercury absolute pressure. Such a series of oils can be obtained from a residuum or still bottoms resulting from ordinary distillation of a naphthenic base crude. The data given below is for the lubricating oils distilled directly from such a residuum by the present process without re-running.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Gravity (°Bé.)	18.5	18.2	18.0	17.5	17.0
Flash (°F.)	440	455	470	490	520
Flash range (°F.)	420–450	440–470	460–480	480–500	500–540
Fire (°F.)	530	545	560	575	600
Viscosity of sample (Saybolt sec. at 212° F.)	70	85	100	125	150
Viscosity range	60–80	80–90	90–110	110–140	140–170
Color (N. P. A.)	4½	5	5½	6	6½
Pour test (A. S. T. M.)	5	5	5	10	15
Initial B. P. (°F.)	475	490	520	550	575
All distilled over at (°F.)	490	520	550	575	590

In general, lubricating oils manufactured in accordance with my invention are most readily distinguishable from comparable prior oils by comparison of their respective ranges of viscosity and distillation temperatures or boiling points, and of the relative proportions distilling over up to a given temperature. The new oils are all characterized by narrow viscosity ranges that are far narrower than those found in prior available oils. Oils of the novel type herein decribed, having viscosities up to 150 seconds Saybolt universal at 100° F., show viscosity ranges as low as 50 seconds; while a range of 100 seconds is common, and a range of 250 seconds is approximately the maximum for oils of this particular class. The novel oils having viscosities of 150 seconds (at 100° F.) and upwards are characterized by viscosity ranges as low as 20 or 30 seconds (at 212° F.) for the very heavy oils; and by typical limiting viscosity ranges of 250, 500, and 700 seconds (at 100° F.) for commercial grades of lighter oils of this

class. It is well known that such narrow ranges of viscosity are not approached by comparable oils heretofore known. Similarly, light oils are readily obtainable by my novel process having viscosities of 200 seconds (at 100° F.) or less but whose boiling or distillation range at 5 mm. mercury pressure or below is not over 50° F. in some instances; and limiting ranges of 75° F. and 100° F. are typical in other cases. In the case of heavy oils having viscosities upward of 70 seconds (at 212° F.), a distillation range as small as 50° F. is also characteristic of narrow cut oils obtainable by my process.

Further classification of oils manufactured in accordance with the invention may be made as follows, the data given being based on results obtained in operating commercially on naphthene base crudes and still bottoms.

Viscosity (seconds).	Flash point not less than (°F.).	Fire point not less than (°F.).	Viscosity range (seconds) (5 mm. distillation.)
Up to 150 (100° F.)	280	340	50–200 (100° F.).
150–250 (100° F.)	310	370	125–300 (100° F.).
250–350 (100° F.)	320	380	250–400 (100° F.).
350–550 (100° F.)	340	400	300–700 (100° F.).
550–900 (100° F.)	380	440	500–1000 (100° F.).
60–100 (212° F.)	390	450	50–120 (212° F.).
100–150 (212° F.)	440	500	90–175 (212° F.).

Another characteristic distinguishing the present novel straight overhead non-acid-treated lubricating distillates from lubricating oils heretofore available commercially, practically all of which latter having viscosities up to 750 seconds (at 100° F.) are acid treated, is the fact that the oils of the present invention show little or no tendency to form emulsions with water when subjected to severe emulsifying tests, but on the contrary separate from water quickly and clearly. Commercial oils heretofore available, on the other hand, invariably emulsify with water to a substantial extent, and often emulsify excessively. This is due to the practical impossibility of removing all traces of the complex alkali-sulfonic acid compounds always formed when oil is treated with acid and alkali. The importance of being able to obtain non-emulsifying lubricating oils by straight overhead distillation, which nevertheless are of as good or better color than acid-treated oils, and which are therefore free of asphaltic contamination, is sufficiently apparent.

What I claim is:

1. As a new article of manufacture, a mineral lubricating oil having a viscosity not exceeding about 150 seconds Saybolt universal (at 100° F.), and further characterized by the fact that when a sample of said oil is substantially completely distilled under an absolute pressure of 5 mm. mercury or less and under non-oxidizing conditions, the first ten per cent fraction and the last ten per cent fraction of the distillate differ in viscosity by not more than 250 seconds Saybolt universal (at 100° F.).

2. As a new article of manufacture, a mineral lubricating oil having a viscosity not exceeding about 150 seconds Saybolt universal (at 100° F.), and further characterized by the fact that when a sample of said oil is substantially completely distilled under an absolute pressure of 5 mm. mercury or less and under non-oxidizing conditions, the first ten per cent fraction and the last ten per cent fraction of the distillate differ in viscosity by not more than 100 seconds Saybolt universal (at 100° F.).

3. As a new article of manufacture, a mineral lubricating oil having a viscosity not exceeding about 150 seconds Saybolt universal (at 100° F.), and further characterized by the fact that when a sample of said oil is substantially completely distilled under an absolute pressure of 5 mm. mercury or less and under non-oxidizing conditions, the first ten per cent fraction and the last ten per cent fraction of the distillate differ in viscosity by not more than 50 seconds Saybolt universal (at 100° F.).

4. As a new article of manufacture, a mineral lubricating oil having a viscosity of 200 seconds or less, Saybolt universal (at 100° F.), which oil distils substantially completely under non-oxidizing conditions at or below 5 mm. mercury absolute pressure between initial and final boiling points differing by not more than 100° F.

5. As a new article of manufacture, a mineral lubricating oil having a viscosity of 200 seconds or less, Saybolt universal (at 100° F.), which oil distils substantially completely under non-oxidizing conditions at or below 5 mm. mercury absolute pressure between initial and final boiling points differing by not more than 75° F.

6. As a new article of manufacture, a mineral lubricating oil having a viscosity of 200 seconds or less, Saybolt universal (at 100° F.), which oil distils substantially completely under non-oxidizing conditions at or below 5 mm. mercury absolute pressure between initial and final boiling points differing by not more than 50° F.

7. As a new article of manufacture, a mineral lubricating oil having a viscosity of at least 150 seconds Saybolt universal (at 100° F.), and further characterized by the fact that when a sample of said oil is substantially completely distilled under an absolute pressure of 5 mm. mercury or less and under non-oxidizing conditions, the first ten per cent fraction and the last ten per cent fraction of the distillate differ in viscosity by not more than 700 seconds Saybolt universal (at 100° F.).

8. As a new article of manufacture, a mineral lubricating oil having a viscosity of at least 150 seconds Saybolt universal (at 100° F.), and further characterized by the fact that when a sample of said oil is substantially completely distilled under an absolute pressure of 5 mm. mercury or less and under non-oxidizing conditions, the first ten per cent fraction and the last ten per cent fraction of the distillate differ in viscosity by not more than 500 seconds Saybolt universal (at 100° F.).

9. As a new article of manufacture, a mineral lubricating oil having a viscosity of at least 150 seconds Saybolt universal (at 100° F.), and further characterized by the fact that when a sample of said oil is substantially completely distilled under an absolute pressure of 5 mm. mercury or less and under non-oxidizing conditions, the first ten per cent fraction and the last ten per cent fraction of the distillate differ in viscosity by not more than 250 seconds Saybolt universal (at 100° F.)

10. As a new article of manufacture, a mineral lubricating oil having a viscosity of 150 seconds or greater, Saybolt universal (at 100° F.), which oil distils substantially completely under non-oxidizing conditions at or below 5 mm. mercury absolute pressure between initial and final boiling points differing by not more than 50° F.

11. As a new article of manufacture, a mineral oil whose viscosity is 150 seconds or greater, Saybolt universal (at 100° F.), and which distils substantially completely under non-oxidizing conditions at or below 5 mm. mercury absolute pressure between boiling points differing by not more than 100° F.

12. As a new article of manufacture, a mineral oil whose viscosity is 150 seconds or greater, Saybolt universal (at 100° F.), and which distils substantially completely under non-oxidizing conditions at or below 5 mm. mercury absolute pressure between boiling points differing by not more than 75° F.

13. As a new article of manufacture, a straight overhead lubricating oil distillate derived from a naphthenic base oil and having a viscosity of not less than 90 seconds Saybolt universal (at 212° F.), said distillate being substantially free of tarry matter.

14. As a new article of manufacture, a straight overhead lubricating oil distillate derived from a naphthenic base oil and having a viscosity exceeding 100 seconds Saybolt universal (at 212°), said distillate being substantially free of tarry matter.

15. As a new article of manufacture, a straight overhead lubricating oil distillate derived from a naphthenic base oil, and having a viscosity exceeding 150 seconds Saybolt universal (at 212° F.), said distillate being substantially free of tarry matter.

16. As a new article of manufacture, a straight overhead lubricating oil distillate derived from a naphthenic base oil and having a viscosity of about 170 seconds Saybolt universal (at 212° F.), said distillate being substantially free of tarry matter.

17. As a new article of manufacture, a mineral lubricating oil having a viscosity of at least 70 seconds Saybolt universal (at 212° F.), and further characterized by the fact that when a sample of said oil is substantially completely distilled under an absolute pressure of 5 mm. mercury or less and under non-oxidizing conditions, the first ten per cent fraction and the last ten per cent fraction of the distillate differ in viscosity by not more than 30 seconds Saybolt universal (at 212° F.).

18. As a new article of manufacture, a mineral lubricating oil having a viscosity of at least 70 seconds Saybolt universal (at 212° F.), and further characterized by the fact that when a sample of said oil is substantially completely distilled under an absolute pressure of 5 mm. mercury or less and under non-oxidizing conditions, the first ten per cent fraction and the last ten per cent fraction of the distillate differ in viscosity by not more than 20 seconds Saybolt universal (at 212° F.).

19. As a new article of manufacture, a lubricating oil whose viscosity is 70 seconds or greater, Saybolt universal (at 212° F.), and which distils substantially completely under non-oxidizing conditions at or below 5 mm. mercury absolute pressure between initial and final boiling points differing by not more than 50° F.

20. As a new article of manufacture, a mineral lubricating oil having a viscosity of not more than about 150 seconds Saybolt universal (at 100° F.), a flash point of not less than 280° F., and a fire point of not less than 340° F., said oil yielding no fraction, upon distillation under non-oxidizing conditions at 5 mm. mercury or less absolute pressure, having a viscosity of less than 50 seconds or greater than 200 seconds, Saybolt universal (at 100° F.).

21. As a new article of manufacture, a mineral lubricating oil having a viscosity lying between about 150 seconds and about 250 seconds, Saybolt universal (at 100° F.), a flash point of not less than 310° F., and a fire point of not less than 370° F., said oil yielding no fraction, upon distillation under non-oxidizing conditions at 5 mm. mercury or less absolute pressure, having a viscosity of less than 125 seconds or greater than 300 seconds, Saybolt universal (at 100° F.).

22. As a new article of manufacture, a

mineral lubricating oil having a viscosity lying between about 250 seconds and about 350 seconds Saybolt universal (at 100° F.), a flash point of not less than 320° F., and a fire point of not less than 380° F., said oil yielding no fraction, upon distillation under non-oxidizing conditions at 5 mm. mercury or less absolute pressure, having a viscosity of less than 250 seconds or greater than 450 seconds, Saybolt universal (at 100° F.).

23. As a new article of manufacture, a mineral lubricating oil having a viscosity lying between about 350 seconds and about 550 seconds, Saybolt universal (at 100° F.), a flash point of not less than 340° F., and a fire point of not less than 400° F., said oil yielding no fraction, upon distillation under non-oxidizing conditions at 5 mm. mercury or less absolute pressure, having a viscosity of less than 300 seconds or greater than 700 seconds, Saybolt universal (at 100° F.).

24. As a new article of manufacture, a mineral lubricating oil having a viscosity lying between about 550 seconds and about 900 seconds, Saybolt universal (at 100° F.), a flash point of not less than 380° F., and a fire point of not less than 440° F., said oil yielding no fraction, upon distillation under non-oxidizing conditions at 5 mm. mercury or less absolute pressure, having a viscosity of less than 500 seconds or greater than 1,000 seconds, Saybolt universal (at 100° F.).

25. As a new article of manufacture, a mineral lubricating oil having a viscosity lying between about 60 seconds and about 100 seconds, Saybolt universal (at 212° F.), a flash point of not less than 390° F., and a fire point of not less than 450° F., said oil yielding no fraction, upon distillation under non-oxidizing conditions at 5 mm. mercury or less absolute pressure, having a viscosity of less than 50 seconds or greater than 120 seconds, Saybolt universal (at 212° F.).

26. As a new article of manufacture, a mineral lubricating oil having a viscosity lying between about 100 seconds and about 150 seconds, Saybolt universal (at 212° F.), a flash point of not less than 440° F., and a fire point of not less than 500° F., said oil yielding no fraction, upon distillation under non-oxidizing conditions at 5 mm. mercury or less absolute pressure, having a viscosity of less than 90 seconds or greater than 175 seconds, Saybolt universal (at 212° F.).

27. The process of producing useful mineral oil distillates which comprises distilling, under an absolute pressure not exceeding 25 millimeters mercury, mineral oil material containing substantially no constituents as volatile as gasoline.

28. The process of producing useful mineral oil distillates which comprises distilling mineral oil material under an absolute pressure not substantially exceeding 5 millimeters mercury.

29. The process of producing useful mineral oil distillates which comprises distilling mineral oil material under an absolute pressure not substantially exceeding 1.5 millimeters mercury.

30. The process of producing useful mineral oil distillates which comprises distilling with the aid of water vapor mineral oil material containing substantially no constituents as volatile as gasoline, while maintaining a distillation pressure of not substantially above 25 millimeters mercury absolute and restricting the distillation temperatures to below about 620° to 630° F.

31. The process as set forth in claim 30, in which the pressure is from 1 to 5 mm. mercury absolute.

32. The process of manufacturing mineral oil lubricants which comprises subjecting mineral oil material containing substantially no constituents as volatile as gasoline to distillation under an absolute pressure not substantially exceeding 25 mm. mercury and cutting the distillate between predetermined limits of viscosity.

33. The process of manufacturing mineral oil lubricants which comprises subjecting mineral oil from which lighter products have been removed to distillation under an absolute pressure not substantially exceeding 5 mm. mercury, and cutting the distillate between predetermined limits of viscosity.

34. The process of manufacturing mineral oil lubricants which comprises subjecting mineral oil from which lighter products have been removed to distillation under an absolute pressure of between 1 and 5 mm. mercury and cutting the distillate between predetermined limits of viscosity.

35. The process of producing mineral oil lubricants, which comprises fractionally distilling under an absolute pressure not substantially exceeding 5 mm. mercury mineral oil containing substantially no fractions of a viscosity lower than 50 seconds Saybolt universal (at 100° F.), and condensing the distillate under substantially the pressure of distillation.

36. The process of producing mineral oil lubricants, which comprises fractionally distilling under an absolute pressure not substantially exceeding 5 mm. mercury a stripped crude oil, and condensing the distillate under substantially the pressure of distillation.

37. The process as set forth in claim 36, in which the pressure employed does not substantially exceed 1.5 mm. mercury absolute.

38. The process of producing mineral oil lubricants, which comprises fractionally distilling under an absolute pressure not substantially exceeding 5 mm. mercury still

bottoms derived from distillation of crude petroleum, and condensing the distillate under substantially the pressure of distillation.

39. The process as set forth in claim 38, in which the pressure employed does not substantially exceed 1.5 mm. mercury absolute.

40. The process of manufacturing mineral lubricating oils by overhead distillation without acid treatment or filtration, which comprises subjecting lubricant-containing mineral oil to distillation under pressure not exceeding 5 mm. mercury absolute while avoiding substantial refluxing of the distillate, and conducting off and condensing lubricating oil distillate at substantially the same pressure, the distillation temperature being controlled so as not to exceed 620° to 630° F. as a maximum.

41. The process as set forth in claim 40, in which the pressure employed does not substantially exceed 1.5 mm. mercury absolute.

42. The process of manufacturing mineral lubricating oils which comprises subjecting mineral oil, such as crude oil or still bottoms of naphthenic base origin to distillation under pressure not exceeding 5 mm. mercury absolute while avoiding substantial refluxing of the distillate, controlling the distillation temperature to prevent its going above 620° F. to 630° F., obtaining overhead lubricating cuts, the distillation being continued until at least 60 per cent of the original charge has distilled over.

43. The process as set forth in claim 42, in which lubricating cuts having viscosities up to as high as 150 seconds Saybolt universal (at 212° F.) are distilled over.

44. The process of manufacturing mineral lubricating oils which comprises distilling mineral oil with the aid of steam introduced thereinto, maintaining the pressure in the distilling chamber at or below about 5 mm. mercury absolute, increasing the distillation temperature to a maximum not exceeding about 620°–630° F., and collecting heavy lubricating oil as overhead distillate.

45. In the manufacture of lubricating oils, the process which comprises distilling a lubricant-containing mineral oil material at an absolute pressure not substantially exceeding 15 mm. of mercury and under non-oxidizing conditions.

46. In the manufacture of lubricating oils, the process which comprises distilling a lubricant-containing mineral oil material at an absolute pressure not substantially exceeding 10 mm. of mercury and under non-oxidizing conditions.

47. In the manufacture of lubricating oils, the process which comprises distilling a lubricant-containing mineral oil material at an absolute pressure of between 1 and 5 mm. of mercury and under non-oxidizing conditions.

48. The process of manufacturing mineral lubricating oils by overhead distillation without acid treatment or filtration, which comprises subjecting lubricant-containing mineral oil distillation under pressure not exceeding 5 mm. mercury absolute while avoiding substantial refluxing of the distillate, and conducting off and condensing lubricating oil distillate at substantially the same pressure, the distillation temperature being controlled so as not to exceed a temperature at which substantial cracking occurs.

49. The process as set forth in claim 48 in which the pressure employed is between 1 and 5 mm. mercury absolute.

In testimony whereof I hereunto affix my signature.

JOHN E. SCHULZE.