Feb. 8, 1944. R. D. EVANS ET AL 2,340,947

PROCESS FOR THE MANUFACTURE OF LUBRICATING OILS

Filed Sept. 2, 1941 4 Sheets-Sheet 1

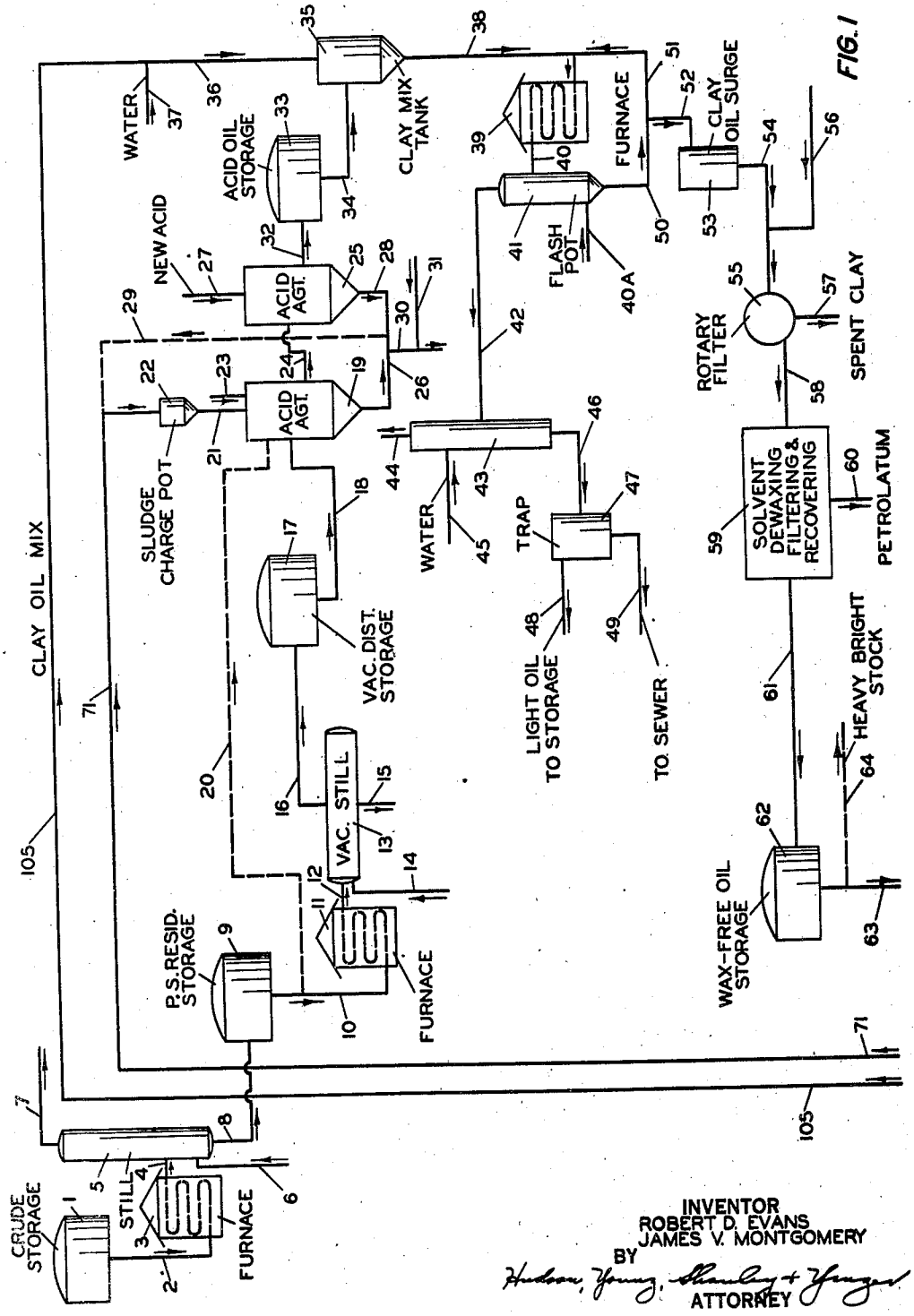

FIG. 1

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PROCESS FOR THE MANUFACTURE OF LUBRICATING OILS

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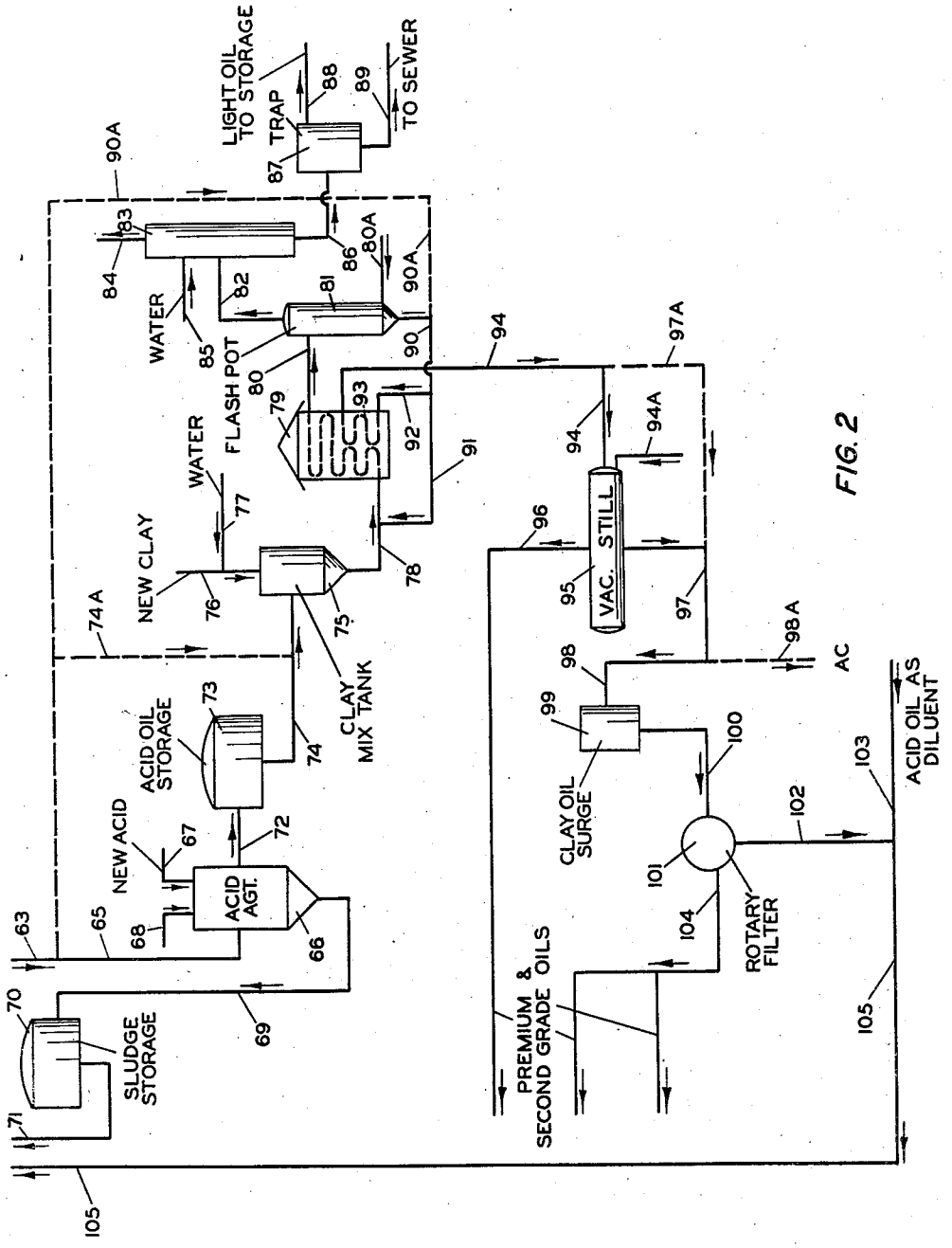

FIG. 2

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PROCESS FOR THE MANUFACTURE OF LUBRICATING OILS

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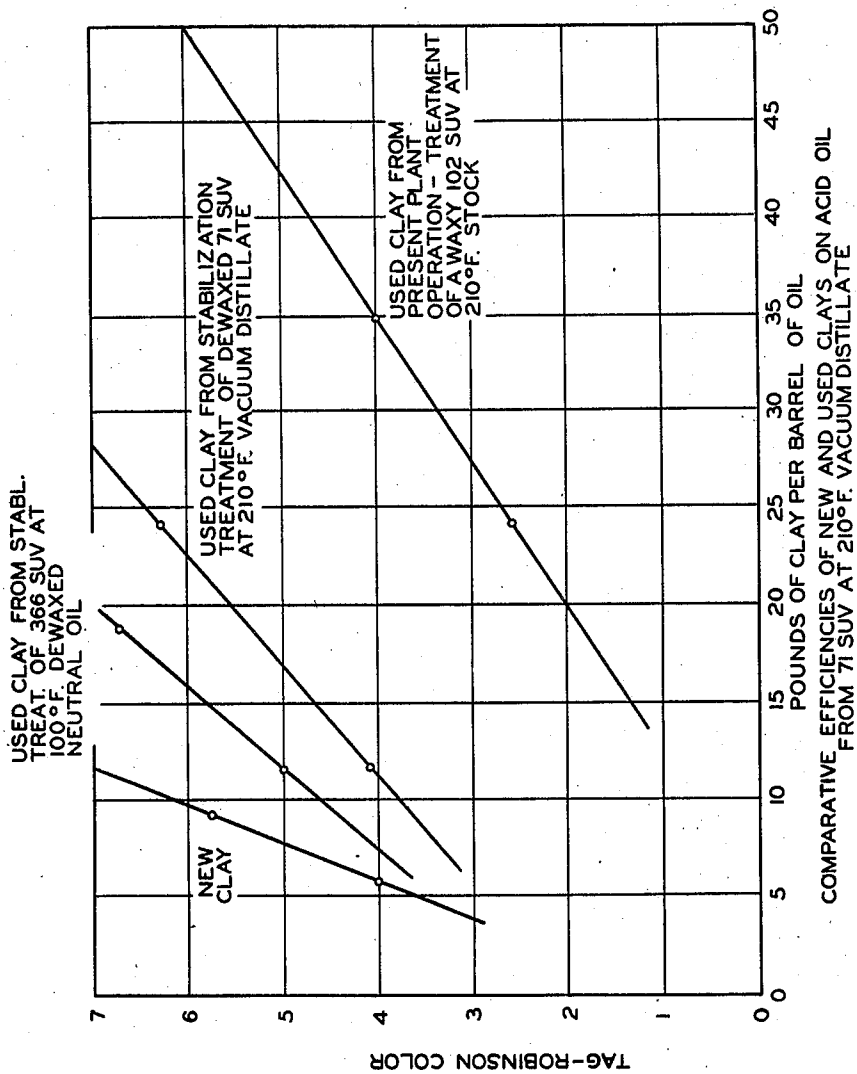

FIG. 3

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PROCESS FOR THE MANUFACTURE OF LUBRICATING OILS

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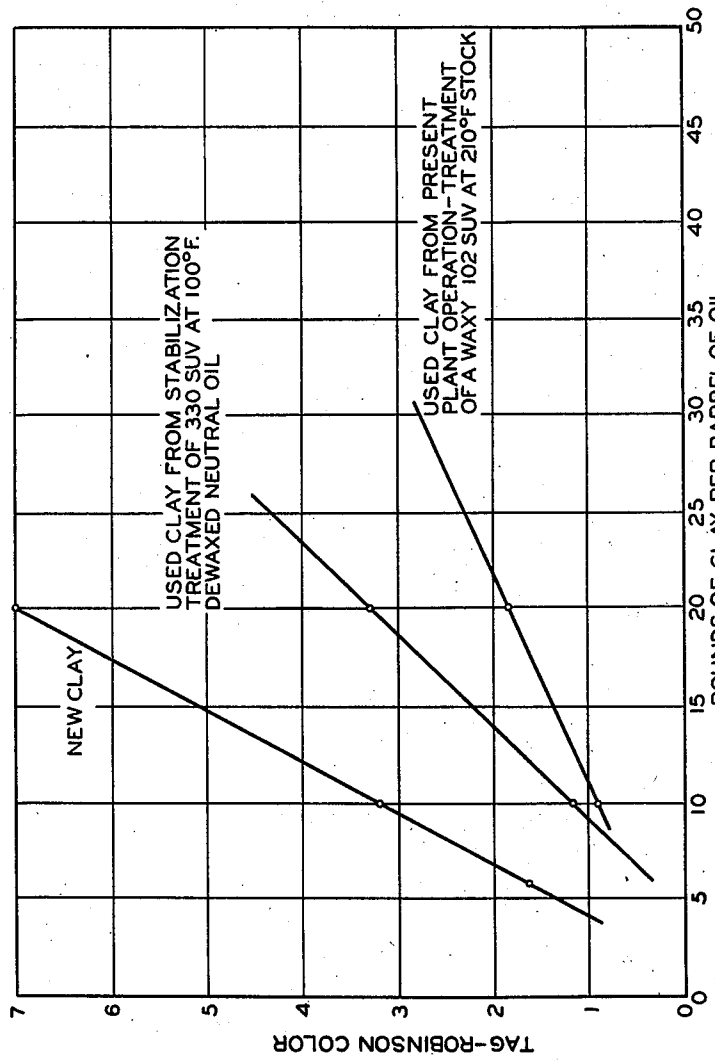

COMPARATIVE EFFICIENCIES OF NEW AND USED CLAYS ON ACID OIL FROM A 102 SUV AT 210°F. BLEND OF 80% PIPE STILL RESIDUUM AND 20% VACUUM DISTILLATE

FIG. 4

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UNITED STATES PATENT OFFICE

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PROCESS FOR THE MANUFACTURE OF LUBRICATING OILS

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Application September 2, 1941, Serial No. 409,280

8 Claims. (Cl. 196—40)

The present invention relates to a process for refining mineral oils with acid and activated clay, and is more particularly concerned with the treatment of mineral oils with these materials to produce lubricating oils of greater stability and improved characteristics than heretofore attainable.

Acid and clay refining have been employed alone and in combination for the treatment of lubricating oils, and are well known for the beneficial effects which they impart thereto. Such prior methods, however, are directed mainly to treatment of waxy lube stock which results in the clay becoming completely exhausted, and therefore have proven a rather costly mode of procedure. Further methods have been proposed which involve acid-clay treatment of dewaxed oils which have not previously been refined to accomplish the removal of "pour point depressors." These materials consist mainly of asphaltic and/or tarry matter and when present prevent thorough dewaxing due to their adverse effect on wax crystallization. Likewise, when the oil has not been treated specifically to remove pour point depressors, subsequent treatment with acid causes a very substantial increase in the pour point of dewaxed oil.

An object of the invention is to produce lubricating oils more highly refined and of greater stability than attainable by acid and clay refining methods heretofore. A further object is to provide a process of refining lubricating oils which is economical and efficient. Another object is to accomplish the removal of pour point depressants prior to dewaxing. A still further object is to provide a process which will result in acid-free distillates and avoid the corrosion of equipment. Another object is to provide an oil of improved color. Another object is to provide an oil of improved gravity.

The present invention provides a process which involves a primary acid treatment preferably with sulfuric acid, whereby pour point depressors are substantially removed with other impurities, followed by contact with activated clay for the adsorption of principal color body and asphaltic content and neutralization of the acid oil. This enables a very thorough dewaxing of the lube oil stock, and thereafter the oil is subjected to a further acid-stabilizing treatment. The final treatment with acid results in a stable oil unaltered by subsequent treatment and without substantial change in pour point. The latter effect is due to the removal of constituents by the primary acid treatment, which if present during dewaxing and if removed in the stabilization treatment would cause a substantial rise in pour point. The invention further contemplates the use of acid sludge from the stabilizing step for treatment of the waxy lube stock, thereby providing a substantial economy. The acid oil from the stabilization treatment is treated with contact clay for the removal of traces of color bodies and impurities not previously removed and neutralization of the acid oil. Clay derived from the treatment of stabilized acid oil is preferably employed in treatment of acid oil from the primary acid treat. It has been found that spent clay from ordinary plant processes, where initial contact is affected in the presence of wax, asphaltic and tarry constituents, is substantially spent and of such low efficiency that it must be either discarded or reactivated. It is a feature of this invention that fresh activated clay used to treat oil from which wax, asphaltic and other impurities have been substantially removed, is employed to neutralize waxy acid oil and remove the greater portion of the asphalt and color bodies prior to dewaxing. This clay retains sufficient activity and adsorptivity to adsorb a substantial amount of asphaltic constituents, and at the same time neutralize the waxy acid oil derived from the primary acid contact. Dewaxed oil which has received a final stabilizing and clay contact treatment in accordance with this invention has been found to retain better stability and to be much more highly refined than oil produced by known methods. An important phase of the process is the distillation of the clay treated stabilized oil in the presence of the clay. By methods previously known, a certain amount of acid, not physically or chemically bound to the clay, remains in the oil, and an essential feature of this invention consists in flashing off this acid just prior to distillation.

Briefly, we propose to produce finished lubricating oils of improved characteristics by separating residual lube stock into an overhead waxy lube stock and residual tar by distillation at controlled temperatures, either at atmospheric pres-

sure or above or below atmospheric pressure, with or without the use of steam or other diluents. The distilled waxy lube stock is then treated with partially spent sulfuric acid contained in sulfuric acid sludge formed during the further treatment of dewaxed lube stock with fresh sulfuric acid, as later described, and preferably at a temperature within the range of from 80 to 140° F. Optionally, the waxy acid oil may be further treated with fresh sulfuric acid, preferably 98 percent sulfuric acid. The waxy acid oil is then contacted at controlled elevated temperatures with clay obtained from the contacting of dewaxed acid oil with fresh clay, as later more fully described. The contacting step with clay is preferably carried out by multipass in furnace tubes with or without steam and/or added water at temperatures in the range of from 400 to 600° F. Other temperature ranges may be employed, but it has been found that this temperature is sufficient to bring the activity of the partially spent clay to the desired point. As an integral part of the contacting step, acid materials not physically or chemically bound to the clay are flashed off in a clay-oil flash pot, later described in detail. The clay-oil mix is then filtered and the treated waxy lube distillate is dewaxed, preferably by filter dewaxing from solution in an acetone-benzol-toluene or similar dewaxing solvent. The dewaxed lube stock is then stabilized by treatment with fresh sulfuric acid at controlled temperatures and with either 98 percent acid or "fuming" 104 percent acid, or if dilution is employed, the treatment may be carried out at temperatures as low as 0° F. We prefer to operate upon the undilute oil with 98 percent sulfuric acid at or near atmospheric temperature, such as from 60 to 120° F. The acid sludge from this treatment retains a sufficient acid value for the removal of pour point depressors from waxy lube stock of relatively low viscosity in the primary treat. The dewaxed acid oil or dewaxed acid oil solution is then contacted with fresh activated contact clay in furnace tubes at controlled elevated temperatures. A contact method may be either a single-pass or multiple-pass, with or without steam or added water, and the temperature depends upon the material being treated, the contact time and whether or not the diluents are present. Acidic materials not physically or chemically bound to the clay are thereupon flashed off at elevated temperature, i. e., from 400 to 600° F., in a clay-oil flash pot and the clay-oil mixture is further heated in a furnace coil or similar apparatus and charged to distillation equipment where separation is effected into an acid-free distillate, consisting of a highly improved lube oil of relatively low viscosity and a residual, greatly improved lube oil of relatively high viscosity containing clay. The distillation is carried out in conventional equipment, and at controlled temperatures to avoid injury to the oil. Steam or low boiling diluents may be used to aid in the distillation, if it is carried out at atmospheric pressure. Vacuum distillation is advantageous, either with or without steam or other diluent; however, we prefer to employ dry flash vacuum distillation.

The residual lube oil is filtered to remove clay, producing a highly improved acid-free lube oil of relatively high viscosity. The distillate and residual lube oil are highly improved, stable lube oils, and may be used separately or blended in any desired proportions. The clay from the latter step remains approximately 50 percent efficient, and may be employed in treatment of fresh waxy lube stock for the removal of pour point depressors, other impurities, and neutralization of the oil.

The contacting of the waxy acid oil with clay obtained from treatment of dewaxed oil is sufficient to effect substantial neutralization of the acid content of the oil, thereby avoiding the use of neutralizing agents commonly employed, such as caustic, ammonia, lime and the like, which promote the formation of emulsions and production of soluble soaps which are difficult to remove from the oil. The clay from the secondary clay contact treatment is effective to the desired degree when used to contact the oil in furnace tubes at elevated temperatures, whereas mere filtration of the oil through a cake of partially spent clay does not develop the necessary activity. We have found, however, that oil so treated retains a small amount of acid not physically or chemically bound to the clay, which it is difficult or impossible to render inactive irregardless of the quantity of clay employed. The presence of this acid not physically or chemically bound to the clay is objectionable, particularly in the oil following the second contact stage with fresh clay which will result in acid distillates, as well as promote corrosion of equipment. In accordance with this invention, we flash off this acid not physically or chemically bound to the clay at elevated temperatures, i. e., from 400 to 600° F. in the presence of the clay, and prior to distillation in the second stage.

The stabilization with fresh acid on dewaxed oil produces a highly improved lube oil and is much more effective as a stabilization measure than when acid treatment is made in the presence of wax. This treatment is likewise economical since the expensive treating agent is used on the lube stock only and after asphalt and wax have been removed. This final stabilization step is sufficiently late in the refining process to be practically unaffected by subsequent refining steps and the oil so treated remains stable even under the influence of relatively high temperatures. Likewise, a substantial rise in pour point of the dewaxed oil is not experienced, due to the fact that pour point depressors were removed prior to dewaxing. The final clay contact with new clay effects neutralization of the acid oil and is highly effective to accomplish the removal of color-forming materials and traces of residual impurities, thereby producing a highly stable and refined lubricating oil. Contacting the oil with clay removes all acid residues, both with the aid of steam and consequent removal from the flash pot, and by chemical and physical action within and upon the clay particles, causing said material to be bound to and adsorbed by the clay and thereby removed from the oil. This allows distillation to take place without corrosion of equipment, and without the production of acid lube distillates.

Figures 1 and 2 illustrate diagrammatically an apparatus suitable for carrying out the process of this invention, Figure 2 being a continuation of Figure 1. Figure 3 is a graph illustrating the comparative efficiencies of new and used clays on acid oil from 71 S. U. V. at 210° F., vacuum distillate. Figure 4 is also a graph illustrating the comparative efficiencies of new and used clays on acid oil from a 102 S. U. V. at 210° F. blend of 80% pipe still residuum and 20% vacuum distillate.

Referring to Figure 1, crude mineral oil from

storage tank 1 is flowed through line 2 to furnace 3 whence it is withdrawn through line 4 to still 5. Furnace 3 and still 5 may be the well known pipe still-bubble tower combination, or may be any other conventional distillation unit used in the art to separate crude mineral oil into overhead distillates and residual lube stocks. Steam from line 6 may be introduced into still 5 to aid in distillation. Overhead products are withdrawn as through line 7, and the residual lube stock of desired flash and viscosity is withdrawn through line 8 to storage tank 9. The residual lube stock from storage tank 9 is flowed through line 10 to furnace 11 and thence withdrawn through line 12 to still 13. Still 13 may be a conventional atmospheric still where distillation is effected by use of steam admitted through line 14, or may be a vacuum still where either steam or low boiling hydrocarbon is admitted through line 14 to aid in distillation. We prefer to use "dry" flash vacuum distillation, wherein line 14 is omitted. In the case of vacuum distillation, the reduction in pressure is effected by means of mechanical vacuum pumps or by steam jet ejectors, not shown. If desired, still 13 may contain reboiler tubes, not shown, through which heated liquid is circulated to assist in stripping the tarry residue. In any case the distillation steps in stills 5 and 13 may be carried out in conventional equipment, and the method of distillation is not considered a part of our invention. From still 13, the asphaltic residue, or tar, is withdrawn through line 15 to storage, not shown. Waxy lube distillate is taken overhead from still 13 through line 16, through condensing equipment, not shown, and to storage tank 17, thence to acid treating equipment 19 through line 18. If desired, residual lube stock from storage tank 9 may be flowed directly through line 20 to acid treating equipment 19. If desirable, the oil charge to acid treating equipment 19 may be a combination of waxy lube distillate from still 13 and waxy residual lube stock from tank 9. Acid sludge is admitted to acid treating equipment 19 through line 21 from sludge charge pot 22. Acid treating equipment 19 may be conventional acid treating equipment, either batch or continuous. If desired, acid treatment may be carried out in solution, in which case naphtha or other suitable diluent may be introduced through line 23. In case the diluent is propane or other similar material of high vapor pressure, apparatus 19 must be of suitable material and construction to permit of usage at above atmospheric pressure. The acid oil, or acid oil solution, is withdrawn from treater 19 through line 24 to acid treating equipment 25. This equipment may be similar in design and operation to equipment 19, or may be other conventional acid treating equipment. New acid is admitted to 25 through line 27, from storage not shown. Acid sludge from 19 is withdrawn through line 26 and thence through line 30 to storage not shown. Acid sludge from 25 is withdrawn through line 28 and thence may be combined with sludge from line 26 and flowed to storage through line 30, or when and as desired, may be flowed through line 29 to sludge charge pot 22. If desired, "gas oil" or other suitable diluent may be added to the acid sludge in line 30 from line 31, to impart desired fluidity to the sludge to permit pumping and other handling. Acid-oil, or acid-oil solution from 25 is withdrawn through line 32 to storage tank 33, and thence to line 34 and clay-mix tank 35 to which clay from the stabilization treatment is added through line 36. If desired, water may be added to line 36 through line 37 from source not shown. The clay-oil mix in 35 may be obtained in conventional manner. We prefer to use mechanical agitation as by recirculating pumps or by motor driven stirrer. The clay-oil mix from 35 is flowed through line 38 to furnace 39 and thence through line 40 to flash pot 41. In flash pot 41, volatile acid compounds, steam, and low boiling diluent (if present) are withdrawn through line 42. If desired, steam or low boiling diluent may be added to flash pot 41 through line 40—A. The volatile acidic materials, steam and/or low boiling diluent from line 42 are flowed into tower 43 to which cooling water or other cooling and absorption medium is admitted through line 45. Non-condensed vapors are withdrawn through line 44. If propane or other similar low boiling diluent has been used, it is withdrawn through line 44. Water, acid materials, and any light lube oil fractions which may have been distilled from flash pot 41 are condensed in tower 43 and flowed through line 46 to separator 47 whence mineral oils are withdrawn through line 48 to storage not shown and water and acidic materials are withdrawn through line 49 to discard. Hot clay-oil mix from flash pot 41 is withdrawn through line 50. A portion is recirculated to furnace 39 through line 51 and the balance is withdrawn through line 52 to clay-oil surge tank 53. The temperature of the above described clay-contacting process is controlled as desired, in furnace 39. We prefer to operate in the approximate range of 400 to 600° F., but other temperatures are permissible and may at times be desirable. When clay from the stabilization treatment is employed, this procedure is found preferable. The contacting in furnace 39 may be "single-pass," or "multiple-pass," as we have described. The clay-oil mix from surge pot 53 is flowed through line 54 to filter equipment 55. If desired, diluent may be added through line 56. Filter apparatus 55 may be any conventional filter equipment, such as the well known "Oliver rotary filter," or the "Sweetland filter press" type, or other similar equipment. Spent clay is withdrawn from 55 through line 57, and may be discarded, re-claimed, or processed to recover contained oil, as desired. Filtered oil, or filtered oil solution, is withdrawn through line 58 to dewaxing equipment 59. Dewaxing may be by conventional method. We prefer to use filter dewaxing with suitable solvent as propane, acetone-benzol-toluene, etc. The method and act of dewaxing are known art, however, the point in the entire refining process at which dewaxing is carried out is highly critical in the present invention. Petrolatum or wax from dewaxing equipment 59 is withdrawn through line 60 to storage not shown, and the dewaxed oil from 59 is withdrawn through line 61 to storage tank 62. A draw-off 64 is shown for low grade lube oils which may be used for blending purposes. The dewaxed lube oil stock is withdrawn from tank 62 through line 63 and thence through line 65 to stabilization acid treating equipment 66. New acid is added to 66 through line 67 from source not shown. If desired, propane, low boiling naphtha, or other suitable diluent may be added to 66 through line 68 from source not shown. Acid-treating equipment 66 may be conventional acid-treating equipment, either batch or continuous, and may or may not be carried out in solution in low boiling diluent. The temperature may be controlled, as desired. We prefer to treat undiluted lube stock

at approximately 60 to 120° F., but treatment may be carried out in solution in propane or other diluent, at sub-atmospheric temperatures as at 0° F., or lower. Acid sludge, containing valuable partially spent acid, is withdrawn from 66 through line 69 to storage tank 70, and thence through line 71 to sludge charge pot 22 for use in treating waxy lube stock in 19, as previously described. If desired, the acid treatment in 66 may be preceded by separation of the dewaxed lube stock into fractions of different viscosity by distillation, or "propane fractionation" in conventional manner in equipment not shown. Acid-oil, or acid-oil solution, from 66 is withdrawn through line 72 to storage tank 73, and thence through line 74 to clay-mix tank 75. New activated contact clay, such as "Filtrol" contact clay is added to 75 through line 76. If desired, water is added to line 75 through line 77. Agitation may be by conventional means. We prefer to use recirculating pumps or motor driven stirrer. The clay-oil mix from 75 is flowed through line 78 to furnace 79 and thence through line 80 to flash pot 81. In flash pot 81, volatile acid compounds, steam and low boiling diluent, if present, are withdrawn through line 82. If desired, steam or low boiling diluent may be added to flash pot 81 through line 80—A. The volatile acidic compounds, steam and/or low boiling diluent from line 82 are flowed into tower 83 to which cooling water or other cooling and absorption medium is admitted through line 85. Non-condensed vapors are withdrawn through line 84. If propane or other similar low boiling diluent has been used, it is withdrawn through line 84. Water, acidic materials and any light lube oil fractions which may have been distilled from flash pot 81 are condensed in tower 83 and flowed through line 86 to separator 87 whence mineral oils are withdrawn through line 88 to storage not shown, and water and acidic materials are withdrawn through line 89 to discard. Hot clay-oil mix from flash pot 81 is withdrawn through line 90. A portion is recirculated to furnace 79 through line 91, and the balance is withdrawn through line 92 to heating coil 93. Heating coil 93 may be a part of the furnace 79, or, if desired, may be in a separate furnace. From heating coil 93 the hot clay-oil mix is withdrawn through line 94 to still 95. The temperature of the above clay-contacting process is controlled as desired in furnace 79. We prefer to operate in the approximate range of 400 to 600° F., but other temperatures are permissible and may at times be desirable. The contacting in furnace 79 may be "single-pass," or "multiple-pass," as we have described. In any case, the method in flash pot 81 is an essential feature for in this manner we avoid the presence of acidic and corrosive materials in still 95. The temperature in heating coil 93 is controlled in the necessary range to effect the desired distillation in still 95. Still 95 may be an atmospheric still of conventional design where distillation is effected by the use of steam admitted through line 94—A, or may be a vacuum still. We prefer to use "dry" flash vacuum distillation, wherein line 94—A is omitted. In the case of vacuum distillation, the reduction in pressure is effected by means of mechanical pumps or by steam jet ejectors, not shown. If desired, still 95 may contain reboiler tubes, not shown, through which heated liquid is circulated to assist in stripping the residual oil. Distillation of the oil from which volatile acidic materials have been flashed off previously in the presence of clay promotes better adsorption of the impurities by the clay, and avoids acid distillates. From still 95, the distillate consisting of highly improved lube oil of relatively low viscosity is withdrawn through line 96, and thence through condensing and cooling equipment and separating equipment if steam has been used, not shown, and on to storage. The residual oil and clay is withdrawn from still 95 through line 97 and thence through line 98 to clay-oil surge pot 99. The clay-oil mix from surge pot 99 is flowed through line 100 to filter equipment 101. Filter apparatus 101 may be any conventional filter equipment, such as the well known "Oliver rotary filter," or the "Sweetland filter press" type, or similar equipment. Clay is withdrawn from 101 through line 102 and thence is recirculated to clay-oil mix tank 35, as previously described. If desired, acid oil from acid oil storage tank 33 may be added to the clay from the stabilization treatment in line 102 and thence is recirculated to clay-oil mix tank 35, as previously described. Also, if desired, acid oil from acid oil storage tank 33 may be added to the clay from the stabilization treatment in line 102 through line 103 to impart necessary fluidity for pumping. Filtered oil, consisting of highly improved lube oil of relatively high viscosity is withdrawn from 101 through 104 to storage, not shown.

If desired, wax-free oil from storage tank 62 may be flowed through line 63 and 74—A, direct to clay-oil mix tank 75, thus omitting the acid stabilization step. In some cases, both acid stabilization and clay-contacting may be omitted, in which case wax-free oil from storage tank 62 is withdrawn through lines 63, 90—A, 90 and 92 to heating coil 93, and thence to fractionating still 95. Unless previously refined, oils so treated are of inferior quality.

Clay-oil mix from heating coil 93 may be flowed through lines 94, 97—A, 97 and 98, direct to clay-oil surge pot 99, when fractionation is not necessary.

In addition to the highly improved oils which result from the specific mode of treatment in accordance with this invention, substantial economies are effected, first by the use of acid sludge from the stabilization step for the treatment of the waxy lube which serves to recover any valuable lube stock contained in the sludge from those treating steps and likewise permits the full utilization of the acid. It has been found, for instance, that this sludge possesses an acid value equivalent to about 40 percent of the weight of the entire amount of new acid employed in the stabilization step. Thus, the maximum amount of fresh acid is used in the final treatment where it is most effective and also obviates waste of useful acid in the sludge.

The use of clay from the stabilization treatment for contacting waxy acid oil under the influence of heat is a convenient and economical method for effecting neutralization. Of course, new clay or clay derived from other sources or employed in contacting partially refined oils having the required activity may be employed for this purpose, the specific mode of treatment being responsible for the improved lube oil herein disclosed. The clay obtained by this process has about 50 percent of the efficiency of new clay and contains an appreciable quantity of useful oil adsorbed in the secondary treatment when removed from the filter. By using this clay to contact waxy acid oil this oil is re-

covered, we believe, by displacement from the clay by selective adsorption of resinous and asphaltic materials present in the waxy acid oil. In addition, excessive and unnecessary refining of by-products, such as wax, is avoided since the treatment of the waxy lube stock is carefully controlled so as to remove only asphalt, tar and other undesirable materials, such as pour point depressors, so that these materials are not present to contaminate the wax during dewaxing.

Figures 3 and 4 illustrate graphically the advantages and economies derived in this process by the use of clay from the stabilization treatment on waxy acid oil in the initial contact stage. The pounds of clay per barrel of oil are plotted against a Tag-Robinson color scale.

Referring to Figure 3, the comparative efficiencies of new and used clays on acid oil from 71 S. U. V. @ 210° F. vacuum distillate are compared. The line marked "New Clay" shows the Tag-Robinson colors that can be obtained by contacting the vacuum distillate with various amounts of new Filtrol clay. Note that eight pounds of new clay per barrel of oil will give 5 Tag-Robinson color. To compare efficiencies, the line 5 Tag-Robinson color is used for the basis of comparison and eight pounds per barrel of new Filtrol clay is arbitrarily taken as 100% efficient. It takes twelve pounds per barrel of used clay from a stabilization treatment of 366 S. U. V. @ 100° F. dewaxed neutral oil to make 5 Tag-Robinson color on acid oil from 71 S. U. V. @ 210° F. vacuum distillate. As the neutral oil was highly refined before it was contacted with the clay, the clay still retained 67 percent of the efficiency of new clay when it was reused in contacting vacuum distillate.

Using clay from a stabilization treatment of dewaxed 71 S. U. V. @ 210° F. vacuum distillate, it takes 17 pounds of the used clay per barrel of oil to make 5 Tag-Robinson color. This is an efficiency of 47 percent. The efficiency is lower than that of the clay from stabilizing neutral oil because the dewaxed 71 viscosity vacuum distillate is a slightly heavier oil than the neutral oil and it is not quite so highly refined.

When clay from the treatment of a waxy 102 S. U. V. @ 210° F. stock is employed, it takes 42.5 pounds of the used clay per barrel of oil to make 5 Tag-Robinson color. This is an efficiency of 19 percent. The stock originally treated with this clay is heavier and less highly refined than either of the other two.

From this graph, four general conclusions can be drawn:

1. The more highly refined an oil is when contacted with clay, the greater is the efficiency of the used clay.

2. The lower the viscosity of an oil when it is contacted with clay, the greater is the efficiency of the used clay.

3. A spent clay from a stabilization treatment of a dewaxed distillate is substantially more efficient than the one which has resulted from the treatment of a waxy distillate as in usual plant operation.

4. Considerable economies are effected inasmuch as much less clay is necessary to obtain a given Tag-Robinson color using new clay for treating dewaxed oil and thereafter for treatment of waxy acid oil.

Referring to Figure 4, the comparative efficiencies of new and used clays on acid oil from a 102 S. U. V. @ 210° F. blend of 80% pipe still residuum and 20% vacuum distillate are compared. As before, the line marked "New Clay" shows the colors that can be obtained by contacting the blend with new clay. This has a darker color originally than the vacuum distillate of the other graph and therefore requires more clay to obtain the same color of contacted oil. This blend, for example, requires 15 pounds of new clay per barrel of oil to make 5 Tag-Robinson color, whereas the vacuum distillate requires only 8 pounds of new clay per barrel of oil. To compare efficiencies on this graph, use the line 2 Tag-Robinson color. Seven pounds of new clay per barrel of oil are required to make 2 Tag-Robinson color; this is arbitrarily taken as 100% efficient.

Using clay from the stabilization treatment of 330 S. U. V. @ 100° F. dewaxed neutral oil, 13½ pounds of used clay per barrel of oil are required to make 2 Tag-Robinson color. This is an efficiency of about 52 percent.

Using clay from the contacting of a heavier, less highly refined oil, a waxy 102 S. U. V. @ 210° F. stock, requires 23 pounds of used clay per barrel of oil to make 2 Tag-Robinson color. This is an efficiency of about 30 percent.

This graph confirms the general conclusions drawn from Figure 3 in demonstration of economies afforded by the present invention.

The following example of the operation of our process is cited, all yields being based on the original crude oil.

EXAMPLE I

Mixed-base crude oil from the Oklahoma City field in the Mid-Continent area was charged to atmospheric still 5 at a temperature of 775° F., where it was reduced, with steam, to a 35% yield of a residual lube stock of 95 Saybolt Universal viscosity @ 210° F. This residual stock was dry flash vacuum distilled in still 13 to a 29% yield of waxy lube stock distillate 71 S. U. V. @ 210° F. This waxy stock was batch treated at 130° F., in agitator 19, with 18# of partially spent acid per barrel of waxy oil. This partially spent acid was contained in sludge withdrawn from agitator 66. The 27% yield of acid oil from agitator 19 was charged to batch agitator 25 where it was treated at 130° F. with 10# of fresh 98% sulfuric acid per barrel of original waxy oil (to 19). The 25.5% yield of 66.5 S. U. V. acid oil from agitator 25 was contacted by multiple-pass at 500° F. in furnace 39 with 11.6 pounds of clay per barrel of acid oil. The contact time was 50 minutes, with added steam. This clay was obtained from filter 101. The clay-oil mix was withdrawn through 52, and surge pot 53 and filtered hot, without dilution, in filter apparatus 55. There was no decrease in oil volume at this point since the clay from 101 was already saturated with oil which was displaced by asphalting materials and color bodies adsorbed during the contact period in furnace 39. The 25.5% yield of 67 S. U. V. contacted waxy oil was filter dewaxed at −10° F. with acetone-benzene-toluene solution in dewaxing apparatus 59. A 21% yield of dewaxed lube stock of 74 S. U. V. @ 210° F. and 0° F. pour and cloud point was secured. The dewaxed lube stock was batch acid treated at 100° F., without dilution, in acid agitator 66, with 25# of fresh 98% sulfuric acid per barrel of dewaxed oil. A 19.8% yield of 73 S. U. V. @ 210° F. acid oil was obtained. The acid sludge from 66, containing partially spent acid, was charged to sludge charge pot 22 for reuse in treating waxy lube distillate as described. The acid oil from 66 was contacted by multiple-

pass at 500° F. in furnace 79 with 15# of new "Super Filtrol" contact clay per barrel of acid oil. Contact time was 20 minutes, with steam and added water. The clay-oil mix was withdrawn through line 92, heating coil 93 and line 94 to "dry" flash vacuum still 95. A 11.5% yield of highly improved lube oil of 50 S. U. V. @ 210° F. was distilled overhead. The residual oil and clay from 95 was filtered hot, without dilution, in 101. A 7.7% yield of highly improved lube oil of 165 S. U. V. @ 210° F. was secured. The clay from 101 was recirculated to clay-oil mix tank 35 where it was used to treat waxy acid oil from agitator 25. A portion of the clay-oil mix from heating coil 93 was withdrawn directly to the clay-oil surge pot 99 and thence to clay filter 101. By this method a 19.2% yield of highly improved lube oil of 71 S. U. V. @ 210° F. was secured.

Properties of the oils from the various treating stages are shown below in Table I.

TABLE I

Properties of intermediate and finished lube oils produced by special acid and clay refining process

Product	Yield on crude oil	A. P. I. gravity	S. U. V. @ 210° F.	Flash	C. C. R.	Color	Pour	Cloud
	Percent			*°F.*			*°F.*	*°F.*
Okla. City crude oil	100	38.2					5	
Residual lube stock from still 5	35		95	450	3.5	400 Lov		
Waxy lube distillate from still 13	29	24.7	71	460	1.5	2,030 O. D		
Acid-oil from agt. 19	27		68.5		0.7	800 O. D		
Acid-oil from agt. 25	25.5		66.5		0.5	270 O. D		
Contacted oil from filter 55	25.5		67		0.5	5 T. R		
Wax-free oil from dewaxer 59	21	25.2	74	465	0.5	4 T. R	0	0
Acid-oil from agt. 66	19.8		73					
Unfractionated lube oil from filter 101	19.2	26.6	71	465	0.25	2¾ A.S.T.M.	5	5

The following table illustrates the comparative acid and clay requirements for lube oils processed in accordance with this invention compared to requirements for conventionally refined lube oils.

TABLE II

Comparative acid and clay requirements for specially processed lube oils vs. conventionally refined lube oils

ORIGINAL VACUUM DISTILLATE FROM OKLA. CITY REDUCED CRUDE

S. U. V. @ 210° F. 71
Yield on crude ..... per cent.. 29

	Special refining process	Conventional refining process (vacuum distillate, acid treated, clay contacted, dewaxed)	
		A	B
Acid used per bbl. finished oil pounds	42.425	43.2	58.5
Clay used per bbl. finished oil	15.45	22.5	22.5
Finished lube oil yield, percent on crude	19.2	20.3	19.8
Tests:			
A. P. I. gravity	26.6	26.2	26.6
Flash °F	465	430	440
Fire °F	545	515	520
S. U. V. @ 210° F	71	66.5	66.5
C. C. R.	.25	.3	.25
A. S. T. M. color	2¾	3¼	3
Indiana oxidation test at 341° F:			
Hours to 10 mg. sludge	52	30	35
Hours to 100 mg. sludge	87	65	86
Increase in viscosity at 50 hours percent	8	16	13.5

The table below illustrates comparative tests on SAE 20 lube oils prepared in accordance with this invention compared with oils prepared by conventional acid and clay refining.

TABLE III

Comparative tests on SAE 20 lube oils as prepared by special process vs. oils prepared by conventional acid and clay refining

	Special S. A. E. 20	Conventional S. A. E. 20
A. P. I. gravity	29.1	27.3
Flash ° F	440	420
Fire ° F	500	480
S. U. V. @ 210° F	52	52
A. S. T. M. color	1¾	3¾
Ramsbottom carbon residue per cent	0.073	0.153
Indiana oxidation test:		
Hours to 10 mg. sludge	30	20
Hours to 100 mg. sludge	106	52
Increase in viscosity at 50 hrs per cent	7	12
O. D. color stability:		
Original O. D. color	5.2	58
Color after heating 4 hrs. @ 302° F	12.9	108
Underwood test (results on used oil):		
Naphtha insoluble per cent	.450	.792
Chloroform soluble do	.393	.766
Spray chamber deposit	(1)	(2)

[1] Stain, no deposit. [2] Little soft sludge.

In order to demonstrate the advantages of the present process over conventional acid and clay refining, the following example is given in which lube oil specially processed in accordance with this invention is compared with oil refined by ordinary plant process.

EXAMPLE II

A lube oil is produced by ordinary plant operation as follows: A blend of 80% pipe still residuum and 20% vacuum distillate is charged to the acid agitators. It is given two treats with 98% sulfuric acid. The acid oil is mixed with Super-Filtrol clay and 1 to 3% water added. The mixture is charged to the oil heater and contacted at 525° F. to 550° F. At this temperature, the water and acid vapors flash off in the evaporator. The contacted oil is diluted 50% with naphtha and the solution run through Sweetland presses to remove the clay. The solution is further diluted to 36% oil and chilled at a slow rate to −44° F. It is then centrifuged to remove wax. The solution is charged to a still, and the naphtha is recovered. At the same time, the wax-free oil is fractionated to neutral oil and 125 S. U. V. @ 210° F. bright stock. This method hereafter will be referred to as present plant operation.

A blend of 80% pipe still residuum and 20% vacuum distillate was specially processed in accordance with the present invention as follows: This blend was treated with acid sludge from the stabilization of wax-free oil, and then given a second acid treat using fresh 98% acid. The waxy acid oil was neutralized by contacting with clay from the stabilization treatment of wax-free oil. Acid was flashed off and the waxy contacted oil was solvent dewaxed and wax-free oil

recovered. The wax-free oil was stabilized by treating with 98% acid, and contacted with clay. Acid was flashed off and the oil was fractionated in the presence of the clay into a neutral oil and bottoms of 125 S. U. V. @ 210° F. bright stock. The clay was filtered from the bottoms and saved for neutralization purposes in the primary treatment. In the ensuing table, oil produced by this process is designated as case I.

A variation of the process was carried out in the same manner as in case I, with the exception that the first acid treat using acid sludge from the stabilization of wax-free oil was omitted. Before dewaxing, the oil was given only one acid treat and that with 98% acid. This method will hereafter be referred to in the table as case II.

The following table gives the laboratory tests on the finished neutral oils and bright stocks made by the foregoing three methods.

TABLE IV

	Present plant oper.		Specially processed case I		Specially processed case II	
	Neutral oil	Bright stock	Neutral oil	Bright stock	Neutral oil	Bright stock
Gravity, A. P. I.	28.1	24.6	28.6	25.2	28.4	25.1
Flash	410	505	395	535	375	525
Fire	470	580	480	620	460	605
Pour	25	10	0	0	10	5
Color, A. S. T. M.	2		1	4¼	1¼	4¼
Color, T. R.		1¾		8¼		6½
S. U. V. @ 100° F.	217.7	2,074	231	2,412	210	2,202
S. U. V. @ 210° F.	46.6	122	47.3	135.8	46.0	126.9
V. I.	84.8	82.2	82.6	85.3	80.7	83.1
C. C. R.	0.02	1.05	0.01	0.91	0.02	0.86
Indiana oxidation:						
Hr. for 10 mg. sludge.	22	84	26	Nil	23	Nil
Hr. for 100 mg. sludge.	68	94	90	Nil	78	Nil
50 hr. S. U. V. @ 210° F.	51.1	144	51.8	152	50.8	143
Percent increase.	10	18	9.5	12	10	13
90 hr. S. U. V. @ 210° F.	55.1	185	55.1	178	54.4	169
Percent increase.	18	51	16	31	18	35

A number of outstanding improvements in oils specially processed in accordance with this invention over present plant oils shown in the table are as follows:

1. Oxidation stability of both neutral oil and bright stock, as measured by the Indiana oxidation test, shows much improvement.

2. The color of the finished oil is very light and is much better than present oils.

3. Conradson carbon residue of the oils is reduced.

4. An oil of improved gravity is obtained.

The material costs of proposed process, case I, were practically the same as for present plant operation. Proposed process, case II, yielded oils nearly identical with those yielded by proposed process, case I, but at a slightly lower material cost.

The strength and quantity of acid necessary in the primary acid contact depends principally on the viscosity of the original oil under treatment. In the case of relatively light, low viscosity oils, it is ordinarily sufficient to treat with sludge acid alone, while slightly heavier oils require a further light treatment with full strength acid. Heavier oils of intermediate viscosity are best treated by a single treatment with full strength acid, whereas, heavy oils of relatively high viscosity will ordinarily require a double treatment with full strength fresh acid.

It is thus apparent that lubricating oils produced in accordance with this invention are of highly improved characteristics over those produced by conventional methods. These results are likewise obtained without sacrifice of efficiency and with improvement in economy.

We claim:

1. A method of refining lubricating oils which comprises treating wax containing lubricating oil stock with acid and separating acid sludge therefrom, contacting the resultant waxy acid oil with clay and flashing off acid not physically or chemically bound to the clay in the oil, dewaxing to desired pour characteristics, acid-stabilizing the dewaxed stock, treating the separated acid oil with activated clay, flashing off acid not physically or chemically bound to the clay in the oil and distilling the same in the presence of the clay to recover an acid-free highly improved lubricating oil.

2. A process of refining lubricating oils wherein wax containing oils are subjected to acid and clay contact before and after dewaxing, which comprises treating the oil with acid, contacting the resultant waxy acid oil with partially spent activated clay derived from the treatment of dewaxed oil with fresh clay, dewaxing said oil to desired pour characteristics, acid-stabilizing the dewaxed stock and treating the separated acid oil with fresh activated clay for the recovery of a highly refined lubricating oil.

3. A process for the refining of lubricating oils wherein wax containing oils are subjected to acid and clay contact before and after dewaxing, which comprises treating the oil with acid of sufficient strength to remove pour point depressants, contacting the resultant waxy acid oil with partially spent activated clay obtained from the subsequent contact of dewaxed oil with fresh clay, and dewaxing the separated neutralized oil to desired pour characteristics, acid-stabilizing the dewaxed stock, treating the separated acid oil with fresh activated clay, and recovering highly refined lubricating oil.

4. A process for the refining of lubricating oils wherein wax containing oils are subjected to acid and clay contact before and after dewaxing, which comprises treating the oil with acid of sufficient strength to remove pour point depressants, contacting the resultant waxy acid oil with partially spent activated clay obtained from the subsequent contact of dewaxed oil with fresh clay, and dewaxing the separated neutralized oil to desired pour characteristics, acid-stabilizing the dewaxed stock, treating the separated acid oil with fresh activated clay, flashing off acid not physically or chemically bound to the clay in the oil, thereafter distilling the oil in the presence of the clay and recovering an acid-free highly refined lubricating oil.

5. In a process for the refining of lubricating oils wherein said oils are subjected to acid contact followed by clay contact both before and after dewaxing, the step of utilizing clay which has been contacted with said oil subsequent to dewaxing for contact with said oil prior to dewaxing thereof.

6. A process according to claim 5 wherein the acid with which the oil is contacted is sulfuric acid and in which acid sludge resulting from treatment subsequent to dewaxing is contacted with said oil prior to dewaxing.

7. A process for producing stable lubricating oils of a relatively high degree of purity which comprises substantially removing pour point de-

pressants from wax containing oil by treatment with acid prior to dewaxing, separating acid sludge therefrom, contacting the resultant waxy acid oil with activated clay, and dewaxing to desired pour characteristics, acid stabilizing the dewaxed stock, treating the separated acid oil with activated clay and recovering highly refined lubricating oil.

8. A process for producing stable lubricating oils of a relatively high degree of purity which comprises removing pour point depressants from wax containing lubricating oil by treatment with sulfuric acid prior to dewaxing, separating acid sludge therefrom, contacting the resultant waxy acid oil with activated clay and dewaxing the same to the desired pour characteristics, acid stabilizing the dewaxed stock with sulfuric acid, treating the separated acid oil with activated clay, and recovering acid free refined lubricating oil.

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