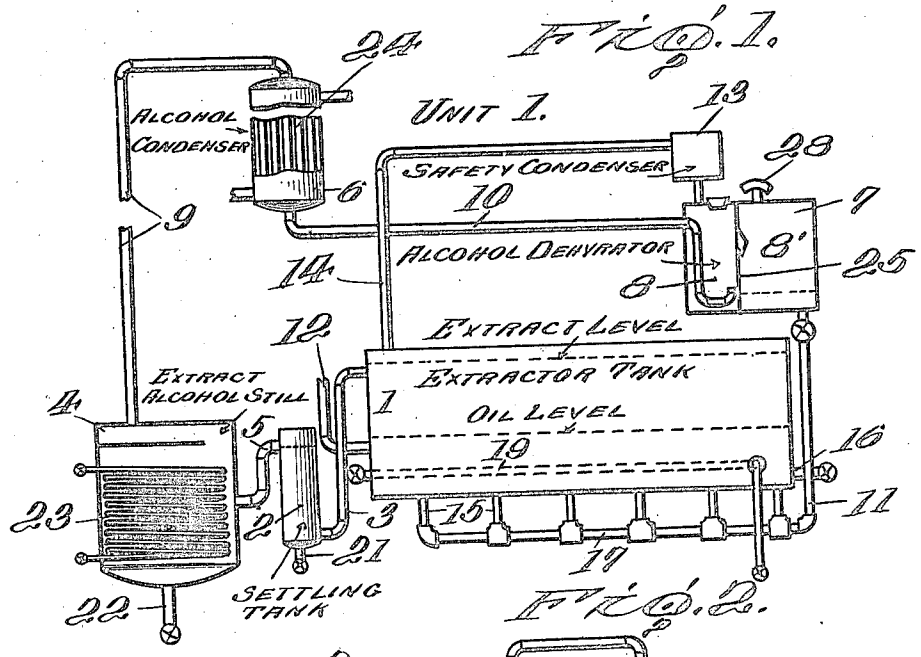
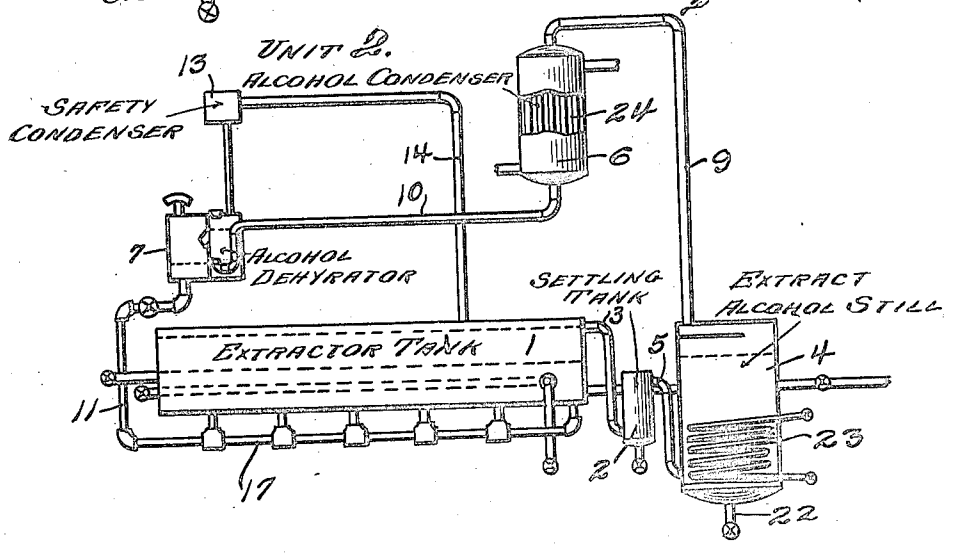
Aug. 14, 1928. 1,680,353

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APPARATUS FOR THE FRACTIONAL EXTRACTION OF PETROLEUM HYDROCARBONS WITH ALCOHOL

Original Filed Nov. 19, 1924 3 Sheets-Sheet 1





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Aug. 14, 1928. 1,680,353

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APPARATUS FOR THE FRACTIONAL EXTRACTION OF PETROLEUM HYDROCARBONS WITH ALCOHOL

Original Filed Nov. 19, 1924 3 Sheets-Sheet 2

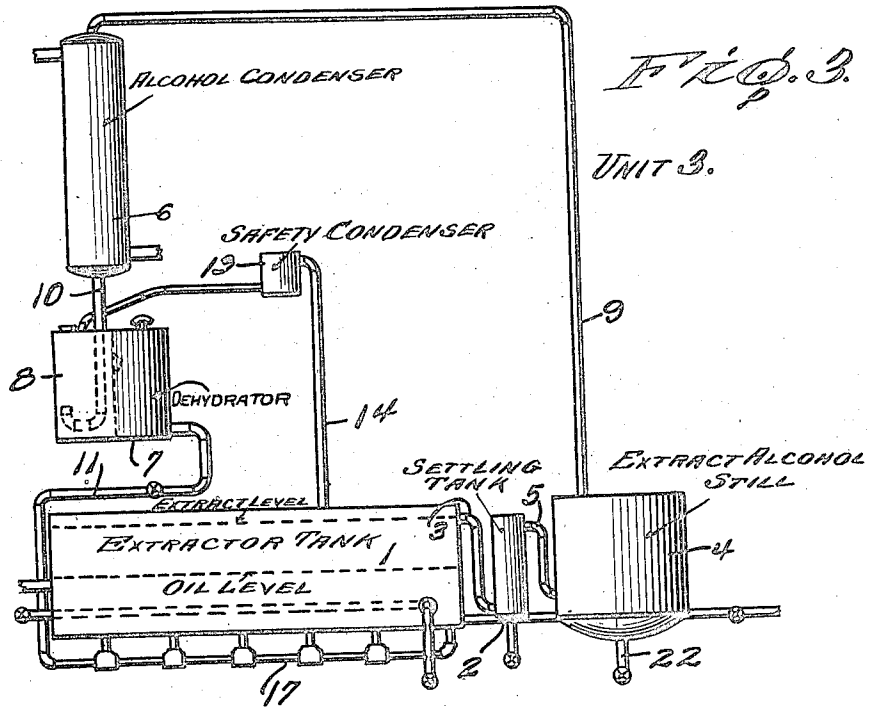


FIG. 3.

UNIT 3.

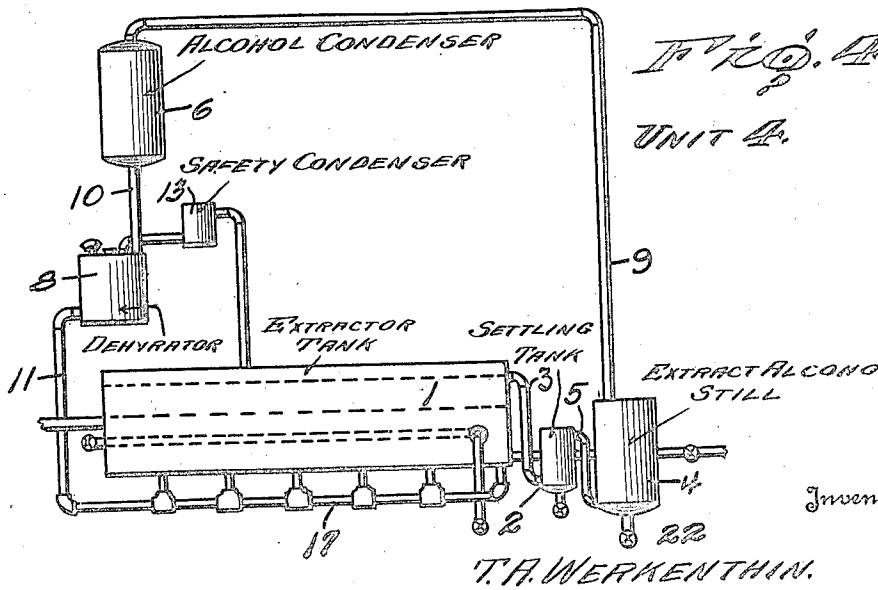


FIG. 4.

UNIT 4.

Inventor

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Attorney

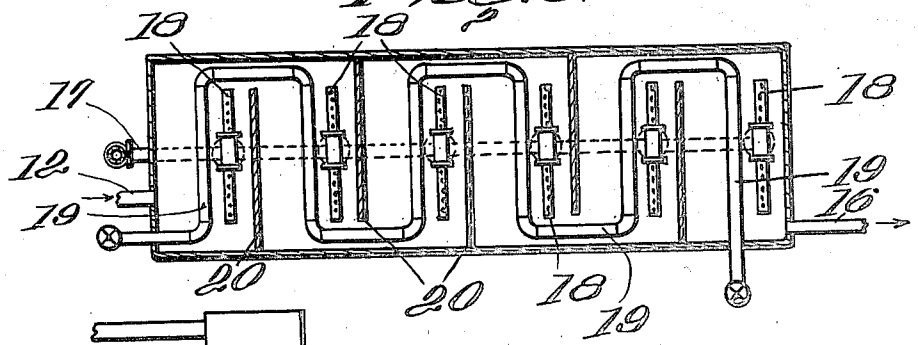
Aug. 14, 1928. 1,680,353

T. A. WERKENTHIN

APPARATUS FOR THE FRACTIONAL EXTRACTION OF PETROLEUM HYDROCARBONS WITH ALCOHOL

Original Filed Nov. 19, 1924 3 Sheets-Sheet 3

Fig. 5.



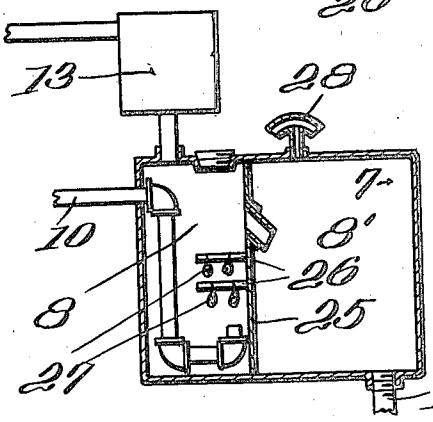


Fig. 6.

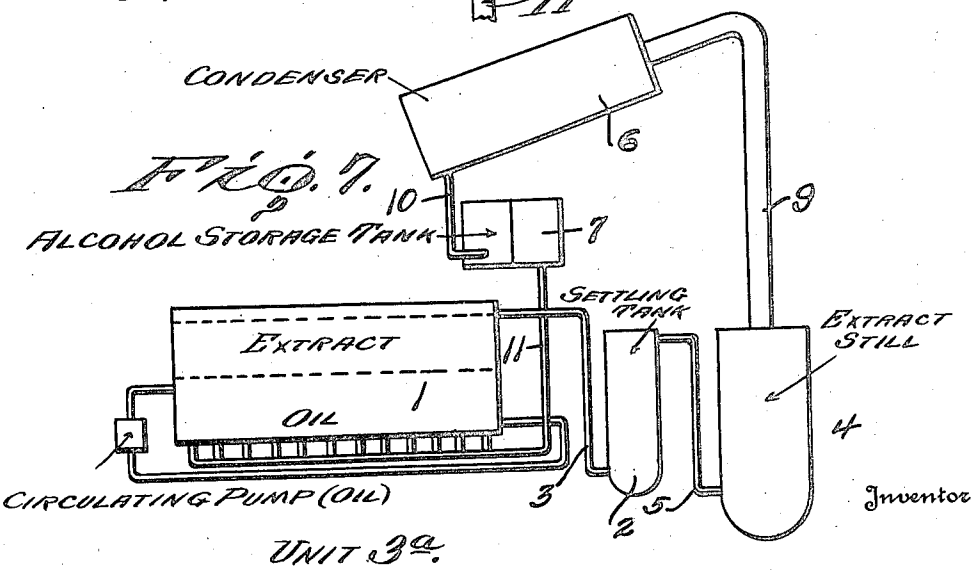


Fig. 7.

UNIT 3a.

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By

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Patented Aug. 14, 1928. 1,680,353

UNITED STATES PATENT OFFICE.

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APPARATUS FOR THE FRACTIONAL EXTRACTION OF PETROLEUM HYDROCARBONS WITH ALCOHOL.

Original application filed November 19, 1924, Serial No. 750,783. Divided and this application filed November 4, 1925. Serial No. 66,727.

My invention relates to an apparatus for the fractional extraction of petroleum hydrocarbons with alcohol to produce a cracking stock and various grades of lubricating oils, and is a divisional application of my application filed November 19, 1924, Serial No. 750,783, for a process of and apparatus for the fractional extraction of petroleum hydrocarbons with alcohol.

According to my invention petroleum hydrocarbons are successively extracted from skimmed crude in a continuous manner with alcohol at a low temperature and in the absence of any substantial pressure whereby a cracking stock is produced and a yield of lubricating oils is obtained which is much greater than possible by the present method of overhead distillation. This may be readily understood when it is considered that in the overhead method of producing lubricating stock, the oil suffers marked cracking of the heavy molecules into gases such as methane and ethane with the corresponding production of first unsaturated compounds and finally by complete dehydrogenation of the hydrocarbon molecules, passes into coke. In the production of this coke the most valuable lubricating components are destroyed.

In carrying out my invention, skimmed crude oil is utilized as a starting material; a cracking stock and lubricating oils are selectively extracted therefrom with alcohol. The crude skimmed oil, that is one deprived of its gasoline and kerosene content, is extracted first with alcohol so as to dissolve the most soluble components, this constituting the cracking stock. Thereafter the remaining oil which has been deprived of the cracking stock is repeatedly subjected to an alcohol extraction treatment to produce a series of lubricating oils of remarkably high character, and a residuum or asphalt notable for its low free carbon-content. This residual oil or asphaltum furnishes an ideal binder free from grit and impurities. The entire process is carried out at a very low temperature, the specific temperature employed being of course, determined somewhat by the character of the material undergoing treatment. To furnish the necessary heat, steam coils are preferably employed and the extract is maintained at a temperature that, as stated may vary, but usually ranges between 150 and 175° F. The process, as compared to the overhead method of distillation, is characterized by its great fuel economy since the heat is saved necessary to raise the oil from the temperature at which cracking commences which in the skimming operation represents the end point of the distillation of the crude to be used in the process, to the temperature of coking which runs about 800° F., and is the end point of the ordinary coking distillation. Additionally, the heat required to reduce the paraffin distillate after cold pressing to the overhead light lubricating oils and the residual red oils, is substantially entirely saved, for the separation is effected by solution and extraction with alcohol at a relatively low temperature. Further, the red oils produced in the reducing stills need to be steamed on an average three times in order to produce satisfactory results with the shake tests while the oils resulting from the present process need only to be steamed once. In this connection, it should be noted that not only is there a saving in steam but the time necessary for the steaming operation is greatly reduced. In comparing the overhead distillation system with my process, it will be seen that all the fuel expenditure required in the latter is that necessary to keep the starting material and the intermediate products at a temperature of 150 to 175° F., and to vaporize the alcohol in the continuous system, since, the recovery and reuse of the alcohol is contemplated. In considering the heat necessary to vaporize the alcohol at the temperature stated, it should be noted that the heat of vaporization of alcohol is only 370 B. t. u. per pound of alcohol whereas the heat of vaporization of water at the same temperature is about three times as large. It is therefore obvious that the extraction process employing alcohol effects a great saving in fuel. Exhaust steam may be employed as the fuel, and this is the only source of heat necessary to produce the various products.

Apparatus suitable for carrying out my invention is illustrated in the accompanying drawings in which:

Figs. 1, 2, 3 and 4 are elevations of successive extraction units;

Fig. 5 is a general plan view of extractor unit No. 3, which is typical of the other units and shows the arrangement of the extractor baffle plates, the exhaust steam coils and the perforated alcohol pipes;

Fig. 6 is a detail of the alcohol dehydrator and storage tank;

Fig. 7 is a diagrammatic representation of a supplementary unit whereby crude red oil stock may be brought, within certain limits, to any desired viscosity.

The apparatus set forth in Fig. 1 which for convenience will be referred to as unit 1 will be described in detail. Figs. 2, 3 and 4 show successive extraction units, similar to extraction unit 1 and will be referred to as units 2, 3 and 4. The size of the different elements of these latter units differ somewhat from those of unit 1 but otherwise there are no essential differences between the various units and the description of Fig. 1 will therefore adequately serve for the others.

Referring to Fig. 1 unit 1, comprises an extraction-tank 1, a settling tank 2, a conduit 3 therebetween, an extract alcohol still 4 connected to the settling tank 2 by the conduit 5, an alcohol condenser 6, and an alcohol storage tank 7 having as an integral part thereof an alcohol dehydrator chamber 8, the construction of which will be described later on. Conduits 9, 10 and 11, serve to connect the various elements to make the unit operative. The extraction tank 1 is provided with an oil inlet 12 and outlet 16 to unit 2 and is in operative connection with the safety condenser 13 by means of the conduit 14. The conduit 11, connects with the bottom alcohol pipe 17, provided with branches 15 which terminate in perforated alcohol coils 18 as shown in Fig. 5. The heat necessary to carry out the process is furnished by the extractor stream coils 19 as indicated more in detail in Fig. 5. This figure also indicates the arrangement of the baffle plates 20.

The settling tank 2 is provided with a conduit 21 to allow the removal of any undissolved oil which may be mechanically carried over from the extractor tank 1. Conduit 22 of the alcohol still 4 allows the collection of the portion of the oil extracted by the alcohol. The alcohol still 4 is heated to the necessary temperature by means of the steam coils 23. The alcohol condenser 6 is provided with the usual water pipes 24. The alcohol storage tank 7 is divided by the partition 25 so as to form a dehydrator chamber 8 which is provided with means for holding a dehydrating chemical whereby the small traces of water which may have been extracted from the oil and distilled over with the alcohol may be removed. This may comprise rods or plates 26 carrying bags or canvas plates 27. The alcohol storage tank 7 is also provided with a vent 28.

The process may be carried out as follows:

The oil introduced into the system may be either a paraffin base crude oil or an asphalt base crude oil or a mixed asphalt-paraffin base crude oil. All the natural gasoline and refined oil is topped from the crude oil, the exact amount taken depending on the nature of the crude which naturally has varying amounts of light fractions in it. It is important that in the topping operation care be taken to avoid cracking as this breaks up some of the lubricating stock. If a paraffin base oil is used the extracted fractions of oils must be chilled and have the paraffine cold pressed but if an asphalt base oil is used, the latter may be directly introduced into the system without any subsequent treatment of the extracted oils other than color treatment.

The skimmed crude oil produced as described, for example, 100 barrels is pumped into the extractor tank 1 of unit 1 and allowed to flow through the baffled compartments thereof while the alcohol introduced through coils 15 and 17 is extracting the light portion or cracking stock from the oil. The dissolved oil-extract is allowed to run into the settling tank 2 to allow any undissolved oil, which may have been carried along mechanically to settle out. The oil-extract overflows into still 4 where the alcohol is distilled off and passes into the water condenser 6 to be condensed. The condensed alcohol runs into storage tank 7 first flowing into compartment 8 to be dehydrated by means of a dehydrating chemical suitably suspended therein. From the storage tank 7 the alcohol is returned by gravity to the bottom of the extractor 1 and rises through the oil dissolving the lightest portion thereof; again overflowing into the small settling tank. The oil or cracking stock produced would amount to thirty-five barrels or generally speaking 35% of the oil introduced into the system.

The remaining undissolved oil flows by gravity into the extractor of unit 2 and there has its light lubricating components extracted by alcohol. The dissolved oil-extract produced in the extractor of unit 2 passes into a settling tank similar to that of unit 1 and thereafter to an alcohol still where the alcohol is removed by distillation from the extract and the extracted oil which is a light lubricating oil having the characteristics later referred to sinks to the bottom to be withdrawn as it accumulates just as in the first unit. The quantity of this light lubricating oil is about 10 barrels or 10%

of the oil introduced into the system. The alcohol is returned to the extractor of unit 2 and used over and over again. The size of the extractor, the ratio of oil to alcohol, and the length of time that the oil remains in the extractor determines the amount and also to some extent the quality of the oil extracted.

The remaining oil deprived of its cracking stock components and light lubricating oil components is run by gravity into the extractor of unit 3 which is similar to the other two units but larger in size in all its parts such as alcohol still, condenser and etc. In unit 3 the lubricating oil of 250–310 viscosity is extracted from the oil in the same manner as the preceding two units. The quantity of lubricating oil extracted in unit 3 is about thirty-five barrels or 35% of the oil introduced into the system. The undissolved oil is allowed to run by gravity to the extractor of unit 4 where heavy lubricating oil of high viscosity may be extracted. The heavy lubricating oil obtained from unit 4 represents about a 10% fraction of the oil introduced into the system as well as does the residuum so each of these would be 10 barrel fractions, assuming as stated that the initial amount of crude oil introduced into the system is 100 barrels. The residuum from this last extraction will, in general, be of the nature of asphaltum, its precise qualities depending on whether asphalt base oil or paraffin base or mixed base oil is used in the process. The carbon content of the residual asphaltum will be directly proportional to the carbon content of the topped crude; that is, all the free carbon is apparently left behind in the residuum and will roughly be ten times that of the carbon content of the original topped crude as it will have been concentrated from one hundred volumes to ten volumes of oil. For example, if the topped crude has one-fourth of one per cent free carbon then the free carbon of the residue will be two and one-half per cent.

The oil which is drawn off from the alcohol extract still of each unit is dried to recover any traces of alcohol except in the case of the cracking stock, which may, if desired, be sent to the pressure stills immediately upon being drawn off from the bottom of the alcohol still. In some cases, the number of units may be increased and different grades of oil produced.

Crude red oil stock as produced in unit 3 may be brought to any desired viscosity (within certain limits) by being circulated through a supplementary unit 3^A indicated diagrammatically in Fig. 7 and extracted there with alcohol kept at a slightly lower temperature, say 130 degrees F. This unit is run independently of the four units of the system and is part of the lubricating finishing plant. The oil extracted from the crude red oil as derived from unit 3^A may be returned to the crude to be run through the system again or used the same as the light oil extracted in unit 2. By this method a small portion of the red oil is extracted but those components which are diluting the oil are gotten rid of, thus leaving the unextracted oil from unit 3^A, the red oil of the desired viscosity. After pumping the oil through the supplementary unit 3^A continuously for the required length of time for example, three hours which it takes to extract the light portion of the crude red oil, it is freed of any traces of alcohol and after a treatment for color is ready for the market. Supplementary unit 3^A is intended to be used when necessary only as a corrective medium.

The properties, nature and amounts of the different products obtained by the process set forth is indicated by the following: Since the initial starting material is the product which has been skimmed of gasoline and kerosene content just below the point at which cracking commences as previously described, this skimmed crude oil has all the lubricating components and some light components found in the spindle oils left in. Some Gulf Coastal crudes may be used directly. As an example of the basic stock suitable for use in the process the following is given: gravity 18° Bé., flash point 500° F.

This stock is extracted by means of the alcohol in such a way that the more soluble components are dissolved first. These more soluble components are low gravity and low viscosity oils between 23–25° Bé. gravity for the 85 to 100 seconds Saybolt viscosity cracking stock while the less soluble components have up to 26.6 degrees Bé. gravity and the high viscosity of 400–500 seconds Saybolt of heavy lubricating oils. This phenomenon of low gravity and low viscosity and vice versa have been observed in the products obtained in the process from asphalt as well as from paraffin base oils which seems to indicate that it is not always the low gravity oil that possesses the high viscosity as has been generally assumed.

A feasible explanation of this is that the molecular components containing oxygen and sulfur have a tendency to lower the gravity but have no particular influence on the viscosity of the oil.

The cracking stock oil which is extracted in unit 1 will vary from 20% to 35% depending on the nature of the skimmed crude used as a starting point. It will have a gravity of 23–25° Bé., a viscosity of 85 to 100 seconds Saybolt at 100° F., a flash point of 250° F., and a fire point of 290° F. This stock is suitable for light spindle oils but as it constitutes such a large percentage of the crude it is advisable to use it as cracking stock. It is intended to use this oil with-

out completely recovering the traces of alcohol after it is drawn off the alcohol extract still. An example of the cracking stock obtained is as follows:

Gravity	24.4° Bé.
Flash	305° F.
Viscosity	112 seconds at 100° F.
Cold test	36° F.

The light lubricating oil produced in unit 2 has a viscosity of 180–215 seconds Saybolt at 100° F. and a gravity of about 25 to 25.5° Bé., a flash point of 350° F. and a fire point of 390° F. The oil constitutes about 9–12% of the oil charged. It shows a fair steam or shake test without steaming out but, in order to show a perfectly acceptable test, it will have to be steamed out once unless clayed with an acid-clay treatment to produce the desired color. The untreated oil in a thin film has a golden yellow color while in a four ounce bottle it is deep ruby in color or opaque. An example of the light lubricating oil obtained in unit 2 is as follows:

Gravity	25.9° Bé.
Flash	340° F.
Viscosity	160 seconds at 100° F.

The third and most important product of the process is an oil of 290–350 seconds Saybolt viscosity at 100° F. This high grade oil forms from about 23% to 38% of the oil charged into the system. It has a flash point of about 430° F. and a fire point of 480° F. It has a remarkable high gravity of 26° Bé. to 26.8° Bé. This oil will also require a slight steaming to stand up to the shake or steam test perfectly. Its color is the same as the lighter oil and will require acid-clay or acid treatment to produce the desired color. An example of the medium lubricating oil is as follows:

Gravity	26.1° Bé.
Flash	370° F.
Viscosity	306 seconds at 100° F.

The fourth product which results to the extent of 8–10% of the oil charged does not necessarily have to be separated but may be included in the third unit if desired. This heavy oil of from 450–300 seconds Saybolt viscosity has a gravity of about 26° Bé. and a flash point of 483° F. and a fire point of 531° F. This high viscosity high gravity oil requires the same treatment for finishing as does the oil produced in unit 3. An example of the heavy lubricating oil obtained is as follows:

Gravity	26.5° Bé.
Flash	390° F
Viscosity	496 seconds Saybolt at 100° F.

It is to be especially noted that the various lubricating oils have to be cold pressed if a paraffin base oil or mixed base oil has been used as a basis for the topped crude. This cold pressing is accomplished just as ordinarily in cold pressing lubricating oil stock but as the extracted oils the way they come from the extract-alcohol still contain a small quantity, say one-fourth to three-fourths of one per cent of alcohol, they have a remarkable low viscosity due to these traces of alcohol and can be easily pumped and otherwise handled for color treatment and cold pressing and presents them in a very favorable condition for chilling and cold pressing. After the color has been obtained and the oil freed from its paraffin content, the remaining traces of alcohol may be removed.

The residuum or asphalt comprises about 8–11% of the stock charged into the system and is best converted to true asphalt by blowing to produce the desired consistency. At 100° F. this residue-oil flows very slowly, has a shiny black appearance and is sticky to the touch. A remarkable feature of the asphalt is that only a small per cent of free carbon is present unless found in such fine colloidal suspension that it does not show up when the mass is dissolved in benzine and filtered.

Any of the standard methods for dehydrating alcohol may be employed to obtain the anhydrous product used in the process. The alcohol may be made anhydrous in several ways but the one which I have found most satisfactory is the following:

The alcohol is stirred in a tank for about twenty-four hours with the theoretical quantity of fresh lime (calcium oxide). The purer the grade of lime used, the less will be the loss due to mechanical absorption of the alcohol. The lime is now allowed to settle and the clear or slightly limpid alcohol is decanted off and is mixed with dehydrated powdered copper sulphate or blue stone and placed in the still. The distillate from this is water free alcohol. It is not essential to use absolutely water free alcohol, but one that does not indicate a blue color when tested with the white anhydrous copper sulphate has been found to give the best results when used in the process. The copper sulphate left in the still is dissolved in hot water and allowed to recrystallize in a tank. The blue stone thus obtained is again made anhydrous and may be used over and over. The alcohol which remains in the lime may be regained by steaming out the lime accumulated from several batches and concentrating the dilute alcohol in fractionating stillheads but whether this method of recovery is employed or not depends on the market price of the alcohol used.

Only the initial amount of alcohol required for the process is large and the amount required later on is just that needed

to replace the slight loss from evaporation from the continuous system.

In order to insure the anhydrous nature of the alcohol as it is kept circulating around in the continuous system, chamber 8 of the alcohol storage tank 7 is provided with bags or canvas plates 27 filled with anhydrous copper sulphate which is in intimate contact with the alcohol thus taking out small traces of water that may have been extracted from the oil and distilled over with the alcohol. From this chamber the thus dehydrated alcohol overflows into chamber 8' which serves as the real storage tank. The copper sulphate is removed from time to time and examined. Its color will indicate whether it is anhydrous or has taken up its five molecules of water of crystallization. The copper sulphate in its anhydrous form has by weight roughly four times the efficiency of lime in removing water from alcohol and has the additional advantage of being economically recovered.

The various impurities usually contained in the commercial grades of alcohol do not effect the amount of oil dissolved by the alcohol in the minute quantities that they are present excepting possibly pyridine bases which impart a somewhat disagreeable odor to the oil. It may be feasible to obtain alcohol free from this undesirable component.

The alcohol needs no purifications, unless dehydrating the traces of water that are carried along with the alcohol from the extract alcohol still to the condenser, may be spoken of as purification. That is one of the advantages of the process that the alcohol needs no troublesome process of revivifying and can be used an indefinite length of time.

It is desired to indicate that the total yield of lubricating oils obtainable when using my process may be as high as 30 per cent of the crude which is almost two and one-half times the usual quantity obtainable with the overhead distillation processes now in use. On the other hand if it is not desired to produce this maximum amount of lubricating oils, my process still represents the most economical method of producing cracking stock for the pressure stills.

The contention of superior quality oil produced by my process is based on the following considerations: The light gravity oil produced contains a homogeneous series of hydrocarbons that, as shown by a series of carbonization tests, will withstand high temperature better and with the production of less carbon than the oils produced by ordinary distillation.

The substances may have almost identical boiling points and differ in other essential properties. This state of affairs occurs without end in organic chemicals and also applies to components of crude petroleum. Thus, two substances may have identical vaporization temperatures yet may differ widely in the temperature at which decomposition occurs. The differential solubility of the components of crude oil in the alcohol eliminates this extensively.

The total value of all the products produced in the process as compared with the total value of the products ordinarily produced will show a good margin in favor of my process.

Another big factor of economy of the process is the construction of the various units. As there is no pressure on them, they may be of light construction effecting a great saving of material in the structural and foundation as well as in the boiler construction. The highest temperature experienced in the process will be the boiling point of the anhydrous alcohols which is never more than 212° F.

Furthermore, no fire of any kind is in contact or in the vicinity of the oil or alcohol during the operation of the process; thus giving a reduction in the fire hazard with a corresponding saving on the insurance rates. To a large extent the fuel consumption and power production may be centralized and by the use of steam the process may be made entirely automatic if the temperature control of the extractor and the rate of flow of the skimmed crude through the system is automatically regulated. The extracting of the oil by the alcohol is automatic as designed, and depends on the rate of distillation of the alcohol from the extract in the extract alcohol still. A saving in labor cost is effected by the automatic operation of the process.

While it is preferred to use as indicated, ethyl alcohol, the process may be carried out with other alcohols, such as methyl and propyl alcohol or with mixtures of alcohols.

What I claim is:—

1. In an apparatus for extracting hydrocarbons with an alcohol, the combination in operative relation of an extractor-tank having means for introducing alcohol, means for withdrawing alcohol therefrom, means for introducing a hydrocarbon oil, and means for withdrawing a hydrocarbon oil after extraction with alcohol; an extract alcohol-still for recovering alcohol and hydrocarbon, a settling chamber intermediate the extractor-tank and the extract alcohol-still provided with means for receiving an alcoholic extraction-product from said extractor tank and means for conducting the extraction-product after settlement into the alcohol extract-still; a combined alcohol storage and dehydrator tank having means for conducting the hydrated alcohol to said extractor-tank; and an alcohol condenser having means for receiving uncondensed alcohol from the extract alcohol-still, and

means for conducting condensed undehydrated alcohol to the storage and dehydrator-tank.

2. In an apparatus for extracting hydrocarbons with an alcohol, the combination in operative relation of an extractor-tank having a series of perforated coils for introducing alcohol, means for withdrawing alcohol therefrom, means for introducing a hydrocarbon oil, means for baffling oil, and means for withdrawing a hydrocarbon oil after extraction with alcohol; and extract alcohol-still for recovering alcohol and hydrocarbon, a settling chamber intermediate the extractor-tank and extract alcohol-still provided with means for receiving an alcoholic extraction-product from said extractor tank and means for conducting the extraction-product after settlement into the alcohol extract-still; a combined alcohol storage and dehydrator tank having means for conducting the hydrated alcohol to said extractor-tank; and an alcohol condenser having means for receiving uncondensed alcohol from the extract alcohol-still, and means for conducting condensed undehydrated alcohol to the storage and dehydrator-tank.

3. In an apparatus for extracting hydrocarbons with alcohol, the combination of an extractor tank having means for introducing alcohol, means for withdrawing alcohol therefrom, means for introducing a hydrocarbon oil, and means for withdrawing a hydrocarbon oil after extraction with alcohol; of an alcohol storage and dehydrating chamber provided with means for receiving undehydrated alcohol, and means for conducting dehydrated alcohol to said extract alcohol-still.

4. In an apparatus for extracting hydrocarbons with alcohol, the combination of an extractor tank having means for introducing alcohol, means for withdrawing alcohol therefrom, means for introducing a hydrocarbon oil, and means for withdrawing a hydrocarbon oil after extraction with alcohol; and a dehydrating chamber provided with means for suspending in said chamber a dehydrating material, means for receiving undehydrated alcohol, and means for conducting dehydrated alcohol to said extract alcohol-still.

In testimony whereof I hereunto affix my signature.

THEODORE A. WERKENTHIN.