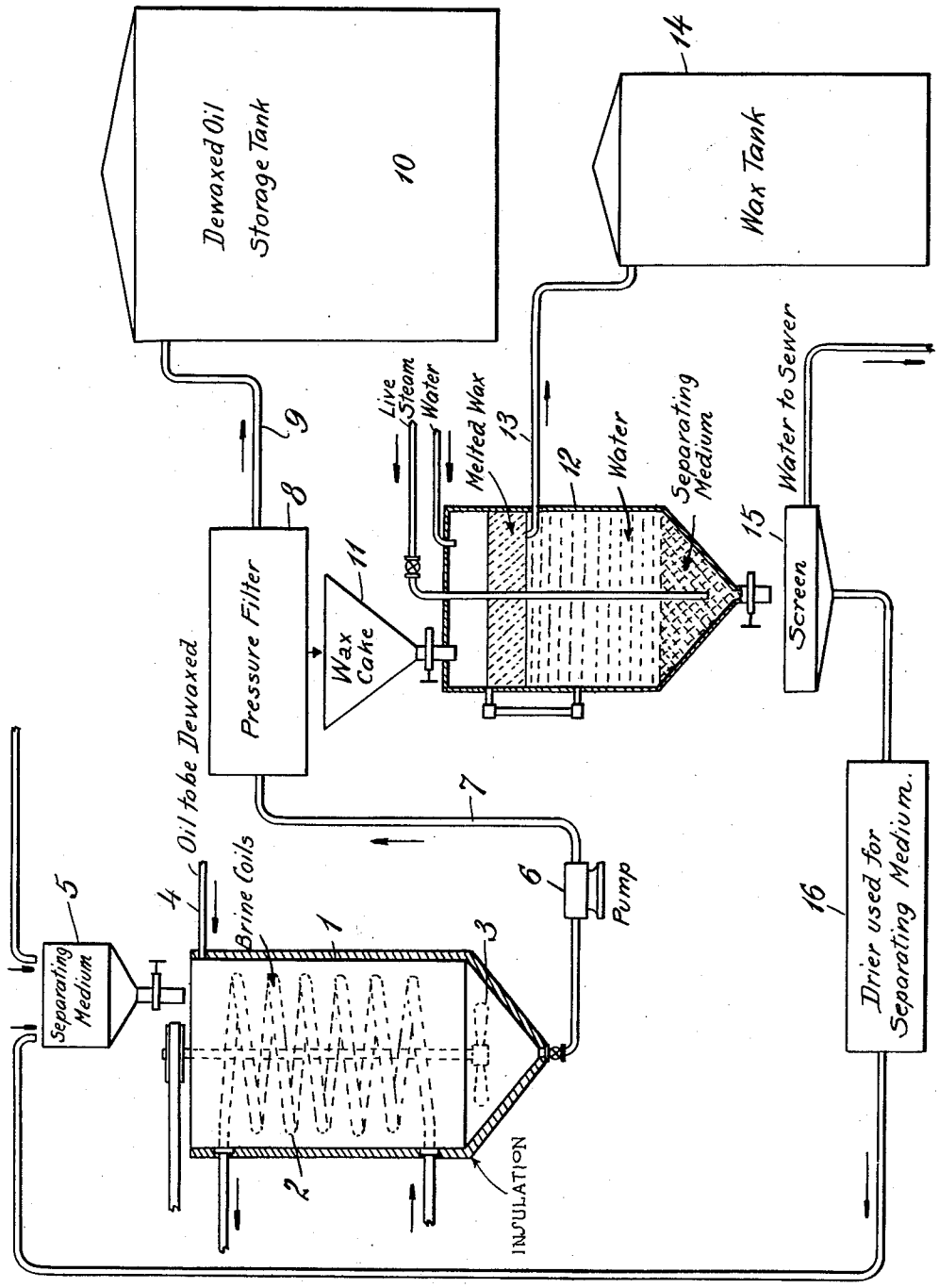
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DEWAXING OF OIL

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INVENTORS
Ernest B. Phillips
James G. Stafford
BY
Pennie, Davis, Marvin & Edmonds
ATTORNEY

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ERNEST B. PHILLIPS, OF EAST CHICAGO, INDIANA, AND JAMES G. STAFFORD, OF CHICAGO, ILLINOIS, ASSIGNORS TO SINCLAIR REFINING COMPANY, OF CHICAGO, ILLINOIS, A CORPORATION OF MAINE.

DEWAXING OF OIL.

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This invention relates to improvements in the dewaxing of oils, and particularly to the separating of wax from lubricating oils. The invention relates particularly to an improved method and apparatus for dewaxing oils. This application is a division of an application filed February 19, 1924, Serial No. 693,770.

One of the troublesome groups of compounds in crude oils are the paraffin waxes. These bodies belong to the saturated or paraffin series of hydrocarbons and vary in character from low melting point amorphous bodies to high melting point crystalline bodies. Of themselves, these waxes possess very little lubricating value. In the pure state and at temperatures well above their melting points they have many of the properties of kerosene, particularly as regards specific gravity and internal friction or viscosity. Further objection to these bodies is found in their tendency to become semi-fluid or solid at low temperatures. Oils intended for use in fluid condition at low temperatures must be cleared of their dissolved waxes, else free movement of the lubricating medium over moving parts of machinery will be lost.

From the beginning of the oil industry refiners have been striving to improve commercial methods for removal of wax from their products. Two principal methods of accomplishing this end have reached the stage of practically universal application: 1st—separation by cold pressing; 2nd—separation by cold settling.

A brief outline of refinery practice on straight paraffin base crudes will show the essentials of the two methods. This type of crude is distinguished by the fact that simple distillation with steam at atmospheric pressure will produce a residue of high quality. Such residues are called steam refined cylinder stocks and find use as internal lubricants for steam engines. Since the refiner is concerned with obtaining these residues in as good condition as possible, the whole system of distillation is directed to this end. Temperature of stills, rate of distillation and steam supply are carefully regulated so as to prevent injury to the residue. The ordinary break-up of crude into fractions is as follows: 1—crude naphtha; 2—kerosene stock; 3—300° burning oil stock; 4—gas oil; 5—wax distillate; 6—residue—steam refined stock. The first four fractions listed contain little or no wax and therefore may be disregarded.

During the time the wax distillate is being collected every effort is made to drive over as much wax from the residue as possible. Such practice makes for rough separation of waxes originally present in the crude into two groups. Wax distillate will contain a preponderance of crystalline waxes and the residue will hold waxes in amorphous form. The two principal methods for wax removal owe their development to the unlike character of these two stocks.

Waxes present in the wax distillate fraction from crude oil do not lend themselves to separation by cold pressing because of contamination with amorphous wax from the original still residue. To further change these waxes a secondary distillation is resorted to. Under the influence of high temperature and scant steam supply many of the amorphous wax bodies are converted into crystalline, or high-melting point bodies. In refineries this operation is termed "cracking wax distillate". The distillate obtained is divided into fractions,—the principal one of which is "paraffine distillate". The residue remaining in the still is a viscous dark-colored liquid which contains a large part of the impurities originally in the wax distillate, asphaltic bodies, free carbon and resinous decomposition products.

The "paraffine distillate" fraction carries a considerable percentage of wax which has been so changed in form that it will crystallize when chilled. By cooling paraffine distillate to the proper temperature it is converted into a semi-solid mass which, when cold pressed under high pressure, will give up its oil content as "pressed oil" and leave the wax content as "slack wax" on the blankets of the press. Without further separation of wax the pressed oil at once becomes stock from which all paraffine-base engine oils are made. "Slack wax" after appropriate treatment, is sweated for required melting point, filtered through fuller's earth at elevated temperatures and caked or barrelled for market.

The steam-refined cylinder stock from the original crude distillation—while a market product—commands only a low price. Small amounts of asphaltic material, free

carbon and inorganic impurities prohibit its use in high-class lubrication work. To satisfy the demand for these high-class products the petroleum refiner is required to further process his steam refined stocks to obtain type filtered and bright stocks. As soon as the impurities are removed from cylinder stocks, either by acid treating or by filtration through fuller's earth, the dissolved wax becomes less soluble and high pour tests on the purified oils are invariably found. For instance, if a +35° F. pour test steam refined stock is filtered to color, the end product will solidify at +80° F. or +90° F.

The finished stocks must therefore be dewaxed in order to have them fluid at moderately low temperatures. If naphtha solutions of filtered cylinder oils are gradually cooled, a temperature will be reached at which a large portion of the wax is no longer soluble. If such a chilled solution is allowed to stand for a period (usually about four days) the suspended wax will settle and a clear, cold solution of stock in naphtha can be drawn from the cold settling tanks.

This settled stock mixture, after removal of naphtha and straining through fuller's earth to remove the last traces of impurities, yields the bright cylinder stocks of commerce. Since these are the highest grade products manufactured every effort is made to obtain maximum yields. The settlings from the chilling tanks contain all of the separated wax and in addition a considerable quantity of high-grade cylinder oil. When the settlings are cleared of naphtha they produce crude petrolatum stock from which all grades of petrolatum are made.

The present tedious method of chilling type stock mixtures is used because wax will not settle by gravity if the chilling step is hurried. Observation of type stock mixtures while cooling shows that a nucleus of wax first forms to which strings of amorphous wax attach themselves. If the cooling starts in the upper portion of a tank convection currents are set up which drag down the slightly denser wax and leave a clear layer of oil and naphtha at the top. After a number of days the suspended wax will be found in a more or less concentrated layer at the bottom of the tank while the bulk of the charge is a bright, clear solution of cylinder oil in naphtha. Under these conditions heavy investment in plant equipment is required, relatively high operating cost for refrigeration is involved, large volumes of oil are tied up in the process and maximum yields of high-class cylinder stocks cannot be obtained.

Attempts have been made to overcome the faults of the old cold settling method by causing separation of precipitated wax in cold type stock mixtures by means of high speed centrifuges. On account of the fact, however, that the density of the suspended wax is so nearly that of the mother liquor, a separating medium in liquid form of considerably greater density than the original solution must be used. At temperatures ordinarily met with—+20 to 0° F.—this liquid must have a low freezing point. Calcium chloride brine is generally used for the purpose. This practice, however, introduces complications which in a large measure offset the advantages. Injury to the cylinder stock in the dewaxed mixture is quite likely to result from contamination with the brine. Centrifuge machines are very costly and are capable of handling only small volumes per hour. After the brine and its accompanying wax has been separated, the whole mass must be warmed to release the wax and the recovered brine must again be chilled before a new cycle of operations can begin.

The present invention provides an improved method and apparatus for the separation of wax from cold type stock mixtures, or from crude petrolatum stock produced by present dewaxing methods, or from other fractions from which separation of wax is desired; and the invention enables slow settling by gravity of the chilled type stock mixtures to be replaced by a rapid settling operation, or it enables an increased amount of valuable lubricating oil to be recovered from the crude petrolatum stock obtained by present cold settling methods, while other oils can be similarly dewaxed in a rapid and advantageous manner.

In operating the apparatus of the present invention, there is added to the solution or oil to be dewaxed, a finely divided gathering material or separating medium which has no effect upon the solution or oil but which will serve to gather the suspended wax so as to permit of filter press operations for separation of the wax from the solution or oil. In the case of naphtha-oil solutions, for example, the addition of a small amount of powdered diatomaceous earth of the type of commercial fuller's earth to the type stock mixture, either before or after chilling, will provide a large number of individual mineral particles serving as nuclei about which the amorphous wax can gather. Under such conditions the cooling step can be hurried as much as possible and when wax precipitation is complete a normal filter-press operation will cause physical separation of the mineral-wax and clear naphtha-oil solution. Instead of extending the cooling step over a period as is the case in the gravity separation method, type stock mixtures carrying 1% by weight of the earth can be chilled while being gently agitated in accordance with the improved method of the invention, and filter pressed without elevation of temperature to effect a rapid separation of amorphous wax.

The clear filtrate from the press when

cleared of naphtha and strained through fuller's earth yields type bright cylinder stock. The wax content of the press cake can be recovered if the cake is thrown in boiling water. Wax in melted state rises to the surface and can be withdrawn while the fuller's earth settles to the bottom. After freeing of water and drying in a rotary kiln, the fuller's earth is ready for re-use in the original wax separation step.

By proceeding in the manner above described, the tedious gravity settling operation for separating the wax from the type stock mixture can be eliminated and a rapid separation of the wax effected. The addition of the earth to a super-cooled solution of wax in oil and naphtha apparently induces a rapid crystal growth of wax crystals upon the particles of the earth as nuclei. If the mixture is relatively quiescent, the crystals will tend to be larger, while if the mixture is agitated, the tendency is for smaller crystals to form. In any event, however, a greatly increased rapidity of the wax separation is effected.

The invention will be further described in connection with the accompanying drawing, which illustrates, in a somewhat conventional and diagrammatic manner, an apparatus embodying the invention and adapted for the practice of the improved method of the invention; but it is intended and will be understood that the illustration is diagrammatic and illustrative, and that the invention is not limited thereto.

In the accompanying drawing the apparatus is shown partly in vertical section and partly in elevation. The tank 1 is provided with a conical shaped bottom and is heavily insulated. The tank 1 is equipped with coils 2 for cooling, for example, with cold brine, and with a mechanical stirrer 3 for agitating the contents of the tank. An inlet 4 is provided for the oil to be dewaxed, for example, the type stock mixture, which is pumped in to charge the tank 1. A finely divided gathering or separating medium, such as powdered diatomaceous earth, is stored in the bin 5, and is fed into the tank 1 as required. The charge can be chilled to the proper temperature and mild agitation can be kept up or maintained by the mechanical stirrer 3. When the charge is chilled to the proper temperature, rapid separation of the wax takes place. The batch is then transferred, without loss of refrigeration by the pump 6 and line 7 to the pressure filter shown conventionally at 8, where the physical separation of the clear oil-naphtha solution and the suspended mineral-wax takes place. The clear, cold filtrate goes forward by the line 9 to the dewaxed oil storage tank 10. The original press cake after washing with fresh cold naphtha, is dumped from the press into the hopper 11, and is fed into the hot water tank 12. Here the wax portion of the cake is melted and rises to the surface and is withdrawn through line 13 to the wax tank 14. The washings from the filter press go forward with the dewaxed oil through the line 9 to the storage tank 10. The powdered mineral released from the press cake in tank 12 settles to the bottom and is drawn off on to the screen 15. After draining, it is fed to the rotary dryer 16, and finally returned to the bin 5 for further use in the process.

It will thus be seen that the apparatus comprises a refrigerating tank with means for supplying thereto the oil to be dewaxed, and the gathering or separating medium, together with a stirrer for agitating the charge during its treatment in a refrigerated state with the gathering medium, together with a filter press for separating the refrigerated charge into the dewaxed oil and the wax cake. Provision is also made for melting the wax and separating the wax from the gathering or filtering medium, and for separating the filtering medium and drying it for further use in the process.

It will be understood that not only the tank 1, but all lines carrying cold oil, will be heavily insulated, and that the hot water tanks will be placed at some distance from the filter press. Also heat interchange devices (not shown) may be utilized, such, for example, as heat interchangers for passing the fresh incoming type stock mixture in heat interchanging relation with the dewaxed oil, so as to utilize refrigeration of the dewaxed oil for precooling the oil to be dewaxed. The fresh incoming oil to be dewaxed may be passed, for example, through coils in the dewaxed oil storage.

When the type stock mixture is directly treated, in the apparatus of the present invention, the old gravity method of cold settling is eliminated, and a radical change in refinery practice is accordingly effected. Where, however, the refinery already has a plant for the old gravity method of cold settling, this apparatus may be employed in conjunction with the apparatus of the present invention; for example, normal refinery products obtained by routine cold settling operations by the old gravity method can be further treated in the apparatus of the present invention in accordance with the improved process of the invention. The end products of the old gravity method, so far as wax is concerned, consists of crude petrolatum stock having melting points between 100° and 120° F. Such stock can advantageously be treated by the present invention for the recovery of additional lubricating oil, and wax of a higher melting point, therefrom.

It will thus be seen that the present invention enables a materially increased amount of commercial grade cylinder oil to be obtained from the low-priced petrolatum stock

in which it is now contained. The present invention, accordingly, enables such low-priced petrolatum stock to be further treated for the production of a further amount of lubricating oil therefrom, together with wax of materially increased melting point.

In refineries which are not provided with the equipment for present day cold settling methods, or where such equipment is to be replaced by the apparatus of the present invention, the various oils or solutions now subjected to the old cold settling method can be subjected to treatment in the apparatus of the present invention. The naphtha solutions of type stock mixture or of type colored cylinder stocks may thus be treated while avoiding heavy investment in cold settling tanks and refrigerating capacity.

The present invention, accordingly, permits radical change in refinery practice and in refinery equipment and greatly simplifies both.

I claim:

1. An apparatus for dewaxing oils, comprising an insulated tank having refrigerating and agitating means therein, means for supplying oil to be dewaxed and means for supplying a finely divided solid material to said tank, a filter press with a connection for charging the mixture from the tank to the filter press, said filter press being adapted for filtering wax and finely divided solid material from the oil under pressure, means for separating the wax from the finely divided solid material, a dryer adapted to receive the finely divided solid material from the said separating means and means for returning dried finely divided solid material from said dryer to the insulated tank.

2. An apparatus for dewaxing oils, comprising an insulated tank having refrigerating and agitating means therein, means for supplying oil to be dewaxed and means for supplying a finely divided solid material to said tank, a filter press with a connection for charging the mixture from the tank to the filter press, said filter press being adapted for filtering wax and finely divided solid material from the oil under pressure, a melting tank adapted to receive the wax and finely divided solid material from the filter press and permit the separation of the wax from the finely divided solid material, a dryer adapted to receive the finely divided solid material separated from the wax in the melting tank and means for returning dried finely divided solid material from said dryer to the insulated tank.

3. An improved method of dewaxing oils, comprising intimately admixing a small amount of finely divided solid material with the oil to be dewaxed and simultaneously agitating and chilling the mixture, and subsequently subjecting the chilled mixture to a filter pressing operation.

4. An improved method of recovering wax from wax-containing oils, comprising intimately admixing a small amount of finely divided solid material with the wax-containing oil and simultaneously agitating and chilling the mixture, subjecting the chilled mixture to a filter pressing operation to separate wax-free oil from the finely divided solid material and adherent wax, thereafter heating the separated wax mixture and removing the finely divided solid material from the melted wax.

In testimony whereof we affix our signatures.

ERNEST B. PHILLIPS.
JAMES G. STAFFORD.