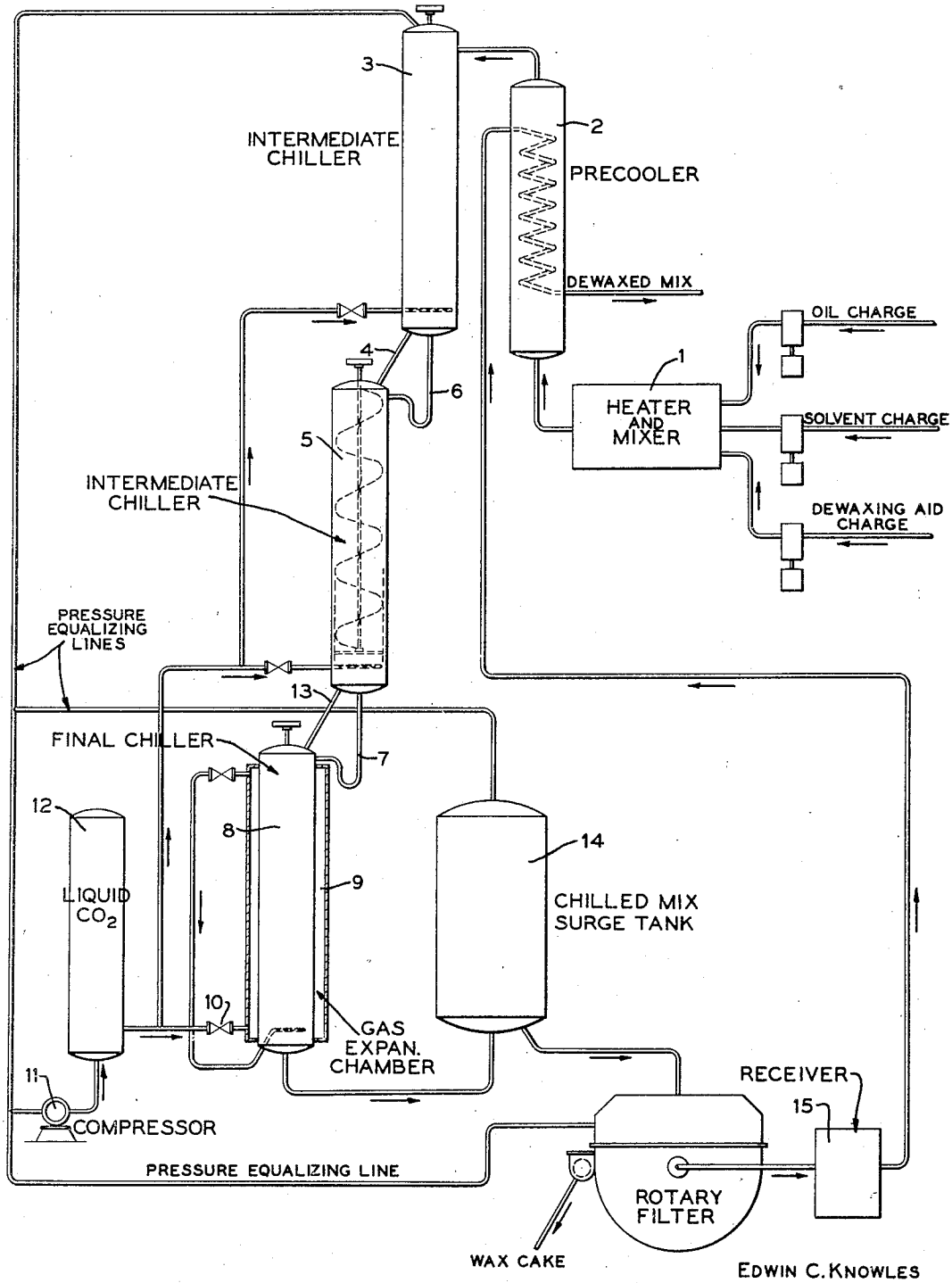
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METHOD OF DEWAXING HYDROCARBON OIL

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EDWIN C. KNOWLES
INVENTOR

BY R. J. Dearborn

ATTORNEY

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## METHOD OF DEWAXING HYDROCARBON OIL

Edwin C. Knowles, Beacon, N. Y., assignor to The Texas Company, New York, N. Y., a corporation of Delaware

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3 Claims. (Cl. 196—18)

This invention relates to dewaxing hydrocarbon oil, and more particularly the dewaxing of wax-bearing mineral lubricating oil.

It broadly contemplates a dewaxing procedure in which the oil is mixed with a solvent and the mixture chilled in part by direct thermal contact with a refrigerant material and in part by indirect thermal contact with the same refrigerant.

More specifically, the invention comprises mixing wax-bearing oil containing either naturally-occurring or artificial wax crystal modifying substances with a selective solvent, such as a mixture of methyl ethyl ketone and benzol, for example, which has substantially complete solvent action upon the oil at temperatures of around 0° F. and below, and which at such temperatures has substantially no solvent action upon the solid hydrocarbon constituents of the oil.

The mixture of wax-bearing oil and solvent is heated to a temperature substantially above the minimum temperature at which the wax and oil appear to be completely dissolved in the solvent so as to condition it. The heated mixture is then chilled by both direct and indirect thermal contact with a normally gaseous refrigerant material. The refrigerant material is utilized as an agitating medium to provide mild agitation in the mixture of wax-bearing oil and solvent during chilling in a manner which will be described in more detail.

I this way, the mixture of wax-bearing oil and solvent is chilled to a temperature of around 0° F. and below in order to precipitate the wax constituents as solid hydrocarbons. The solid hydrocarbons are then removed from the cold mixture advantageously by filtration.

The refrigerant materials which I contemplate employing may comprise ammonia, carbon dioxide, propane, dichloro-difluoro-methane, etc.

For dewaxing solvents, I prefer to use a solvent of the selective type, such as mixtures of acetone or methyl ethyl ketone and benzol. Instead of benzol, other aromatic hydrocarbons may be used as, for example, toluol, or mixtures of benzol and toluol. Aliphatic ethers, such as ethyl ether and isopropyl ether, may be used as modifying solvents in conjunction with acetone or methyl ethyl ketone. Mixtures of low and high molecular weight ketones may be used, the low molecular weight ketones such as acetone and methyl ethyl ketone acting as wax anti-solvents, while the higher molecular weight ketones provide solvents for the oil constituents.

Other well known wax anti-solvents may be used, however, selected from such groups as aldehydes, acetates, formates, etc. These may be employed in conjunction with various oil solvents, such as benzol, chlorbenzol, aliphatic ethers, etc.

In my co-pending application, Serial No. 41,393, I have disclosed a process for dewaxing hydrocarbon oil containing either naturally-occurring or artificial wax crystal modifying materials in which the mixture of oil and solvent is heated to an elevated temperature prior to chilling in order to condition the mixture containing the wax crystal modifying material so as to obtain high rates of wax removal, high yields of dewaxed oil, and less voluminous wax filter cakes.

The present invention involves a method of practicing the invention disclosed in my earlier application. It concerns particularly a method of chilling the heated mixture of wax-bearing oil and solvent liquid. A feature of this method of chilling is the utilization of a normally gaseous refrigerant material to supply both refrigeration and mild agitation of the mixture undergoing chilling.

As disclosed in my earlier application, it is highly essential to avoid subjecting the wax-bearing mixture to excessive agitation or settling during the chilling step since I have found that excessive agitation tends to destroy the beneficial effect obtained by conditioning the mixture at elevated temperature prior to chilling.

In order to illustrate the method of my invention, reference will now be made to the accompanying drawing in which I will describe the application of the invention to the dewaxing of a wax distillate of about 75 Saybolt Universal seconds viscosity at 210° F. and derived from Mid-Continent crude. In dewaxing oils having a viscosity of around 75 seconds or less, it is advantageous to employ an artificial wax crystal modifying material, such as crude montan wax, metallic soaps of higher fatty acids, such as aluminum stearate, or mixtures of crude montan wax and such soaps.

Oils of higher viscosity apparently contain naturally occurring modifying substances which impart their modifying action upon the structure of the wax crystals, especially when the mixture of oil and solvent is conditioned by heating to an elevated temperature prior to chilling.

Referring to the drawing, the wax distillate is conducted from a source not shown and delivered to a combination heater and mixer 1. This may consist of a heating coil. The selective solvent, such as a mixture of methyl ethyl ketone and

commercial benzol containing around 30% or 40% methyl ethyl ketone, is also delivered from a source not shown to the heater and mixer 1. The solvent mixture may be mixed with the oil in the proportion of about two to four parts of solvent to one part of oil. A wax crystal modifying substance of the type mentioned above is also incorporated in the mixture as shown, in the proportion of about 0.1 to 0.25% by weight of the oil charge.

The combined mixture is then heated to a temperature of about 170° F. or to a temperature ranging from about 150° to 180° F., and as a result of which heating the wax crystal modifying material imparts the desired modifying action upon the wax crystal structure during the subsequent chilling step.

The heated mixture, at a temperature of about 170° F., is then precooled by passage through a precooler 2 wherein it is advantageously brought into indirect contact wtih a stream of cold dewaxed filtrate leaving the system. In this way, the heated mixture may be cooled to a temperature of around 110° F.

At this temperature, the precooled mixture is introduced to the upper portion of a vertical chilling chamber. This chamber comprises a vertical vessel 3 through which a body of wax-bearing oil and solvent descends by gravity. The vessel is provided with a scraping mechanism of the spiral ribbon type adapted to scrape the interior walls of the vessel and thus prevent any substantial deposition of wax upon the interior vertical surfaces of the vessel. The scraping mechanism is operated at a slow rate of rotation so as to avoid excessive agitation which would destroy the free-filtering qualities of the wax crystals.

As the body of oil and solvent descends through the vessel, vaporized and vaporizing normally gaseous refrigerant material, such as carbon dioxide, bubbles upwardly through the mixture. This refrigerant material is introduced to the bottom of the vessel through a pipe 4, leading from a preceding vessel 5, as will now be more fully described.

The partially chilled mixture is conducted from the bottom of the vessel 3 through a seal 6 to the next vessel 5. The vessel 5 is similar to vessel 3 in construction and operation.

From the bottom of the vessel 5, the chilled mixture is similarly conducted through a seal 7 to another vessel 8. The vessel 8 is provided with an annular jacket 9. This annular space provides a gas expansion chamber into which the liquefied carbon dioxide is introduced through a valve 10 from a storage tank 12.

Liquid carbon dioxide under high pressure is thus introduced to the expansion chamber wherein it is permitted to expand and vaporize, subtracting heat from the oil and solvent mixture within the vessel 8. The vaporized carbon dioxide, still under relatively high pressure, is removed from the top of the expansion chamber at a temperature of about −20° F. and injected into the body of oil and solvent within the vessel 8. The injected refrigerant bubbles upwardly through the body of liquid, subjecting it to the desired type of gaseous agitation with avoidance of any disrupting action upon the structure of the wax crystals.

The gaseous refrigerant collecting in the top of the vessel 8 is then removed through the pipe 13 and injected into the lower portion of the body of liquid maintained within the vessel 5. It thus bubbles upwardly through this body of liquid and escapes through the pipe 4 into the body of liquid contained in the vessel 3.

Thus, the gaseous refrigerant, which is flowing countercurrently through the body of oil and solvent within the vessels 8, 5 and 3, both agitates and chills the mix. It is removed from the top of the vessel 3 at or near atmospheric pressure, and picked up by a compressor 11, by which means it is liquefied and returned to the storage tank 12.

It is contemplated, of course, that all portions of the chilling apparatus will be covered with heat insulating material. If desired, liquefied refrigerant may be injected directly to the body of liquid contained in each of the three chilling vessels.

The chilled mixture of wax-bearing oil and solvent, at a temperature of about −15° F., is withdrawn from the bottom of the vessel 8 and conducted to a surge tank 14. From this tank it is delivered to a filtering means advantageously of the rotary drum type wherein the solid hydrocarbons are removed in the form of a filter cake, producing a dewaxed filtrate.

This dewaxed filtrate is drawn off to a receiving tank 15. This filtrate, being at a temperature of around 0° F. or below, is advantageously passed through the precooler 2, previously referred to, and wherein it gives up its heat to precool the heated mixture passing through the precooler 2.

The thus warmed dewaxed mixture may then be passed through a suitable stripping means wherein the solvent is recovered from the dewaxed oil, leaving an oil having a pour test of around 0° to −10° F.

In carrying out the procedure described above, it is advantageous to select a refrigerant material which is comparatively insoluble in the oil and solvent mixture, and which does not react with the solvent. Thus, when using a mixture of methyl ethyl ketone and benzol as the selective solvent, carbon dioxide is entirely satisfactory.

It will be seen, therefore, that my invention has for its object the use of a refrigerant medium to supply internal agitation and cooling as well as direct external refrigeration to the solvent-oil mix. This permits employing gaseous agitation to the substantial exclusion of mechanical agitation such as is obtained when using paddles or mechanical stirring means. Mechanical agitation is objectionable because it is difficult to avoid substantial destruction of the wax crystal structure.

By using vertical chilling vessels of the type described above, a gravity flow system is permitted which eliminates pumping with its resultant tendency to disrupt or injure the structure of the wax crystals.

The invention has also for its object the application of this method of chilling to the dewaxing of wax-bearing oil in conjunction with wax crystal modifying material, and wherein it is extremely desirable to condition the mixture by heating to an elevated temperature prior to chilling.

As a result of my invention, it is possible to obtain a very free-filtering wax relatively free from oil. The filter cakes of wax are relatively dry and quite compact. They are less bulky, being about one-third less in bulk than those obtaining where the conditioning step of my process is omitted.

High yields of dewaxed oil are obtained coupled with a low yield of slack wax. Furthermore, these results are obtained by using a reduced ratio of solvent to oil.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. In the dewaxing of wax-bearing mineral lubricating oil, the method comprising mixing the oil with a dewaxing solvent liquid, passing the mixture to the top portion of the uppermost of a plurality of vertical chilling vessels arranged one above the other and each of height relatively great with respect to the cross-sectional area, maintaining said vessels full of wax-bearing mixture gravitating therethrough, surrounding at least in part the lowermost vessel with a body of expanding refrigerant consisting of a normally gaseous refrigerant thereby indirectly chilling the mixture, injecting cold expanded refrigerant into the body of oil and solvent within said lowermost vessel, injecting liquefied refrigerant in the gravitating liquid mixture at intervals throughout its passage through the chilling vessels, passing the vaporized injected refrigerant upwardly through the succeeding vessels in amount sufficient to mildly agitate the gravitating body of liquid without disrupting the crystal structure of the wax, and removing the chilled wax-bearing mixture from the bottom of the lowermost vessel.

2. In the dewaxing of wax-bearing mineral lubricating oil, the method comprising mixing the oil containing wax crystal regulating material with dewaxing solvent liquid, heating the resulting mixture to a temperature in the range 150 to 180° F. to condition the mixture, passing the mixture to the top portion of the uppermost of a plurality of vertical chilling vessels arranged one above the other and each of height relatively great and with respect to the cross-sectional area, maintaining said vessels full of wax-bearing mixture gravitating therethrough, surrounding at least in part the lowermost vessel with a body of expanding refrigerant consisting of a normally gaseous refrigerant thereby indirectly chilling the mixture, injecting cold expanded refrigerant into the body of oil and solvent within said lowermost vessel, injecting liquefied refrigerant in the gravitating liquid mixture at intervals throughout its passage through the chilling vessels, passing the vaporized injected refrigerant upwardly through the succeeding vessels in amount sufficient to mildly agitate the gravitating body of liquid without disrupting the crystal structure of the wax, and removing the chilled wax-bearing mixture from the bottom of the lowermost vessel.

3. In the dewaxing of wax-bearing mineral lubricating oil, the method comprising mixing the oil with a dewaxing solvent liquid, passing the resulting mixture to the top of an elongated vertical chilling zone of height relatively great with respect to its cross-sectional area, maintaining said zone full of wax-bearing mixture gravitating therethrough, surrounding at least in part the lowermost portion of said chilling zone with a body of expanding refrigerant consisting of a normally gaseous refrigerant in indirect thermal contact with the wax-bearing mixture thereby chilling the mixture, injecting cold expanded refrigerant into the body of oil and solvent within said lowermost portion of the chilling zone, injecting liquefied refrigerant in the gravitating liquid mixture at intervals throughout its passage through the chilling zone, passing the vaporized injected refrigerant upwardly through said chilling zone and in direct contact with the gravitating liquid mixture in amount sufficient to mildly agitate the gravitating liquid mixture without disrupting the crystal structure of the wax, and withdrawing the chilled mixture from the bottom of said chilling zone.

EDWIN C. KNOWLES.