June 29, 1965 R. E. SPARKS ETAL 3,192,125

APPARATUS FOR DEOILING WAX

Filed Aug. 1, 1961 2 Sheets-Sheet 1

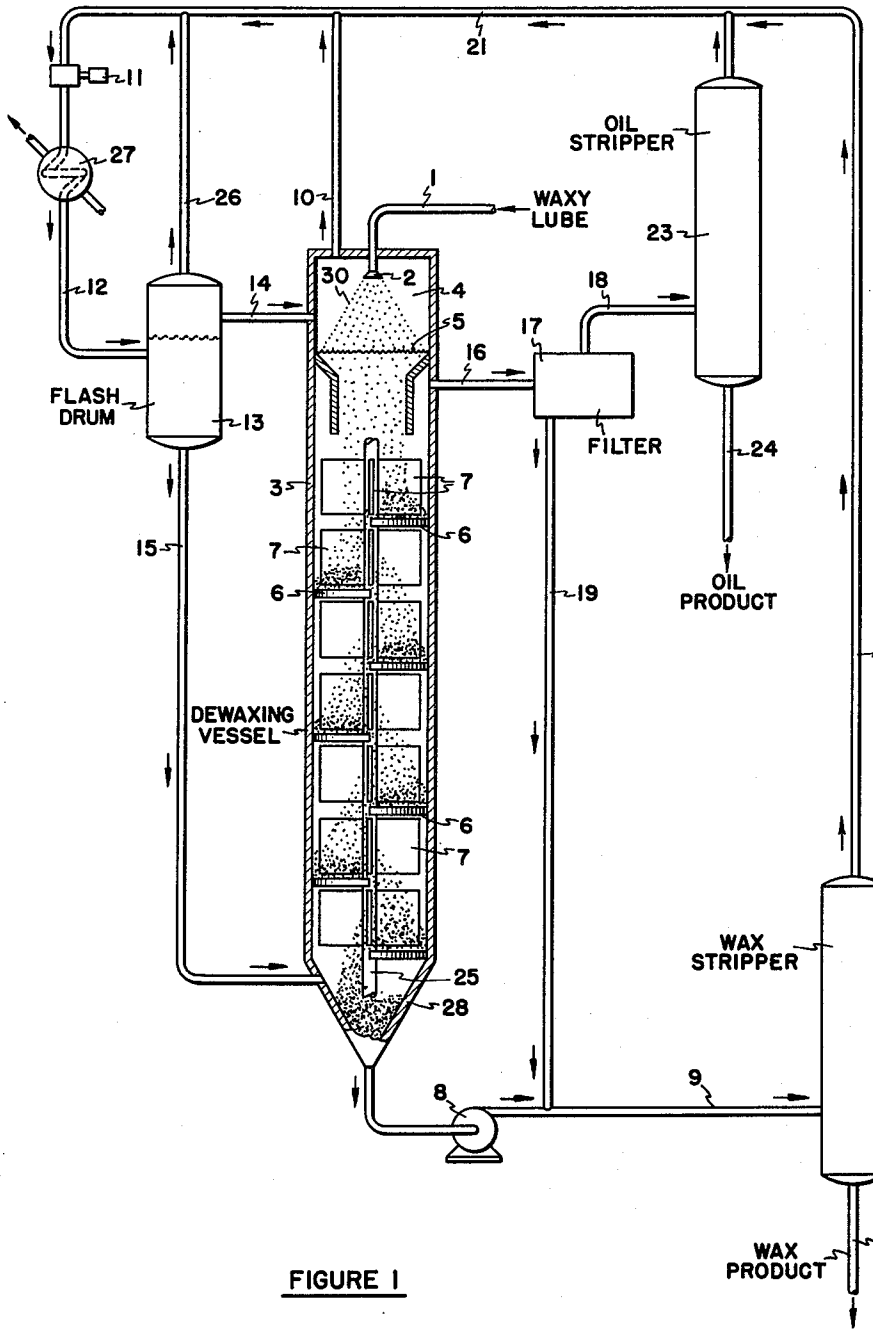


FIGURE 1

ROBERT E. SPARKS INVENTORS
STEPHEN F. PERRY
BY Richard N. Nagel
PATENT ATTORNEY

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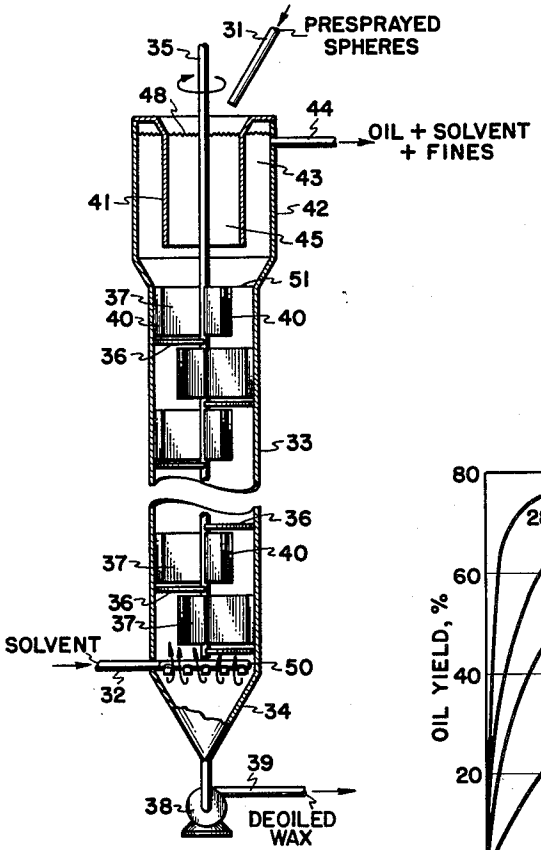


FIGURE 2

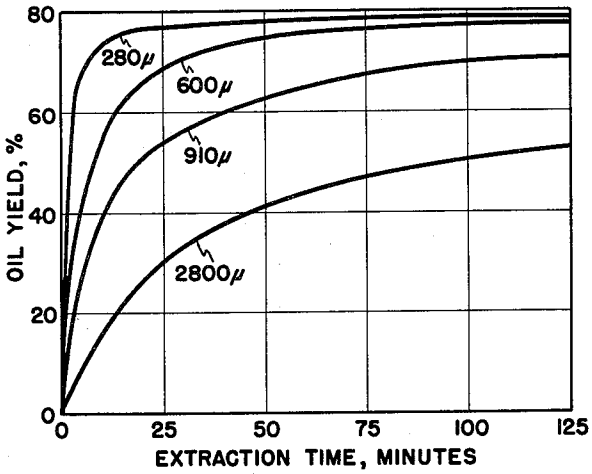


FIGURE 5

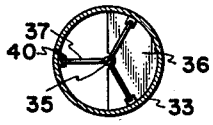


FIGURE 3

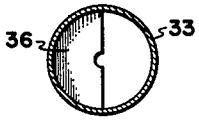


FIGURE 4

ROBERT E. SPARKS INVENTORS
STEPHEN F. PERRY

BY Richard H. Nagel

PATENT ATTORNEY

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APPARATUS FOR DEOILING WAX

Robert E. Sparks and Stephen F. Perry, both of Westfield, N.J., assignors to Esso Research and Engineering Company, a corporation of Delaware

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8 Claims. (Cl. 196—14.5)

This invention relates to improvements in the art of dewaxing of petroleum oil fractions. This invention is particularly concerned with an improved process for dewaxing lubricating oil fractions. In accordance with the invention, a waxy oil feed is sprayed in the form of small droplets which solidify by direct contact with a cold fluid, followed by extraction of the oil from the solidified droplets with an appropriate solvent. An advantage of the invention is that the solidified wax droplets are easily separated from the dewaxed oil product.

Petroleum oil fractions obtained from paraffinic crudes contain various amounts of wax. This is particularly true of lubricating oil fractions. In order to obtain lubricating oils which will flow at low operating temperatures, i.e., have low cloud and pour points, it is necessary to remove from the lubricating oil stock the wax present. The wax recovered in dewaxing paraffinic lube oil stocks is itself a valuable product.

There are several commercial solvent dewaxing processes now in use. The two most widely known are propane dewaxing and ketone dewaxing. In propane dewaxing, the waxy oil is mixed continuously with liquid propane under pressure and charged alternatively to two batch chillers. The rate at which the propane waxy oil mixture is cooled is critical. If the mixture is cooled too rapidly, shock chilling results causing the wax to form as fine particles which are difficult to filter. The chillers are used alternatively; while one is chilling a charge of waxy oil, the other is being cleaned and emptied. The contents of the chillers are then filtered. In order to produce dewaxed oil with a pour point of 15–20° F., it is necessary to dewax with propane at —25 to —35° F. In normal operations, the filter cloth used to filter the dewaxed oil from a precipitated wax gradually blinds or becomes clogged and requires a periodic hot wash with a solvent, such as kerosene, at intervals of about 4 hours or so.

In ketone dewaxing, a mixture of MEK and toluene is generally used as the solvent. In this process, the waxy oil is mixed with the ketone solvent and charged to double-pipe scraped surface heat exchangers and then to chillers of similar construction wherein the mixture is chilled continuously to the desired filtering temperature. On chilling, the waxy oil-solvent mixture precipitates the wax and a slurry is formed. The cooled wax slurry is then charged to a rotary filter where the wax is separated from the dewaxed oil and solvent. A filtering temperature of about 0° to 10° F. is required to produce a dewaxed oil of 15–20° F. pour.

Another method of dewaxing oils which has been tried is to feed the waxy oil directly into a cold solvent; (i.e. at a point beneath the surface of the solvent or just above the surface), such as liquid propane, to precipitate the wax and to extract the oil from the solid wax particle. In accordance with this process, coarse, flake-like crystals are formed which are easily broken and which make fines, which are difficult to filter. The size of the crystals were relatively large, and the extraction of oil from the crystals was not efficient. More recently, a process has been developed for separating small amounts of oil from crude paraffin waxes; i.e., a decoiling process. It has been reported that, in accordance with this process, a crude petrolatum wax containing 2–5% oil is sprayed into a vessel containing a cooling gas. The cooling gas will solidify the petrolatum if the oil content is low enough. The

cooled solid grains of wax are collected at the bottom of the vessel and are scraped off and subsequently treated in a separate vessel with a deoiling solvent. The resulting mixture must be centrifuged or filtered to separate the wax from the oil and solvent. This process has proved inefficient and ineffective in separating wax from waxy oil feeds which contain large amounts of oil. When waxy oil feeds containing large amounts of oil or more than about 30% are sprayed in accordance with that process, they are only partially solidified in the cold gas present and form agglomerates which stick together in the bottom of the vessel. In this condition, they cannot easily be scraped out of the vessel nor can they be effectively deoiled and filtered. Further, this process is not operative in removing oil from residuals stocks regardless of oil content, since these stocks contain high molecular weight waxes which do not solidify and form stick agglomerates.

The prior art processes have not provided an economical, efficient, or continuous method of dewaxing high oil-content waxy oil fractions that produces a wax that can be easily deoiled, and effectively filtered or centrifuged, or otherwise separated from the dewaxed oil. The propane and ketone dewaxing processes require a considerable investment in equipment. The propane process is not a continuous process, but rather a batch or semi-continuous process. The ketone process requires a large investment in complicated scraped-surface exchangers and both processes require well-controlled chilling rates. Both processes require large investments in rotary filtration equipment to remove the small wax crystals. Neither process produces the wax material in a form which is readily filtered, and in which the oil can be readily separated from the wax material. The spray deoiling process is not effective in that the oil in high oil-content feeds cannot be separated from wax in this manner, and the process requires in addition a filtration or centrifugation step.

It is an object of this invention to provide an improved process for separating wax from waxy oil fractions which is efficient and economical. It is another object of this invention to provide a continuous process for separating wax from lube oil fractions, which results in a wax which is easily filtered or separated from the dewaxed oil. A further object of this invention is to provide a process of separating wax from waxy lube oil fractions which results in a high dewaxed oil yield, and a wax and dewaxed oil which are easily separated.

In accordance with a preferred embodiment of this invention, a waxy petroleum oil fraction is heated to a temperature slightly above its pour point and charged to a cooling tower or vessel through an atomization device to give droplets of waxy oil of a critical size to provide maximum extraction rate of the oil, as well as allowing a simplified method of separating the resulting solidified wax droplets from the oil-solvent solution. The waxy droplets are cooled by contacting them with cold vapor which cools the droplets sufficiently to crystallize enough of the wax in the droplets so that when the droplets contact the liquid deoiling solvent at the bottom of the tower, they are in spherical shape, which shape is not greatly deformed on contacting the liquid solvent. The remainder of the wax present in the droplet is solidified while in contact with liquid solvent while descending to the bottom of the vessel. As the wax in the droplet solidifies in the liquid solvent, the major portion of the oil present in the wax droplet is extracted. At the bottom of the tower wax droplets which are substantially reduced in oil content are collected. Fresh liquid solvent is introduced at one or more points in the tower and removed at the top of the liquid layer, together with the extracted oil. The supernatant liquid may contain a small amount of wax fines which may be readily filtered or

centrifuged. The wax at the bottom of the tower may be removed from the bottom of the vessel and taken and stripped of any excess solvent. For most operations, the separation is good enough that the bulk of the wax does not have to be filtered or centrifuged to remove oil. The solvent is removed by flashing it off from the wax. The temperature of the liquid solvent is warm enough to extract the desired amount of oil from the wax droplets, but not sufficiently warm to dissolve an appreciable amount of wax from the droplets. The solvent will be sufficiently cold to solidify any liquid wax remaining in the droplet.

When the above process is carried out in a liquid solvent having a density lower than that of the feed, the extraction takes place while the solidified feed droplets are descending countercurrently through the liquid. If proper internal apparatus is inserted in the extraction tower, well-controlled countercurrent motion of solid particles and liquid can be obtained. This renders the process especially economical, since many countercurrent equilibrium extraction stages can be obtained in the tower, requiring less solvent for extraction of a given oil yield than would be required for simply mixing the solids with the solvent. The amount of oil extracted from the solid droplets can be closely controlled by the number of equilibrium stages obtained and the volume of solvent employed.

Our process has several advantages over the known processes of dewaxing lubricating oil stocks; namely—the equipment required is much simpler and much less expensive, the process obtained is continuous, the wax droplets obtained are more easily separated from the dewaxed oil, and the holdup time or residence time of the droplets in the dewaxing vessel is favorable. The wax droplets formed are of aproximately spherical shape and sufficiently hard by the time the oil is removed and they do not agglomerate or cake, and therefore allow the solvent and dewaxed oil to be easily separated from them.

The nature and objects of the invention will be better understood when reference is made to the accompanying drawings in which:

FIGURE 1 is a flow plan of a preferred embodiment of our dewaxing plant.

FIGURE 2 is a detailed drawing of the internal structuer of the deoiling zone.

FIGURE 3 shows a top view of the paddles used in the extraction column.

FIGURE 4 shows a top view of a left horizontal baffle used in the extraction tower.

FIGURE 5 shows the effect of droplet diameter and extraction time on oil yield.

The waxy petroleum oil fractions which may be used in accordance with our process usually boil above 460° F. Pour points of the feed stocks are generally above 30° F. Petroleum stocks having a wax content of from about 5 to 98% by weight wax can be dewaxed in accordance with this invention. Preferably distillate and residual lube oil stocks having about a 12 to 25% by weight wax and boiling in the range above 525° F. and having a pour point of about 90° F.—140° F. are treated.

The cooling gases used to initially cool the waxy oil droplet forming the sphere may be light hydrocarbons, such as methane, ethane, propane, and butane, or air, ammonia, nitrogen dioxide, carbon dioxide, SO_2, Freons, and the like. Propane vapor, however, is preferred. Propane has an advantage of being an autorefrigerant as well as a solvent. The waxy oil droplet is contacted with the cool gaseous vapor and forms a sphere of sufficient hardness so that when the droplet contacts the liquid oil-extracting solvent near the bottom of the vessel, it is not appreciably deformed. The temperature of the cooling vapor will be below the pour point of the waxy oil feed. Generally, temperatures of −162° to +100° F. can be used. The time that the waxy oil droplet is present in the gaseous cooling vapor will be a matter of a few seconds. This is the time that it takes the droplet to fall from the spray nozzle to the surface of the liquid cooling solvent. The height of the gaseous cooling column, and the temperature of the cooling gas will be determined by the temperature of oil feed and its wax content. The difference in the temperature between the feed and the cooling gas will be regulated so that about 1/10 to 9/10 of the B.t.u.'s which are necessary to completely solidify the wax in the droplet will be transferred to the gaseous cooling vapor in the time that it takes the droplet to fall from the spray nozzle to the surface of the liquid cooling solvent. The remaining B.t.u.'s which must be transferred to completely solidify the wax in the droplet will be absorbed by the liquid cooling solvent.

In a preferred embodiment, liquid propane functions as the cooling liquid, as well as the oil-extracting solvent, and as the source of cold vapor. The volume throughput of the cooling vapor will be determined by the throughput of waxy oil feed and the desired amount of cooling in the vapor space. The amount of cooling vapor employed may be easily regulated within wide limits by removing part of the vapor before it cools the droplets or by adding more vapor if desired.

In another embodiment of the invention, instead of using a cooling gas to form the initial uniform spheres of waxy oil droplets, liquids which are poor solvents or antisolvents for waxy oil may be used. Such materials are liquid ammonia, methanol, water, aqueous solutions, saturated oil-solvent solutions, and the like. The high interfacial tension between the wax and the nonsolvent forms a sphere immediately on contact of the waxy oil droplet with the nonsolvent. In this embodiment, the atomizing nozzle will be only far enough above the liquid surface to allow the droplets to be formed before hitting the liquid. The nonsolvent may be kept in a vessel separate from the extracting solvent.

The deoiling solvent may be selected from liquefied light hydrocarbons, such as ethane, propane, butane, pentane, and hexane; ketones such as MEK, MIBK, and mixtures such as MEK/toluene, MEK/MIBK, and the like. The deoiling solvent also functions to complete the cooling of the waxy oil droplet. About one-half to nine tenths of the solidification or cooling of the droplet takes place in the deoiling solvent. After the waxy oily droplet has partially solidified in the cooling vapor, it contacts the cooling solvent. Sufficient solidification has taken place in the vapor so that when the droplet contacts the cooling solvent, its shape is not appreciably deformed.

In one embodiment of the invention, liquid propane is used as a cooling and deoiling solvent because of its autorefrigerant characteristics, its low solubility for wax, and high solubility for oil at low temperatures. When the waxy oil droplet is contacted with liquid propane, the oil in the droplet is extracted by the liquid propane. Substantially all the oil present in the droplet may be extracted into the propane at high dilutions. Liquid propane solvent enters the dewaxing vessel at the bottom of the vessel and is removed at the top of the solvent phase. This effects a countercurrent extraction of the oil from the droplets. The oil may be so well removed from the droplets that further treatment of the hardened wax droplets is not necessary. After the waxy droplet is removed from the vessel, all that is required is that any excess solvent present on the droplets be removed by flashing or stripping. One of the most important advantageous of this process is that no centrifugation or filtering step is required for removing the oil saturated solvent from the crystallized wax droplet. The solvent, however, may also be removed by centrifuging or filtering. The uniform spherical shape of the droplets, and the fact that they are not deformed and are allowed to form almost perfect spheres, allows easy separation and flow of the solvent around each of the droplets. The wax in spherical shape also has less tendency to break into small

particles which would be difficult to separate from the solvent. The droplets do not cake or agglomerate and subsequent filtration or centrifuging, if desired, is relatively simple.

The temperature of the extracting solvent, for example, propane, is dependent upon the pour point of the desired dewaxed oil, and the content of the wax in the waxy oil droplets. Solvent temperatures of −162° to +100° F. may be used. Where liquid propane is used as the solvent, the dewaxing vessel is maintained at a pressure of about 5 to 20 p.s.i.g. in order to keep substantially all of the solvent in the liquid phase. Autorefrigeration is effected, however, by partially vaporizing a portion of the solvent, thereby cooling the remainder. The solvent that is vaporized is collected, compressed, condensed, and recycled to the bottom of the vessel. The ratio of solvent to feed for extracting of about 1/1 to 10/1 can be used. The ratio of solvent to feed is dependent upon the desired pour point of the resulting oil, the wax content of the feed, and the amount of oil desired to be extracted. The dilution and, hence, the flow rate of solvent will determine, to a certain extent, the holdup time or residence time of the waxy oil droplets in the dewaxing vessel. The residence time of the waxy oil droplets in the deoiling solvent is between 5 minutes and 10 hours. Naturally, the shorter the residence time, the higher throughput and the greater the dewaxing capacity of the vessel. Depending on the characteristics of the waxy oil feed, residence time selected will be such that it is sufficient to extract substantially all of the oil present.

The droplet size of the atomized waxy oil feed in this invention is critical. The physical form of the droplet when it contacts the liquid deoiling solvent is also critical. Flake-like crystals, though easy to extract oil from, are difficult to handle and almost impossible to filter. The slightest agitation causes them to break into fines, which make filtration and subsequent handling very difficult. Droplets of uniform spherical shape are preferred. Once these droplets harden, there are areas between the droplets for solvent to go through and extract the oil. This also provides for ease of separation of dewaxed oil and solvent from the wax droplets. Wax droplets of large size, however, are undesirable because it takes an exceptionally long time to extract substantially all of the oil from these droplets, as shown in FIGURE 5. This would require an excessively long holdup time and lower the capacity of a given dewaxing vessel. On the other hand, exceptionally small droplets are also undesirable as they decrease settling rate, and tend to pack closely and/or entrain overhead causing the filtration and separation of the dewaxed oil and solvent from the droplets to be difficult. Narrow size distribution spheres are preferred for ease of handling and uniformity of extraction. Droplets of fairly wide size distribution, such as obtained from conventional spray nozzles can, however, be used.

Waxy oil droplets of a diameter at 50% cumulative volume referred to as volume median, of between 20–5000 microns can be used. However, spheres of 300–1000 microns are preferred, though diameters of 100–2500 can also be used. As previously stated, the size of these waxy oil spheres is critical. Not only is the size critical, but the physical shape of the droplet is also critical. By contacting the waxy oil droplet with a cooling gas, as stated above, such as propane, the droplet is allowed to form a spherical particle and allowed to become sufficiently hard so that, when the sphere contacts the liquid extracting solvent, it is not appreciably deformed and enters the extracting solvent in approximately spherical shape. In this state, the oil is easily extracted from the sphere, and the droplet solidifies in the shape of a sphere. When these spheres stack or collect at a stage or in the bottom of the dewaxing vessel, there are interstices or spaces between the droplets between which the extracting solvent may flow. In this manner, substantially all of the oil is removed from the droplets efficiently and effectively in a relatively short time. This manner of treating the waxy oil droplets also obviates the necessity of filtering dewaxed oil and solvent from the bulk of the waxy oil droplets, since substantially all of the oil and solvent solution is removed in this manner and the wax patricles are separated simply by settling. The wax droplets are then withdrawn from the bottom of the vessel through a gear or screw pump and any excess solvent stripped from the wax.

The temperature at which the dewaxing, cooling, and extraction is carried out will, of course, depend upon the temperature of the feed and upon the pour point of the dewaxed oil desired. Temperatures of cooling vapor of −162° to +100° F. can be used. However, temperatures of the cooling vapor of −35° to +40° F. are preferred.

The temperature of the cooling solvent will depend to a certain degree on the temperature of the cooling vapor. Where propane is used as a cooling and deoiling solvent, temperatures of −35° to 0° F. are preferred. However temperatures of −44° to +40° F., as well as temperature of −162° to +100° F. can be used. The temperature, of course, is dependent upon the particular deoiling solvent used.

Pressure in the vessel is generally about atmospheric pressure. However, pressures of 5 to 300 p.s.i.a. can be used, but pressures of 15–40 p.s.i.a. are preferred. The residence time of the waxy oil droplet in the vessel is the time that it takes to fall through the cooling gas or vapor, plus the time in the deoiling solvent. This time in the deoiling solvent may be controlled by the rate of flow of propane countercurrently through the droplets and by constructing baffles or stages within the vessel to hold up the droplet. Residence times of 30 to 60 minutes are preferred. However, depending upon the oil content of the droplet, residence times of 30 minutes to 5 hours, as well as 5 minutes to 10 hours, can also be used. To obtain maximum throughput and maximum capacity of a given piece of equipment, however, a shorter residence time for a specific oil yield makes for greater throughput.

The ratio of solvent to feed is, of course, dependent upon the particular extracting solvent used and the temperature at which the oil is extracted from the droplets. Ratios of 1/1 to 10/1 can be used. However, a ratio of 1/1 to 5/1 and, specifically, for economic reasons, a ratio of 1/1 to 3/1 are used. The flow rate of the extracting solvent is countercurrent to the gravity flow of the waxy oil droplet. This rate of flow is naturally contingent upon other variables and should be set as low as possible to minimize entrainment of fine or small spheres in the oil-solvent stream. The droplet size is determined by the design of the spray nozzle, the pressure drop across the nozzle and the viscosity and surface tension of the sprayed waxy oil feed.

The temperature at which the waxy oil feed is charged to the dewaxing vessel will be above its pour point. The pour point and viscosity of a feed may be reduced by addition of pour point inhibitors and/or solvents for the oil, and/or light hydrocarbons. In view of the variety of feeds that may be used and the wax content of the feeds, as well as the viscosity of the feeds, this encompasses feed temperatures of 5° to 360° F. The lubricating oil stocks that are to be dewaxed in accordance with this invention will have feed temperatures of about 40–220° F. The wax content of the feed will vary, depending on its crude source, as well as the particular cut that is taken. Oil contents as high as 98% by weight can be handled. However, it would be more common to have wax concentrations in the stock of 10–65%. Where the lubricating oil stocks are used, wax concentrations in the nature of 12–25% will be more common.

For a typical 2500 barrel/day rate of throughput of feed, a vertical vessel approximately 10–80 feet in height and 8–25 feet in diameter can be used. The height of

the cooling gas column can be 5–40 feet; wheras, the height of the cooling solvent may be 5–70 feet. The height of either of these two columns may be easily regulated and will depend upon the type of feed that is being treated, the coolants used, and the internal apparatus in the tower.

In a preferred embodiment of the invention, propane vapor is used over a liquid propane deoiling and cooling solvent. The dewaxing is carried out at about atmospheric pressure, and the vessel is maintained at a temperature of about —30° F. This temperature is attained by vaporizing part of the propane liquid, thus cooling the remainder. This is an autorefrigerated process. Where MEK-toluene is used as the extracting solvent, the MEK-toluene is generally cooled externally. This may be done through heat exchange with propane or ammonia refrigerants. In another embodiment of the invention, a nonsolvent or antisolvent for the wax may be used to form the uniform spherical shaped droplets. In such case, two vessels may be used; one of them to form the droplets, and the other to deoil the droplets.

An understanding of various aspects of the invention may be aided by referring to the accompanying drawings and the discussion thereof. The drawings show arrangements of apparatus which can be used in the practice of an embodiment of the invention. It will be readily appreciated that these drawings are in the nature of flow diagrams and that numerous pieces of individual equipment, for purposes of simplification, have been omitted.

Referring now to FIGURE 1 of the drawings, a waxy paraffinic lube oil fraction having a pour point of 90° F., a boiling range of 525–850° F. and having a viscosity of 4 centistokes at 210° F. is charged to dewaxing vessel **3** through line **1** and is atomized by spray nozzle **2**, forming waxy oil droplets **25** of volume median diameter 300–1000 microns. The lube oil fraction has a wax content of 10–25% by weight and is fed to vessel **3** at a temperature of 40–220° F. The pressure in vessel **3** in the vapor phase **4** is about atmospheric pressure or sufficient to prevent violent boiling of the liquid propane.. Vapor space **4** is filled with propane vapor at a temperature of —44 to +40° F. The atomized waxy oil feed on contacting the cold propane vapor forms spheres of wax and oil and partially solidifies prior to contact with the liquid propane in the vessel. The waxy droplets contact liquid propane **5**, which is at a temperature of —44 to 0° F. The residence time of 30 minutes to 5 hours of the droplets in the liquid propane is sufficient for the droplets to completely solidify, and the oil in the droplets to be substantially extracted. The ratio of solvent to oil is 1/1 to 5/1. By means of baffles **6** and paddles **7**, the droplets descend in a spiral motion countercurrently to the rising propane solvent which enters the vessel through line **15**, and the holdup time is controlled by the number of baffles **6**, the height of the liquid column and the speed of rotation of paddles **7** on shaft **25**. The hardened droplets collect at the bottom of the dewaxing vessel in cone **28** wherein the fresh liquid propane is introduced and effectively extracts any remaining oil present in the droplets. The deoiled solidified droplets **26** collect in the bottom of the vessel formed by cone **28** and are removed from the vessel by gear or screw pump **8** and through line **9**, and are taken to a solvent stripper **20** from which any excess propane solvent is removed from the wax. The stripped solvent is recycled to flash drum **13** via lines **21** and **12**. One of the big advantages of my invention is that sufficient separation of wax, and dewaxed oil and solvent solution is obtained by the settling action of the droplets which makes it unnecessary to subsequently centrifuge or filter the wax. The liquid propane cooling and extracting solvent entering through line **15** passes countercurrently through the hardened wax droplets in cone **28** upwardly in a spiral motion through the liquid solvent column **3** and is withdrawn through line **16** and passes through cartridge filter **17**. A small amount of wax fines, less than about 1–3% by weight of the total feed is present in the dewaxed oil and propane solution withdrawn through line **16**. These fines are removed from the oil solvent mixture by centrifuge or cartridge filters **17** and are taken via lines **19** and **9** to the wax stripper **20**. The dewaxed oil and propane solvent are removed from cartridge filters **17** by conventional means and are taken via line **18** to an oil stripper where the propane solvent is stripped from the dewaxed oil. The dewaxed oil is removed for further treatment and the stripped solvent is recycled to propane compressor **11**. Propane vapor is withdrawn from vessel **3** via line **10** and is taken to compressor **11** wherein it is compressed and passed via a condenser **27** and line **12** to propane flash drum **13**. In flash drum **13**, the temperature and pressure are controlled so that a sufficient amount of propane vapor may be withdrawn through lines **14** and **26** and charged to compressor **11** and vapor space **4**, in vessel **3**, to control the cooling temperature and pressure of the propane vapor in space **4**. The remainder of the recycled propane in liquid form from flash drum **13** is withdrawn through line **15** and charged to the bottom of dewaxing vessel **3**. The wax removed from the bottom of vessel **3** is substantially reduced in oil content. The dewaxed oil removed through line **18** has a pour point of about 20° F.

By controlling the volume median diameter of the waxy oil droplets atomized from spray nozzle **2** within a critical size range of 300–1000 and controlling the temperature of the propane vapor, solidification of the droplet in the vapor is sufficient so that when the droplets strike the liquid propane solvent, they are sufficiently hard that they are neither deformed nor broken up. In the propane solvent, the solidification is completed and the oil is extracted from the droplets while they pass countercurrently to the propane solvent. Due to the approximately spherical shape of the droplets, as they collect in the bottom of the dewaxing vessel **3** in cone **28**, there is sufficient space between the drops so that substantially all the oil is removed by the propane introduced through line **15**, and that the wax removed via screw pump **8**, and line **9**, is substantially free of dewaxed oil and has only to be separated from the propane deoiling solvent by wax stripper **20**. Screw pump **8** is operated in such a manner that most of the interstitial solvent present in the settled wax solids is squeezed from the wax droplets and remains in the column, while the wax substantially free of solvent and oil is pumped out. This combination of steps is critical in obtaining the ease and efficiency of the separation of wax from waxy oil stocks in accordance with my inventive process.

In FIGURE 2 of the drawings is shown a staged extraction zone which may be used in one embodiment of my invention. This apparatus was used to deoil a waxy lube stock containing 87.5% by weight oil (as measured by the ASTM oil content procedure with secondary butyl acetate at 0° F.). In this embodiment, the droplets of waxy lube stock were prepared externally from the oil extraction zone. The lube stock used had a pour point of 90° F. and a cloud point of 95° F. and a kinematic viscosity of 4 centistokes at 210° F. The feed was heated to 220° F. and sprayed through a swirl-type pressure nozzle. The spray droplets were received in methanol at temperatures between +15 and +45° F. The distance of the surface of the methanol from the nozzle is not critical, when using an antisolvent to form the spheres, and in this instance was about 18 inches. The spray droplets had a wide size distribution and a median diameter of approximately 500 microns. The droplets were spherical in shape and showed no tendency to agglomerate or to stick to metal or glass surfaces. The droplets were cooled to the desired extraction temperature of —20° F. in cold methanol, then separated

from the cold methanol by filtration and subsequently washed with methylethylketone and then hexane.

Instead of solidifying the drops in methanol they may, as has been previously described, be solidified by falling through cold propane vapor. A similar spray distribution of the same feed stock, as was discussed immediately above, was allowed to fall 10 feet through a rising stream of propane vapor at a temperature of 0 to +20° F. After falling this distance through the propane, the sprayed droplets fell into a body of hexane at −20 to −40° F. Upon entering the solvent, the droplets had solidified sufficiently to remain as separate spherical particles. Either of these methods may be used to obtain solidified droplets for extraction with the apparatus described in FIGURE 2.

Now referring to FIGURE 2, waxy oil droplets obtained from the methanol soldification process were fed through line **31** to the extracting tower **33**. The droplets contacted the surface **48** of cold hexane deoiling solvent maintained at a temperature of −20° F. in the droplet receiving zone **45** at the top of the extraction tower. The droplets were fed intermittently into the top of the tower and fall slowly through zone **45** to line **51** in the column where the bed level is maintained. From line **51** downward, the bed contains 10–60% solids depending on the throughput rate of solids and liquids. The solids move slowly downward through the column following a spiral path and are removed at the bottom of the column by screw pump **38**. Cold hexane solvent is introduced into the column **33** via line **32** and through distribution ring **50** in a downward direction and subsequently passes upward through the column in a spiral path countercurrently to the descending waxy oil droplets. During the countercurrent contact, the oil in the droplets is extracted by the ascending hexane solvent. Wax fines are collected in zone **43** which is made up by annular baffle **41** and the outside wall of the tower **42** and are withdrawn with the supernatant solvent through line **44**. These fines are separated from the solvent by either centrifugation or filtration with a cartridge filter. Solvent was introduced into the bottom of the column at a ratio of 3.7 to 1 based on the feed rate of waxy oil. The takeoff rate at the bottom of the column was adjusted until the ratio of interstital liquid to bulk sphere vloume was 2.2 to 1. Hence, the total volume of liquid rising up the column and being removed at the top was 1.5 to 1 based on the feed volume. The waxy oil droplets, with a substantial amount of the oil removed, were collected in the bottom of the tower in zone **34** and were compressed in screw pump **38**, squeezing out most of the interstitial solvent present in the settled droplets, which solvent remains in column **33**, while the deoiled wax is removed through line **39**. The oil content of the wax in this run was reduced from 87.5% to 25%. The dewaxed oil removed by line **44**, at the top of the column after separation of the wax fines is separated from the hexane solvent by distillation. A dewaxed oil yield of 75%, based on feed, was obtained. The pour point of the oil obtained from this process was +20° F. and the cloud point of the oil was 2 to 6° higher.

Referring again to the apparatus in FIGURE 2, the waxy droplets from which oil is to be extracted is charged through line **31** into zone **45** which is filled with extraction solvent to level **48**. The droplets as they descend through zone **45** and column **33** are caused to descend in a spiral motion by alternately contacting horizontal baffles **36** and by the rotary motion of vertical paddles **37**. Baffles **36** are situated one-half column diameter apart throughout the height of the column, each baffle havnig the shape of a half disc (as shown by FIGURE 4) extending halfway across the column. Successive baffles are placed on alternate sides of the column. At the level of each baffle is stiuated a paddle **37** approximately one-half column diameter in height and attached to a central shaft **35** in such a manner that there is only a small clearance between the paddle blade, the walls of the columns, and the baffles. Each paddle consists of three vertical blades placed 120° apart and each blade having attached to it a short extension **40** of a suitable material, such as "Teflon," of sufficient length to touch the wall of column **33**. Each paddle is attached to shaft **35** in such a manner that each of its blades is in the same vertical plane of the corresponding blades of the paddles above and below it. A mechanical drive, not shown, is attached to central shaft **35** allowing it to be driven over a wide range of rotational speeds. In this manner, all of the paddles are rotated at the same speed. By this arrangement of internals, for a portion of the time during which a droplet is on a baffle **36**, it is isolated from two-thirds of the cross-section of the column at that point. The portion of the fluid solid mixture in which it exists is bounded by two of the half baffles **36** and on each side by four blades **37** of two paddles, the blades being aligned one above the other. In this manner, each particle of solids is isolated for a portion of each paddle revolution from that part of the column at which there is upflowing solvent. This isolated portion can be considered as a "mixer and settler." It is evident that by controlling paddle r.p.m. and baffle distance and solid and liquid throughput rates, that a wide range of throughputs, dilution ratios and residence times can be obtained.

The above described apparatus overcomes many of the problems associated with countercurrent extraction of solids with light solvents. One of the problems encountered is large scale vertical channeling. Channeling occurs when solvent introduced in the bottom of the tower moves upward and the solids introduced in the top of the tower move downward in "channels" and bypass each other rather than countercurrently contacting each other. This particular apparatus allows positive control in processes where the density of the entering solvent is less than that of the component being extracted from the solid. Further, in a situation such as this, where the density of the liquid phase increases with the distance it moves up the column, due to the presence of increasing amounts of extracted oil, control of the liquid stream and solids, and countercurrent motion becomes quie difficult. The tower internals described in FIG. 2 eliminate the strong channeling tendencies in such a column, and permit controlled countercurrent motion. If an upward moving channel of solvent tends to form in one compartment, proper adjustment of the rotational speed of the paddles will allow this developing channel to be moved under the next baffle above it so that it cannot propagate upward, since all the paddles are turning in the same direction and the entire extraction bed turns. In this manner, all channeling having a scale larger than the distance between two baffles on the same side of the column can be eliminated, in order to obtain an efficient countercurrent extraction operation, channeling must be eliminated.

Another problem associated with extraction of liquids from solids is the poor distribution of the entering liquid at the bottom of the column. Generally, in fluidized bed systems, there exists above the fluid distributor localized areas in which dilute phase fluidization occurs with downflow of packed solids between the areas of fluidization. This phenomena tends to decrease countercurrency and the efficiency of the extraction. The phenomena is eliminated by the apparatus used in this embodiment of the invention since, when the paddles turn, the entire bed of solids rotates and this phenomena is eliminated. Fluidization of the solids is also minimized by injecting the deoiling solvent through an annular ring with openings pointed downward rather than upward into the packed solids.

Still another problem associated with countercurrent extraction of solid particles of wide size distribution is the different rate at which the particles of different size descend through the ascending solvent. The heavier particles, of course, would move through the column too rapidly to have the oil contained therein removed. The

apparatus described in FIGURE 2 allows control of the residence time of the heavy particles. In a column without internals, the largest particles fall rapidly through the column being extracted only slightly. In the present apparatus, these heavy particles would fall onto a baffle **36** and could fall no further until swept off the baffle by slow-moving paddle **37**. Therefore, the minimum residence time for any droplet in a tower having the internals shown in FIGURE 2 would be equal to the product of the number of the baffles in the column, and the time required for a paddle to describe one-half revolution. The apparatus similarly restricts the maximum rising velocity of any entering fresh solvent which may have a tendency to bypass or channel. The rotational speed of the paddles and the geometry of the system therefore give positive control over the speed of movement of both the liquid and the sprayed solids through the extraction column. The paddles may be rotated at speeds between $\frac{1}{20}$ to 10 r.p.m.; preferably at speeds of $\frac{1}{4}$ to 2 r.p.m.

There are several variations of this apparatus which will appear to one skilled in the art. There may be more or fewer horizontal baffles used and the baffles may be other than half-moon in shape; e.g. pie-shaped, extend more or less than half way across the column. They may be more or less than a half diameter apart. There may be more than three paddles attached to the shaft at any one pint, for example 2 to 6, and consequently the angle between the paddles may be other than 120°. The height of the paddles need not be that of the distance between two horizontal baffles. The paddles may be slanted to the horizontal instead of normal to them, and the horizontal baffles may be slanted to the horizontal or conical in shape rather than forming a plane.

Our invention is further exemplified by the following example:

In accordance with a preferred embodiment of this invention, a typical 5,000 barrel a day feed rate dewaxing plant is used. The waxy lubricating oil fraction having a 90° F. pour point and a wax content of 12.5% (by secondary butyl acetate at 0° F.) is charged to the vessel at a temperature of 160° F. having a vapor pressure in the vessel of 19 p.s.i.a. The waxy oil feed is sprayed through a nozzle into the cooling vapor of propane which is at a temperature of −35° F. The nozzle atomizes the waxy oil feed resulting in droplets of wide size distribution having a volume median diameter of 400 microns. About one-third of the B.t.u.'s required to solidify all the wax present in the droplets is absorbed by the cooling propane vapor. Sufficient solidification occurs so that when the droplet hits the liquid propane filling the bottom half of the tower, the droplet's physical shape is not appreciably deformed. The liquid propane which is used to complete cooling of the droplet, as well as to extract the oil present, is at a temperature of −35° F. The liquid propane absorbs sufficient B.t.u.'s from the partially solidified oil droplet to completely solidify the droplet. The droplet passes from the top of the liquid propane solvent to the bottom of the solvent in a countercurrent motion as the oil is extracted from the droplet. The residence time of the waxy oil droplet in the liquid propane is about 60 minutes. A dewaxed oil yield of 75% is obtained having a pour point of 20° F.

Our invention is fairly exemplified by the following data:

Table I shows that the content of the oil in the waxy oil feed is critical, as well as the degree of cooling the droplet attained. It can be readily seen from the data below that waxy oil feeds having a large amount of oil present, which are not sufficiently cooked in a gaseous vapor prior to contacting the bottom of the spray vessel, form spongy agglomerates which are difficult to transport and filter and otherwise difficult to handle.

TABLE I

Deoiling tower does not work on high oil content or residual stocks

Stock	Oil content (percent by SBA at 0° F.)	Approx. diameter (microns)	Cooling vapor and temp (° F.)	Distance of fall (ft.)	Condition of drops hitting solid surface near bottom of column	Condition of drops on falling into liquid solvent
Paraffin lube	87.5	1,300	Air (45°)	18	No solidification	
Do	87.5	450	Air (5-20°)	14	Particles stick together.	Single particles. No sticking or agglomeration.
Do	87.5	280	Propane (5-35°)	12	do	Do.
Residual lube stock	58	280	do	12	Particles *very* sticky	Do.
Middle distillate	90	280	do	12	Particles soft, partially agglomerated.	Do.

In order to show the operability of the present invention in forming droplets in a non-solvent, feeds containing various amounts of oil were sprayed into cold methanol and then the oil was extracted with various solvents. The results are given below in Table II.

TABLE II

Process operability on stocks having wide range of oil contents

Data for batch extraction of sprayed droplets of wide size distribution having median diameters of approximately 400 microns

[Drops solidified by spraying into methanol]

Stock	Oil content (percent by secondary-butyl acetate at 0° F.	Solvent	Dilution ratio	Extraction temperature (° F.)	Oil yield (percent)	Filter rate (gal. dewaxed (oil) (hr.-Ft.^{2}) for 40% filter submergence
Residual petrolatum	29.6	50 MEK/50 toluene	3.0/1	45	42.8	4.26
Medium paraffinic lube	87.5	Hexane	2.0/1	−20	74.0	21.7
Middle distillate	90	85 MEK/15 methanol	1.5/1	0	94.9	15.8

The droplet diameter also has a direct effect on the time it takes to extract the oil present in the droplet and the percent of oil yield obtained. Data were obtained with waxy oil droplets having a median mean diameter of 2800, 910, and 600 microns, using MEK as the deoiling solvent at a temperature of 35° to 40° F. with a solvent to feed ratio of 4/1. A run was also made with 280 micron diameter droplets using a 50/50 MEK/toluene deoiling solvent at a solvent to feed ratio of 2/1. In this run, 20% by volume of the deoiling solvent was added to the feed before spraying the feed. The data obtained is presented graphically in FIGURE 5 of the drawings. It can be seen from the drawing that the larger droplets take a longer time to extract a specific amount of oil.

From the above examples and data, it is evdient that the droplet size, the degree of cooling of the droplet, prior to striking a liquid or solid surface, and the physical shape of the wax droplets are critical as related to the efficiency of filtering and/or centrifuging the resulting dewaxed oil, and the rate of extracting the oil from the droplet.

The scope of this invention is not to be limited by the specific examples and the embodiments herein presented and described, but is limited only by the claims appended hereto.

What is claimed is:

1. Apparatus for removing oil from waxy oil droplets which comprises in combination: (a) a vertical cylindrical vessel, (b) means for introducing waxy oil into said vessel, (c) means for introducing solvent into said vessel, (d) a plurality of spaced baffles on alternate sides of said vessel throughout its height, said baffles extending less than all the way across said vessel, (f) a plurality of paddles connected to a central shaft and located between each set of two baffles, said paddles having three blades, the blades being spaced approximately equidistant apart, the outer edge of said blades being in constant contact with the interior walls of said vessel and the lower edge of each blade being located so as to make continuous contact with the baffle immediately below it.

2. The apparatus of claim **1** wherein each blade has a resilient tip on its outer edge, said resilient tip making a continuous contact with the interior wall of said baffle.

3. The apparatus of claim **2** wherein each blade has a resilient element on its lower edge and is adapted to make continuous contact with the baffle beneath it whenever it passes over said baffle.

4. The apparatus of claim **2** wherein the blades extend from the central shaft outward to the walls of the vessel and extend from the top of one baffle to the bottom of the baffle next above it.

5. The apparatus of claim **2** wherein the vessel is provided with a means at the bottom of said vessel for collecting and settling the waxy droplets and for removing them from the bottom of the vessel.

6. The apparatus of claim **2** wherein the baffles are situated one-half column diameter apart throughout the height of the column, each baffle having the shape of a half disc, extending about halfway across and placed on alternate sides of the column.

7. The apparatus of claim **6** wherein there is situated between successive baffles, at the level of each baffle three bladed paddles, the blades being 120° apart and approximately one-half column diameter in height and attached to a central shaft so that all paddles rotate at the same time.

8. An apparatus for removing oil from partially solidified waxy oil droplets which comprises a vertical cylindrical vessel with a means at the top of said vessel for feeding into the vessel said waxy oil droplets, and with a means at the bottom of said vessel for feeding into the vessel a deoiling solvent, and contained within the vessel horizontal baffles spaced on alternate sides of said vessel throughout a portion of its height, said baffles extending less than all the way across said vessel, and spaced between said horizontal baffles, vertical paddles which are connected to a central shaft in such a manner that they may rotate in a plane normal to said horizontal baffles, said paddles having three blades, the outer portion of said blades being comprised of a resilient material which makes continuous contact with the interior walls of said vessel and wherein the bottom portion of said blades is comprised of a resilient material adapted to make continuous contact with the baffle below it, the net effect of any two blades passing over a baffle being to create a tight compartment of which the bottom portion is the baffle, one side is the interior wall of said vessel, another side is one blade of said paddle and the last side is a second blade of said paddle.

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ALPHONSO D. SULLIVAN, *Primary Examiner.*

DANIEL E. WYMAN, *Examiner.*