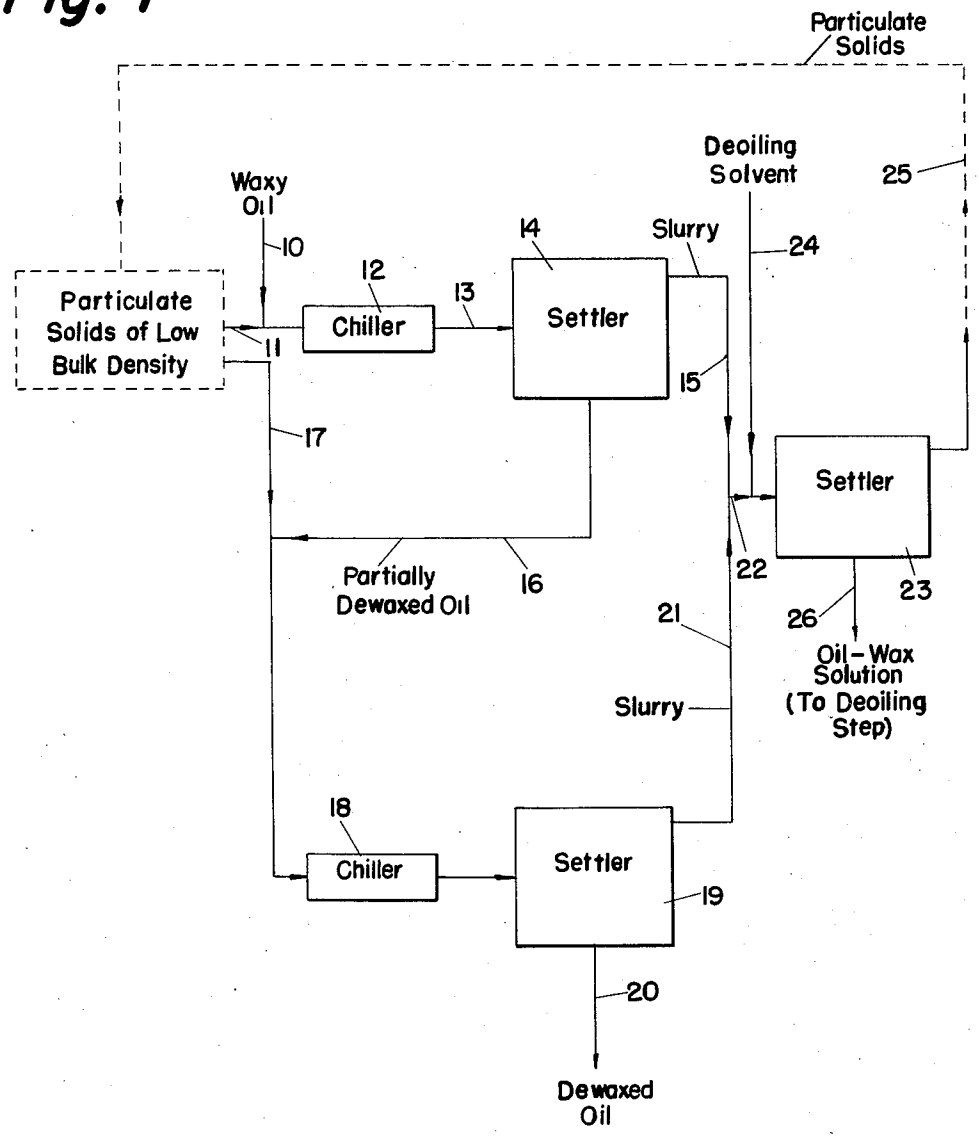
Aug. 16, 1960 J. L. JEZL 2,949,418

SEPARATION OF WAX FROM OIL

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Fig. 1



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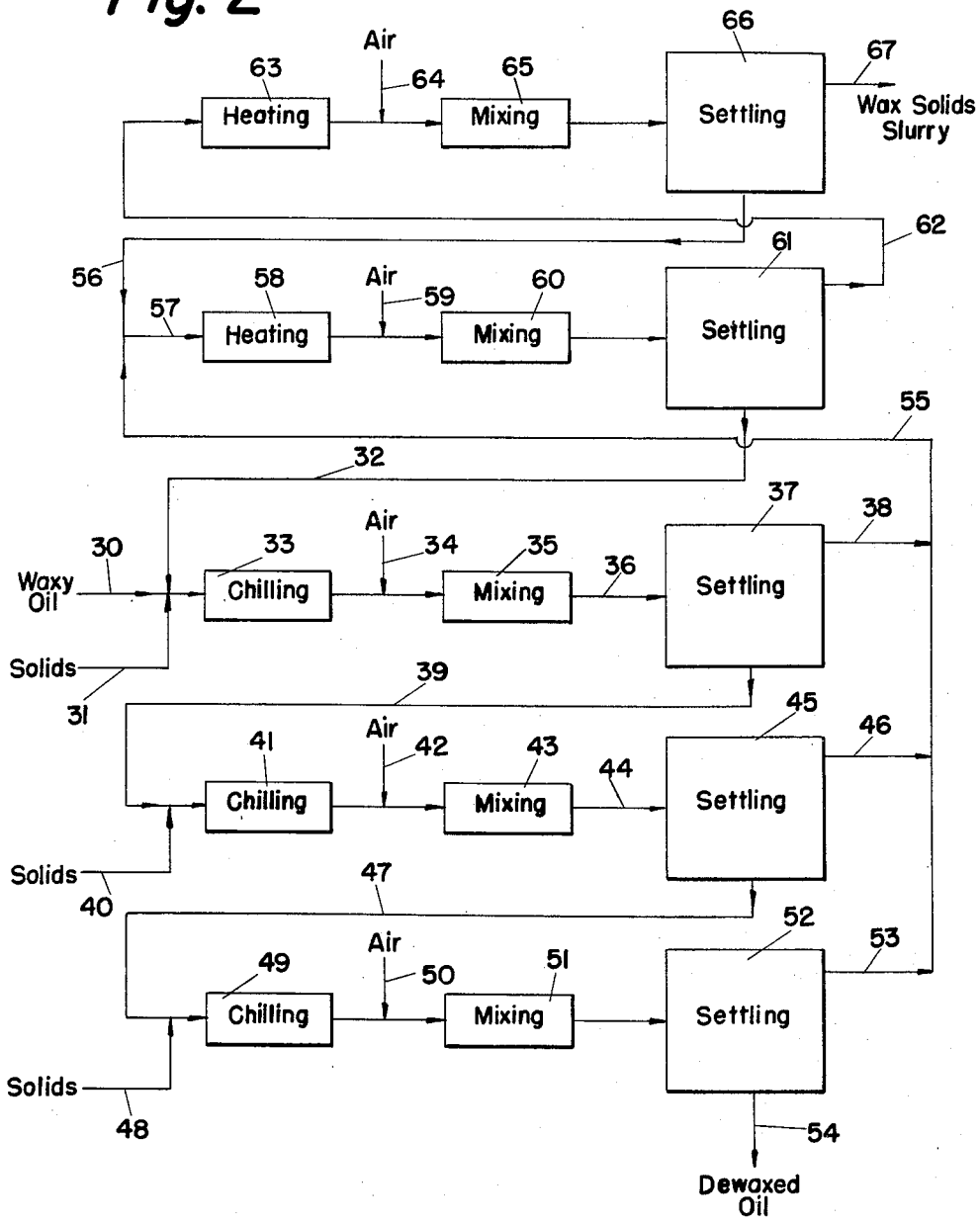
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Fig. 2



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2,949,418

SEPARATION OF WAX FROM OIL

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6 Claims. (Cl. 208—31)

This invention relates to the separation of wax from hydrocarbon oil and more particularly is directed to a simple and inexpensive method for obtaining a wax concentrate from wax-bearing hydrocarbon stocks containing paraffin wax.

Lubricating oil stocks obtained by distillation of most wax-bearing srude oils generally have relatively low wax contents such as for example 5–20% wax. In conventional refinery practice these stocks are subjected to a dewaxing operation in which a suitable solvent is used for separating wax from the oil. The most common solvent employed for this purpose is methyl ethyl ketone in admixture with an aromatic hydrocarbon such as benzene or toluene. The slack wax obtained from this operation generally has a wax content in the range of 60–90%. In order to obtain marketable wax products this material is subjected to a deoiling operation in which the same type of solvent may be used, although operating conditions, such as temperatures and solvent ratios, generally are different from the conditions maintained in the previous step of dewaxing the oil.

For effective deoiling of waxy stocks to produce wax products of suitably low oil content, it is generally necessary that the charge material have a wax content in excess of 40%. Stocks having lower wax content first must be treated to obtain the wax in a more concentrated form before it can be effectively deoiled. Hence the conventional practice in processing typical refinery oils entails the two steps described above of solvent dewaxing the charge oil and subsequently solvent deoiling the slack wax.

The present invention provides an inexpensive way of obtaining from waxy oils wax concentrates having sufficiently high wax contents so that solvent deoiling can be effectively accomplished by conventional solvent deoiling procedures. Practice of the invention eliminates the need for treating the charge oil with a solvent to obtain the wax concentrate and hence avoids the expenses entailed in employing and recovering solvent as done in conventional solvent dewaxing operations.

According to the invention a particulate or finely divided solid material whihc has a particle density less than the density of the charge oil is added to the waxy oil as an aid in effecting gravity separation of wax from the oil. Preferably, the particulate solid material is first added to the charge oil and the mixture is then chilled to precipitate the wax, although the particulate solids may be added subsequent to the chilling if desired. After chilling the mixture it is also distinctly preferable to agitate the mixture in the presence of a gas, such as air or flue gas, so as to incorporate fine gas bubbles in the mixture, although separation of wax can be effected without the use of such gas. The chilled mixture is then allowed to stratify, whereby a wax concentrate admixed with the particulate solids forms as a layer above the oil. This layer is separately withdrawn and the particulate solids are separated from the hydrocarbons. This yields

a wax concentrate having a substantially higher wax content than that of the original charge oil.

The hydrocarbon charge stocks for which the present invention is applicable may be distillate oils containing paraffin waxes or topped crude oils containing both the paraffin and microcrystalline waxes. In any event the charge should contain paraffin waxes for the process to to be effective. Residual stocks containing only the microcrystalline waxes generally cannot be handled effectively in the present process.

There are various materials which are suitable for use as the particulate solids in practicing the invention. Examples are expanded or foamed plastics of the unicellular type, such as vinyl plastics, polyurethane foams and phenolic "Microballoons." Powdered unfused polyethylene or polypropylene and powdered polyvinyl alcohol are other examples of suitable plastic materials. Another type of material which can be used is vesiculated volcanic glass, such as sintered perlite, volcanic ash and pozzolana. Any of these materials for use in practicing the invention should have a relatively small particle size, for example, a diameter suitably within the range of 0.0001 to 0.02 inch. The material selected should, of course, be insoluble in oil at the temperatures employed in the process, and it is essential that it have a particle density substantially less than the density of the hydrocarbon stock being treated.

A preferred manner of practicing the invention comprises adding the particulate solids to the waxy charge oil and then chilling the mixture to a temperature at which only a part of the wax is precipitated. Air or other relatively inert gas preferably is incorporated in the chilled mixture in the form of small bubbles and the mixture is then allowed to stratify. The upper layer, which is in a foamed condition if gas has been added and which contains the particulate solids and precipitated wax, is removed. A further amount of the particulate solids is then added to the partially dewaxed oil, and the mixture is chilled to a still lower temperature to precipitate an additional amount of wax. Again it is preferable to incorporate gas bubbles in the mixture, after which stratification again is permitted to occur. This procedure may be repeated as many times as is desired until all of the wax has been removed: Operation in this manner is advantageous in that it avoids the formation of thick mixtures which may be difficult to stratify. In each stage of chilling and stratification the amount of particulate solids used may vary widely but typically may be from 0.005% to 5.0% based on the weight of oil used. The number of stages which should be employed to achieve complete dewaxing will vary depending on the charge stock, particularly on its wax content and viscosity. For stocks of low wax content and relatively low viscosity, one stage may be sufficient whereas several stages may be needed when the wax content and viscosity are relatively high. If the viscosity of the waxy stock is high, a small amount of light hydrocarbon solvent may be added, such as, for example, up to 25% by volume based on the stock.

The slurries of wax and particulate solids as obtained from the stratification steps also contain considerable amounts of oil. If desired, these may be processed, either separately or in admixture with each other, to obtain wax concentrates having lower oil contents. One manner of reducing the oil content comprises subjecting the slurry to a sweating operation. Another manner, hereinafter more specifically described, involves raising the temperature of the slurry moderately and then subjecting it to stratification to cause separation of oil and low melting wax from higher melting wax and particulate solids.

Fig. 1 of the accompanying drawings diagrammatically illustrates one manner of practicing the invention wherein, for purposes of illustration, two stages of chilling and stratifying are employed and the use of gas bubbles to aid the separation is omitted. Waxy charge oil to be treated enters the system through line **10** and is admixed with a suitable amount of particulate solids introduced through line **11**, for example, from a hopper. The mixture passes through chiller **12** wherein the temperature is reduced sufficiently to cause a portion of the wax to precipitate from solution. The particles of solid material in the mixture serve as nuclei on which the wax can separate from the oil. The mixture then flows through line **13** to a settler **14** wherein it is allowed to separate into layers. The solid particles, being lighter than the oil, rise to the top and carry the precipitated wax along with them. The so-formed upper layer can be skimmed off or allowed to overflow through line **15**.

From the bottom of settler **14** partially dewaxed oil is withdrawn through line **16**. This stream is admixed with a further amount of the particulate solids as indicated by line **17**, and the resulting mixture is fed into chiller **18**. The mixture is brought to a lower temperature in chiller **18** than that attained in the preceding chilling step, so that an additional amount of wax is precipitated which wax occludes to the particles of solid material. The chilled mixture is passed into settler **19** wherein it stratifies to form an upper layer comprising particulate solids and wax concentrate. Dewaxed oil is withdrawn from the bottom of the settler through line **20** while the upper layer is removed through line **21**.

Since the slurries of wax concentrate and solid particles obtained from settlers **14** and **19** contain waxes precipitated at different temperatures, it may be desirable in some cases to process them separately in order to obtain different grades of wax products. However, for purposes of illustration, the accompanying drawing shows these materials as being processed together. The two streams from lines **15** and **21** are admixed and passed through line **22** to settler **23**. A solvent which is preferably of the type used in the subsequent deoiling operation, such as a mixture of methyl ethyl ketone and benzene, is fed into the mixture through line **24**. The purpose of the solvent is to dissolve the wax and oil hydrocarbons constituting the wax concentrate to effect separation thereof from the particulate solids. The solids rise to the top in settler **23** and may be skimmed off and returned for re-use as indicated by dotted line **25**. If desired, the small amount of solvent withdrawn with the solids may be evaporated therefrom and recovered before the solid material is re-used. Alternatively, the solids may be re-used without removal of the solvent, in which case provision should be made for stripping the dewaxed oil obtained from line **20** so that solvent which leaves the system admixed with the oil will be recovered. From the bottom of settler **23** the solution of wax concentrate in solvent is withdrawn through line **26** and is then sent to a conventional deoiling operation (not shown) for obtaining the desired wax product of low oil content.

The foregoing embodiment represents one manner of practicing the invention and it is apparent that numerous modifications may be made. The process may be conducted either batchwise or in continuous manner. In place of gravity separation in the settling zones, centrifuging of the mixtures may be employed. Also, separation of the wax concentrate from the particles of solid material may be accomplished, if desired, by washing with a hydrocarbon solvent such as pentane or naphtha rather than with a conventional deoiling solvent or by sweating rather than by washing with a solvent. However, since the wax concentrate has to be mixed with a deoiling solvent later in order to obtain wax having the desired low oil content, it is advantageous to use a deoiling solvent in the manner described in connection with Fig. 1 to aid in separating the hydrocarbons from the solid material.

Fig. 2 diagrammatically illustrates another embodiment of the invention wherein the wax-solids slurries obtained are subjected to settling treatments at increased temperatures and the resulting liquid hydrocarbons are recycled in the process. Also, a gas such as air is utilized as an aid in stratifying the mixtures in each of the settling steps.

Referring to Fig. 2, waxy oil, which enters the system through line **30**, is admixed with particulate solids from line **31** and with recycle material from line **32**. The mixture passes to a chilling zone **33** wherein the temperature is reduced sufficiently to cause a portion of the wax contained in the charge oil to precipitate. The chilled mixture is sent along with air introduced through line **34** into a mixing zone **35** where agitation is effected in a manner suitable for dispersing the air into the mixture in the form of fine bubbles. The mixture then passes through line **36** to settling zone **37** and therein is allowed to stratify. Separation into layers readily occurs with the upper solids-containing layer being in the form of a froth. The presence of the particulate solids aids in holding the air bubbles, thus tending to stabilize the froth. The frothy layer comprising wax, oil and particulate solids may be skimmed off or allowed to overflow through line **38**.

Oil from the bottom of settler **37** is sent through line **39** to another stage of chilling and settling. Another portion of particulate solids is introduced as indicated by line **40**, the mixture is chilled in zone **41** to a temperature suitable for precipitating a further quantity of wax, air is introduced through line **42** and agitation is then effected in zone **43** to disperse the air in the mixture. The mixture then passes through line **44** to settler **45** wherein it separates into an upper foam layer containing wax and solids along with oil and a lower oil layer. The upper layer is removed through line **46**, and the oil layer is passed through line **47** to a third stage of chilling and settling. After addition of solids as indicated by line **48**, the mixture is chilled in zone **49** to precipitate a still further amount of wax, air is added via line **50**, mixing is effected in zone **51** and the mixture is then settled in zone **52**. The wax-containing froth layer flows out through line **53** and dewaxed oil is removed from the system by means of line **54**.

As shown in Fig. 2 the wax-containing slurries obtained from the three settling steps above-described, are combined and passed through line **55** for further treatment adapted to remove oil and yield a wax concentrate of lower oil content. As illustrated, this treatment involves two stages of heating and settling. In the first stage the combined slurries from line **55** are mixed with recycle material from line **56**, and the mixture flows through line **57** into a heating zone **58** wherein it is subjected to moderate heating to raise the temperature sufficiently to liquify lower melting waxes. Air is then introduced through line **59** and is incorporated as fine bubbles in the mixture by suitable agitation in mixing zone **60**. The mixture then flows into settling zone **61** wherein it readily stratifies into an upper foam layer and a lower liquid layer. The latter is composed of oil and the lower melting waxes and preferably is recycled to one of the previously described chilling and settling stages. As illustrated in Fig. 2, this material is passed through line **32** and is admixed with the charge oil passing to the first of such stages. In some instances, however, it may be more advantageous to recycle this material to either the second or third stages, depending upon the temperature required to precipitate waxes contained in the recycle material. It will be understood that Fig. 2 is merely illustrative of one manner of carrying out such recycling, and that the most advantageous manner of recycling can be selected in any given case for the particular charge

stock being treated and the particular temperature conditions maintained in the various stages.

The wax-containing slurry leaves settler **61** through line **62** and passes to a further stage of purification. The mixture is heated moderately again in zone **63** to melt a further quantity of wax and then is mixed with air from line **64** in mixing zone **65**. The mixture is then allowed to stratify in settler **66**. The liquid layer of oil and wax, which wax is generally higher melting than that contained in the lower layer in settler **61**, preferably is recycled through line **56**. By operating in this manner, most of the wax contained in the charge will eventually flow from the system as a component of the froth layer or slurry obtained from settler **66** through line **67**. The hydrocarbon portion of this material will constitute a wax concentrate of relatively high wax content. The hydrocarbons can be separated from the particulate solids by employing a deoiling solvent as described in connection with Fig. 1 and may then be deoiled in conventional manner.

While the system illustrated in Fig. 2 involves five settling stages, it will be understood that any desired number of such stages may be incorporated in the system. Also, the operation may be modified so that only the wax-containing slurry from settler **37** is sent through line **55** for effecting oil removal, with the slurries from settlers **45** and **52** being recycled to the preceding settling operations.

The following examples are illustrations of simple batch treatments of waxy oil carried out in accordance with the invention:

Example I

The charge material was a distillate lubricating oil having a wax content of 13.5% by weight and a solidification point of +80° F. 200 cc. of the charge were mixed at about 85° F. with 1 gram of powdered unfused polyethylene and the mixture was cooled to about 60° F. to cause precipitation of wax. The mixture was agitated in the presence of air both during and after cooling, thus causing air bubbles to be formed therein. The mixture then was permitted to stratify into an upper froth layer and a lower liquid layer having a volume of about 160 cc. The lower layer was separated and the same procedure was repeated with 1 gram of additional polyethylene being added. This produced another froth layer and a lower liquid layer having a volume of 124 cc. The procedure was repeated a third time by adding 1 gram of the polyethylene to the lower layer after separation. Upon separating the froth layer from the liquid layer after the third stage of treatment, 112 cc. of oil having a solidification point of +66° F. were obtained. This shows that the resulting oil had substantially reduced wax content and that the wax had concentrated in the foam layers.

Example II

The same oil as used in Example I was treated in a similar manner in two stages but in each stage only 0.01 gram of powdered unfused polyethylene was used. The first stage yielded 162 cc. of oil as the lower layer and the second stage yielded 124 cc. having a solidification point of +70° F. This shows that a very small amount of particulate solids, when employed in combination with air dispersed in the mixture, is capable of removing substantial quantities of wax from the oil.

Example III

The procedure of Example II was repeated with the same charge stock in another two-stage treatment. In each stage 0.5 gram of "Microballoons" prepared from phenolic resin and having a particle diameter in the range of .0002–.005" was used. Expanded plastic material of this type is described in "The Oil and Gas Journal," July 13, 1953, pages 74–75. The first stage of treatment yielded 158 cc. of oil layer while the second stage of treatment yielded 136 cc. This treated oil had a solidification point of +76° F.

Example IV

Another three-stage treatment was conducted in the same manner as described in Example I utilizing the same amounts of materials, except that finely divided polyvinyl alcohol was used as the particulate solid material. From the third stage 104 cc. of oil product was obtained having a solidification point of +66° F.

Example V

A two-stage treatment of the same charge oil was carried out as in Example II employing 0.01 gram of finely divided polyvinyl alcohol in each stage. 170 cc. of oil layer were obtained from the first stage and 138 cc. were obtained from the second stage. This oil product had a solidification point of +76° F.

In the embodiment of the invention described above in connection with Fig. 2 wherein a gas is utilized in cooperation with particulate solids to effect separation of the wax from the oil, the gas is illustrated as being introduced into and dispersed in the mixture after it has been chilled to precipitate the wax. It is also permissible to disperse the gas in the mixture before the wax has been precipitated. In either event air generally is satisfactory for this purpose, since it is essentially inert toward oil at the relatively low temperatures employed in practicing the invention. However, other fixed gases such as flue gas, carbon dioxide or nitrogen may be used if desired.

I claim:

1. Method of obtaining a wax concentrate from an undiluted wax-bearing hydrocarbon oil containing paraffin wax which comprises forming an admixture of the wax-bearing hydrocarbon oil with particulate solids, having a particle density less than the density of said hydrocarbon oil, selected from the group consisting of polyethylene, polypropylene, polyvinyl alcohol, foamed plastics of the unicellular type, and vesiculated volcanic glass, subjecting said admixture to stratification at a temperature at which at least a portion of the wax is solidified to form an upper layer comprising a wax concentrate in admixture with particulate solids and a lower layer comprising oil of reduced wax content, and removing wax concentrate in admixture with said particulate solids from oil of reduced wax content.

2. Method of obtaining a wax concentrate from an undiluted wax-bearing hydrocarbon oil containing paraffin wax which comprises adding to the wax-bearing hydrocarbon oil particulate solids, having a particle density less than the density of said hydrocarbon oil, selected from the group consisting of polyethylene, polypropylene, polyvinyl alcohol, foamed plastics of the unicellular type, and vesiculated volcanic glass, chilling the mixture to precipitate wax from oil, subjecting the mixture to stratification to form an upper layer comprising a wax concentrate in admixture with particulate solids and a lower layer comprising oil of reduced wax content, and removing wax concentrate in admixture with said particulate solids from oil of reduced wax content.

3. Method of obtaining a wax concentrate from an undiluted wax-bearing hydrocarbon oil containing paraffin wax which comprises adding to the wax-bearing hydrocarbon oil particulate solids, having a particle density less than the density of said hydrocarbon oil, selected from the group consisting of polyethylene, polypropylene, polyvinyl alcohol, foamed plastics of the unicellular type, and vesiculated volcanic glass, chilling the mixture to precipitate wax from the oil, incorporating a gas in the form of bubbles in the oil, subjecting the mixture to stratification to form an upper layer comprising a wax concentrate in admixture with particulate solids and gas bubbles and a lower layer comprising oil of reduced wax content, and separating said layers.

4. Method according to claim 3 in which said upper

layer is admixed with a wax deoiling solvent at a temperature sufficient to dissolve the wax and oil hydrocarbons, the particulate solids are separated from the resulting hydrocarbon solution, and the hydrocarbon solution is then cooled to a temperature at which the wax precipitates to obtain a deoiled wax product.

5. Method according to claim 3 additionally comprising adding to said lower layer said particulate solids having a particle density less than the density of the lower layer, chilling the mixture to a temperature lower than that reached in the preceding chilling step to precipitate an additional amount of wax, incorporating a gas in the form of bubbles in the chilled mixture, subjecting the resulting mixture to stratification to form an upper layer comprising a second wax concentrate in admixture with particulate solids and gas bubbles and a lower layer comprising oil having a lower wax content than the oil obtained from the preceding stratification step, and separating the last-mentioned layers.

6. Method according to claim 3 wherein said upper layer after separation is heated to melt a portion of the wax contained therein, gas is incorporated in the form of bubbles in the heated mixture, the mixture is subjected to stratification to form another upper layer comprising particulate solids, gas bubbles and wax of higher concentration than that in the first-mentioned upper layer and another lower layer comprising oil and lower melting waxes, and separating said layers.

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