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PROCESS FOR DEWAXING OIL

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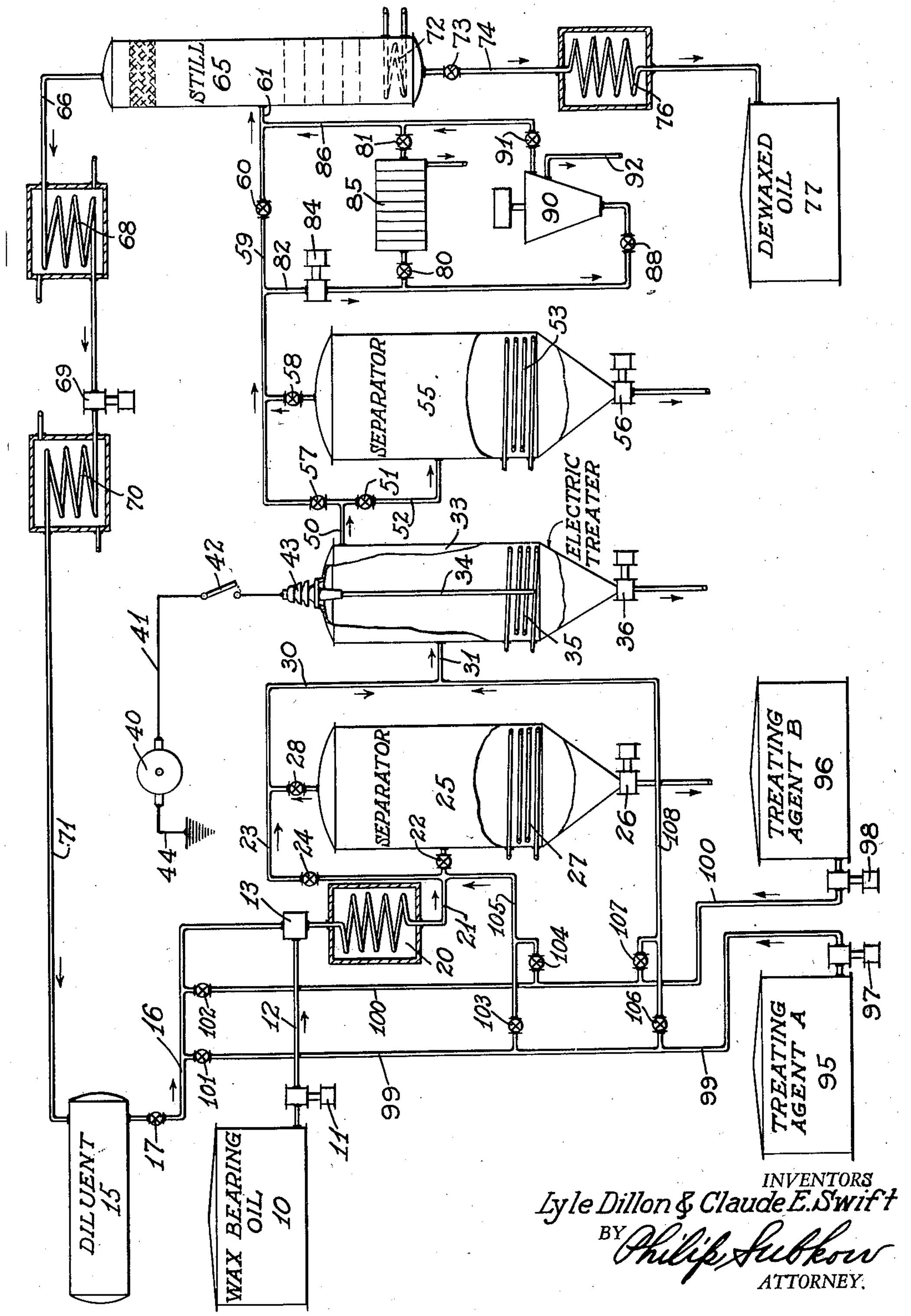

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PROCESS FOR DEWAXING OIL

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This invention relates to wax separation from wax-bearing oil. This invention relates more particularly to the separation of precipitated wax from suspension in oil.

Many crude oils from which lubricating oil is produced contain paraffin or wax. It is found associated with the lubricating oil fractions of paraffin base crude oil, asphalt base crude oil and mixtures or blends of lube oil fractions of both paraffin and asphalt base crude oils. The wax is not only of doubtful lubricating value but limits the minimum temperature at which lubricating oils containing it can be used, by congealing at low temperatures. Therefore, in the production of lubricating oil from petroleum fractions containing wax or paraffin, it is customary to remove a substantial portion of the wax or paraffin present in the oil in order to lower its "pour point" or the temperature at which it congeals.

The separation of wax from wax-bearing lubricating oil fractions has been accomplished by several processes in the past, the two most common and oldest of which are the "cold settling process" and the "cold pressing process".

In the "cold settling process" the wax containing oil is first diluted with a quantity of a light hydrocarbon fraction, such as naphtha, gasoline, or kerosene. The diluted wax-containing oil is then slowly chilled by suitable refrigerating means for a period of 20 to 50 hours until a temperature is reached at which a substantial portion of the wax is precipitated. The chilled oil and precipitate mixture is then allowed to stand for a period of several weeks to allow the wax to settle to the bottom of the chilling tank. Objections to this process are the cost of refrigeration for the necessary long periods of time, the large capacity of refrigeration and storage equipment, and the poor separation of wax and oil obtained.

In the "cold pressing" process the wax-containing oil is chilled slowly, as in the above described "cold settling" process. The chilled mixture of precipitated wax and oil is then pumped through a filter press at a high pressure. The wax precipitate is collected upon the filter and the oil is removed as a pressed distillate relatively free from wax. This process has found commercial application only in conjunction with oil having wax present in a crystalline form. Amorphous and/or micro-crystalline wax has been found extremely difficult and impracticable to separate by filtration methods.

It has been found that the enumerated disadvantages and other disadvantages inherent in the common methods of wax separation may be overcome by the process which will be described hereinafter.

We have discovered that wax-bearing oils may be mixed with suitable diluents, chilled to a temperature at which wax precipitates from solution and the resulting mixture of wax-bearing oil, diluent and precipitated wax subjected to an electric field. A portion of the precipitated wax acted upon by the electric field is separated from the mixture in the form of a deposit on the electrodes between which the said treating field is established. That portion of the precipitated wax which is not removed from the mixture in the form of a deposit is agglomerated and otherwise conditioned to be more readily filtered, centrifuged or settled. The diluent may be recovered by distillation subsequent to the separation of the wax from the solution according to the process described above.

In some cases where the quantity of wax to be separated from the wax-bearing oil is great it is advantageous, after refrigerating the oil and diluent mixture to a temperature at which wax is precipitated from solution, to subject the mixture to a preliminary settling stage wherein a portion of the wax which is more readily settled is removed. Following this preliminary settling stage the solution containing the remaining precipitated wax is then subjected to an electric field to deposit a portion thereof from solution and to render the wax remaining in solution more readily filtered, centrifuged or settled. Accordingly, the oil, diluent and the precipitated wax remaining therein following electrical treatment is withdrawn to a final settling stage where the remaining wax precipitate is settled and removed. The solution comprising the diluent and the dewaxed oil is removed from the final settling stage to a still where the diluent is separated from the oil, recovered and recycled through the system. The dewaxed oil and diluent mixture may, instead of being run directly from the final separating stage to the still, be filtered or centrifuged prior thereto. Or in some cases it is desirable to filter or centrifuge the oil, diluent and precipitated wax mixture immediately after electrical treatment without the intermediate final settling stage, as described above.

The preferred and most usual method of treatment, however, comprises chilling the wax-bearing oil and diluent solution to precipitate the wax, removing the wax by depositing it on the treater electrodes under the influence of the electric field in the electrical treater and separating the oil and diluent in the still directly after the electrical treatment without further settling.

The addition of certain electrolytes to the wax-bearing oil-diluent solution following refrigeration, aids in both the preliminary settling process without electrical treatment and in the separation by electrical treatment. The electrolyte remaining in solution is also beneficial in obtaining a thorough separation of the precipitated wax from the solution in the final settling stage. Electrolytes which have been found effective in aiding separation, according to the above described process are; inorganic acids, such as sulphuric, hydrogen chloride; organic acids, such as formic, acetic, oleic, stearic and naphthenic, and palmetic; metallic halides, such as aluminium chloride, ferric chloride, stannic chloride and zinc chloride. Also solutions of sulphur dioxide, carbon dioxide, ammonia and numerous soluble organic bases act as electrolytes to aid in the separation of the precipitated wax.

It is often desirable to add the electrolyte to the wax-bearing oil-diluent solution subsequent to refrigeration in order to confine said electrolyte to the liquid phase of the mixture, under which condition separation of the wax both by settling and by electrical treatment is most effective. However, the electrolyte may be introduced into the wax-bearing oil-diluent solution prior to refrigeration and in some cases, this is advantageous in aiding the subsequent process.

The addition of finely divided substances to the wax-bearing oil-diluent solution prior to refrigeration aids in settling the precipitated wax both before and after electrical treatment. The finely divided substance apparently forms a nucleus upon which the wax particles may form, agglomerate or adhere thus increasing the weight and size of the resultant wax particles which decreases its time of settling. Also, the presence of finely divided material in the wax particle which has a dielectric constant or conductivity which is materially different from that of the surrounding liquid materially aids deposition and agglomeration of the said particles under the influence of the electric treating field or current. These particles may become charged electrically and aid in the wax separation.

In some cases it is advantageous to introduce simultaneously finely divided solids and electrolytes into the wax-bearing oil-diluent solution. The solids in this case are introduced prior to refrigeration and the electrolyte subsequent to refrigeration according to the processes described above. Finely divided solids which we have discovered applicable to this process are iron, aluminium, lead, zinc, tin, litharge, graphite, iron oxide, carbon such as lamp-black or gas-black, asphalt, diatomaceous earth, clay, sawdust and wood flour. A number of these solids, in addition to being beneficial in the settling and electrical separation processes, also serve as filter aids. Fractions obtained by treating asphalt with appropriate solvents have also been found effective in some cases as aids in separating wax from oil by electrical precipitation. For example, an asphaltic residue or pitch which has been produced by the distillation of an asphaltic crude oil, or by cracking an asphaltic oil, may be extracted with a lubricating oil fraction and the lubricating oil solution of soluble bodies recovered from these residues or pitches may be added in relatively small quantities to the waxy oil as aids in the separation of the wax by the electrical methods above described. We may also employ high molecular weight bodies produced by the condensation of a chlorinated paraffinic hydrocarbon, such as paraffin wax and an aromatic hydrocarbon, such as naphthalene with aluminium chloride.

When finely divided solid materials are employed to aid settling and separation, according to the above processes, they are removed from the final dewaxed oil-diluent solution by settling and/or filtration.

The wax-bearing oil is dissolved in a diluent prior to refrigeration, according to the above described processes, for the purpose of preventing the refrigerated wax-bearing oil from congealing and to maintain the mixture sufficiently fluid to allow the precipitated wax to be readily separated from the mixture. Diluents which we have found suitable for this purpose are propane, pentane, butane, petroleum ether, naphtha, gasoline, kerosene, acetone, benzol, mixtures of acetone and benzol, methylchloride and halogenated hydrocarbons, such as monochlorodifluoromethane, dichlorodifluoromethane and dichloroethylene and trichloroethylene, ethers, alcohols and various mixtures thereof. A number of these solvents, such as propane, butane, methylchloride are normally gaseous and may, by a reduction of pressure, be made to serve as refrigerants in addition to solvents, as will be described hereinafter.

A number of diluents, such as liquid sulphur dioxide, analine, chloranaline, nitrobenzol, dichlorether, alcohol, acetone and acetone and benzol may be used as selective solvents and a stage of solvent extraction be employed simultaneously with the preliminary settling stage.

Refrigeration of the wax-bearing oil-diluent solution is accomplished either by means of external indirect heat exchange with a refrigerant, internal indirect heat exchange by means of a refrigerant circulating through cooling coils in the settling and electrical treating chambers or by direct cooling by means of evaporation of a normally gaseous liquid diluent from the wax-bearing oil solution. Diluents which may be used for refrigeration are propane, butane and methylchloride. It has also been found possible to cool the contents of the separator and the electrical treater chambers by mixture therein of liquid sulphur dioxide, carbon dioxide or ammonia.

The currents and/or potentials which may be employed in treating the refrigerated solution of wax-bearing oil and diluent containing precipitated wax are either continuous direct current or interrupted direct current. When direct current is employed, deposition of a portion of the precipitated wax on the electrodes immersed in the mixture takes place and the remainder of the precipitated wax is agglomerated or otherwise effected so that it is readily settled or separated by filtration or centrifuging. An alternating potential may also be imposed on the solution containing precipitated wax to agglomerate it and render it more readily separated by the above mentioned processes of separation, such as settling, filtering and centrifuging.

It has been found that in some cases where the kind of wax being treated has a dielectric constant, which is materially different from that of the surrounding oil-solvent solution, a high frequency alternating potential may be used to advantage for agglomeration and separation. High frequency is also advantageous where the solids or electrolytes which have been added to the solution have materially changed the dielectric constant or conductivity of the precipitated particles or of the surrounding solution. For example, where clay or other material having a dielectric constant which is materially greater than oil is utilized as the nucleus for formation of the precipitated wax particle the said particle will have an effective dielectric constant greater than the surrounding oil body in which it is dispersed. A body having greater dielectric properties than its surrounding material when subjected to a non-uniform electrostatic field tends to move towards the region of greater field intensity. Thus by proportioning the electrode sizes in the treater a non-uniform field of any desired variation of gradient can be obtained, and when these electrodes are energized by either a direct current or an alternating current the particles move towards the electrode around which the field is most intense. This condition obtains unless the polarity of the charge on the dielectric particle is of such polarity and potential that its attraction to the pole in the region of the weakest field is greatest. By reversal of polarity these two forces may be caused to assist one another in moving the wax particle out of the liquid to the desired electrode surface. Potential gradients of 5,000 to 60,000 volts per inch through the solution containing precipitated wax have been found most effective for deposition and agglomeration. Some wax precipitates exhibit a definite negative charge and are, therefore, deposited in greatest quantity on the positive electrode.

An example of operation according to the invention is as follows: A wax-bearing lubricating oil stock distillate from Santa Fe Springs crude oil was dissolved in a light hydrocarbon diluent, having a boiling point range between 300 and 400° F., at a ratio of 30% diluent to 70% distillate, and chilled to a temperature at which wax was precipitated from solution. The wax-bearing distillate-diluent and precipitated wax mixture was subjected to the action of a unidirectional electric field having a potential gradient of 45,000 volts per inch between electrodes immersed in the mixture, for a period of fifteen minutes. At the end of this period the positive electrode was found to have a heavy coating of wax which had been deposited or plated thereon. The negative electrode was without any wax coating.

Materials which have been effectively used for electrodes are iron, aluminium, copper, zinc and lead.

Simultaneous cooling and electrical treating has been found advantageous in reducing the quantity of diluent necessary to successful treating and separation. Thus the wax precipitate is electrically removed from the cooling solution as it is formed without accumulating or causing the mixture to congeal. In other words, by simultaneous treating and cooling the pour point of the solution is continuously lowered, as the treatment progresses, at such a rate that the lowering temperature follows closely the said lowering pour point. By this method it is possible to wax some lubricating oils without the use of diluents. The decrease in temperature in the treater is accomplished either by evaporation of a normally gaseous liquid in solution with the oil at reduced pressure or by indirect heat exchange through cooling coils.

Objects of this invention are to overcome the enumerated disadvantages and other disadvantages of the common wax separation methods and to provide a novel process for separating wax from oil which will be efficient, economical, of high capacity and less costly in time and equipment than the processes heretofore employed.

Other objects are to provide a process for separation of precipitated wax from wax-bearing oil which will be complete, in which the time of settling and separation of the wax is greatly reduced, and in which the time and energy consumption of refrigeration is a minimum and by which fine precipitates both crystalline and amorphous can be effectively separated. Another object of this invention is to provide a method wherein wax can be separated from wax-bearing oil which has been quickly cooled or "shock chilled".

In general these objects are attained according to the invention through treating the mixture of oil and precipitated wax by an electrical field or current. These objects are also attained according to the invention through treating the wax-bearing oil precipitate mixture with chemicals and/or finely divided solid materials. These objects are also attained according to the invention through the combined treatment by chemicals and/or finely divided solid materials and an electric field or current.

The invention is embodied in apparatus capable of performing the process of the invention comprising chilling a wax-bearing oil, or a solution of such an oil in a suitable diluent, to a temperature at which wax precipitation therein takes place, allowing the mixture to settle, separating a portion of the precipitated wax therefrom, subjecting the mixture containing the remaining wax to an electric field, depositing and/or settling the remainder of the precipitated wax from the mixture and separating the dewaxed oil from the diluent. The embodiment of the invention also comprises apparatus for adding chemicals and/or finely divided solid materials to the wax-bearing oil-diluent-precipitate mixture either in the refrigerating stage, the preliminary settling, the electrical treating, or final settling stages.

The invention broadly stated comprises a method of treating wax-bearing oil with an electric field or current to aid separation of wax therefrom. The invention more specifically stated comprises a process for treating wax-bearing oil and/or wax-bearing oil containing precipitated wax, by an electric field or current, to aid in, agglomerating and settling the precipitated wax. The invention also comprises a process for treating wax-bearing oil and/or oil containing precipitated wax by an electric field or current between immersed electrodes to remove wax from said oil by depositing or plating of said wax on one or more of said electrodes. The invention also comprises the combined method of treating wax-bearing oil with chemicals and/or finely divided solid materials and an electric field or current to aid in separation of the wax therefrom. The invention specifically stated comprises the process of treating wax-bearing oil in which a solution of wax-bearing oil and a diluent is "shock chilled" to precipitate wax, chemicals added to the solution containing the precipitated wax, the mixture subjected to an electric field or current to agglomerate and/or deposit the wax; the remaining agglomerated wax removed by settling and the dewaxed oil and diluent separated. The invention also includes the addition of finely divided solid materials to the wax-bearing oil-diluent solution either with or without chemicals and either before or after chilling to aid in settling, depositing and agglomerating the wax.

Other objects and advantages and features of the invention will be evident hereafter.

The electrical treater unit structure comprises a gas-tight vertical cylinder having an upper spherical head and an inverted conical bottom. A cylindrical electrode is situated axially in the electrical treater shell and is supported by and electrically connected through a high tension lead-in insulator extending through the center of the top spherical head. The electric potential is maintained between the said cylindrical electrode and the wall of the treater shell, by a suitable high voltage generator or transformer. Precipitated wax which settles to the bottom of the electrical treater shell moves downward toward the apex of the inverted conical bottom where it enters a pump by means of which it is ejected from the system. Refrigeration of the electrical treater contents may in some cases be directly attained by evaporation of a normally gaseous liquid within the treater from solution with the waxy oil undergoing treatment. The treater shell is, therefore, constructed to withstand the pressure associated with this type of operation. Cooling coils are also provided in the inside of the electrical treater shell through which a refrigerant may be circulated for the purpose of cooling the treater contents or maintaining its temperature constant. The wax-bearing oil-diluent solution is introduced at a point in the electrical treater shell about midway of the top and the bottom. The electrical treater outlet is situated near the top thereof. Suitable mechanical means, such as scrapers or stirrers may be provided for continuously or intermittently removing deposited wax from the walls and electrodes of the electrical treater and directing it to the outlet in the conical bottom. In some cases where mechanical means for removing wax from the treater walls and electrodes are not used, it has been found satisfactory to utilize a battery of two or more treaters in parallel so that they can be operated intermittently and alternately, allowing the ones not in operation to be entered and the accumulated wax removed.

The accompanying drawing illustrates one embodiment of the invention.

Wax-bearing oil at a temperature above its congealing point is stored in tank 10. This oil is withdrawn from tank 10 by pump 11 and forced through line 12 to a mixing valve 13 where it meets and is mixed with a stream of a light hydrocarbon diluent supplied from diluent storage tank 15 through valve 17 and line 16. The solution of wax-bearing oil and diluent passes from the mixing valve 13 into refrigerator 20 where it is chilled to a temperature at which wax is precipitated from solution. The mixture of wax-bearing oil, diluent and wax precipitate flows from refrigerator 20 through line 21 and valve 22 into the settling chamber or separator 25 where the more readily settling portion of the precipitate is allowed to settle. The wax settlings are removed from the conical bottom by means of pump 26. The wax-bearing oil, diluent and the remaining precipitate mixture is withdrawn from the top of the separator through valve 28 and flows through lines 30 and 31 into the electrical treating chamber 33 where it is subjected to an electric field between the treater wall and the electrode 34 therein. A major portion of the remaining wax precipitate is deposited on the electrical treating chamber wall and electrode. This deposited wax along with other wax which settles is removed from the interior surfaces of the electric treater chamber and withdrawn through the conical bottom thereof by means of pump 36. A high potential electric field is established through the solution containing precipitated wax in the electric treater between the central electrode 34 and the treater wall, by means of a high voltage supplied by a generator 40 through the requisite electrical connections comprising conductor 41, switch 42 and treater lead-in insulating bushing 43. The electrical return circuit from the treater shell is completed through the ground and ground connection 44.

The electrically treated wax-bearing oil-diluent solution is withdrawn from the electrical treater through line 50, valve 51, line 52 and introduced into settling chamber 55 where a final separation of the precipitated wax and/or solid bodies, if any remain therein, is allowed to take place. The finally separated wax and solid materials are removed from the conical bottom of the separator 55 by means of pump 56.

The clear, dewaxed oil-diluent mixture is withdrawn from the top of separator 55 through valve 58, line 59, valve 60 and is introduced through inlet 61 into a still 65 where separation of the said dewaxed oil and diluent takes place. The diluent vapors from the still 65 are withdrawn through vapor line 66 and in the case where the diluent is normally gaseous, the vapors are cooled in cooler 68, compressed by compressor 69, condensed in condenser 70 and the condensate returned through line 71 to diluent storage tank 15. In the case where the diluent is normally liquid the vapors from the still are condensed in cooler 68 and returned by means of pump 69 to the diluent storage tank 15. Heat is supplied to the still 65 by means of heating coil 72. The still bottoms consisting of the treated dewaxed oil is withdrawn through valve 73, line 74 and cooler 76 to the dewaxed oil storage tank 77.

In many cases it is found that final settling after electrical treating is unnecessary the wax having been completely removed from the mixture by deposition on the electrodes, and when this takes place valves 51 and 58 are closed, valve 57 opened and the dewaxed oil-diluent solution run directly from the electrical treater 33 through line 50, valve 57 and lines 59 and 61 to the still 65.

It has been found, as explained above, that electrical treatment of the precipitated wax renders it more readily filtered and centrifuged and, therefore, in some cases it is desirable to filter or centrifuge the mixture directly after electrical treatment or after the final settling stage. When it is desired to filter, valve 60 is closed and valves 80 and 81 opened, allowing the solution to flow through line 82, pump 84, filter 85, lines 86 and 61 to the still. Pump 84 serves to supply the additional pressure necessary for filtration. When it is desired to centrifuge, the valves 80 and 81 remain closed and valves 88 and 91 are opened allowing the solution to flow through the centrifuge 90. Wax is removed from the centrifuge through line 92.

Two treating agent storage tanks 95 and 96 are provided for storing treating agents A and B, respectively. Treating agent A comprises chemicals, such as the oil soluble electrolyte, acids and bases enumerated hereinbefore. Treating agent B comprises finely divided solid material in suspension in a suitable carrying medium as, for example a portion of the wax-bearing oil being dewaxed or in the diluent, also as enumerated hereinbefore. Treating agents A and B are transferred by means of pumps 97 and 98 into manifolds 99 and 100, respectively. Suitable manifolding and valves are provided as shown in the drawing for making it possible to introduce these treating agents either separately or together into the diluent stream to the mixing valve 13 through valves 101 and 102, or either of them may be introduced through valves 103 and 104 through line 105 to the chilled wax-bearing oil diluent solution from the refrigerator 20 at line 21 or either one or both of said treating agents may be introduced through valves 106 and 107 through line 108 to the solution entering the treating chamber through line 31.

It has been the preferred operation to introduce treating agent B through manifold line 100 and valve 102 into the diluent stream to the mixing valve 13 so that the wax-bearing oil-diluent solution will have present in it, during refrigeration in refrigerator 20, the finely divided solid materials to act as nuclei for precipitated wax particles which form during refrigeration. It has been the preferred practice to introduce the treating agent A through manifold 99 to the oil-diluent solution after chilling through line 105 or 108.

In cases where the amount of precipitated wax is not great it is sometimes desirable to eliminate the preliminary settling and separation stage, and this is accomplished by by-passing separator 25 by line 23. In this case valves 22 and 28 are closed and valve 24 open.

The separator 25, electrical treater 33 and separator 55 are provided with cooling coils 27, 35 and 53, respectively, by means of which the temperatures of the contents of the said chambers may be lowered, regulated or maintained. When refrigeration of the wax-bearing oil in the various chambers is accomplished by evaporation of a normally gaseous liquid, the release and reduction of pressure is governed by the adjustment of the outlet valves, such as 51 and 57 of the electrical treater chamber.

Acid treatment of the oil containing wax may be carried on in separator 25. The acid sludge and oil mixture may be withdrawn to the electrical treater through line 30, while the precipitate may be withdrawn through pump 26 at the bottom. Similar treatment with metallic halides, such as aluminium chloride, may be performed in separator 25.

The process and apparatus is not to be limited to the treatment of oils for the removal of wax but is applicable to the treatment of similar substances for the removal of asphalt, asphaltines, petrolatum, sludges and other substances and impurities both solid and plastic.

The foregoing is merely illustrative of one apparatus and method and the invention is not limited thereby but may include any method and apparatus which accomplishes the same within the scope of the invention.

We claim:

1. A process for separating wax from wax-bearing oil comprising dissolving the wax-bearing oil in naphtha, mixing lampblack into the solution, chilling the mixture to precipitate wax, subjecting the mixture to an electric field and separating the wax from the oil.

2. A process for the separation of wax from a wax-bearing oil which comprises adding a wax filter aid to said wax-bearing oil to thereby condition said oil to facilitate the separation of wax therefrom, chilling the wax-containing oil to precipitate wax, subjecting the chilled oil containing precipitated wax to the influence of an electric field and removing the precipitated wax from the chilled oil.

3. A process for the separation of wax from a wax-bearing oil which comprises adding a finely divided solid to said wax bearing oil to thereby condition said oil to facilitate the separation of wax therefrom, chilling the wax containing oil to precipitate wax, subjecting the chilled oil containing precipitated wax to the influence of an electric field and subsequently filtering the chilled oil to remove the wax therefrom.

4. A process according to claim 3 in which the finely divided solid is lampblack.

5. A process according to claim 2 in which the wax filter aid is a petroleum residue.

6. A process according to claim 2 in which the wax filter aid is petroleum asphalt.

7. A process according to claim 2 in which the wax filter aid is asphalt and in which the wax is removed from the oil by filtration.

8. A process according to claim 2 in which the wax filter aid is asphalt and in which the wax is removed from the oil by settling.

9. A process according to claim 2 in which the wax filter aid is a petroleum residue and in which the wax is separated from the oil by filtration.

10. A process according to claim 2 in which the wax filter aid is a petroleum residue and in which the wax is separated from the oil by settling.

11. A process according to claim 2 in which the waxy oil is commingled with a diluent and in which the wax filter aid is a petroleum residue.

12. A process according to claim 2 in which the waxy oil is commingled with liquid propane and the wax filter aid is a petroleum residue.

13. A process for the separation of wax from a wax-bearing oil which comprises adding a finely divided solid to said wax-bearing oil to thereby condition said oil to facilitate the separation of wax therefrom, chilling the wax-containing oil to precipitate wax, subjecting the chilled oil containing precipitated wax to the influence of an electric field in the presence of said finely divided solid, and subsequently removing the precipitated wax from the chilled oil.

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