Jan. 8, 1952 J. L. BILES ET AL 2,581,573

METHOD FOR SEPARATING WAXY AND OILY MATERIALS

Filed June 9, 1948 3 Sheets-Sheet 1

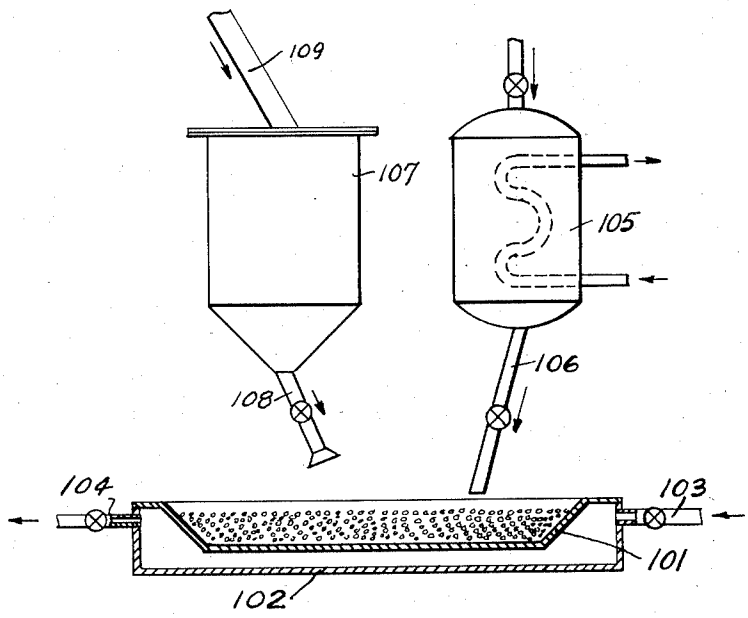


Fig. 1

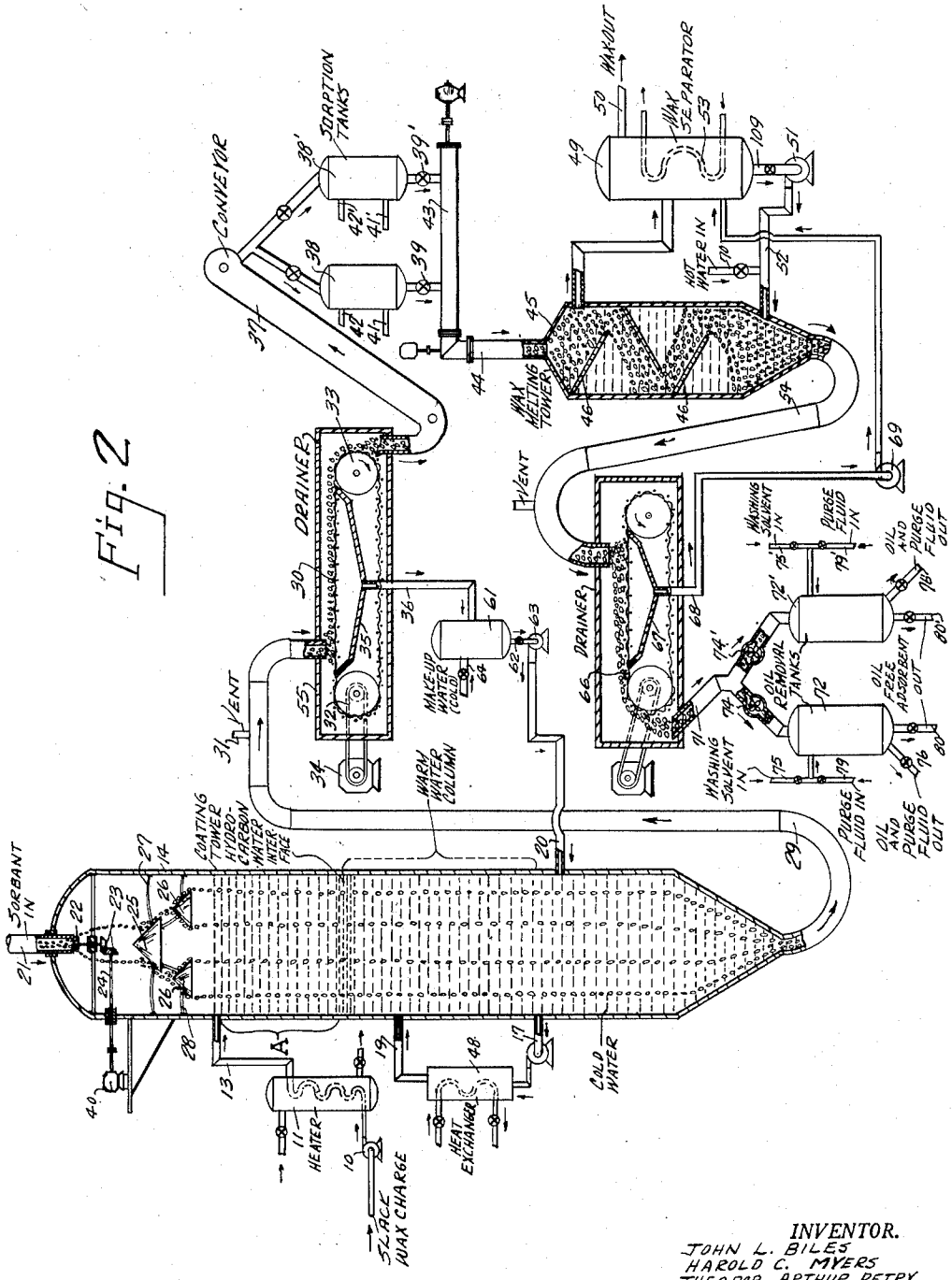
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FIG. 2



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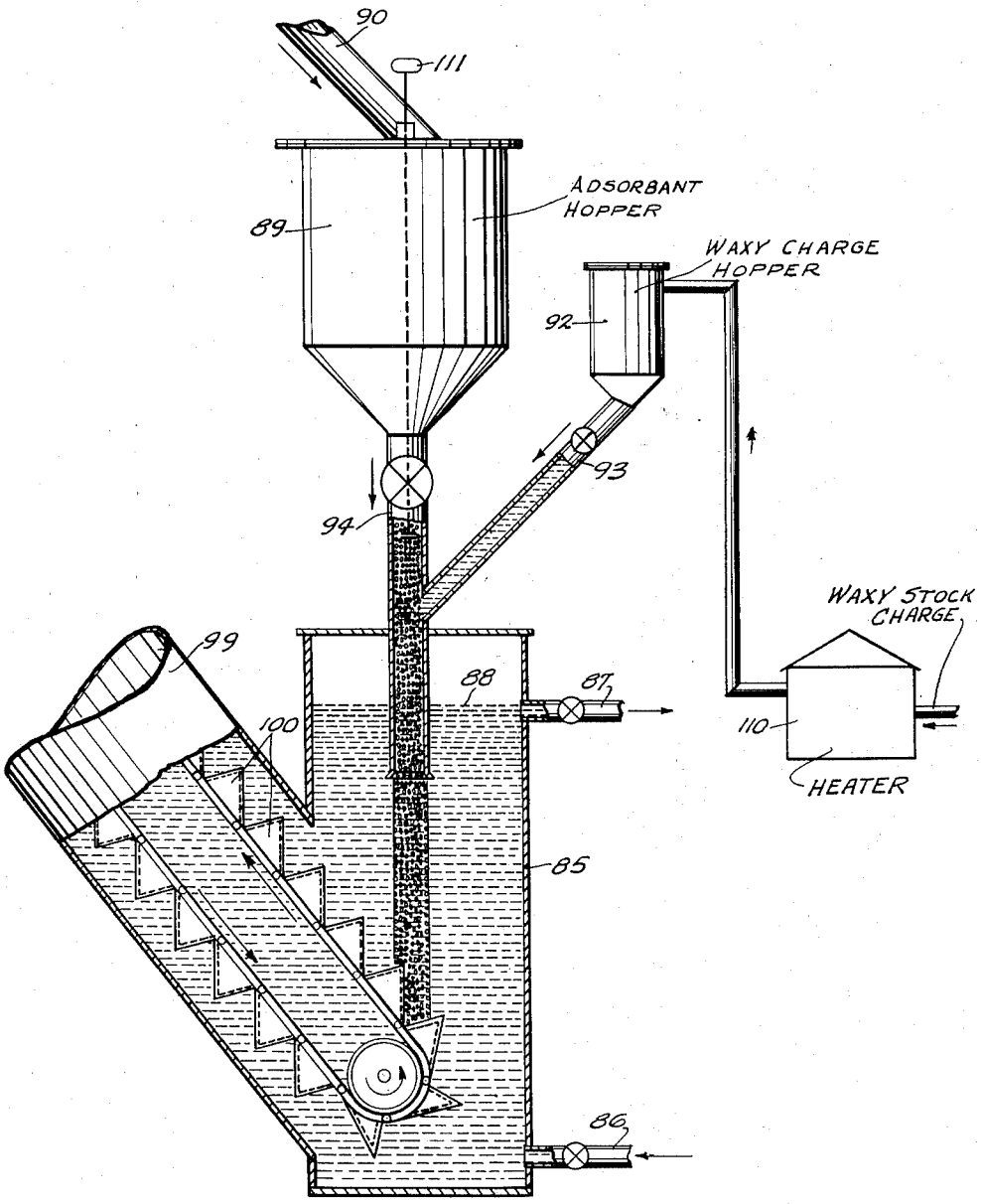
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Fig. 3



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UNITED STATES PATENT OFFICE

2,581,573

METHOD FOR SEPARATING WAXY AND OILY MATERIALS

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17 Claims. (Cl. 196—20)

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This invention relates to a process for the separation of wax and oily constituents present in a wax bearing hydrocarbon stock and more particularly to a process for deoiling waxy petroleum fractions such as slack wax and the like.

The present process is broadly applicable to the problem of separating wax and/or petrolatum and the like from hydrocarbon oils in substantially oil free form. The present process is particularly directed to the deoiling of crystallizable wax present in high waxy stocks such as in slack wax.

A process commonly employed heretofore for the deoiling of wax is the well known sweating process wherein the slack wax is chilled in pans to cause congealing of the wax after which the mass is slowly heated to effect sweating out of the liquid oil. The efficiency of this process is low as compared with other methods from the standpoint of wax yields. Moreover, the process is conducted batchwise and requires a considerable length of time and delicate temperature control during the heating period.

Another process employed is the solvent deoiling process in which the slack wax is mixed with a suitable solvent such as propane or benzol-acetone, for example, and then chilled and filtered.

Still another process currently employed is the emulsion deoiling process in which the slack wax is mixed with a non-viscous non-solvent while in molten state after which it is cooled to congeal the wax. Then the congealed wax is separated from the oil in non-solvent emulsion by means of a basket type centrifuge lined with a filter material. Such processes involve extensive wax recycle to provide satisfactory yields of wax with low oil content.

It has been customary in the prior art to employ filter aids such as diatomaceous earth in powdered form to act as an aid in the dewaxing of oils by the filtration of the wax from the liquid oil. In such a process the liquid oil from which most of the wax has been crystallized is withdrawn free of the filter aid and the waxy material. The process has not ben found practicable as a method for deoiling waxes to obtain oil free wax. As a matter of fact the waxy material left behind with the filter aid is generally known as slack wax and contains substantial amounts of oil.

In United States Patent 1,278,023, dated September 3, 1918, there is disclosed a process for dewaxing of oils wherein the waxy oil stock is wholly absorbed by a solid porous material such

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as fuller's earth after which the fuller's earth is chilled to effect congealing of the sorbed wax. The fuller's earth is then treated with a suitable oil solvent whereby the liquid oil is removed leaving behind the wax within the pores of the adsorbent. The wax is subsequently separated from the solid adsorbent. This process is unsatisfactory because of the difficulty in obtaining satisfactory wax yields and the difficulty of removing the wax from within the pores of the adsorbent without use of a second solvent for the wax.

A major object of this invention is the provision of a new, improved and economical process for the separation of wax and liquid oils which overcomes many of the disadvantages of the prior art processes.

A specific object is the provision of a novel continuous process for the deoiling of slack wax by means of porous solid adsorbent materials.

These and other objects of this invention will become apparent from the following description of the invention.

The present invention broadly comprises a process wherein the waxy stock such as slack wax is brought into intimate contact with a suitable particle form solid adsorbent material under temperature conditions at which the wax constituents of the wax bearing oil are congealed and become and remain coated on the outer surface of the adsorbent particles while the non-congealed liquid oil constituents are sorbed into the pores of the adsorbent. Thereafter the wax is removed from the surface of the adsorbent leaving behind the adsorbent bearing in its pores the liquid oil. The oil may be subsequently separated from the adsorbent by any of a number of different methods. In order to obtain the optimum yields of wax it is highly important in this process that the temperature be controlled such that the waxy constituents in the waxy stock are in a congealed or crystallized state either prior to, or substantially immediately after being brought into contact with the solid adsorbent particles or are congealed substantially simultaneously upon being contacted with the adsorbent. Also the waxy constituents should remain congealed at least until the step of removing the wax from the adsorbent commences. It will be readily understood by those skilled in the art that such expressions as "congealed wax constituents" and "non-congealed liquid oil constituents" and the like as used in describing and claiming this invention do not necessarily mean pure oil-free wax or pure wax-free oil since the

amount of wax which will congeal from a wax-oil mixture is to some extent dependent upon the temperature of the mixture. For example, if the mixture were cooled to 90° F. some waxy constituents might congeal but in the non-congealed liquid oil there very probably will be present in non-congealed state some material which chemically should be classified as a wax. For the purposes of describing and claiming this invention a wax which is free of oil shall be taken as meaning one in which the oil content is zero as determined by the A. S. T. M. method for determining oil contents of waxy stocks, A. S. T. M. Test Number D721–43T.

The invention may be more readily understood by reference to the drawings attached hereto in which Figure 1 is a highly diagrammatic elevational view of an apparatus arrangement adapted for conducting this invention. Figures 2 and 3 are elevational views, partially in section, showing modified systems for conducting the method of this invention. All of these drawings are highly diagrammatic in form.

Turning now to Figure 1, there is shown a system adapted for conducting the method of this invention batchwise. In Figure 1, 101 is a shallow pan provided with a cooling jacket 102. A cooling fluid inlet 103 and outlet 104 connect into the cooling jacket. A layer of waxy charging stock is supplied to pan 101 from heated tank 105 via pipe 106. The waxy constituents are caused to congeal by means of the cooling fluid passed through jacket 102 so as to provide a pasty layer of charging stock on the bottom of pan 101. Adsorbent particles are then passed from hopper 107 via pipe 108 into pan 101 in sufficient amount to cover over the layer of waxy stock with a thin layer of adsorbent. The adsorbent is then pressed into the layer of wax by a large spatula or other suitable means and the process is then repeated until the pan is filled with a mass of congealed waxy charge mixed with adsorbent particles. The mass is chilled to insure the complete desired precipitation of wax constituents and permitted to stand under these conditions until the oil constituents have been sorbed in the pores of the adsorbent. Thereupon the wax may be separated from the surface of the particles by removing the particles from the pan 101 and mechanically agitating them together so as to break off the crystallized wax from the surface of the wax particles. Alternatively, the wax may be melted from the particles by contacting them with steam or hot water followed by separation of the melted wax from the adsorbent particles which still hold the oily constituents in the adsorbent pores. The oily constituents may then be removed from the adsorbent by means of a suitable solvent such as a naphtha fraction. This latter alternative may be conducted in pan 101 if desired, the liquid being poured from the pan at the proper time. The adsorbent particles are then purged free of solvent by means of steam and then returned to tank 107 via pipe 109 for reuse.

If desired the cooling of the waxy stock and the temperature of the solid adsorbent charge to pan 101 may be so controlled as to accomplish crystallization of the waxy constituents substantially simultaneously upon contact with the particles of adsorbent, which is preferable, or substantially immediately after such contact.

The process of this invention may be conducted continuously as well as batchwise. A suitable arrangement for conducting the process continuously is shown in Figure 2. In this system a waxy stock such as slack wax is pumped by pump 10 through a heater or heat exchanger 11 wherein it is heated to a temperature slightly above that at which the waxy constituents begin to congeal. The heated slack wax then passes via pipe 13 into the upper section of the elongated vertical vessel 14. A column of the molten slack wax is maintained within section A of the coating tower 14. A column of water or other suitable cooling liquid is maintained within a lower section of tower 14. This liquid should be of greater density than the slack wax and a non-solvent as to both wax and oil. The water in that portion of the tower 14 just below the slack wax column is maintained at a temperature sufficiently high to avoid congealing of wax at the interface between the slack wax and water column. This is accomplished by circulating water through pipe 17 into and through heat exchanger 18 and back into the water column via pipe 19 just below the interface. Cold water enters the water column via pipe 20 below the level of warm water outlet pipe 17. Particle form porous adsorbent material which may preferably be of spherical form enters the tower 14 via pipe 21 at about the same temperature as the slack wax or at a somewhat lower temperature. In general, the inlet temperature of the adsorbent should usually be below about 100° F. and preferably below about 80° F. The rate of introduction of adsorbent is controlled by adjustment of the height of the outlet end of pipe 21 from conical spreader 22 and by rotation of spreader 22. The spreader is rotated by means of gears 23, shaft 24 and motor 40. Upright conical baffles 25 and 26 are supported by rods 27 and 28 properly positioned below the spreader 22 in such a manner as to distribute the particles of adsorbent uniformly over the entire cross section of the tower 14. The adsorbent particles drop downwardly through the column of slack wax and become coated on their surface with a film of slack wax. The particles then drop into the water column and the cool water acts to congeal the wax constituents on the surface of the particles. When the difference between the particle density and cooling liquid is small it is desirable to add some substance such as potassium oleate to the water or other cooling liquid to lower the interfacial tension at the water-slack-wax interface. This will prevent hold up of adsorbent particles at this interface. The particles of adsorbent bearing the congealed material are washed by the water from the bottom of tower 14 through the curved pipe 29 onto a moving screen belt drainer 30. The pipe 29 is provided with a vent 31 to break the siphon effect, and the level of the highest point along pipe 29 is such as to maintain the surface of the wax column substantially constant as indicated in the drawing, the water introduced into tower 14 via pipe 20 being equal in volume to that passing from the tower through pipe 29.

The screen 30 is of a continuous belt type, moving over rollers 32 and 33, one of which is driven by motor 34. The screen is encased in suitable housing 55. A pan 35 positioned under the screen catches the water which is withdrawn via pipe 36 to accumulator 61. The water is passed from accumulator 61 via pipe 62, pump 63 and pipe 20 back to the tower 14. Make up cooling water is added to the accumulator 61 via pipe 64. The adsorbent particles bearing the congealed waxy material are retained by

the screen and discharged into conveyor 37. The adsorbent is discharged from the conveyor into one of the sorption tanks 38 and 38', these tanks being several in number although only two are shown and being employed in cycle. When one of the tanks 38 is filled the adsorbent is permitted to stand therein while the temperature is controlled by means of heat transfer tubes (not shown) at a level at which the wax constituents of the slack wax will remain congealed. A suitable cooling fluid may be supplied to the heat transfer tubes within each of the tanks 38 via pipe 41 and withdrawn via pipe 42. The adsorbent is retained within the tank 38 or 38' until substantially all of the non-congealed liquid oil constituents of the slack wax are sorbed from the congealed mass on the surface of the particles into the pores of the particles leaving substantially only the waxy constituents coated on the outer surface of the adsorbent particles. The adsorbent is then withdrawn through outlets 39 and 39' and conveyed by screw conveyors 43 and 44 into the upper section of the wax melting tower 45 which is maintained substantially filled with a column of hot water. The adsorbent particles drop through the column of hot water in a zig zag path provided by baffles 46 so that the wax deposited on the surface of the particles is melted off from the particles and is passed from the upper section of tower 45 via pipe 48 to the wax separator 49. The molten wax is withdrawn from the upper section of separator 49 via pipe 50 and the separated water is returned via pipe 109, pump 51 and pipe 52 to the lower section of the wax melting tower 45. The water is maintained substantially above the melting point of the wax by means of the heating coil 53 within separator 49. The adsorbent particles which still retain the liquid oil within the pores of the particles are carried from the bottom of tower 45 in a water stream via conduit 54 and discharged onto the moving belt screen drainer 66 which is similar to the screen 30 described hereinabove. The highest level of conduit 54 is such as to permit maintaining tower 45 substantially filled with liquid. The hot water passing through the screen 66 is collected in pan 67 and returned via pipe 68 and pump 69 to the separator 49. Hot water make up is added to the system via pipe 70. The filtered adsorbent material passes from the end of moving screen 66 via duct 71 into one of several oil removal tanks 72 and 72' (only two being shown). These tanks are used in cycle, the empty tank being opened to the duct 71. When one of the tanks 72 has become filled to the desired level with adsorbent, it is closed off from duct 71, as by stopping the rotation of the star valve 74 and 74', and a suitable oil solvent is introduced via conduit 75 or 75' into the tank 72 or 72' and passed through the adsorbent mass until all the sorbed oil is removed. The solvent bearing removed oil is withdrawn from tank 72 via pipe 76 and the oil and solvent may then be separated in suitable equipment which is conventional in the art for that purpose. The solvent employed may be a heated naphtha fraction, benzol, hexane, butyl alcohols, ethyl carbonate and acetone or other suitable oil solvents. After removal of the oil, the adsorbent is drained and then purged free of solvent by means of steam, flue gas or other suitable purge fluid entering via pipe 79. The purge fluid is withdrawn from tank 72 via pipe 76. The reclaimed adsorbent is then discharged from tank via pipe 80 and may be reused in the deoiling process.

After long periods of continued reuse a deposit of carbonaceous material may accumulate on the adsorbent which is not removed in the reclaiming steps. Inasmuch as this material may eventually plug up the pores of the adsorbent and decrease its efficiency in the present process, the carbonaceous contaminant should be periodically removed from the adsorbent either by means of suitable solvents or by means of burning with air at elevated temperatures in a manner well known to those skilled in the art.

It will be readily understood that this invention is not limited to the particular details of apparatus arrangement or process step technique shown in Figures 1 and 2. For example, a number of methods may be employed for accomplishing the initial coating of the surface of the adsorbent with the waxy stock. An alternative method is shown in Figure 3 in which is shown an apparatus arrangement which may be substituted for the coating tower 14 in the system of Figure 2. In Figure 3, there is shown a confined elongated chamber 85 which may be supplied with cold water through pipe 86 so as to maintain a column 88 of cold water therein. The water is continuously withdrawn from the upper section of vessel 85 via pipe 87 so as to permit continuous circulation of the water through column 88. An adsorbent supply hopper 89 supplied with adsorbent via pipe 90 is positioned above chamber 85. A feed pipe 94 extends vertically downward from hopper 89 into chamber 85 and terminates a substantial distance below the surface level of the water column in chamber 85 but preferably within the upper section of the water column. A slack wax supply hopper 92 is also positioned above the chamber 85, and a pipe 93 extends downwardly from hopper 92 to connect into feed pipe 94 a short distance above the surface level of the water column 88. Slack wax is heated in heater 110 and supplied to hopper 92 in molten condition. It then flows via pipe 93 into pipe 94 where it mixes with adsorbent from hopper 89 at a temperature only slightly above the congealing temperature of the wax constituents of the slack wax charge. The liquid charge stock fills in the void spaces between the stream of solid particles flowing in pipe 94 and solidifies as the stream reaches the column of cool water 88. If desired, the congealing of the wax may be aided by supplying the adsorbent from hopper 89 at a temperature somewhat below that required to congeal the wax constituents of the molten slack wax charge. Due to the head of adsorbent in pipe 94 above the solidified mass near its outlet, a rod or ribbon of adsorbent encased in solidified waxy charge stock is extruded from the lower end of pipe 94 into the water column. The extrusion may be aided, if desired, by a mechanically agitated rod or other suitable device 111 within the pipe 94 which may be operated from an external location above the hopper 89. If desired the temperature of the waxy stock may be so regulated in hopper 92 as to cause the waxy constituents to be partially crystallized as they flow through pipe 93 or as to provide for crystallization of the waxy constituents substantially simultaneously upon initial contact with the adsorbent in pipe 94. The rod or ribbon of extruded material drops through the column of cooling water 88 and becomes further cooled so as to complete the congealing of the waxy constituents throughout the cross section of the rib-

bon. The extruded ribbon may be caused to break up to some extent into chunks of solidified charging stock encasing adsorbent particles as it falls through the water column 86 and the material is removed from the lower section of the chamber 85 by means of the continuous bucket conveyor 99 which connects into chamber 85. The buckets 100 of this conveyor may be perforated so as to permit draining of liquid from the mass of adsorbent particles encased in congealed waxy stock once the buckets rise above the surface level of column 86. If desired, adsorbent may be further drained free of water by delivery from conveyor 99 into the drainer 55 shown in Figure 2. In many operations adequate draining may be accomplished as the material is elevated in conveyor 99 and the adsorbent material may be conveyed directly to the adsorption tanks 36 and 36' shown in Figure 2.

When the method described in Figure 3 is employed the pipe 94 should preferably be subdivided near its lower end by means of vertical partitions so as to form a number of vertical passages having a maximum horizontal average diameter of about one half inch in diameter. The diameter of the ribbons is thereby limited to a size which will permit rapid transfer of heat into the center of the ribbons so as to accomplish quick congealing of the wax throughout the ribbon cross section. In general, the pipe 94 should extend about 0.5 to 10 inches below the surface of water column 86 depending on the water temperature, and being less the lower the water temperature and higher the congealing temperature of the waxy constituents. The waxy stock should enter the pipe 94 about 0.5 to 24 inches above the surface of water column 86.

It will be readily understood that apparatus and methods other than that shown in Figure 2 may be employed to accomplish the transfer of materials between vessels, the adsorption step and the draining and wax melting and oil recovery steps. Moreover, the removal of wax from the surface of the adsorbent particles may be accomplished by methods other than by the melting of the wax. For example, the wax may be removed from the particles while in solid form by mechanical attrition. This latter method is particularly applicable when the wax is of brittle texture and where the adsorbent particles are spherical in form. One method for accomplishing the mechanical separation is to rotate the adsorbent particles in a closed drum for a period of time to crack off the brittle wax. The particles of wax may then be separated from the adsorbent particles by elutriation, i. e. suspension in a stream of gas the flow rate of which is controlled to carry off the wax particles without entraining the adsorbent.

The step of removing the oil from the pores of the adsorbent particles may be accomplished by methods other than those employing oil solvents. For example, the adsorbent may be heated and steamed to remove the oil.

A wide variety of porous adsorbent materials may be employed in the process of this invention, for example, bauxites, fuller's earth, activated charcoal, synthetic silica-alumina or silica and alumina gel catalysts and other materials of similar porosity. Certain porous sorptive silica glasses such as are described in United States Patent 2,106,744 issued February 1, 1938, to Hood et al. may be employed. In general, the pore size of the adsorbent material should be adapted to effect rapid sorption thereinto of the oily constituents of the waxy charge stock. The adsorbent particles should be of substantial size as distinguished from powdered adsorbents. When powdered adsorbents of size less than about 100 mesh Tyler are employed the waxy constituents tend to be sorbed into the pores along with the oily material before complete congealing of the waxy constituents can be accomplished thereby preventing the desired separation. In general, it has been found that the adsorbent particles should be broadly at least about 0.01 inch average diameter and preferably at least about 0.022 inch and less than about 0.5 inch average diameter. A preferred adsorbent is a synthetic silica-alumina gel catalyst in spherical form prepared in the manner described in United States Patent 2,384,946 issued September 18, 1945, to Milton M. Marisic.

The operation should be conducted so as to effect congealing of the waxy constituents immediately on contact or as soon as possible after the initial contacting with the adsorbent.

The ratio of adsorbent to waxy charge stock employed in the process of this invention will depend to some extent upon the oil sorption capacity of the adsorbent, the percentage of oil present in the waxy stock and other operating variables. In general, for synthetic gel catalysts the ratio should be of the order of 0.5 to 10 pounds of adsorbent per pound of waxy stock. In any case, sufficient adsorbent should be employed to sorb substantially all of the oily constituents in the waxy charge.

The length of time to be devoted to the sorption period during which non-congealed liquid constituents are sorbed into the pores of the adsorbent will vary depending upon the thickness of the waxy stock coating on the adsorbent particles and upon the particular adsorbent involved and the viscosity and molecular size of the oily constituents under the sorption temperature conditions required to maintain the waxy constituents in a congealed state. In general, it has been found that with adsorbent particles of about 0.09 to 0.19 inch diameter and having a porosity similar to a synthetic silica-alumina gel catalyst, the length of the sorption period should be at least about 0.1 hour and should preferably be of the order of about 1 to 24 hours.

In general, the average thickness of the waxy stock coating around each adsorbent particle should be less than about 0.1 inch and preferably less than about 0.05 inch.

As an example of the process of this invention the deoiling of a waxy stock by the general method shown in Figure 2 may be considered. The waxy charge stock was a paraffinic petroleum stock having a melting point of 116.9° F. as determined by the test procedure recommended by the American Society for Testing Materials, Test Number A. S. T. M. D87–42 and an oil content of 19.2 as determined by A. S. T. M. tentative Test Number D–721–43T. The adsorbent employed was a synthetic silica-alumina gel bead catalyst prepared by the method described in United States Patent 2,384,946 dated September 18, 1945. The catalyst had a bulk density of about .74 as determined by pouring the catalyst into a measured container and weighing. The individual particle density was about 1.15. The catalyst particle size was about 0.09 to 0.19 inch diameter. The catalyst beads were dropped through a column of molten waxy stock one inch in depth and maintained at about 126 to 133° F. The weight ratio of catalyst to waxy stock charge was about

3.5 to 1. The catalyst beads bearing a coating of waxy stock then dropped through a column of cooling water maintained at about 70° F. About 0.3–0.5% potassium oleate was added to the water to reduce the interfacial tension at the water wax interface. The catalyst bearing the congealed coating of waxy stock was permitted to stand about 4 hours at about 80° F. after which the wax was removed by attrition from the surface of the particles. The recovered wax had a melting point of 125.3° F. and an oil content of 3.2% by weight and the yield of recovered wax amounted to 58% by weight based on the waxy stock charge or 72% by weight of the wax present in the charge as determined by A. S. T. M. Test Method D–721–43T. By way of comparison the yield of wax obtained by the method described above using a minimum cooling water temperature of 70° F. amounted to 83% by weight of the yield of wax obtained by solvent deoiling the same waxy stock employing benzol-methyl ethyl ketone as the solvent at a temperature of zero degrees F. The wax obtained by the solvent deoiling process contained 2.4% by weight oil.

In another experiment employing the same conditions outlined above except that the sorption period was increased from 4 to 20 hours a final wax product containing only 1.4% oil was obtained but the wax yield based on the charge was somewhat lower.

In still another experiment conducted similarly to the one first described the sorption period was increased from 4 to 20 hours and the absorbent to oil charge ratio was decreased from 3.5 to about 1.4. The wax yield was increased to 61% by weight of the original waxy charge but the oil content in the recovered wax increased to about 6.7% of the wax.

In another experiment conducted according to the method described in connection with Figure 3, a waxy charge stock having a melting point of 113.5° F. and an oil content of 20.3% oil by weight was deoiled employing the same adsorbent. Referring to Figure 3, the adsorbent feed pipe **94** measured one half inch internal diameter and molten charge entered the pipe **94** about one inch above the surface of water column **88**. The one half inch rod extruded from pipe **94** dropped into a cold water bath maintained at about 70° F. The adsorbent to waxy charge stock weight ratio was about 1.8 to 1.0. The extruded material was permitted to stand at 80° F. for 3 hours after which the wax was removed by attrition in a ball mill. The wax yield amounted to 68% of the wax present in the charge stock as determined by A. S. T. M. tentative Test Number D–721–43T and the wax product contained 4.3% oil and had a melting point of 123.3° F.

In an experiment conducted on the same charge stock and with the same type of adsorbent by the batchwise method described in connection with Figure 1 and employing an adsorbent to waxy charge ratio of 2.0 to 1.0 and a sorption period of 66 hours at 80° F. the yield of wax containing 4.6% oil was about 60% of that in the waxy charge.

In this latter experiment the waxy stock was cooled in pan **101** to about 70° F. to accomplish crystallization of the waxy constituents before the adsorbent was added. The wax remaining on the surface of the adsorbent particles after the sorption period was removed by mechanical attrition.

It should be understood that the specific details of operation and of apparatus arrangement and the specific modifications of this invention given hereinabove are intended as exemplary and the invention is not to be construed as being limited thereto or otherwise limited except as limited by the following claims.

We claim:

1. The method for separating wax and oily constituents present in a wax bearing mineral oil which comprises: subjecting the wax bearing oil to an intimate contacting with a particle form solid adsorbent material composed of particles of average diameter within the range 0.022–0.5 inch, maintaining the wax to be separated in congealed state by control of the temperature beginning at a time falling within the period of any time prior to the contacting to substantially immediately after initial contacting of the wax bearing oil with the adsorbent and throughout at least most of said contacting at a level at which wax constituents of said wax bearing oil are congealed whereby the congealed wax constituents remain deposited on the surface of said adsorbent and the non-congealed liquid constituents are sorbed into the pores of said adsorbent, and thereafter removing said wax constituents from the surface of said adsorbent while leaving said liquid constituents within the pores of said adsorbent.

2. The method for removing oily constituents from a waxy hydrocarbon stock which comprises: subjecting said waxy stock to an intimate contacting with a particle form solid adsorbent material of at least 0.01 inch average particle diameter, maintaining the temperature of the waxy stock during at least most of said contacting at a level at which waxy constituents of said stock are precipitated and beginning at a time falling within the period of any time prior to the initial contacting to not more than ten minutes after the initial contacting, whereby the non-precipitated liquid constituents are sorbed into the pores of said adsorbent while the precipitated waxy constituents remain deposited on the outer surface of the adsorbent particles, thereafter effecting removal of said precipitated waxy constituents from said adsorbent separately of said sorbed oily constituents and finally effecting removal of said non-precipitated, sorbed liquid constituents from said adsorbent.

3. The method for removing oily constituents from a waxy hydrocarbon stock which comprises: subjecting said waxy stock to an intimate contacting with a particle form solid adsorbent material in which the average particle diameter is at least 0.01 inch, maintaining said waxy stock in contact with said adsorbent for a period of at least about 0.1 hour, chilling the waxy stock to effect congealing of at least most of the waxy constituents therein beginning within the period of any time prior to the contacting to substantially immediately after initial contact of the waxy stock with the adsorbent and maintaining said waxy stock chilled during the contacting, whereby the non-congealed liquid constituents of said waxy stock are sorbed into the pores of said adsorbent particles while the congealed waxy constituents are left deposited upon the surface of said adsorbent particles, effecting removal of the congealed waxy constituents from said adsorbent particles in a separate zone while leaving substantially all of said liquid constituents still sorbed in the particle pores and finally separately removing the sorbed liquid constituents from said adsorbent.

4. The method for separating wax and oily constituents present in a waxy mineral oil stock

which comprises: intimately contacting the wax bearing oil with a particle form solid adsorbent material in which the average particle diameter is at least 0.01 inch, substantially excluding the sorption of the waxy constituents in said mineral oil stock into the pores of said adsorbent particles by maintaining said waxy constituents in congealed form while permitting the non-congealed liquid constituents to be sorbed into the pores of said adsorbent, and after substantially all of said liquid constituents are sorbed in the pores of said adsorbent effecting a separation of the adsorbent bearing said liquid constituents from said waxy constituents in a separate zone.

5. The method of separating oily constituents from waxy constituents present in a waxy hydrocarbon stock which comprises: cooling said waxy stock to effect at least partial crystallization of the waxy constituents and then coating the waxy stock onto the surface of particles of solid adsorbent material of greater than about 0.01 inch average diameter, permitting the adsorbent particles to remain coated with said waxy stock for a period within the range 0.1 to 24 hours and maintaining the temperature of the waxy stock during substantially said entire period at a level at which waxy constituents in said stock are congealed whereby the non-congealed liquid constituents are sorbed into the pores of said adsorbent particles while the congealed waxy constituents remain on the surface of said particles, thereafter effecting removal of said waxy constituents from the surface of said adsorbent particles while leaving sorbed said non-congealed liquid constituents.

6. The method for removing oily constituents from a waxy hydrocarbon stock which comprises: subjecting said waxy stock to an intimate contacting with a particle form solid adsorbent material having an average particle diameter of at least 0.01 inch, effecting sorption of the liquid oily constituents of said waxy stock into the pores of said adsorbent particles while substantially preventing sorption of the wax constituents by maintaining the temperature during substantially the entire contacting at a level at which the wax constituents are congealed, and thereafter melting the congealed wax constituents from the surface of said adsorbent particles while leaving the oily constituents sorbed in the pores of said particles and collecting the melted wax separately from the adsorbent particles and sorbed oily constituents.

7. The method for removing oily constituents from a waxy hydrocarbon stock which comprises: effecting substantial congealing of the waxy constituents in the waxy stock, thereafter subjecting said waxy stock to an intimate contacting with a particle form solid adsorbent material composed of particles of at least 0.01 inch average diameter under conditions of temperature wherein the waxy constituents of said stock remain congealed, continuing said contacting until substantially all of the non-congealed liquid constituents of said stock are sorbed into the pores of said adsorbent particles while leaving the congealed wax on the surface of said particles, thereafter heating said adsorbent particles to melt the congealed wax constituents from the surface thereof, collecting the melted wax, separately treating the adsorbent freed of wax with a suitable solvent to remove the sorbed oil therefrom, effecting removal of the solvent from the adsorbent and reusing said adsorbent for contacting waxy stocks as aforesaid.

8. A method for deoiling waxy petroleum fractions which comprises: chilling the waxy fraction in a suitable container to effect at least partial congealing of the waxy constituents, whereby a congealed semi-solid mass is formed, mixing particles of a suitable porous adsorbent material of at least 0.01 inch average particle diameter with said congealed mass and permitting the particles to remain mixed in said mass until substantially all of the non-congealed oily constituents are sorbed into the pores of said adsorbent particles, then removing the waxy constituents from the surface of said particles in a separate zone while leaving the liquid oily constituents sorbed in the pores of said particles, finally separately removing the oily constituents from the pores of said particles and reusing said particles to deoil additional slack wax as aforesaid.

9. A method for deoiling waxy petroleum fractions which comprises: chilling the waxy fraction in a suitable container to effect at least partial congealing of the waxy constituents, whereby a congealed semi-solid mass is formed, pressing particles of a suitable porous adsorbent material into said congealed mass, said particles being of at least about 0.01 inch average diameter, permitting the adsorbent particles to remain in said semi-solid mass while maintaining the waxy constituents congealed for a period of at least about 0.1 hour whereby the non-congealed oily constituents of the waxy fraction are sorbed into the pores of said adsorbent particles leaving the waxy constituents substantially unsorbed, then melting the waxy constituents and collecting them separately of the adsorbent particles which still bear the liquid oily constituents.

10. The method of separating oily constituents from waxy constituents present in a waxy hydrocarbon stock which comprises: coating said waxy stock onto the surface of particles of solid adsorbent material of greater than about 0.01 inch average diameter, permitting the adsorbent particles to remain coated with said waxy stock for a period of at least about 0.1 hour and maintaining the temperature of the waxy stock during substantially said entire period at a level at which waxy constituents in said stock are congealed whereby the non-congealed liquid constituents are sorbed into the pores of said adsorbent particles while the congealed waxy constituents remain on the surface of said particles, thereafter dropping the particles of adsorbent through a bath of water heated to a temperature sufficiently high to melt said waxy constituents off of said particles, separating the water and molten waxy constituents from the adsorbent particles, and separating the waxy constituents from said heated water in a separate zone.

11. The method for removing oily constituents from a waxy hydrocarbon stock which comprises: subjecting said waxy stock to an intimate contacting with a particle form solid adsorbent material of at least 0.01 inch average particle diameter effecting sorption of the liquid oily constituents of said waxy stock into the pores of said adsorbent particles while substantially preventing sorption of the wax constituents by maintaining the temperature during said contacting at a level at which the wax constituents are congealed and thereafter physically removing the waxy constituents from the surface of the adsorbent particles still in congealed form.

12. The method for separating wax and oily constituents present in a wax bearing mineral oil which comprises: subjecting the wax bearing oil with the waxy constituents initially in liquid

phase to an intimate contacting with a particle form solid adsorbent material comprising particles of at least 0.01 inch diameter, thereupon quickly cooling the mixture and maintaining the temperature during most of said contacting at a level at which wax constituents of said wax bearing oil are congealed whereby the congealed wax constituents remain deposited on the surface of said absorbent and the non-congealed liquid constituents are sorbed into the pores of said adsorbent, and thereafter removing said waxing constituents from the surface of said adsorbent while leaving said liquid constituents within the pores of said adsorbent.

13. The method for removing oily constituents from a waxy hydrocarbon stock which comprises: cooling the waxy stock to a temperature only slightly above that at which the waxy constituents are congealed and then subjecting said waxy stock initially in liquid form to an intimate contacting with a particle form solid adsorbent material of at least 0.01 inch average particle diameter, lowering the temperature of said waxy stock shortly after the initial contacting and maintaining the temperature thereof during at least most of said contacting at a level at which waxy constituents of said stock are precipitated whereby the non-precipitated liquid constituents are sorbed into the pores of said adsorbent while the precipitated waxy constituents remain deposited on the outer surface of the adsorbent particles, thereafter effecting removal of said precipitated waxy constituents from said adsorbent separately of said sorbed oily constituents and finally effecting removal of said non-precipitated, sorbed liquid constituents from said adsorbent.

14. The method of separating oily constituents from waxy constituents present in a waxy hydrocarbon stock which comprises: coating said waxy stock as a liquid onto the surface of particles of solid adsorbent material of greater than about 0.01 inch average diameter, substantially immediately chilling the coated adsorbent to effect congealing of wax constituents in said waxy stock coated on said adsorbent particles, permitting the adsorbent particles to remain coated with said waxy stock while maintaining said wax constituents in congealed form until substantially all of the non-congealed liquid constituents of said waxy stock are sorbed into the pores of said particles leaving the congealed waxy constituents on the surface of said particles, thereafter physically removing said wax constituents from the surface of said adsorbent particles still in congealed form.

15. The method of separating oily constituents from waxy constituents present in a waxy hydrocarbon stock which comprises: coating said waxy stock onto the surface of particles of an inorganic oxide gel adsorbent consisting of particles of generally spheroidal shape and of an average diameter of at least about 0.01 inch, permitting the adsorbent particles to remain coated with said waxy stock for a period within the range 0.1 to 24 hours and maintaining the temperature of the waxy stock during substantially said entire period beginning at least substantially immediately after initial contact with said adsorbent at a level at which waxy constituents in said stock are congealed whereby the non-congealed liquid constituents are sorbed into the pores of said adsorbent particles while the congealed waxy constituents remain on the surface of said particles, thereafter effecting removal of said waxy constituents from the surface of said adsorbent particles while leaving sorbed said non-congealed liquid constituents.

16. The method of deoiling slack wax stocks which comprises: coating said slack wax stock in liquid form onto the surface of particles of adsorbent material in an adsorbent coating zone, said adsorbent particles being of at least 0.01 inch average diameter, chilling the coated adsorbent particles to effect precipitation of wax constituents in said slack wax stock coated thereon at least within about 10 minutes of the beginning of the adsorbent coating, maintaining the wax constituents in precipitated form on said absorbent particles for a period of at least 0.1 hour until substantially all of the non-precipitated liquid constituents of said slack wax are sorbed into the pores of said adsorbent particles leaving the precipitated wax on the surface of said particles, effecting removal of the precipitated wax from the surface of said adsorbent particles while leaving the liquid constituents still sorbed in the pores of said adsorbent particles, separately effecting removal of the sorbed liquid constituents from the adsorbent particles and reusing said adsorbent particles in said coating zone as aforesaid.

17. A method for separating oily constituents from waxy constituents present in a waxy hydrocarbon stock which comprises: mixing particles of a suitable solid adsorbent of at least 0.01 inch average diameter with said waxy stock while it is in liquid form and then quickly cooling the mixture to effect crystallization of the waxy constituents of said stock, whereby the adsorbent particles become coated with a layer of waxy stock in which the waxy constituents are crystallized, permitting the adsorbent particles to remain coated with said waxy stock until substantially all the oily constituents are sorbed into the pores of the adsorbent particles leaving the crystallized waxy constituents on the surface of the particles, thereafter effecting removal of said waxy constituents from the surface of said adsorbent particles while leaving the non-congealed liquid oily constituents still sorbed in the pores of the adsorbent particles and separately removing the sorbed oily constituents from said adsorbent particles.

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