

**April 6, 1954**

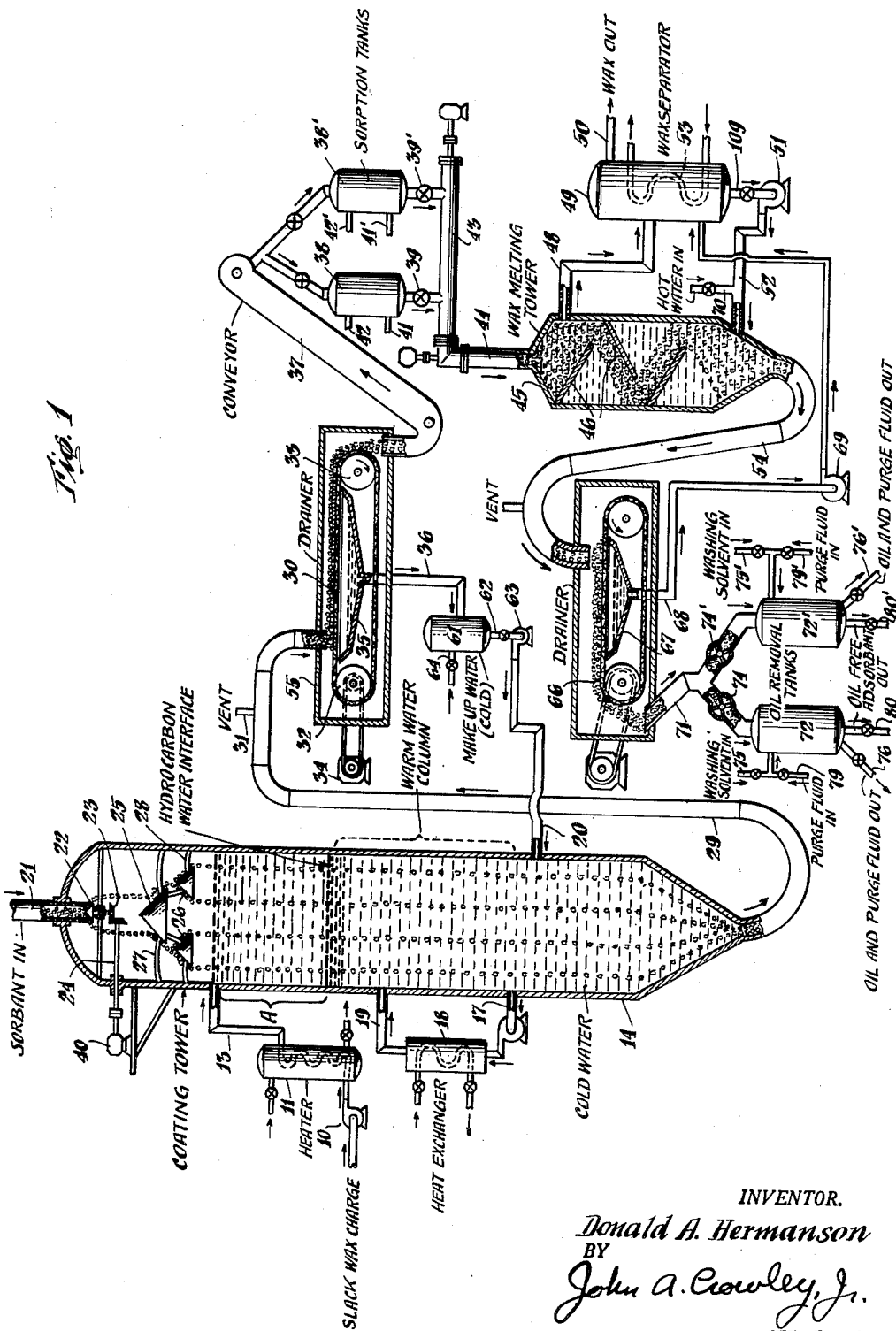
D. A. HERMANSON

**2,674,564**

# METHOD FOR SEPARATING WAXY AND OILY MATERIALS

Filed Oct. 12, 1951

2 Sheets-Sheet 1



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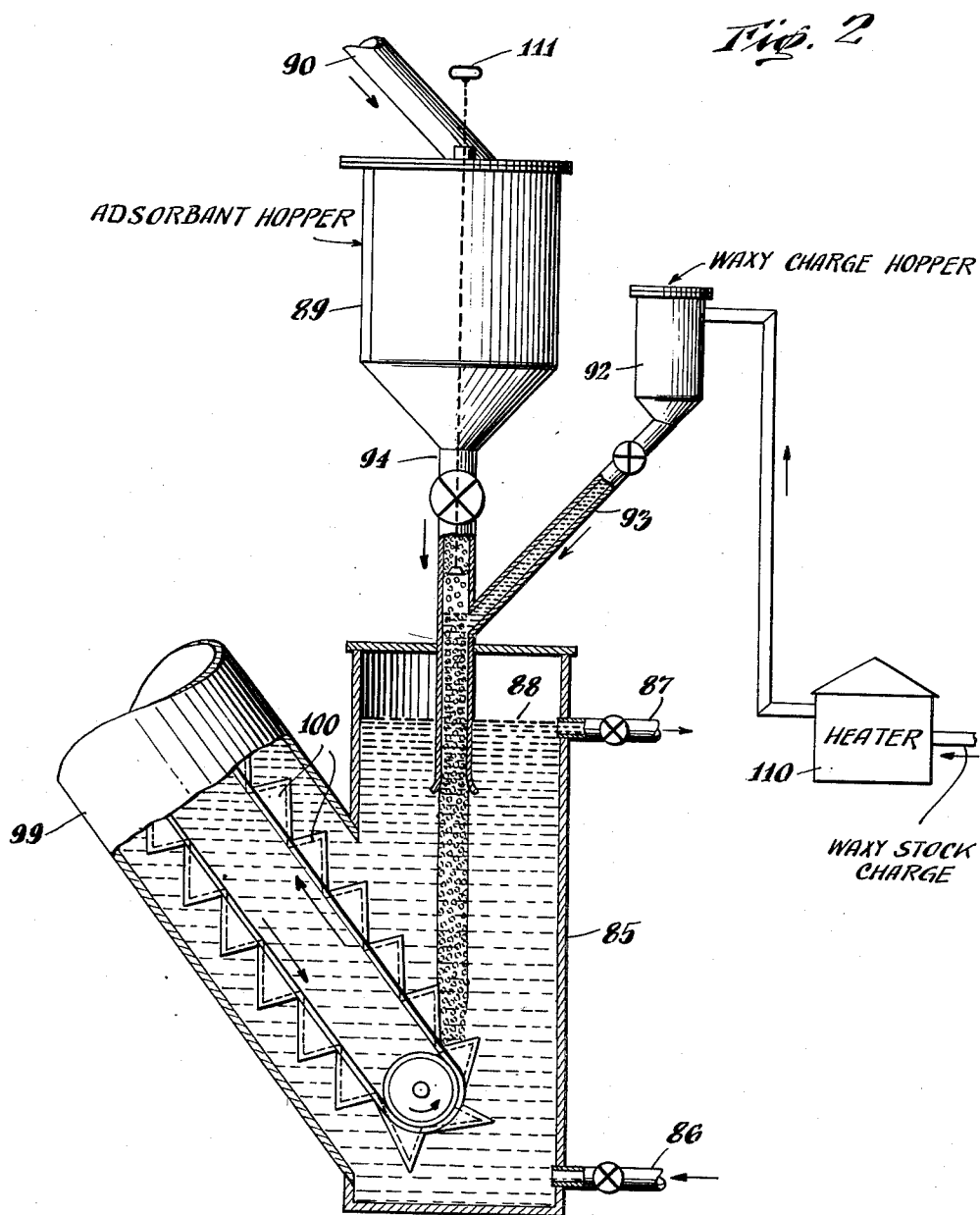
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2 Sheets-Sheet 2



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## UNITED STATES PATENT OFFICE

2,674,564

## METHOD FOR SEPARATING WAXY AND OILY MATERIALS

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Application October 12, 1951, Serial No. 251,109

11 Claims. (Cl. 196—18)

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This application is a continuation-in-part of my application Serial Number 32,017, filed in the United States Patent Office June 9, 1948.

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 also 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 been found practicable as a method of 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 Sep-

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tember 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 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.

There is disclosed in United States application Serial Number 31,948, filed June 9, 1948, a process wherein the waxy stock such as a 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 that 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 are maintained in congealed condition at least until the step of wax removal from the adsorbent.

The present invention is directed to an improved method for continuously conducting one

form of the above described wax-oil separation process on a commercial scale. In a preferred form of the present invention the adsorbent particles are passed continuously through a first region wherein the waxy stock is contacted while it is in liquid form. Conditions of the contacting are preferably controlled so that in effect a film of liquid waxy stock surrounds each adsorbent particle to a thickness of less than about 0.1 inch. Coated particles are substantially immediately cooled at least in part by dropping them through a body of a suitable cooling liquid in which the constituents of the waxy stock are insoluble, thereby causing the waxy constituents to congeal on the surface of the adsorbent particles. The adsorbent is then permitted to remain at the wax congealing temperature levels until the oily constituents of the waxy stock become sorbed into the adsorbent pores leaving the congealed waxy constituents on the surface thereof. The waxy constituents are then removed from the surface of the adsorbent by suitable means such as by melting or by physical means and the oily constituents may be later separately removed by suitable methods.

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 an elevational flow plan, partially in section of a preferred form of the invention and Figure 2 is an elevational view, partially in section, of a modified form of a portion of the system in Figure 1. Both of these drawings are highly diagrammatic in form.

Turning now to Figure 1 for a description of the apparatus and its operation, 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 supported by rods 27 and 28 are 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, potassium stearate, diethanol amine, sodium wax phenol sulfonate, etc. 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

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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 39 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 or 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 Figure 1. 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 2 in which is shown an apparatus arrangement which may be substituted for the coating

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tower 14 in the system of Figure 1. In Figure 2, 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. 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 ribbon. 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 88 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 88. If desired, the adsorbent may be further drained free of water by delivery from conveyor 99 into the drainer 55 shown in Figure 1. In many operations adequate draining may be accomplished as the material is elevated in conveyor 99 and the adsorbent may be conveyed directly to the adsorption tanks 38 and 38' shown in Figure 1. When the method described in Figure 2 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 88

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 88.

It will be readily understood that apparatus and methods other than that shown in Figure 1 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 therein 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.

In conducting the methods described in connection with Figures 1 and 2, the temperature of the waxy stock as brought into initial contact with the adsorbent should preferably be only several degrees above that at which the waxy constituents will commence to congeal. The temperature of the cooling fluid employed to cause the congealing of wax constituents and to maintain them congealed during the sorption period will of course vary somewhat depending on the melting point of the waxy constituents involved. For many operations, a cooling water temperature of about 70° F. has been found satisfactory. The operation should be conducted so as to effect congealing of the waxy constituents as soon as pos-

sible after the initial contacting with the adsorbent. The waxy constituents should be congealed at least within about 10 minutes of the initial contacting and preferably within about less than one minute thereof.

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. In the method disclosed in Figure 1, the wax coating is limited below 0.1 inch thickness by proper control of the temperature of the adsorbent and waxy stock. In the method of Figure 2, the effective coating thickness is controlled by proper control of the waxy stock to adsorbent feed ratio to the ribbon forming zone.

As an example of the process of this invention, the deoiling of a waxy stock by the general method shown in Figure 1 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 D721-43T. 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 for 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 135.3° 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 adsorbent 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 2, 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 2, 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.

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.

I claim:

1. The method for separating wax and oily constituents present in waxy hydrocarbon stocks which comprises, continuously passing particles of a suitable solid adsorbent of at least 0.01 inch average diameter into contact with said waxy stock existing in the liquid phase in a contacting region, withdrawing the contacted adsorbent particles with waxy stock on the surface thereof from said contacting region before any substantial amount of the wax constituents are sorbed into the pores of the adsorbent particles and substantially immediately dropping the particles downwardly through a body of a suitable cooling liquid in which the constituents of the waxy stock are insoluble to effect congealing of the waxy constituents on the surface of the adsorbent particles, withdrawing the chilled

adsorbent from said body of liquid and then maintaining the coated particles under conditions in which said waxy constituents remain in congealed condition in a separate region 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 and thereafter effecting removal of the waxy constituents from the surface of said adsorbent particles while leaving said liquid constituents within the pores of the adsorbent.

2. The method for separating wax and oily constituents present in waxy hydrocarbon stocks which comprises, continuously passing particles of a suitable solid adsorbent of at least 0.01 inch average diameter into contact with said waxy stock existing in the liquid phase in a first region to effect coating of waxy stock as a liquid onto the surface of the particles of solid adsorbent, controlling the conditions of contacting so as to limit the average thickness of waxy stock coating on the particles below about 0.1 inch, limiting the length of contact time in said first zone below that at which any substantial amount of the wax constituents would be sorbed into the pores of said adsorbent, then substantially immediately effecting congealing of the waxy constituents on the surface of said adsorbent at least partly by withdrawing the coated adsorbent from said first region and dropping the adsorbent downwardly through a body of a suitable cooling liquid in which the constituents of the waxy stock are insoluble maintained in a second region below said first region, withdrawing the chilled adsorbent from said body of liquid and then maintaining the coated particles under conditions in which said waxy constituents remain in congealed condition in a separate region 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 and thereafter effecting removal of the waxy constituents from the surface of said adsorbent particles while leaving said liquid constituents within the pores of the adsorbent.

3. The method of claim 2 further characterized in that the coated adsorbent is cooled in said second region within less than one minute of the time of the initial contact of the adsorbent with waxy stock in said first region.

4. A method for deoiling wax-oil petroleum stocks which comprises: maintaining a liquid column of said wax-oil stock at a temperature slightly above that at which the waxy constituents begin to congeal, maintaining below and contiguous with the bottom of said column of wax-oil stock a column of water, circulating the water in the upper portion of said column thereof through an external heater and then back into the upper portion of said column to maintain the temperature of the water in the upper portion of the water column near that of the wax-oil stock, introducing cold water into the intermediate portion of said column to maintain the temperature in the remainder of said water column at a temperature at which the waxy constituents of said stock will congeal, dropping particles of solid adsorbent comprising particles of at least 0.01 inch average diameter downwardly through said column of wax-oil stock to cause said particles to become coated with wax-oil stock, causing the coated particles



to drop downwardly into and through said column of water to cause the waxy constituents in the stock coating said particles to become congealed, removing the particles bearing the coating of wax-oil stock from said water column along with some of the cold water, and thereafter maintaining the coated particles at a temperature below the congealing temperature of said waxy constituents until substantially all the non-congealed constituents of the wax-oil stock coating said particles are sorbed into the pores of said adsorbent particles while leaving the waxy constituents on the surface of said particles, then removing the waxy constituents from the surface of said particles and collecting the waxy constituents separately of the adsorbent particles and said sorbed oily constituents.

5. A method for separating oily constituents from waxy constituents present in a waxy hydrocarbon stock which comprises: continuously passing particles of a suitable solid adsorbent of at least 0.01 inch average diameter downwardly by gravity through a first region wherein said particles are brought into intimate contact with said waxy stock, whereby some of the waxy stock becomes coated around the surface of each adsorbent particle, said first region being maintained at a temperature at which said waxy stock is present in the liquid phase, then before the waxy constituents can become sorbed into the pores of said adsorbent particles, passing the adsorbent downwardly through a cooling region to effect congealing of the waxy constituents on the surface of said particles, maintaining a body of suitable cooling liquid throughout at least a substantial portion of said cooling region and causing the adsorbent particles to drop downwardly through said body, withdrawing the adsorbent from said body of cooling liquid and maintaining it at a temperature at which said waxy constituents remain congealed until substantially all of the oily constituents of the stock coated on the particles becomes sorbed into the pores of the particles leaving the waxy constituents on the surface thereof, thereafter effecting removal of the waxy constituents from the surface of said particles while leaving the non-congealed oily constituents still sorbed in the pores of the particles.

6. A method for deoiling wax-oil petroleum stocks which comprises: maintaining a liquid column of said wax-oil stock at a temperature slightly above that at which the waxy constituents begin to congeal, dropping particles of solid adsorbent material of at least 0.01 inch average diameter through said column to deposit a film of said waxy stock on the surface of said adsorbent particles, controlling the temperature of the waxy stock and of the adsorbent particles supplied to said column to limit the thickness of said film on said particles below about 0.1 inch, substantially immediately cooling said adsorbent particles to effect congealing of the waxy constituents of said wax-oil stock, permitting the adsorbent particles to remain coated with said wax-oil stock while maintaining the waxy constituents in a congealed state until substantially all the non-congealed constituents are sorbed into the pores of said particles, thereafter effecting removal of the waxy constituents from the surface of said adsorbent particles while leaving said non-congealed liquid constituents sorbed in the pores of said particles and separately effecting removal

of the sorbed liquid from the wax free adsorbent particles.

7. A method for deoiling wax-oil petroleum stocks which comprises: maintaining a liquid column of said wax-oil stock at a temperature slightly above that at which the waxy constituents begin to congeal, dropping particles of solid adsorbent material having an average particle diameter of at least 0.01 inch through said column to deposit a film of said waxy stock on the surface of said adsorbent particles, immediately dropping said adsorbent particles bearing said film of waxy stock into a bath of a suitable cooling liquid maintained at a temperature suitable for congealing the waxy constituents of said wax-oil stock, permitting the adsorbent particles to remain coated with said wax-oil stock while maintaining the waxy constituents in a congealed state until substantially all the non-congealed constituents are sorbed into the pores of said particles, thereafter effecting removal of the waxy constituents from the surface of said adsorbent particles while leaving said non-congealed liquid constituents sorbed in the pores of said particles and separately effecting removal of the sorbed liquid from the wax freed adsorbent particles.

8. A method for deoiling waxy petroleum fractions which comprises: converging together a stream of said waxy fraction in liquid form with a stream of particle form solid adsorbent material of at least 0.01 inch average particle diameter in a confined zone whereby the liquid waxy stock fills in the void spaces in the stream of adsorbent particles, chilling the resulting mixed stream to effect congealing of wax constituents of the waxy stock and extruding a ribbon of the mixed adsorbent particles and waxy stock into a suitable bath of cooling liquid to effect further congealing of wax constituents of said waxy stock, maintaining the extruded and chilled ribbon at a temperature at which the wax constituents will remain congealed until substantially all the non-congealed liquid constituents of the waxy fraction are sorbed into the pores of the adsorbent particles while the waxy constituents remain coated on the surface of said particles, then removing the waxy constituents from the surface of said particles and separately removing the non-congealed liquid constituents from the pores of said adsorbent particles.

9. A method for deoiling wax-oil petroleum stocks which comprises: maintaining a liquid column of said wax-oil stock at a temperature slightly above that at which the waxy constituents begin to congeal, maintaining below and contiguous with the bottom of said column of wax-oil stock a column of water, maintaining a short length of the column of water immediately below the column of wax-oil stock at a temperature near that of the wax-oil stock and maintaining the remainder of said column of water at a temperature at which the waxy constituents of said stock will congeal, dropping particles of solid adsorbent comprising particles of at least 0.01 inch average diameter downwardly through said column of wax-oil stock to cause said particles to become coated with wax-oil stock, causing the coated particles to drop downwardly into and through said column of water to cause the waxy constituents in the stock coating said particles to become congealed, removing the particles bearing the coating of wax-oil stock from said water column and permitting the particles to stand at a temperature below the congealing temperature of said waxy constituents until substantially all the



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non-congealed constituents of the wax-oil stock coating said particles are sorbed into the pores of said adsorbent particles while leaving the waxy constituents on the surface of said particles, then removing the waxy constituents from the surface of said particles and collecting the waxy constituents separately of the adsorbent particles and said sorbed oily constituents.

10. The method of claim 9 characterized in that the water in at least the upper portion thereof contains a suitable added material to reduce the interfacial tension at the water-waxy stock interface.

11. A method for deoiling slack wax which comprises: forming a solidified ribbon consisting of particles of a suitable porous solid adsorbent material of greater than about 0.01 inch average diameter surrounded by the slack wax in which the waxy constituents are substantially crystallized, maintaining said ribbon at a temperature at

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which the wax constituents remain solidified for a period of at least 0.1 hour until substantially all the liquid oily constituents are sorbed in the pores of said adsorbent particles leaving the crystallized wax on the surface of said particles, then removing the wax 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.

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