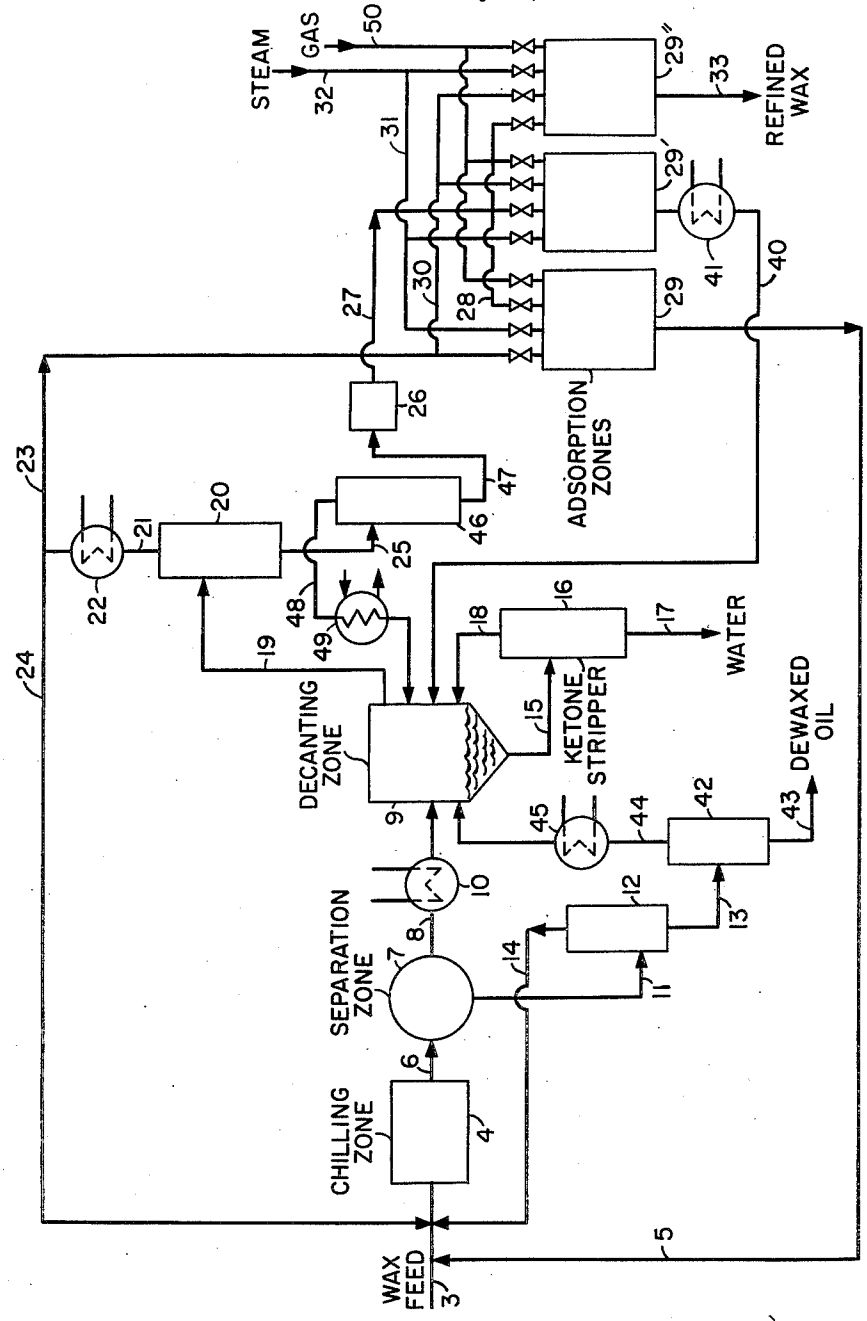
July 2, 1957 S. F. PERRY ET AL 2,798,028

REFINING OF HYDROCARBON WAX

Filed May 26, 1954



STEPHEN F. PERRY } *INVENTORS*
HERMAN J. ZOELLER }

BY J. A. Reilly ATTORNEY

United States Patent Office 2,798,028 Patented July 2, 1957

2,798,028

REFINING OF HYDROCARBON WAX

Stephen F. Perry, Westfield, and Herman J. Zoeller, Union, N. J., assignors to Esso Research and Engineering Company, a corporation of Delaware

Application May 26, 1954, Serial No. 432,366

8 Claims. (Cl. 196—20)

The present invention concerns an improved process for obtaining increased yields of hydrocarbon waxes having improved color and odor characteristics from waxy petroleum fractions. The invention particularly relates to a refining process for improving the color and odor of a petroleum-type wax which has been deoiled by means of solvents. Solvent combinations of concern to the present process are those that comprise an aliphatic ketone in admixture with an aromatic hydrocarbon. The combination of toluene and methyl ethyl ketone is of particular interest. Higher ketones such as the methyl, propyl and methyl, butyl ketones and di-ethyl ketone may also be used, without the addition of aromatics.

The present invention has application to that phase of wax refining in which a wax is improved in its color and odor characteristics by contact with an absorbent material such as particulate bauxite, clay, alumina, charcoal or the like. In this connection, the invention is especially concerned with the treating of micro-crystalline waxes that are derived from the dewaxing of heavy residual waxy petroleum fractions. The invention further relates to a method of restoring the activity of the aforementioned adsorbent materials by washing them with the solvents identified above.

The waxes present in a petroleum crude oil are concentrated in the high boiling distillate fractions and in the residuum. They are present to some extent in almost all types of crude oil, but are found primarily in the paraffinic and mixed base crudes. Examples of such crude oils are the paraffinic stocks from the Pennsylvania fields such as the Buckeye, Bradford and West Virginia crudes. Examples of mixed base stocks are the East Texas, Mid-Continent and Panhandle crudes.

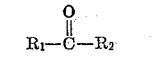
The waxy high boiling fractions of a petroleum crude oil are separated from the lighter fractions by an initial distillation of the crude known as a "topping operation" or atmospheric distillation in which the naphtha, kerosene and lighter fractions are taken off. The topped crude is then fed to a vacuum pipe still and the waxy lubricating oil fractions are removed as overhead, sidestream and bottoms fractions. The overhead or "paraffin distillate" fraction usually has a boiling range of about 580° F. to 850° F. and a viscosity of about 80 S. U. S. at 100° F. The heavy lubricating oil distillate sidestream generally has a boiling range of about 800° F. to 1000° F. and a viscosity of about 50–70 S. U. S. at 210° F. The residuum comprises all of the hydrocarbons boiling above this point and generally has a viscosity of about 150 to 200 S. U. S. at 210° F. The proportions of these three fractions may vary considerably depending upon the particular crude oil in question, but it is general practice to produce these three fractions.

It has been found that wax exists in petroleum crude oils in two major crystalline forms. The first type of wax known as the "crystalline" or "paraffin" variety is present largely in the paraffin distillate fraction of a crude oil, and has a melting point range of about 120–150° F. This type of wax is characterized by large well-formed crystals

that can be readily separated from the oil. Further, this type generally contains a relatively small amount of oil and can be refined with comparative ease.

The second type consisting of the "micro-crystalline" waxes, or "petrolatums," are derived from the heavy lubricating oil distillate and the residual fractions of crude oils. This type of wax is characterized by very minute crystalline forms so small that these waxes were originally thought to be amorphous in structure. The petrolatums, which melt from about 145–190° F. are more difficult to refine than are the paraffin waxes. Good odor and color characteristics are especially difficult to obtain in petrolatums as compared to paraffin waxes. The petrolatums derived from heavy distillate fractions may include considerable paraffin wax and are sometimes referred to as mixed microwaxes or semi-crystalline waxes. The normal paraffinicity of the petrolatums also varies considerably with crude source, causing variations in crystal appearance, hardness and other properties.

The general technique of dewaxing a lubricating oil fraction consists basically in lowering the solubility of the wax in the oil so that a physical separation can be made. This can be done by chilling the oil to low temperatures preferably with the use of solvents. The solvents serve to main functions; (1) they aid the formation of the wax crystals in a structure that can be readily removed from the oil; and (2) they reduce the viscosity of the oil sufficiently to make rapid filtration possible. Once crystallized, the wax may be separated from the oil by means of a rotary filter, a plate and frame filter press, a centrifuge or the like. The present invention is concerned with dewaxing processes that employ ketone type solvents, alone or in combination with an aromatic hydrocarbon. Ketones that are suitable for use in the present invention are the aliphatic ketones that contain a total of from 3 to 6 carbon atoms. These ketones may be represented by the formula



where R_1 and R_2 are alkyl groups that contain from 1 to 4 carbon atoms each. Examples of such ketones include acetone, methyl ethyl ketone, diethyl ketone, the methyl propyl ketones, the ethyl propyl ketones, and the methyl butyl ketones. The first two are used in conjunction with an aromatic solvent, preferably benzene or toluene. A particularly effective and desirable solvent combination is one employing about 50 to 75 volume percent of methyl ethyl ketone with the balance being toluene. With acetone, a higher proportion of aromatic hydrocarbon, up to about 85%, would be used.

Following dilution with one of the above solvent combinations, the oil to be dewaxed is conventionally chilled by passage through double pipe heat exchangers where it is cooled by indirect heat exchange with refrigerants. The waxy oil flows through the inner pipe, and the refrigerant flows through the outer pipe. The inner pipe is conventionally provided with a suitable scraping device for continuously removing precipitated wax from the inner wall surface of the inner pipe. It will be noted that the solvent combination may be added to the oil all at one time or in increments as the oil is being chilled.

Once the wax has been precipitated and separated from the oil, the problem then becomes one of reducing the oil content of the wax, purifying it, improving its color and odor, and segregating it into the various melting point grades. The exact manner in which a wax is refined may vary depending upon the type of wax being processed. With crystalline waxes derived from the paraffin distillates, two methods of deoiling are possible: (1) sweating and (2) solvent deoiling. The present invention is concerned mainly with the latter of these two

procedures for reasons that will be readily apparent in the description which follows.

The solvent deoiling method of reducing the oil content of a wax can be used on both paraffin and microcrystalline types of wax; and any given wax can be solvent deoiled in one of two ways: first, it can be completely dissolved in from 4 to 14 volumes of a solvent such as methyl ethyl ketone and at a temperature from 40° F. to 100° F. above the dewaxing temperature. The solution is then cooled, the wax recrystallized and filtered from the solvent. Alternatively, the chilled, solvent-containing wax cake from the dewaxing operation can be "repuddled" or agitated into a slurry with a lesser amount of fresh, cold solvent (about 2 to 12 volumes) and then refiltered. Either technique is very effective in reducing the oil content of the wax. The repuddling method is generally preferred because of its lower cost, but the method of solution and recrystallization may give a more complete separation in certain cases.

Following the deoiling step, a crystalline paraffin wax will generally contain about 0.1 to 0.5% oil. A semi-crystalline or micro-crystalline wax may contain about 0.5 to 5% oil.

The deoiled waxes may then be chemically treated, usually with sulfuric acid, to remove what are commonly referred to as "carbonizable" substances. The latter are more properly identified as unstable reactive impurities. This procedure is necessary to insure high purity waxes for the food packaging industry. Mild hydrogenation of wax at about 600° F. and 200 p. s. i. g. has been found to be substantially as effective as sulfuric acid treating for paraffin waxes. Somewhat more severe hydrogenation conditions, for example a higher pressure, may be desirable with micro-crystalline waxes.

After a wax has been deoiled and chemically treated, two major refining steps remain: (1) separation into the desired melting point grades, and (2) processing to a suitable odor and color. It is the latter finishing operation with which this invention is primarily concerned. The former step is a conventional one, and it is not a critical factor in the present invention. Hence, a detailed discussion of that step is not included in the present description.

The customary method for decolorizing and deodorizing a wax is to percolate it through a bed of a color-adsorbent material at a temperature sufficient to keep the wax in a fluid state. The adsorbents most generally employed are bauxite, silica gel, and various activated clays. A paraffin or crystalline wax is decolorized by heating it until it becomes fluid, allowing any water to settle out and then passing it through a bed of one of the adsorbent materials mentioned above. The filtering rate employed is generally about ½ to 2 tons of wax per ton of adsorbent per hour and the operating temperature is usually in the range of 160° F. to 200° F. The yield of wax obtained per volume of adsorbent employed will depend upon a number of factors including the color of the feed, the desired color of the product, and the capacity of the adsorbent.

Paraffin waxes generally are decolorized to a color shade of +30 as determined by the Saybolt chromometer. A yield of about 25 tons of fully refined paraffin wax per ton of bauxite is normally obtained before the bauxite requires regeneration.

Owing to the greater viscosity of the semi-micro waxes and the petrolatums, these wax types are sometimes diluted with a suitable solvent to render their percolation through the adsorbent bed more rapid. One such solvent in general use is a petroleum naphtha which is characterized by a 300–400° F. boiling range and a relatively low aromatic content. However, for the combination process described herein, it is preferred that the percolation be carried out without dilution of the feed, at a temperature high enough to give the desired mobility.

The semi-crystalline waxes are essentially light colored and give slightly lower filter yields than the paraffin waxes. The petrolatums, however, are very dark in color; and it is often necessary to recycle these materials in the decolorizing step before suitable color ratings can be obtained. Filter yields for petrolatums accordingly are substantially less than for paraffin waxes. Petrolatums having color ratings of about 10 to 14, as determined by the modified Tag-Robinson colorimeter, generally are satisfactory. The Saybolt and Tag-Robinson methods of color determination are standard tests in the petroleum industry and descriptions of these methods can be found in the "New and Revised Tag Manual for Inspectors of Petroleum" published by C. J. Tagliabue Manufacturing Company.

The odor characteristics of the final waxes are determined as follows: approximately 50 grams of wax and 100 grams of distilled water are heated in a 250 cc. beaker until the water starts to boil. A watch glass covering the beaker is then removed and the vapors over the sample are sniffed by an odor committee having a minimum of three persons. A wax is rated by each committeeman as having:

1. A very faint or lack of odor
2. An unobjectionable odor, and
3. An objectionable odor.

An average numerical rating of 2.5 or less is regarded as satisfactory.

This test is admittedly subject to variations in the odor perception of the individuals. For this reason, the men performing the odor test are specially trained for this work and the atmosphere in the test area is kept as odor-free as possible. Standard odor wax samples for comparison are arrived at by conducting surveys among wax consumers. This test has proven to be a reasonably accurate method of predicting the acceptability of a wax by the trade so far as its odor characteristics are concerned.

In the percolation step wherein a deoiled petroleum wax is filtered through a bed of adsorbent, it has previously been mentioned that the adsorbent gradually becomes filled with objectionable materials. These objectionable materials include various color or odor-forming bodies that are removed from the wax by the adsorbent. The presence of these bodies eventually decreases the adsorptive capacity of the adsorbent to the point where it is no longer effective in producing a wax having desirable color and odor characteristics. At this point the adsorbent must be regenerated.

A spent adsorbent is conventionally regenerated by (1) washing the adsorbent with a solvent such as naphtha or a light kerosene to remove as much adsorbed wax from the adsorbent as possible; (2) steaming the adsorbent to remove more strongly adsorbed wax; (3) "burning" the adsorbent in suitable kilns in the presence of an oxygen-containing gas whereby the adsorbent is freed of any carbonaceous odor- and color-forming bodies. It will be noted that the solvent treating step of the regeneration procedure is necessary in order to recover as much wax as possible from the adsorbent body. This step is especially vital in the refining of petrolatums since the filter yields of such waxes are relatively quite low. For example, the filter yield, when percolating a petrolatum, is generally of the order of about 1 to 5 tons of wax per ton of adsorbent. As a result, the wax remaining on a spent adsorbent at the start of the regeneration procedure may represent about 20 to 50% of the total feed of deoiled wax to the percolation operation. The conventional percolation regeneration procedure, therefore, has several marked disadvantages: First, it is necessary to employ a distillation step in order to recover wax from the naphtha or other solvent which is employed in the solvent-washing operation to recover wax from the spent adsorbent. As mentioned earlier, the solvents normally

employed for this purpose are materials such as naphtha and light kerosene; and it is necessary to separate these materials from the deoiled wax before the wax can be returned to the deoiling operation or any other step in the dewaxing and/or deoiling process. The recovered wax is not acceptable from a color or odor standpoint and hence must be reprocessed.

A second disadvantage of the conventional method of regenerating a spent adsorbent lies in the burning procedure that is required to remove objectionable materials from the adsorbent. This step requires extensive heating of the adsorbent, usually in equipment other than that used for percolation, with attendant handling problems. It is an expensive and complicating procedure.

Accordingly, it is an object of the present invention to simplify the regeneration procedures that are employed to restore the activity of spent adsorbents derived from the adsorbent-treating of petroleum wax. It is a further object of the invention to improve the yields of refined waxes that are produced by the adsorbent treating operation. These and other objects of the invention will be more apparent in the description which follows:

In accordance with the present invention, a petroleum wax is solvent deoiled by the use of a conventional dewaxing solvent consisting of an aliphatic ketone and an aromatic hydrocarbon, or a higher ketone alone. Ketones and aromatic hydrocarbons that are suitable for this operation have been described at length earlier in this description. In further accordance with the present invention, the solvent deoiled wax is percolated through a bed of a particulate adsorbent, preferably bauxite. The bauxite should have a particle size in the range of about 10 to 80 mesh and especially about 20 to 60 mesh. This bauxite should have been previously heated to a temperature within the range of 700–1200° F. to remove all loosely held water and give a product of high adsorbency.

Alternatively a similarly prepared clay may be used. It will be observed that adsorbents of this type are conventional and well known in themselves in the petroleum industry. Hence, it is considered that a more detailed discussion of these materials is not critically necessary in the present description.

As in conventional adsorbent-treating processes, the percolation step of the present process is continued until the product wax stream fails to pass the required color and/or odor tests. At this point, the flow of deoiled wax to the percolation zone is interrupted, and the adsorbent is regenerated.

The regeneration step in accordance with the present invention is carried out by washing the spent adsorbent with the same solvent which is employed in the deoiling step of the process. The solvent is passed through the adsorbent at a rate of about 1 to 10 w./hr./w. (tons of solvent per hr. per ton of adsorbent) and at a temperature of about 150° to 300° F. The total wash required to remove substantially all of the adherent wax together with selectively adsorbed color and odor bodies should be determined for each type of stock processed, by analyzing spot samples of the effluent and also by observing the effectiveness of the regeneration, as judged by subsequent percolation results. However, a total solvent throughput in the range of 1–5 w./w. (tons of solvent per ton of adsorbent) will usually be found sufficient.

The solution of desorbed wax and solvent is then returned to the deoiling operation where it is combined with the wax being fed to the latter operation.

Upon the completion of the solvent washing step, the bed of adsorbent is freed of any remaining solvent by purging the adsorbent with steam at a temperature within the range of about 212° to 350° F. and in sufficient volume to strip substantially all of the remaining solvent from the adsorbent. The combined steam and solvent vapor mixture is condensed and also returned to the deoiling step of the wax refining process.

Following the steaming operation, the adsorbent bed is dried by contacting it with a stream of air or other dry gas such as nitrogen, which does not deactivate the adsorbent, at a temperature of about 300° to 500° F. The adsorbent can be dried to within 1% of its original water content in about 1–4 hours, the shorter time being associated with the higher temperature. Gas rates in the order of 5–25 cubic feet per hour per pound of adsorbent are suitable for the drying step.

The nature and scope of the present invention may be better understood by reference to the attached figure which illustrates means contemplated for carrying out a preferred embodiment of the invention. In considering the apparatus and process depicted in the figure, it will be assumed that the wax passing through the process is a petrolatum of a type produced by a conventional dewaxing operation. Hence, it will be considered that the petrolatum feed has a melting point of 160° F., an oil content of about 15 wt. percent, a color of about 5 Tag-Robinson and an odor rating of 3.

It will also be assumed that the solvent employed in the process of the figure is a mixture consisting of about 60 volume percent methyl ethyl ketone and about 40 volume percent of toluene. It will further be assumed that the adsorbent is bauxite having the general properties mentioned earlier.

Referring to the figure, the petrolatum flows through line **3** into chilling zone **4** together with the deoiling solvent which enters the zone through lines **5**, **14** and **24**. While all these solvent streams are shown entering the wax feed line at one point, prior to chilling, it will be appreciated that parts of the solvent could be added at various points during the chilling and prior to filtering, and part used for washing the wax cake on the filter, each part being cooled to an appropriate temperature. The wash solvent would of course be chilled to approximately the desired filtering temperature.

It will be noted that the recrystallization type of deoiling operation is illustrated here. For a repuddling operation, the wax feed would comprise the cold wax cake from the dewaxing step, containing roughly two volumes of solvent per volume of wax, and the chilling zone would be omitted. In this case the dilution solvent streams would be cooled as much as necessary in order that the resulting slurry would be at the desired filtering temperature. In either case, a total of 5 to 10 volumes of solvent per volume of wax would be suitable for the deoiling step. The temperature of filtration would normally be in the range of 0° F. to +50° F., depending on the wax properties desired. Lower temperature operation gives a relatively soft wax of high sealing strength, particularly suitable for use in laminating compositions whereas higher temperature separation produces a hard wax, more suitable in compositions for paper coating.

The mixture of solvent and wax flows from chilling zone **4** through line **6** to a conventional rotary filter **7**. Here the wax is separated from the solvent and sent via line **8** to decanting zone **9**. It will be observed that the wax in traversing line **8** is heated sufficiently to melt the wax as by means of a heat exchanger **10**. It will further be observed that the rotary filter **7** may be replaced by any other suitable separation device such as a filter press, a centrifuge, or the like.

The filtrate from the rotary filter **7** flows by means of line **11** into a suitable fractionation zone **12**. Zone **12** ordinarily may consist of a simple flash zone wherein the pressure and temperature conditions are maintained so as to flash or otherwise distill the solvent from the dewaxed oil. An inlet temperature of about 300° F., at essentially atmospheric pressure, or of about 400° F. with 30 p. s. i. g. pressure, is suitable for vaporizing the bulk of the solvent from the oil. This solvent is returned for re-use via line **14**. The dewaxed oil, still containing some residual solvent, goes through line **13** to steam stripper **42**. The overhead from this stripper

passes through condenser 45 via line 44, and into decanting zone 9. The solvent-free dewaxed oil flows from the stripper through line 43 to any desired subsequent refining operation or storage tank. This oil may be of suitable quality for further refining to produce finished lubes, but it frequently happens, since the conditions of the deoiling step are adjusted primarily on the basis of wax quality, that the oil is of too high a pour point for lubes and is used as feed stock for cracking. In some cases streams of this type have value as crystal modifiers or dewaxing aids in the dewaxing of other stocks.

It will be observed that filtering zone 7 is frequently maintained at temperatures below the freezing point of water. For this reason, water contained in the wax feed line 3 is retained by the wax in line 8 and hence enters zone 9 along with the wax. Zone 9 is a decanting zone of a character designed to provide settling time sufficient for wax-solvent solution and water to separate into two distinct layers. As illustrated, decanting zone 9 is conventionally a cylindrical, elongated vessel possessing a conical bottom. Some of the ketone present in zone 9 will enter the water layer.

Water from the water layer in zone 9 containing about 10% MEK, is removed from the zone by means of line 15 and is transmitted to a ketone stripping column 16, typically comprising eighteen bubble cap plates. The operation of this column depends on the formation of constant boiling mixtures of ketone and water, and of benzene or toluene and water, which are lower boiling than water. Steam is injected at the base of the tower to provide sufficient heat, and a solvent mixture containing about 12% water is distilled overhead and recycled to the decanter through line 18. Water leaves the base of the tower through line 17, essentially free of solvent. The tower operates at just above atmospheric pressure, with a temperature of about 165° F. on the overhead and 220° F. on the bottoms.

Solvent plus dissolved wax from zone 9 is transmitted by means of line 19 to a wax fractionation zone 20 wherein the wax is separated from admixed solvent. Conventionally, zone 20 may be a flash tower operated under temperature and pressure conditions that are adapted to flash the solvent from the wax. These conditions are essentially the same as those described for the separation of solvent from the dewaxed oil. Similarly, steam stripper vessel 46 for removing the last traces of solvent from the wax will be either similar or identical to previously described stripper tower 42 in construction and operation.

Solvent from flash zone 20 passes by means of line 21 to condenser 22 and is then transmitted at least in part by means of line 23 to an adsorption zone. The remainder of the solvent from condenser 22 is returned for re-use in the deoiling step via line 24.

Wax flows from zone 46 by means of line 47 to an acid treating or hydrogenation zone 26. Here the wax is treated for the purpose of removing any unstable and reactive impurities from the wax.

Other processing steps, such as distillation for melting point separation or topping for odor improvement, could also be inserted at this point.

The treated wax from zone 26 flows through line 27 and manifold 28 into one of the adsorbent zones 29, 29′ or 29″. In the figure, it will be considered that the valves in the various manifolds associated with the adsorption zones are lined up so as to pass the wax from line 27 into zone 29″.

Each of the adsorption zones is also provided with a solvent manifold 30, a steam manifold 31 and a dry gas manifold 50. Each of the manifolds (e. g. the steam, wax, drying gas and solvent manifolds) is valved to permit separate admission of each of these fluids to each of the adsorption zones. Thus, as illustrated, it will be assumed that wax flows from line 27 through manifold 28 into adsorption zone 29″. Similarly, it will be assumed that solvent is flowing through line 23 and manifold 30 into zone 29 and that steam is flowing through line 32 and manifold 31 into zone 29′, to be followed by drying gas. It will be appreciated that more or less zones than those illustrated may be employed in the process of the present invention without the exercise of additional invention.

Turning first to the wax stream in line 27, it will be observed that this stream flows through manifold 28 into adsorption zone 29″. As the stream is initially introduced within zone 29″, this zone is provided with a bed of particulate bauxite which is capable of removing color- and odor-forming bodies and other impurities from the wax stream. It is preferred that the absorbent in zone 29″ be present in an amount sufficient to co-ordinate the operation of this zone with the operation of zones 29 and 29′. Thus, zone 29″, as well as the other zones, should be sized so as to permit ample time within each of the zones to satisfactorily perform the operation required therein. If necessary, it may be required in some instances to employ more than one zone for one or more of the individual operations in order to properly synchronize the steps. As illustrated in the figure, it will be assumed that each zone is capable of carrying out one of the necessary steps without impairing the operations in the other zones.

Zone 29″ is preferably operated at a temperature of about 200° to 300° F. and at a wax feed rate of about ½ to 2 tons of wax per ton of adsorbent per hour. Particularly preferred conditions for the wax under consideration are about 250° F. and 1 w./hr./w.

Decolorized and de-odorized wax, suitable for sale as refined micro-crystalline wax without further processing, flows from zone 29″ via line 33.

When the wax in line 33 fails to meet the necessary color and/or odor properties, the wax stream in line 27 is diverted to zone 29′. It will be observed that this zone, as illustrated, would be the next zone to be utilized for the adsorption step inasmuch as this zone is undergoing a steaming and drying operation adapted to remove solvent from the zone and to thereby prepare the adsorbent for the wax treating step. The adsorption step having been described in detail, the following description will be devoted to an exposition of the regeneration steps that are required for removing objectionable materials from the spent adsorbent and for in turn removing solvent from the solvent-treated adsorbent.

Once the adsorbent becomes spent in its adsorptive capacity, it is (in accordance with the present invention) contacted with a stream of solvent from line 23. As explained earlier, it has been observed that this type of contacting operation serves to remove any objectionable material from the adsorbent. Turning to the figure, it will be recalled that zone 29 is considered to be in the solvent washing phase of the process. Solvent flowing through line 23 flows through adsorption zone 29 at a temperature of about 150° to 300° F., preferably at the highest temperature consistent with maintaining most of the solvent in liquid phase. Pressures in the range of atmospheric to about 100 p. s. i. g. are contemplated. The solvent preferably flows through the bed at a rate of between 1 to 10 w./hr./w., a total throughput of between 1 and 5 w./w. being used.

Solvent leaves zone 29 by means of line 5 whence it flows directly to the entrance to chilling zone 4. Objectionable materials originally present within the adsorbent in zone 29 therefore also flow through line 5 back to deoiling zone 4. It has been observed that these materials do not tend to re-enter the wax and further contaminate the wax, but instead, congregate within the oil and solvent which is separated from the wax in zone 7. It has been a particular observation that the impurities are largely

withdrawn from the process by means of the dewaxed oil stream 43, the disposition of which was discussed previously.

Having been freed of its objectionable contaminants, the adsorbent in zone 29 is next treated with steam, for the purpose of removing adsorbed solvent from the cleaned adsorbent bed. This step of the process is illustrated in the attached figure as occurring in zone 29'. There it will be observed that steam flows through line 32 into zone 29' and thence through line 40 and condensed 41 into decanting zone 9, preferably entering zone 9 close to the interface between the two phases in said zone. A steam rate of between 5 and 25 cubic feet per hour per pound of adsorbent, at between 212° and 350° F., is continued for a period of from 15 minutes to about one hour. If the steam is superheated, the subsequent drying operation may be shortened considerably. Following the steaming, the adsorbent is purged with dry air or other gas, preheated to a temperature in the range of 300° to 500° F., as previously described. The temperature of the drying gas may be reduced toward the end of the drying period to adjust the adsorbent temperature toward that desired for the subsequent percolation operation.

The following example will serve even better to illustrate the nature of the present invention. In this example, a deoiled paraffin wax of about 132° F. M. P., 0 Saybolt color, 0.2% oil content and 3 odor rating was percolated through a bed of bauxite at a temperature of about 160° F. and a rate of about 2 pounds of wax per hour per pound of bauxite until the color rating of the product wax was less than +30 Saybolt color. At this point separate samples of the spent bauxite were treated according to different regeneration procedures.

In a first procedure, the bauxite was washed with a naphtha boiling within the range of about 300° to 400° F. and possessing a gravity of about 45° API. A total wash amounting to approximately 32 bbls. per ton of adsorbent was used, in a percolation type operation. Following the treatment with the naphtha the bauxite was steamed for about 8 hours with 50 p. s. i. g. steam. A sample of this material, which in conventional plant operation would next go to a burning step, was used for wax percolation at the same conditions previously used. The yield of product wax obtained by the use of this bauxite is included in Table I presented later in this example.

A second sample of the spent bauxite was subjected to the identical naphtha washing and steaming procedure described above. In this instance, however, the sample was further subjected to a burning operation in which air was passed through the sample at a temperature of about 850°–1000° F. and at a rate of about 25 cubic feet/hr./lb. of bauxite for a period of about 30 minutes. At the end of this time, the burned bauxite was cooled and again subjected to use in an adsorption operation for removing objectionable material from the paraffin wax feed, under the previously mentioned conditions. Once again, wax yields as well as the color and odor characteristics of the product wax were obtained. The results of this operation are also presented in Table I.

A third sample of the spent bauxite was thoroughly washed with a mixture of methyl ethyl ketone and toluene containing about 75% by volume of the ketone and 25% by volume of toluene. About 2.5 volumes of solvent per volume of bauxite was used, in a Soxhlet type extraction. The temperature was about 175° F. and the total contacting time was about 2 hours. Following the solvent contacting step, the bauxite was dried by heating in an oven at 180° F. for 16 hours.

Once again the bauxite obtained by this technique was employed to percolate the original paraffin wax feed at the standard conditions.

The yield data and the color and odor characteristics of the wax produced by each one of the above described processing operations are presented in the following table:

TABLE I

Comparison of bauxites for percolation of paraffin wax

Plant Spent Bauxite (Naphtha Washed)			Plant Regenerated by Burning			Lab. Regenerated by Extraction with MEK and Toluene		
T/T Yield***	Color*	Odor**	T/T Yield***	Color*	Odor**	T/T Yield***	Color*	Odor**
0–2	+18	2.8	0–2	+30	1.5	0–2	+30	1.3
			4–6	+30	1.8	4–6	+30	1.8
			8–10	+26	2.0	8–10	+30	2.1
						10–15	+30	2.2
						15–20	+29	2.2

*Saybolt.
**2.5 or less is satisfactory.
***Tons of wax per ton of bauxite.

It is apparent from the above table that the bauxite washed with MEK-toluene was more effective than the naphtha washed- or washed and burned-bauxite for the subsequent decolorization and odor improvement of paraffin wax. The superiority of the MEK-washed bauxite is particularly marked in its decolorizing ability, its odor-improvement qualities being at least as good as the other bauxite samples.

What is claimed is:

1. A method of refining an oil-containing petroleum hydrocarbon wax which comprises, in combination, solvent deoiling the wax with a ketone containing from 3 to 6 carbon atoms to form a deoiled wax cake and a filtrate, fractionating the filtrate to form a dewaxed oil fraction and a recovered solvent fraction, liquefying the deoiled wax cake, introducing the liquefied wax within a decanting zone adapted to separate liquefied wax from water, withdrawing the separated liquefied wax and fractionating same to form a second recovered solvent fraction and a substantially solvent-free wax, chemically treating the solvent-free wax to remove unstable reactive impurities therefrom, contacting the treated wax with a particulate adsorbent to remove color and odor bodies from the wax until the adsorbent is spent, contacting the spent adsorbent with at least a portion of said recovered solvent to dissolve and remove any wax and color and odor bodies remaining on the adsorbent, recycling the resulting wax solution to the solvent deoiling step, contacting the wax-free adsorbent with steam to remove solvent remaining thereon, contacting the steamed adsorbent with a dry non-deactivating gas to dry the adsorbent, and thereafter recontacting the adsorbent with additional solvent-free wax.

2. Process as defined in claim 1 in which the ketone solvent contains at least about 25 vol. percent of an aromatic hydrocarbon that contains from 6 to 7 carbon atoms.

3. Process as defined in claim 2 in which the ketone

is methyl ethyl ketone and the aromatic hydrocarbon is toluene.

4. Process as defined in claim 1 in which the adsorbent is bauxite.

5. Process as defined in claim 1 in which the bauxite is contacted with the non-deactivating gas until the water content of the bauxite is less than about 1% by weight above that originally contained when prepared for use.

6. Process as defined in claim 1 in which the steam and associated solvent vapors are condensed and recycled to the decanting zone.

7. Process as defined in claim 3 in which the ketone solvent contains about 25 vol. percent of toluene.

8. In a process for refining an oil-containing petroleum hydrocarbon wax which includes the steps of solvent deoiling the wax with a ketone containing from 3 to 6 carbon atoms to form a deoiled wax cake and a filtrate, fractionating the filtrate to form a dewaxed oil fraction and a recovered solvent fraction, recovering a substantially solvent-free wax, and contacting the recovered wax with

a particulate adsorbent to remove color and odor bodies from the wax until the adsorbent is spent, the improvement which comprises the steps of contacting the spent adsorbent with at least a portion of said recovered solvent to dissolve and remove any wax and color and odor bodies remaining on the adsorbent, removing solvent from the wax-free adsorbent, drying the adsorbent, thereafter recontacting the dried adsorbent with additional solvent-free wax, and recycling to the solvent deoiling step the wax solution resulting from contacting the spent adsorbent with recovered solvent, whereby color and odor bodies removed from the adsorbent enter the dewaxed oil fraction.

References Cited in the file of this patent

UNITED STATES PATENTS

2,429,727	Macke et al.	Oct. 28, 1947
2,521,357	Furnoy	Sept. 5, 1950
2,550,058	Gee	Apr. 24, 1951
2,571,380	Penick	Oct. 16, 1951