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DEASPHALTING PETROLEUM OILS WITH POROUS CONTACT MATERIAL

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This invention relates to a process for deasphalting petroleum oils and, more particularly, is concerned with a method for separating asphalt from asphalt-bearing petroleum stocks by contacting the latter with a solid porous sorbent particle-form material, whereby oil is selectively sorbed into the pores of said material, leaving asphalt as the unsorbed portion and thereafter removing deasphalted oil of low carbon residue from the pores of said material by a selective solvent extraction.

Heretofore, removal of asphalt from petroleum oil has been accomplished by various means, such as deasphalting by distillation and deasphalting by contacting the stock to be treated with various materials, including clay, acids, metallic halides and organic solvents. While the last named materials have generally been found to be the most satisfactory of the group, methods employing the same have been subject to certain economic and operational disadvantages. Thus, deasphalting processes employing propane and related hydrocarbons to precipitate asphaltic materials from asphalt-bearing stock are necessarily operated at temperatures requiring the use of costly high-pressure equipment. Some attempts have heretofore been made to use other solvents, such as aliphatic alcohols, organic esters and ethers. The deasphalting action of these materials, however, has not been sufficiently effective to give satisfactory results.

In deasphalting by distillation, it is difficult to separate all of the oil from the asphalt since heavy petroleum fractions have low volatility and cannot always be vaporized without decomposition. Clay deasphalting may be effective when the oil is contacted with sufficiently large quantities of clay, but it cannot be used economically unless the asphalt content of the oil is relatively low. In addition, clay removes valuable oil components simultaneously with asphalt. Deasphalting with acids requires high acid dosages and usually results in the removal of valuable oil components in addition to asphalt. These conditions result in low yields and high operating costs. Deasphalting using precipitating agents such as aluminum chloride and similar metallic halides is not employed to any great extent in commercial refining, due to the necessity of installing special equipment, the relative expensiveness of such compounds, and the difficulties encountered in disposing of sludges resulting from such operations.

Now, in accordance with the present invention, a new method has been discovered for de-

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asphalting petroleum oils. This method comprises contacting the stock to be treated with a solid porous sorbent particle-form material having a structure corresponding to that of an inorganic oxide gel having a substantially uniform porosity of low macropore volume with an average pore diameter not exceeding about 125 Angstrom units and a particle size, preferably not smaller than about 30 mesh. Under such conditions, it has been found that the uniform porous sorbent material has the ability to sorb the oily constituents into its pores, leaving the asphaltic constituents unsorbed. Deasphalted oil of low carbon residue is then selectively extracted from the pores of said sorbent material with a paraffinic solvent. The remainder of the sorbed oil of relatively higher carbon residue is extracted with a polar solvent, representative of which is methyl ethyl ketone-benzol mixtures and the like. The oil of higher carbon residue can either be held as a by-product fraction or be recycled through the porous sorbent material along with additional charge stock.

The deasphalting process of this invention is accordingly carried out by bringing the asphalt-containing stock to be treated in contact with a suitable solid porous sorbent particle-form material, separating the asphalt and any unsorbed oil from the oil-saturated material, thereafter solvent-extracting the sorbent with a selective paraffinic solvent to remove deasphalted oil of low carbon residue, and then solvent-extracting the sorbent with a second, more polar solvent to remove the remainder of the sorbed oil from the pores of the sorbed material, said extracted oil having a relatively higher carbon residue than the oil extracted with the paraffinic solvent and which may be used as a separate by-product or recycled through the sorbent medium to effectively reduce the carbon residue to a desirable low value.

The contacting is carried out in a suitable vessel where direct contact between the sorbent particles and the stock to be deasphalted is effected. Separation of asphalt from the oil-containing contact material is accomplished most conveniently by draining, although other methods, such as centrifuging or filtering may be used if desired. Unsorbed material adhering to the surface of the porous sorbent material is removed in a washing or steaming operation. Suitable wash materials include the original charge stock, various solvents, and deasphalted oil obtained from previous operations.

Recovery of deasphalted oil from the pores of

the sorbent is effected by a solvent extraction with a paraffinic solvent. Suitable selective solvents for this purpose include hexane, pentane, petroleum ether, paraffinic naphtha, Stoddard solvent, and the like. In general, the paraffin hydrocarbon solvents or solvents composed largely of paraffins, hereinafter referred to as paraffinic solvents, may be employed in extracting a deasphalted oil characterized by a low carbon residue. The remainder of the sorbed oil is then removed from the pores of the sorbent material by extracting with a second, more polar solvent, notably a ketonic solvent containing a normally liquid ketone such as methyl ethyl ketone, acetone, methyl-isopropyl ketone, and the like. The oil thus recovered is of a relatively higher carbon residue and can be recycled for further treatment with the sorbent or withdrawn as a by-product fraction. The solvents so employed, both the primary paraffinic solvent and the secondary polar solvent, can be recovered upon separation from the treated oil and re-used in the process.

After extraction of the oil from the sorbent, the latter is regenerated by evaporation of the solvent under reduced pressure, by passing air or inert gas over the sorbent, by heating, or by a combination of two or more of these methods, and is then ready for re-use.

The macropore volume of the contact material employed in the present invention should be relatively low so that the pore volume is substantially that of micropores. In general, the volume of macropores, i. e., those pores having radii larger than 100 Angstrom units, should constitute less than about 30 per cent of the total pore volume and, preferably, 10 per cent or less. The measurement of pore size and pore size distribution in various porous materials is discussed in detail by L. C. Drake and H. L. Ritter in Industrial and Engineering Chemistry, Analytical Edition, volume 17, pages 782–791 (1945). The methods described there were essentially those employed in determining the bulk densities, average pore diameters, and other pore measurements of the sorbents employed in the present invention.

The size of the sorbent particles employed in the process of this invention is to some extent dependent upon the variables involved in any particular application of the process. These important variables are: time of contact between the liquid mixture under treatment and the sorbent in the sorption zone, temperature in the sorption zone, viscosity of the liquid charge and, to a lesser extent, the ratio of liquid mixture to sorbent charged to the sorption zone. Increasing time of contact results in a decrease in the efficiency of the desired separation. Decreasing viscosity of the liquid charge has the same effect. On the other hand, both increasing temperature and decreasing viscosity result in more rapid sorption of the lighter, less viscous components of the mixture. If the ratio of sorbent to liquid charge is excessive, some loss in separation efficiency results. By proper control of these variables, some latitude in the average diameter of the sorbent employed may be provided. However, when the diameter of the particles becomes too small, the sorbent preferentially sorbs the heavier, more viscous components from the charge mixture in the same manner as well known decolorizing clays. This is shown in Table I below, in which is tabulated the results obtained upon separation of a Mid-Continent residuum using a silica-alumina gel type sorbent having a bulk density in the 4–8 mesh size range of about 0.7.

Table I

Experiment Number	1	4	5	6	7	2	3
Charge Viscosity S. U. V. at 210° F. sec	116.9	116.9	81.9	81.9	81.9	81.8	340
Charge Ramsbottom Carbon			2.3	2.3	2.3	2.3	5.1
Mesh Size of Sorbent (Tyler)	4–8	30–60	30–60	60–80	30–60	4–8	4–8
Sorption Zone Contact Time	24 hrs.	24 hrs.	2 min.	2 min.	2 hrs.	72 hrs.	4 hrs.
Sorption Zone Temperature ° F	150	150	150	150	150	75	275
Weight Ratio of Sorbent to Liquid Charge	1	1	1	1	1	1	2.2
Properties of Oily Constituent Retained by Sorbent:							
S. U. V. at 210° F	69.7	129.2	75.1	81.9	115.7	49.7	151
Ramsbottom Carbon, percent			1.8	2.3	3.1		2.4
Properties of Materials Washed from Sorbent Surface:							
S. U. V. at 210° F. sec	164	100.1	86.4	80.5	76.0	139.2	650
Ramsbottom Carbon, percent			2.4	2.2	2.0	3.5	6.7

It will be apparent from the above Table I that when the gel type particles were greater than 30 mesh size, even at relatively high temperatures and long contact periods, the oily constituents of low viscosity and carbon residue were sorbed in the pores of the sorbent, while the more viscous, heavier constituents could be washed away with a suitable washing solvent, in this case benzol. On the other hand, in the case of sorbent particles ranging from 30 to 60 mesh size, when the contact period was 24 hours (Experiment 4) or even 2 hours (Experiment 7), the sorbent acted similar to a normal filtering clay and preferentially sorbed the heavier, more viscous constituents; but when the contact time was reduced to 2 minutes (Experiment 5), the 30–60 mesh sorbent exhibited a preference for the lighter, less viscous constituents over the heavier, more viscous constituents. When the particle size was reduced below 60 mesh, the sorbent preferentially sorbed the heavier, viscous constituents, even at very low contact periods (Experiment 6).

The effect of contact time and temperature is shown in Table II below, in which are tabulated the results obtained upon separation of an East Texas residuum having an original Saybolt Universal viscosity of 512 seconds at 210° F. and a Ramsbottom carbon residue of 11.1. In this experiment, a silica-alumina gel type sorbent of 4–8 mesh size and 0.48 bulk density were employed.

Table II

Experiment Number	1	2	3
Sorption Zone Contact Time, Hrs	4	4	2
Sorption Zone Contact Temp., °F	275	300	300
Sorbent to Oil Weight Ratio	1.6	1.4	1.5
Ramsbottom Carbon Residue, percent of sorbed oily constituents	1.9	2.6	2.0

In general, it may be said that the particle size of the sorbent material, particularly in the

case of inorganic oxide gel type sorbents, should be not less than about 60 mesh Tyler and preferably within the range of about 0.022 to 1.0 inch average diameter. The best results may be obtained by limiting the sorbents within the range of 0.03 to 0.20 inch average diameter and of reasonably uniform size. It is pointed out, however, that by proper control of the variables discussed hereinabove and also of the average pore diameter of the sorbent, operation according to the method of this invention may be obtained on sorbent particles outside the size ranges given, although the results will be less satisfactory. It is contemplated that, in its broader aspects, this invention covers these latter operations as well as the operations within the specified preferred limits.

The porosity of the gel particles employed in the process of this invention is of fundamental importance. The degree of porosity is generally reflected in the bulk density of the gel composite used; the lower the bulk density, the greater being the degree of porosity. For the purposes of the present process, porous sorbent particles having bulk densities of between about 0.4 and 1.1 gram per cubic centimeter are preferred. The bulk densities indicated correspond to an average pore diameter of between about 20 and about 125 Angstrom units. Preferably, the sorbent used will have a bulk density between about 0.6 and about 0.8 gram per cubic centimeter. Gel particles having a bulk density greater than about 0.8 have been found to have excellent selectivity but poor sorbing capacity, while particles with a bulk density less than about 0.6 have relatively poor selectivity. However, since the selectivity of the separation process improves with a decrease in temperature, particles with a bulk density of less than 0.6 would be satisfactory for treating stocks which can be processed at low temperatures.

The degree of porosity of a synthetic inorganic oxide gel will, in general, depend on the conditions under which it is prepared and allowed to set to gelation. A particularly convenient method of preparing gel particles used in the process of this invention is described in U. S. Patent 2,384,946, issued September 18, 1945, to Milton M. Marisic. It is there disclosed that spheroidal particles of inorganic oxide gel may be prepared by mixing an acidic stream with a stream of sodium silicate and allowing the resulting sol to be ejected from a nozzle into an oil column, where the gel sets in the form of bead-like spheroids. The resulting gel spheres, after washing, drying and tempering, were of a size varying between about 4 and about 20 mesh. The gel beads so produced had a bulk density of between about 0.4 and about 1.1 and an average pore diameter of between about 20 and about 125 Angstrom units. They proved to be excellent selective sorbents for use in the process of this invention.

Likewise, irregularly shaped porous sorbent fragments or particles having the structure of inorganic oxide gels may be used. However, in general, spheroidal particles are to be preferred, since attrition losses are then at a minimum and contamination with gel fines of the asphalt-bearing stock is substantially eliminated.

In general, inorganic oxide gel particles will be used in the process of this invention. Thus, silica, zirconia, alumina, beryllia, and other inorganic oxide gels may be employed as sorbents in the present deasphalting process. The chemical composition of the sorbent medium employed is

of minor importance in comparison to its physical properties, such as pore volume and pore size, discussed above. Usually, however, siliceous gel particles such as silica gel, silica-alumina gel, silica-zirconia gel, silica-thoria gel, and the like, are preferred sorbents. Porous sorptive silica glasses having a structure approaching that of a siliceous gel are likewise contemplated for use in the process described herein, it being necessary, however, that the porous glasses employed have an average pore diameter less than about 125 Angstrom units, and a macropore volume of less than about 30 percent of the total pore volume. The size of the porous glass particles must also be carefully controlled so as to obtain preferential sorption of the lighter, less viscous constituents of the mixture. Usually, particles of less than 60 mesh size are undesirable. It is also contemplated that, within the scope of this invention, other porous materials not of siliceous gel composition which have structures approaching that of an inorganic oxide gel and are within the above specified pore size and particle size may be employed in the selective sorption process of this invention.

Typical of the porous glasses used are those described in U. S. Patent 2,106,744, issued February 1, 1938, to Hood et al. There, it is disclosed that a silica-alkali-boric oxide glass of suitable composition is prepared by a fusion process. Heat treatment of this glass results in separation of the glass into two phases; one phase is rich in alkali-boric oxide and is soluble in acids, while the other phase, which is insoluble in acid, consists of silica with a small amount of boric oxide. Extraction of this heat treated glass with acid results in a porous silica glass which can be employed as a porous sorbent separating medium in accordance with the present invention.

Residual and distillate petroleum stocks from a variety of sources having asphalt contents of from less than 7 per cent to more than 60 per cent have been successfully deasphalted by contacting with the porous sorbent medium described above.

The temperature at which the deasphalting operation is conducted may vary over a wide range, depending upon the type of oil being treated and upon the character of products desired. The temperature should be high enough to give the oil sufficient fluidity to permit rapid sorption, but should be low enough to permit the sorbent to function selectively. The maximum temperature at which deasphalting is carried out is dependent on the viscosity of the stock being treated. The sorption of the oily constituents becomes less selective as the viscosity decreases. The maximum usable temperature, therefore, may vary from below room temperature to a comparatively high temperature, but usually will not exceed about 350° F.

The time required for the deasphalting operation depends upon the conditions of the contact, such as the nature of the mixture being treated, temperature, and the like. In general, saturation of the sorbent particles with the asphalt-bearing stock is not required and excessive contact time is to be avoided since it has generally been found to reduce the selectivity of the operation.

The process of this invention will generally be carried out with a sorbent to asphalt-bearing stock weight ratio of between about 0.1 to 1 and about 20 to 1. With a weight ratio lower than that indicated, the sorbed oily fraction will be very small in proportion to the unsorbed asphaltic

fraction. The higher ratios will usually be employed with the sorbents of higher bulk density, whose sorbing capacity is relatively small. An approximate weight ratio of sorbent to charge stock between about 1 to 1 and about 6 to 1 has been found to be particularly convenient under the usual operating conditions.

Following the sorption step, the bulk of the unsorbed material is removed from the oil-containing sorbent particles by simple draining. This operation leaves the particles coated with high asphalt content oil which must be removed before the deasphalted oil can be recovered from inside the sorbent pores. The most convenient method of accomplishing this is by a quick wash with a hot solvent. By holding the contact time to a minimum, this washing operation can be so controlled that the outer surface of the sorbent particles can be cleaned without displacing any appreciable amount of oil from inside the sorbent pores.

The solvent employed may be any of the conventional oil solvents, the original charge oil, or deasphalted oil obtained from previous operations. Preferably, the solvent will have a boiling point within the range of about 150° F. to about 400° F. The temperature at which the washing operation can be carried out may vary over wide limits. Generally, however, the washing will be carried out at a temperature above 150° F. and preferably above 200° F.

In the choice of a particular wash solvent, consideration should be given to the matter of possible solvent contamination since, at the end of the wash step, a small amount of wash solvent will be left on the sorbent particles and will subsequently be mixed with the extraction solvent in the operation which follows the washing step.

The deasphalted oil is then recovered from the pores of the sorbent by solvent extraction with paraffinic solvent to yield an oil of low carbon residue. After the initial selective solvent extraction with the paraffinic solvent, the remainder of sorbed oily constituents is removed from the pores of the contact material with a polar solvent such as a ketonic solvent mixture of methyl ethyl ketone and benzol.

After sorbent particles have been extracted, their pores are filled with solvent which must be removed before they can be re-used. The preferably employed procedure for removing solvent involves evaporation of the solvent by maintaining the particles at an elevated temperature and sweeping out the solvent vapors from the sorbent pores with an inert gas such as nitrogen or carbon dioxide.

It has been found that after removal of the solvent, the regeneration efficiency of the sorbent particles is considerably improved by steaming the particles for a short interval of time and then purging the residual steam. While this steaming treatment is not essential, it is preferably included in the regeneration procedure since, upon re-use, the sorbing capacity of particles so treated has been found to fall off less rapidly with succeeding cycles than in the case of particles which were not subjected to the steaming treatment.

Generally, a small amount of residual unextractable material remains in the pores of the sorbent particles after each cycle of re-use. This material, if permitted to accumulate, causes a gradual decrease in the sorbing capacity of the particles. When the sorbing capacity of the particles has fallen to an undesirably low level, it can be completely restored by ordinary kiln burning of the particles.

The deasphalting process described herein may be carried out either in batch operation or as a continuous process. The batch operations consist of contacting the asphalt-bearing stock with sorbent, separating the unsorbed oil and asphalt from the oil-saturated sorbent, washing the sorbent particles to remove oil adhering to the surface thereof, removing the deasphalted low carbon residue fraction of sorbed oil by one or more selective solvent extraction treatments with a paraffinic solvent and thereafter extracting the high carbon residue oil remaining in the sorbent particles with one or more portions of an organic polar solvent.

A suitable continuous process consists of slowly percolating asphaltic stock through a column of sorbent maintained at a comparatively high temperature, that is, from about 250° F. to about 350° F. After separating the sorbed oil and asphalt from the oil-saturated sorbent, the sorbent particles are given a quick solvent wash to remove oil adhering to the surface thereof. A fraction of the sorbed oil having a low carbon residue is then removed from the pores of the sorbent by a selective solvent extraction treatment with a paraffinic solvent. The remainder of the sorbed oil of relatively high carbon residue is then removed from the sorbent by solvent extraction with a polar solvent. The solvents are recovered by fractional separation from the oil and re-used. The high carbon residue fraction may be withdrawn as a by-product fraction or charged to the following cycle for re-treatment, together with a mixture of unsorbed oil fraction and a portion of untreated stock. The sorbent particles are dried after removal of the sorbed oil by heating and blowing with an inert gas and steam and are then ready for re-use.

The following detailed examples will serve to illustrate the deasphalting process of this invention without limiting the same. Asphalt removal from the oil was measured by observing the difference in the carbon residue of the oil before and after treatment.

Example 1

A silica-alumina hydrosol was prepared by mixing 1.00 volume of a solution of sodium silicate containing 157.0 grams of SiO_2 per liter with 1.00 volume of a solution containing 39.79 grams of aluminum sulfate and 30.51 grams of sulfuric acid per liter. The resulting colloidal solution was ejected from a nozzle in the form of globules into a column of gas oil whose depth was about eight feet. The globules of solution fell through the oil and gelled before passing into a layer of water located beneath the oil. The time of gelation for the concentrations and proportions of reactants given above was about 4 seconds. The spherical particles of gel were conducted out of the bottom of the column into a stream of water and, on removal from the water, base-exchanged with an aqueous solution of aluminum sulfate and water-washed. The globules were then slowly and uniformly dried in superheated steam at about 300° F. until shrinkage was substantially complete and the drying was continued at a gradually increasing temperature up to about 1050° F., which temperature was maintained for 0.5 hour. The silica-alumina gel resulting retained its spheroidal shape during the washing and drying operations and had a final particle

size of about 4–20 mesh and a bulk density of approximately 0.65 gram per cubic centimeter.

A quantity of 250 grams of an East Texas residuum, having a viscosity of 512 seconds at 210° F. (Saybolt Universal viscosity) and a carbon residue of 11, was contacted with 200 grams of the above prepared gel particles for 4 hours at 300° F. The unsorbed oil was drained from the particles and the oil adhering to the surface of the particles was removed by a quick wash at 170° F. with about 400 cubic centimeters of benzol. The low carbon residue fraction of the sorbed oil was recovered by extracting the oil-filled particles with 5 portions—150 cubic centimeters each—of normal hexane at a temperature of 120° F., permitting a one-half hour contact with each portion. Upon removal of the hexane, 31 grams of a deasphalted oil, having a carbon residue of only 0.7, were obtained.

The high carbon residue oil remaining sorbed in the particles was then recovered by extracting at 165° F., the particles with 3 portions—150 cubic centimeters each—of a solvent mixture containing equal portions of benzol and methyl ethyl ketone, permitting a one-half hour contact with each portion. Twenty-nine grams of an oil having a carbon residue of 8.8 were removed by this extraction.

Example 2

A quantity of 285 grams of the residuum used in Example 1, which had previously been contacted with sorbent to remove a portion of the oily constituents therefrom, and 87 grams of untreated residuum were percolated through 200 grams of gel particles, prepared as described in Example 1, for 4 hours at a temperature of 300° F. The first 35 grams, approximately, of material to drain from the particles constituted the asphalt product. The following 250 grams of oil drained from the sorbent particles were high in asphalt content and were charged to the following cycle. About 20 grams of oil were washed from the surface of the particles by applying 400 cubic centimeters of naphtha at 200° F. The particles were then extracted with five portions of 150 cubic centimeters each of paraffinic naphtha at 230° F., permitting one-half hour contact with each portion. As a result of this extraction, 48 grams of a deasphalted oil, having a carbon residue of 2.3, were obtained.

The residue of the sorbed oil was then extracted from the gel pores of the sorbent particles at 165° F. with three portions of 150 cubic centimeters each of benzol-methyl ethyl ketone mixture, permitting one-half hour contact with each portion. About 15 grams of a high carbon residue material were obtained and this material was recycled to the next sorption cycle. The particles were dried by heating and blowing with an inert gas and steam to complete the initial cycle and then were ready for re-use.

The average results of 18 consecutive cycles gave a yield of 55 per cent by weight (based on the charge stock) of deasphalted oil having a carbon residue of 2.3.

Example 3

The process of Example 2 was repeated with the exception that the high carbon residue benzol-methyl ethyl ketone extract was removed from the system instead of being recycled. The average yield, based on charge material, after 18 consecutive cycles was 55 per cent by weight of deasphalted oil having a carbon residue of 2.4, 16 per cent of the high carbon residue material extracted with benzol-methyl ethyl ketone mixture having a carbon residue of 9.7, and 29 per cent by weight of asphalt.

Example 4

A quantity of about 500 grams of East Texas residuum, which had previously been contacted with sorbent to remove a portion of the oily constituents therefrom, and 131 grams of untreated residuum, having a viscosity of 512 seconds at 210° F. (Saybolt Universal viscosity) and a carbon residue of 11, were percolated through 200 grams of silica-alumina gel particles (5 to 7 mesh size) having a bulk density of 0.48 gram per cubic centimeter, for 2 hours at 300° F. The first 32 grams, approximately, of material to drain from the particles constituted the asphalt product. The following 438 grams of oil drained from the particles were charged to the following cycle. About 62 grams of oil were quick-washed from the surface of the particles by applying 400 cubic centimeters of normal hexane at 180° F. The particles were then extracted with five portions of normal hexane—150 cubic centimeters each—at 150° F., permitting one-half hour contact with each portion. As a result of this extraction, 77 grams of a deasphalted oil, having a carbon residue of 2.0, were obtained.

The residue of sorbed oil was then extracted from the gel sorbent at 165° F. with three portions of 150 cubic centimeters each of benzol-methyl ethyl ketone mixture, permitting one-half hour contact with each portion. About 17 grams of a high carbon residue material were obtained, and this material was withdrawn as one of the products. The sorbent was dried by heating and blowing with an inert gas and steam to complete the cycle and was then ready for re-use.

The average results from 10 consecutive cycles gave a yield, based on the weight of the charge, of 59 per cent by weight of deasphalted oil having a carbon residue of 2.0.

Example 5

The proess of Example 4 was repeated, using 200 grams of silica-alumina gel sorbent having a bulk density of 0.60 gram per cubic centimeter. Five hundred grams of previously contacted oil, together with 98 grams of untreated residuum, were percolated through the sorbent for 4 hours at 275° F. The asphalt product was about 30 grams. About 45 grams of oil were washed from the surface of the sorbent particles by applying at a temperature of 275° F., 400 cubic centimeters of an acid-treated paraffinic naphtha having an A. P. I. gravity of 52.4, an A. S. T. M. initial boiling point of 291° F., an end point of 384° F., and an aromatic content of 3.5 per cent (per cent volume, A. S. T. M. Method E. S. 45a). The sorbent particles were then extracted with five portions of the same naphtha at 275° F. to obtain about 56 grams of a deasphalted oil with a carbon residue of 2.1. The particles were then extracted with three portions of a mixture of the above naphtha and methyl ethyl ketone at 165° F. About 7 grams of a high carbon residue material were obtained and removed from the process.

The average results from 15 consecutive cycles gave a yield, based on the weight of the charge, of 57 per cent by weight of deasphalted oil having a carbon residue of 2.1.

The following examples were carried out em-

ploying various paraffinic solvents for extracting deasphalted oil. The procedure used was that described in Example 1, employing an East Texas residuum oil as the charge stock. The results of deasphalting are summarized below:

Example	FIRST SOLVENT EXTRACTION				SECOND SOLVENT EXTRACTION			
	Solvent	Temp. °F.	Extracted Oil		Solvent	Temp. °F.	Extracted Oil	
			Grams	Carbon Residue			Grams	Carbon Residue
6	Stoddard Solvent	300	64	2.4	Benzol-Methyl Ethyl Ketone	165	9	11.8
7	V. M. and P. Naphtha	150	29	1.9	do	165	38	7.3
8	do	190	51	2.0	do	165	18	7.2
9	n-Hexane	150	37	1.1	do	165	32	8.5
10	Petroleum ether	62	17	1.5	do	165	46	4.7
11	do	85	23	1.5	do	165	39	5.5
12	n-Pentane	62	23	1.1	do	165	40	4.0
13	do	85	25	1.1	do	165	37	6.1
14	ASTM Naphtha	120	28	1.2	do	165	30	8.3

From the above, it will be evident that paraffins are excellent selective solvents for the low carbon residue mineral oil fractions sorbed by porous contact materials having a structure corresponding to that of an inorganic oxide gel having a substantially uniform porosity of low macropore volume and an average pore diameter not exceeding about 125 Angstrom units. It is to be noted that other porous materials not having the above defined characteristics, such as clays and pelleted or extruded synthetic siliceous composites, fail to reduce the carbon residue of the original stock to any appreciable degree and hence are of comparatively little use in the present process. The distinction between the sorbents employed in the present deasphalting process and the clays and pelleted materials indicated above is believed to be in the small, uniform, substantially microporous structure of the former, while the latter contain a high proportion of relatively large voids inherently present or formed therein during the pelleting operation. The low density of pelleted synthetic sorbents indicates that they contain a substantial proportion of large voids having particle diameters of 1,000–10,000 Angstrom units and larger. These relatively large voids present in the non-uniform structure render the material ineffective for use as a sorbent in the present invention.

This application is a continuation-in-part of co-pending application Serial Number 664,708, filed April 24, 1946, and now abandoned.

I claim:

1. A process for deasphalting an asphalt-bearing petroleum stock, which comprises contacting said stock with a porous particle-form inorganic oxide gel type contact material in which most of the pores are micropores and the volume of pores having radii greater than about 100 Angstrom units is less than about 30 per cent of the total pore volume and in which the particles are greater than about 30 mesh size to effect sorption of the oily constituents into the pores of said contact material while asphaltic constituents remain unsorbed, thereafter separating said contact material from said unsorbed asphaltic constituents, selectively extracting said contact material with a paraffinic solvent to remove therefrom a deasphalted product characterized by a low carbon residue content, and thereafter extracting the remainder of sorbed oily constituents with a polar solvent therefor.

2. A process for deasphalting an asphalt-bearing petroleum stock, comprising contacting said stock with uniform, substantially microporous inorganic oxide gel particles having a particle size not less than about 60 mesh and in which the volume of pores having radii greater than about 100 Angstrom units is less than about 30 per cent of the total pore volume to effect sorption of the oily constituents of said stock into the pores of said particles while asphaltic constituents remain unsorbed, thereafter separating said gel particles from said unsorbed asphaltic constituents, selectively extracting said particles with a paraffinic solvent to remove therefrom a deasphalted product characterized by a low carbon residue content, and thereafter extracting the remainder of sorbed oily constituents with a polar solvent therefor.

3. A process for deasphalting an asphalt-bearing petroleum stock, which comprises contacting said stock with uniform, substantially microporous siliceous gel particles having a particle size not less than about 60 mesh and in which the volume of pores having radii greater than about 100 Angstrom units is less than about 30 per cent of the total pore volume to effect sorption of the oily constituents of said stock into the pores of said particles while asphaltic constituents remain unsorbed, thereafter separating said gel particles from said unsorbed asphaltic constituents, removing adhering constituents from the surface of said particles, selectively extracting said particles with a paraffinic solvent to remove therefrom a deasphalted product characterized by a low carbon residue content, and thereafter extracting the remainder of sorbed oil constituents with a polar solvent therefor.

4. A process for deasphalting an asphalt-bearing petroleum stock, which comprises contacting said stock with a contact material in the form of spheroidal siliceous gel particles characterized in that it consists substantially entirely of spheroidal contact material particles having an average diameter greater than about .022 inch and having less than 30 per cent of its pore volume devoted to pores having radii larger than about 100 Angtrom units, the remaining pore volume being devoted to smaller pores, whereby the oily constituents of said stock are sorbed into the pores of said particles while asphaltic constituents remain unsorbed, thereafter separating said gel particles from said unsorbed asphaltic constituents, removing adhering constituents from the surface of said particles, selectively extracting said particles with a paraffinic solvent to remove therefrom a deasphalted product characterized by a low carbon residue content, and thereafter extracting

the remainder of sorbed oily constituents with a polar solvent therefor.

5. A process for deasphalting an asphalt-bearing petroleum stock, comprising contacting said stock with a porous particle-form inorganic oxide gel type contact material in which most of the pores are micropores and the volume of pores having radii greater than about 100 Angstrom units is less than about 30 per cent of the total pore volume and in which the particles are coarser than about 60 mesh size to effect sorption of the oily constituents of said stock into the pores of said particles while asphaltic constituents remain unsorbed, thereafter separating said gel particles from said unsorbed asphaltic constituents, removing adhering constituents from the surface of said particles and selectively extracting said particles with hexane to remove therefrom a deasphalted product characterized by a low carbon residue content and thereafter extracting the remainder of said sorbed oily constituents with a ketonic solvent mixture therefor.

6. A process for deasphalting an asphalt-bearing petroleum stock, comprising contacting said stock with a porous particle-form inorganic oxide gel type contact material in which most of the pores are micropores and the volume of pores having radii greater than about 100 Angstrom units is less than about 30 per cent of the total pore volume and in which the particles are coarser than about 60 mesh size to effect sorption of the oily constituents of said stock into the pores of said particles while asphaltic constituents remain unsorbed, thereafter separating said gel particles from said unsorbed asphaltic constituents, removing adhering constituents from the surface of said particles and selectively extracting said particles with a paraffinic naphtha to remove therefrom a deasphalted product characterized by a low carbon residue content and thereafter extracting the remainder of said sorbed oily constituents with a ketonic solvent mixture therefor.

7. A process for deasphalting an asphalt-bearing petroleum stock, comprising contacting said stock with a porous particle-form inorganic oxide gel type contact material in which most of the pores are micropores and the volume of pores having radii greater than about 100 Angstrom units is less than about 30 per cent of the total pore volume and in which the particles are coarser than about 60 mesh size to effect sorption of the oily constituents of said stock into the pores of said particles while asphaltic constituents remain unsorbed, thereafter separating said gel particles from said unsorbed asphaltic constituents, removing adhering constituents from the surface of said particles and selectively extracting said particles with petroleum ether to remove therefrom a deasphalted product characterized by a low carbon residue content and thereafter extracting the remainder of said sorbed oily constituents with a ketonic solvent mixture therefor.

8. A process for deasphalting an asphalt-bearing petroleum stock, comprising contacting said stock with a particle-form inorganic oxide gel contact material of substantial particle size as distinguished from powdered contact material, said contact material being of a pore structure wherein less than 30 per cent of the total pore volume is occupied by pores of greater than about 100 Angstrom units radius, controlling the relationship between particle diameter and the contact time and temperature to effect the sorption of the oily constituents of said stock into the pores of said particles while asphaltic constituents remain unsorbed, thereafter separating said gel particles from said unsorbed asphaltic constituents and selectively extracting said particles with a paraffinic solvent to remove therefrom a deasphalted product characterized by a low carbon residue content and thereafter extracting the remainder of sorbed oily constituents with a polar solvent therefor.

9. A process for deasphalting an asphalt-bearing petroleum stock, comprising contacting said stock with a porous inorganic oxide gel consisting of particles having a greater average diameter than about .022 inch and having less than about 10 per cent of its pore volume taken up by pores which are greater than 100 Angstrom units in radius, the remaining pore volume being taken up by smaller pores, whereby the oily constituents of said stock are sorbed into the pores of said particles while asphaltic constituents remain unsorbed, thereafter separating said gel particles from said unsorbed asphaltic constituents, selectively extracting said particles with a paraffinic solvent to remove therefrom a deasphalted product characterized by a low carbon residue content and thereafter extracting the remainder of said sorbed oily constituents with a solvent mixture of methyl ethyl ketone and benzol.

10. A continuous process for removing asphalt from a liquid feed mixture containing oily and asphaltic constituents, which comprises contacting said feed with a particle-form porous contact material having an inorganic oxide gel structure in which the pores are mostly micropores, the volume of pores having radii greater than about 100 Angstrom units being less than about 30 per cent of the total pore volume, controlling the relative relationships of contact time and temperature and of particle size to effect sorption of the oily constituents of said feed in the pores of said contact material while leaving the asphaltic constituents substantially unsorbed, separating said contact material from said asphaltic constituents, removing adhering constituents from the surface of the particles of contact material, extracting said particles with a paraffinic solvent to remove therefrom a substantially asphalt-free product characterized by a low carbon residue content, extracting the remainder of sorbed oily constituents from the pores of said particles with a polar solvent, heating the particles to evaporate polar solvent from the pores thereof, and thereafter bringing the dried particles into contact with a fresh feed mixture of oily and asphaltic constituents.

11. A continuous process for deasphalting an asphalt-bearing petroleum stock, which comprises contacting said stock with a porous particle-form inorganic oxide gel type contact material in which most of the pores are micropores and the volume of pores having radii greater than about 100 Angstrom units is less than about 30 per cent of the total pore volume and in which the particles are coarser than about 60 mesh size to effect the sorption of the oily constituents of said stock in the pores of said contact material while leaving the asphalt constituents substantially unsorbed, separating said contact material from said asphaltic constituents, removing adhering constituents from the surface of said contact material, extracting the particles of said contact material with a paraffinic solvent to remove a deasphalted product therefrom, extracting the remainder of sorbed oily constituents from the pores of said particles with a polar solvent, removing polar solvent from the pores of said particles by maintaining the particles at an elevated temperature

and sweeping out resulting solvent vapors with an inert gas, steaming the solvent-free particles and contacting the dried particles with additional asphalt-bearing petroleum stock.

12. A continuous process for deasphalting an asphalt-bearing petroleum stock, which comprises contacting said stock with a particle-form contact material of substantial particle size as distinguished from powdered material, said contact material having an inorganic oxide gel structure and being of a pore structure wherein less than 30 per cent of the total pore volume is occupied by pores of greater than about 100 Angstrom units radius, controlling the relationship between particle diameter and the contact time and temperature to effect sorption of the oily constituents of said stock in the pores of said contact material while leaving substantially unsorbed the asphalt constituents, separating said contact material from said unsorbed constituents, washing the particles of contact material containing sorbed oily constituents with a suitable solvent to remove adhering material on the outer surface of said particles, selectively extracting sorbed oily constituents from the pores of said particles with a paraffinic solvent to yield a deasphalted product characterized by a low carbon residue content, thereafter extracting the remainder of said sorbed oily constituents from the pores of said particles with a polar solvent, heating and blowing the remaining particles with an inert gas and steam to dry the same and bringing the dried particles into contact with additional asphalt-bearing petroleum stock.

13. A process for deasphalting an asphalt-bearing petroleum stock comprising contacting said stock with a porous particle-form sorbent material having an inorganic oxide gel structure in which the pores are mostly micropores and the volume of pores having radii greater than about 100 Angstrom units is less than about 30 per cent of the total pore volume, controlling the contact time, the temperature, and the relative amounts of stock and sorbent contacted to effect sorption of the oily constituents of said stock into the pores of said sorbent while leaving the asphaltic constituents unsorbed, thereafter separating said oil-containing sorbent from said unsorbed asphaltic constituents, selectively extracting said oil-containing sorbent with a paraffinic solvent to remove therefrom a deasphalted product characterized by a low carbon residue content, and thereafter extracting the remainder of sorbed oily constituents with a polar solvent therefor.

14. A process for deasphalting an asphalt-bearing petroleum stock, which comprises sorbing the oily constituents of said stock into the pores of a porous sorbent contact material having an inorganic oxide gel structure, the particles of which are greater than about 60 mesh size and in which less than 30 per cent of the total pore volume is occupied by pores having radii greater than about 100 Angstrom units, while leaving substantially unsorbed the asphaltic constituents, thereafter separating the oil-containing sorbent material from said unsorbed asphaltic constituents, selectively extracting said sorbent material with a paraffinic solvent to remove therefrom a deasphalted product characterized by a low carbon residue content, and thereafter extracting the remainder of sorbed oily constituents with a polar solvent therefor.

15. A process for deasphalting an asphalt-bearing petroleum stock, comprising contacting said stock for a suitable time and temperature with a porous particle-form contact material having an inorganic oxide gel structure in which the pores are mostly micropores and the volume of pores having radii larger than about 100 Angstrom units is less than about 30 per cent of the total pore volume to effect sorption of the oily constituents of said stock into the pores of said contact material while asphaltic constituents remain unsorbed, thereafter separating said contact material from said unsorbed asphaltic constituents, removing adhering constituents from the surface of said contact material, selectively extracting said contact material with a paraffinic solvent to remove therefrom a deasphalted product characterized by a low carbon residue content, and thereafter extracting the remainder of sorbed oily constituents with a polar solvent therefor.

16. A process for deasphalting an asphalt-bearing petroleum stock, comprising contacting said stock for a suitable time and at a suitable temperature with a porous particle-form contact material having an inorganic oxide gel structure in which the pores are mostly micropores and the volume of pores having radii larger than about 100 Angstrom units is less than about 30 per cent of the total pore volume and in which the particles are of greater diameter than about 60 mesh size to effect sorption of the oily constituents of said stock into the pores of said contact material while asphaltic constituents remain unsorbed, thereafter separating said contact material from said unsorbed asphaltic constituents, removing adhering constituents from the surface of said contact material and selectively extracting said contact material with a paraffinic solvent to remove therefrom a deasphalted product characterized by a low carbon residue content, and thereafter extracting the remainder of sorbed oily constituents with a polar solvent therefor.

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