

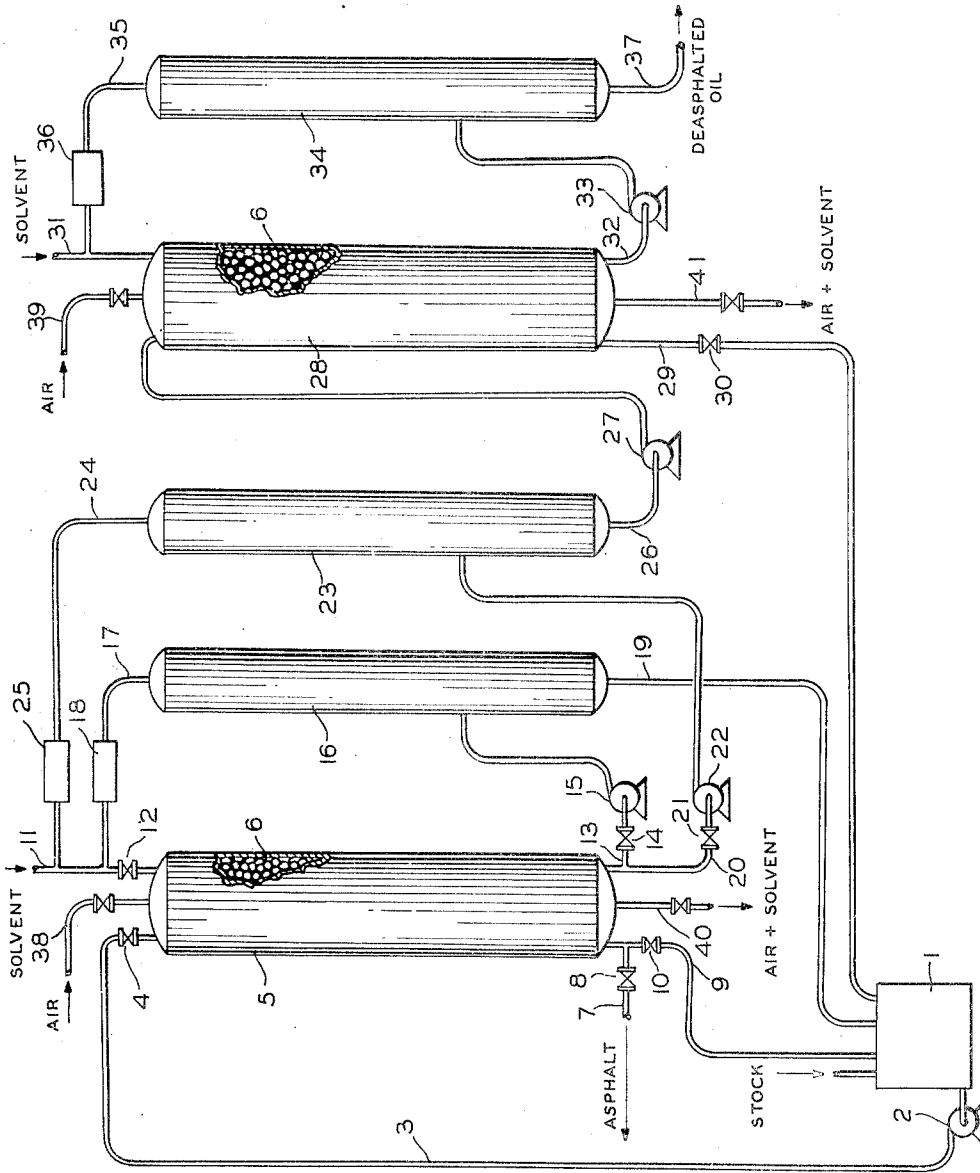
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DEASPHALTING PROCESS

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DEASPHALTING PROCESS

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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 bores of said material, leaving asphalt as the unsorbed portion.

Heretofore, removal of asphalt from petroleum oil has usually been accomplished by one of five methods. These may be summarized as follows:

1. Deasphalting by distillation.
2. Deasphalting with clay.
3. Deasphalting with acids, such as sulfuric acid.
4. Deasphalting by use of precipitating agents, such as the metallic chlorides.
5. Deasphalting with solvents.

While the last named method has generally been found to be the most satisfactory of the group and is most commonly used at the present time, even it is subject to certain economic and operational disadvantages. Deasphalting with solvent is predicated upon the ability of certain solvents, such as propane and related hydrocarbons, to precipitate asphaltic materials from asphalt-bearing stock. The deasphalting processes using light hydrocarbon solvents are relatively expensive, however, being operated at temperatures which require 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 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 a 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

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such compounds, and the difficulties encountered in disposing of sludges resulting from such operations.

In accordance with the present invention, a new method has been discovered for deasphalting 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. This process accordingly affords a new deasphalting method and is a relatively simple operation which does not require the use of corrosive chemicals, high pressures and high temperatures, heretofore involved in conventional deasphalting operations.

The process of this invention is carried out by bringing the asphalt-containing stock to be treated in contact with a suitable solid, porous sorbent particle-form material and thereafter separating the asphalt and any unsorbed oil from the oil-saturated material. The contacting is done 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 oil, various solvents, and deasphalted oil obtained from previous operations.

Recovery of deasphalted oil from the pores of the sorbent is effected by solvent extraction or displacement with steam. Suitable solvents include materials such as benzene-methylethyl ketone solutions and the like. The solvent so employed can be recovered upon separation from the deasphalted 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 Mesh Size of Sorbent (Tyler)	4-8	30-60	2.3	2.3	2.3	2.3	5.1
Sorption Zone Contact Time	24 hrs.	24 hrs.	2 min.	2 min.	2 hrs.	4-8	4-8
Sorption Zone Temperature, °F.	150	150	150	150	150	72 hrs.	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, Per Cent			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, Per Cent			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, per cent 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 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 absorbents for use in the process of this invention.

Likewise, irregularly shaped porous absorbent 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 likewise are 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 per cent 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 absorbent 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. For this reason, it is usually preferable to employ the same solvent for washing as is used in the following extraction step.

Generally, the deasphalted oil will be recovered from the pores of the sorbent by solvent extraction. The solvent so employed should be characterized by a high solvent power for the oil. Conventional oil solvents, such as naphtha, benzene, hexane, and the like, are suitable for this purpose. A particularly effective solvent for use as an extractant is one or more of the above-mentioned oil solvents containing at least a minor proportion of a polar solvent such as, for example, methylethyl ketone or diethyl carbonate.

After the 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 out 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, contacting the asphalt concentrate thus obtained with more sorbent and repeating this cycle until the desired yields of deasphalted oil were obtained upon solvent extraction of the sorbent particles. Each contact was termed a step and generally more than one step was required to effectively deasphalt the stock being treated.

A suitable continuous process consisted of slowly percolating the asphaltic stock through a

column of sorbent maintained at a comparatively high temperature, that is, from about 250° F. to about 350° F. The sorbed oil, having a relatively high carbon residue, is then solvent-extracted from the sorbent. The solvent is recovered by fractional separation from the oil and re-used. The sorbed oil is then percolated through a second column of sorbent maintained at a lower temperature range between about 150° F. and about 250° F. Asphalt is recovered from the high temperature stage and deasphalted oil of low carbon residue from the low temperature stage. Unsorbed oil of relatively high carbon residue obtained from the low temperature stage is transferred to the high temperature stage where it is mixed with the stock being charged to the system. The sorbent particles are periodically regenerated and the deasphalting operation is repeated.

A suitable system for carrying out the continuous process described above is shown in the accompanying drawing. Asphalt-bearing stock is stored in tank 1 from which it is forced by pump 2 through conduit 3 furnished with a valve 4 and passes into tower 5, which is suitably packed with sorbent particles 6. The stock flows through the tower, which is maintained at a temperature between 250° F. and about 350° F. The oily constituents of the charge stock are sorbed, while asphalt passes through the tower and is withdrawn at outlet 7, which is furnished with a control valve 8.

Upon completion of the flow of asphalt, valves 4 and 8 are closed and the unsorbed, asphalt-bearing oil remaining in the tower is drained through conduit 9, furnished with control valve 10, and returns to feed tank 1. After tower 5 is drained, valve 10 is closed and a small amount of solvent is introduced through conduit 11, which is furnished with a control valve 12. Solvent flows down through the tower, removing any unsorbed oil still adhering to the outer surface of the sorbent. The mixture passes through outlet 13, furnished with control valve 14, and is forced by pump 15 to stripping column 16 where the solvent is distilled from the oily constituents, passes as vapor through outlet 17, is condensed to a liquid in condenser 18, and enters the solvent feed line 11, serving to augment the supply of solvent. Stripped oil drains from the bottom of column 16 through conduit 19 and returns to feed tank 1. Then valve 14 is closed and additional solvent is introduced through conduit 11 and control valve 12. This solvent flows down through the tower slowly, extracting sorbed oil of relatively high carbon residue from the sorbent. The mixture of solvent and extracted oil passes out through outlet 20, furnished with control valve 21, and is forced by pump 22 to stripping column 23 where the solvent is distilled from the extracted oil, passes as vapor through outlet 24, is condensed to a liquid in condenser 25, and enters the solvent feed line 11.

Extracted oil is removed from the bottom of column 23 through outlet 26 and is forced by pump 27 to tower 28, which is suitably packed with sorbent particles 6. The oil flows down through the tower, which is maintained at a temperature of between 150° F. and about 250° F. Unsorbed oil of relatively high carbon residue passes through outlet 29, furnished with control valve 30, and returns to feed tank 1. Solvent is then introduced through conduit 31 and flows down the tower, extracting sorbed, deasphalted oil of low carbon residue from the sorbent particles. The mixture of solvent and extracted oil

passes through outlet 32 and is forced by pump 33 to stripping column 34, where solvent is distilled off, passing through outlet 35 and condenser 36 to join the solvent feed line 31.

The product of deasphalted oil is withdrawn from the bottom of column 34 through outlet 37. The sorbent particles are periodically regenerated by passing hot air through conduits 38 and 39 and withdrawing a mixture of air and solvent from outlets 40 and 41, respectively. The solvent may be recovered from this mixture and re-used.

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 SiO₂ 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 operation and had a final particle size of about 4-20 mesh.

A quantity of 500 grams of residuum from a Mid-Continent crude was contacted with 750 grams of the above prepared gel particles for 16 hours at 150° F. The unsorbed oil and asphalt were removed. The sorbent particles were given a quick wash with a solvent mixture containing equal volumes of benzene and methylethyl ketone. The time of contact between solvent and sorbent particles in said wash was insufficient for the solvent to penetrate the pores of the sorbent. The asphalt concentrate previously obtained was contacted with an additional 388 grams of sorbent for an additional 16 hours at 150° F. The sorbent particles were again given a quick wash with the above solvent. Deasphalted oil was then obtained by extracting the two batches of sorbent particles with a solvent mixture containing equal volumes of benzene and methylethyl ketone. The time of contact between sorbent particles and solvent in this instance was sufficient for the solvent to penetrate the pores of the sorbent. Five extractions of 30 minutes each were made to substantially completely remove deasphalted oil from the sorbent particles. Separation of the solvent from the product so obtained permitted the recovery of 330 grams of deasphalted oil, representing a yield of 66 per cent of the charge stock. The carbon residue of the oil was reduced from 4.6 to 1.4.

A summary of the properties of the oil before and after deasphalting are given below:

	Unrefined Residuum	Deasphalted Oil
Gravity, °A. P. I.	21.8	24.6
Pour Point, °F.	90	-----
S. U. V. at 210° F.	155	88.3
Color	Black	Dark Green
Carbon Residue	4.6	1.4

Example 2

A quantity of 2000 grams of the residuum used in Example 1 was contacted with 3000 grams of the gel particles, prepared as described in Example 1, for 16 hours at 150° F. The unsorbed asphalt concentrate obtained was contacted with an additional quantity of sorbent. This operation was repeated three more times to give a five-step process. In each step, the sorbent particles were given a quick wash with a solvent mixture containing equal volumes of benzene and methylethyl ketone to remove unsorbed oil adhering to the surface thereof. Deasphalted oil was then extracted separately from each of the batches of sorbent with a solvent mixture containing equal volumes of benzene and methylethyl ketone. The conditions of contact, together with the amount of deasphalted oil obtained from each step, are listed below:

Step	Time of Contact, Hours	Temp., °F.	Sorbent, Grams	Deasphalted Oil, Grams
1	16	150	3,000	912
2	16	150	1,050	418
3	16	150	910	171
4	16	250	624	143
5	16	250	329	74

The total quantity of sorbent used was, after extraction, combined and again extracted with additional solvent to give an additional 57 grams of deasphalted oil. The total recovery product was 88.3 per cent, based on the charge stock, and the carbon residue was reduced to 2.5.

Example 3

A quantity of 115 grams of the residuum used in Example 1 was slowly percolated over a period of 16 hours through a column containing 353 grams of sorbent particles prepared as described in Example 1. Unsorbed oil and asphalt passing through the column, which was maintained at a temperature of 212° F., were conducted over a period of 16 hours through a second column of 300 grams of sorbent maintained at a temperature of 300° F. Asphalt was removed from the second column and deasphalted oil was solvent-extracted with a benzene-methylethyl ketone mixture from the first column. Sorbed oil from the second column was then extracted and recycled to the first column. A total of 18 cycles of operation were carried out, giving a quantity of deasphalted oil of approximately 95 grams per cycle. The deasphalted oil so obtained had a carbon residue of 1.7 and represented a yield of 82.9 per cent, based on the charge of residuum.

Example 4

A quantity of asphalt-bearing East Texas residuum was contacted with a supply of silica-alumina spheroidal gel particles having a bulk density of 0.685 gram per cubic centimeter and prepared by a method similar to that described in Example 1.

The deasphalting process was carried out by the continuous operation described above, the temperature of treatment being 300° F. in the high temperature stage of the first tower and 212° F. in the low temperature stage of the second tower.

A similar deasphalting process, using spheroidal silica-alumina gel particles having a bulk density

a silica-alumina composite. An East Texas residuum having a carbon residue of 10.5 was used as the charge stock. The contacting conditions and the comparative degree of deasphalting in each example, as indicated by the reduction in carbon residue, are summarized in the table below:

Ex-ample	Porous Medium	Bulk Den- sity	Particle Size	Operating Method	Contacting Conditions			Deasphalted Oil		
					Time, Hrs.	Temp., °F.	Sorbent/Oil Ratio (by wt.)	Yield, per cent wt.		Carbon Resi- due
								Based on Charge	Based on Sorbent	
8.....	Silica-Alumina Gel.....	0.685	4-8 Mesh.....	1-Step Batch..	4	212	0.4	11.7	29.2	1.6
9.....	Silica Gel.....	0.725	3-8 Mesh.....	3-Step Batch..	4	212	1.5	12.6	8.4	3.9
10.....	Superfiltral Pellets.....	0.740	3/16" Diam. x 1/8" Long.	2-Step Batch..	4	212	1.0	7.4	7.4	7.8
11.....	Pellets of a Synthetic Silica-Alumina Com- posite.	0.551	1/8" Diam. x 1/16" Long.	1-Step Batch..	4	212	0.27	10.0	37.0	10.0

of 0.506, was carried out. The contacting conditions and physical properties of the resulting products are summarized in the table below:

From the above, it will be evident that porous contact materials having a structure correspond- ing to that of an inorganic oxide gel having a

Charge Stock	Bulk Density of Sorbent.	Contacting Conditions			Fraction	Yields, Percent Wt.	Physical Properties				
		Time, Hrs.	Temp., °F.	Sorbent/Oil Ratio (by wt.)			S. U. V. at 210° F., seconds	Carbon Residue	Melting Point, °F.	Penetra- tion at 77° F.	Carbon Residue after Solvent Treating
East Texas Residuum.	0.506	4	212/300	3.0	Charge.....	58.0	512	11.1	141	24.5	2.2
					Deasphalted Oil... Asphalt.....						
Do.....	0.685	4	212/300	4.9	Charge.....	57.5	512	11.1	128	28.5	0.5
					Deasphalted Oil... Asphalt.....						

From the results set forth above, it will be seen by a comparison of sorbents of 0.506 and 0.685 bulk density that, on the basis of carbon residue, the higher density sorbent gives a more satisfactory product.

A series of experiments were carried out using silica-alumina gel particles in both the batch and continuous operating methods described above with stocks of different asphalt contents. The contacting conditions and physical properties of the resulting products are given in the table below:

substantially uniform porosity of low macropore volume with an average pore diameter not ex- ceeding about 125 Angstrom units function as excellent sorbents in permitting the deasphalting of an asphalt-bearing petroleum stock. Various other porous materials, such as clays, and pel- leted or extruded synthetic siliceous composites, such as those employed in Examples 10 and 11, fail to reduce the carbon residue of the original charge stock to any appreciable degree and hence are of comparatively little use in the present process. The distinction between the sorbents

Exam- ple	Approx. Asphalt Content (Per cent wt.) of Charge Stock	Bulk Density of Sorbent	Operating Method	Contacting Conditions			Products						
				Time, Hrs.	Temp., °F.	Sorbent/Oil Ratio (by wt.)	Fraction	Yields, Per cent Wt.	Physical Properties				
						S. U. V. at 210° F., seconds			Car- bon Resi- due	Color (Lovibond 1/4" cell)			
5.....	10	0.730	5-Step Batch..	16	150/250	3.4	Charge.....	88.7	155	122.8	4.6	2.5	Black. Dk. Green.
						Deasphalted Oil... Asphalt.....	6.5						
6.....	38	0.685	2-Stage Con- tinuous.	4	212/300	4.9	Charge.....	57.5	512	95.0	11.1	1.7	Black. 550.
						Deasphalted Oil... Asphalt.....	43.6						
7.....	60	0.730	1-Step Batch..	16	250	1.5	Charge.....	30.3	52.9				Black.
						Deasphalted Oil... Asphalt.....	52.9						

It will be seen from the above results that stocks having asphalt contents as high as 60 per cent by weight may be effectively treated to re- move asphalt therefrom by the process of the present invention.

A series of experiments were carried out using, in addition to the inorganic oxide gel sorbents of this invention, various other porous materials such as pellets of Superfiltral clay and pellets of

employed in the present deasphalting process and the clays and pelleted materials indicated above is believed to be in the small, uniform, substan- tially 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 the pelleted synthetic sorbent indicates that it contains a substantial proportion of large voids

having pore diameters of 1000-10,000 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 655,580, filed March 19, 1946, now abandoned.

We claim:

1. A process for deasphalting an asphalt-bearing petroleum stock, comprising contacting said stock with a porous particle-form sorbent material 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 pores of said sorbent, while leaving the asphaltic constituents unsorbed, thereafter separating said oil-containing sorbent from said unsorbed asphaltic constituents and removing sorbed oily constituents from the pores of said sorbent to give a deasphalted product.

2. 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, 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 constituent and removing sorbed oily constituents from the pores of said sorbent to give a deasphalted product.

3. A process for deasphalting an asphalt-bearing petroleum stock, which comprises contacting said stock with a porous particle-form inorganic oxide gel 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 60 mesh size, whereby the oily constituents of said stock are sorbed into the pores of said contact material, while asphaltic constituents remain unsorbed, thereafter separating said contact material from said unsorbed asphaltic constituents and removing sorbed oily constituents from the pores of said contact material to give a deasphalted product.

4. A process for deasphalting an asphalt-bearing petroleum stock, comprising contacting said stock for a suitable time and at a suitable temperature for sorption of the oily constituents of said stock with a porous solid particle-form 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, whereby the oily constituents of said stock are sorbed into the pores of said contact material, while asphaltic constituents remain unsorbed, thereafter separating said contact material from said unsorbed asphaltic constituents and removing sorbed oily constituents from the pores of said contact material to give a deasphalted product.

5. A process for deasphalting an asphalt-bearing petroleum stock, comprising contacting said

stock with a uniform, substantially microporous medium made up of particles in which the volume of pores having radii greater than about 100 Angstrom units is less than about 10 per cent of the total pore volume, controlling the relative relationships of contact time and temperature and particle size to effect sorption of the oily constituents of said stock into the pores of said medium, while asphaltic constituents remain unsorbed, separating said medium from said unsorbed asphaltic constituents and removing sorbed oily constituents from the pores of said medium to give a deasphalted product.

6. A process for deasphalting an asphalt-bearing petroleum stock, which comprises contacting said stock with a uniform, substantially microporous siliceous gel contact material in the form of spheroidal particles having an average diameter greater than about 0.022 inch and having less than 30 per cent of its pore volume devoted to pores having radii larger than about 100 Angstrom 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 particles from said unsorbed asphaltic constituents, washing the particles containing sorbed oily constituents with a suitable solvent to remove adhering material from the outer surface of said particles, solvent-extracting the sorbed oily constituents from the particles and thereafter recovering said sorbed oily constituents from the solvent solution thereof to give a deasphalted oily product.

7. 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, separating said particles from said unsorbed asphaltic constituents, washing adhering material from the outer surface of said particles and thereafter solvent-extracting sorbed oily constituents from the pores of said particles to give a deasphalted product.

8. 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 between about 4 and about 20 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, whereby the oily constituents of said stock are sorbed into the pores of said particles, while asphaltic constituents remain unsorbed, separating said particles from said unsorbed asphaltic constituents, removing unsorbed stock adhering to the surface of said particles and thereafter removing sorbed oily constituents from the pores of said particles to give a deasphalted product.

9. 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 30 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 unadsorbed, separating said particles from said unadsorbed asphaltic constituents, removing unadsorbed stock adhering to the surface of said particles and thereafter removing sorbed oily constituents from the pores of said particles to give a deasphalted product.

10. 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 the particle diameter and the contact time and temperature to effect sorption of the oily constituents of said stock into the pores of said particles, while asphaltic constituents remain unadsorbed, separating said particles from said unadsorbed asphaltic constituents, removing unadsorbed stock adhering to the surface of said particles and thereafter removing sorbed oily constituents from the pores of said particles to give a deasphalted product.

11. A continuous process for deasphalting an asphalt-bearing petroleum stock, comprising slowly percolating said stock through a column of uniform, substantially microporous particle-form contact material maintained at a temperature between about 250° F. and about 350° F., having a particle size not less than about 60 mesh and in which most of the pores are 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, to effect sorption of the oily constituents of said stock into the pores of said particles, while asphaltic constituents remain unadsorbed, separating said unadsorbed asphaltic constituents from said particles and solvent-extracting said sorbed oily constituents from the pores of said particles, passing said extracted constituents through a second column of the aforementioned contact material maintained at a temperature between about 150° F. and about 250° F., recycling material unadsorbed in the second column of contact material to the first column of contact material and solvent-extracting sorbed oily constituents from the pores of said contact material in the second column to give a deasphalted product.

12. A continuous process for deasphalting an asphalt-bearing petroleum stock, comprising slowly percolating said stock through a column of uniform, substantially microporous particle-form contact material consisting of particles of substantial size as distinguished from powder and in which the total pore volume is taken up mostly by micropores, there being less than about 30 per cent of pores having radii greater than about 100 Angstrom units, said column of contact material being maintained at a temperature between about 250° F. and about 350° F., whereby the oily constituents of said stock are sorbed into the pores of said particles, while asphaltic constituents remain unadsorbed, separating said unadsorbed asphaltic constituents from said particles, removing unadsorbed material adhering to the surface of said particles and solvent-extracting said sorbed oily constituents from the pores of said particles, passing said extracted constituents through a second column of the aforementioned sorbent main-

tained at a temperature between about 150° F. and about 250° F., recycling material unadsorbed in the second column of sorbent to the first column of sorbent and solvent-extracting sorbed oily constituents from the pores of said sorbent in the second column to give a deasphalted product.

13. A continuous process for deasphalting an asphalt-bearing stock, comprising slowly percolating said stock through a column of uniform, substantially microporous inorganic oxide gel particles maintained at a temperature between about 250° F. and about 350° F. and having a particle size not less than about 30 mesh and a total pore volume made up mostly of micropores, there being less than about 30 per cent of pores having radii greater than about 100 Angstrom units, whereby the oily constituents of said stock are sorbed into the pores of said particles, while asphaltic constituents remain unadsorbed, separating said unadsorbed asphaltic constituents from said particles, removing unadsorbed material adhering to the surface of said particles and solvent-extracting said sorbed oily constituents from the pores of said particles, passing said extracted constituents through a second column of the aforementioned sorbent maintained at a temperature between about 150° F. and about 250° F., recycling material unadsorbed in the second column of sorbent to the first column of sorbent and solvent-extracting sorbed oily constituents from the pores of said sorbent in the second column to give a deasphalted product.

14. A continuous process for deasphalting an asphalt-bearing petroleum stock, comprising contacting said stock with uniform, substantially microporous spheroidal siliceous gel particles maintained at a temperature between about 250° F. and about 350° F. and having a particle size between about 4 and about 20 mesh and a total pore volume made up mostly of micropores, there being less than about 30 per cent of pores having radii greater than about 100 Angstrom units, whereby the oily constituents of said stock are sorbed into the pores of said particles, while asphaltic constituents remain unadsorbed, separating said unadsorbed asphaltic constituents from said particles, removing unadsorbed material adhering to the surface of said particles and solvent-extracting said sorbed oily constituents from the pores of said particles, passing said extracted constituents through a second column of the aforementioned sorbent maintained at a temperature between about 150° F. and about 250° F., recycling material unadsorbed in the second column of sorbent to the first column of sorbent and solvent-extracting sorbed oily constituents from the pores of said sorbent in the second column to give a deasphalted product.

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