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COMPLETE SPECIFICATION.

Process for Reactivating Inorganic Sorbents.

We, UNIVERSAL OIL PRODUCTS COMPANY, a Corporation organized under the laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This Application relates to a process for reactivating sorbents of the inorganic, thermally stable type, in order to restore the sorbent to an active condition for sorption separation of selected components of organic mixtures. More specifically, this invention concerns a method for reactivating molecular sieve sorbents which have become deactivated during use by accumulation of contaminating substances within the porous structure of the sorbent.

Several processes for the separation of mixtures are known wherein compounds are separated on the basis of their molecular structure and/or chemical composition, utilizing an inorganic sorbent containing pores in which one or more components belonging to a particular class of materials is selectively sorbed from a mixture and retained in the pores of the sorbent while one or more components belonging to another class of substances are rejected by the sorbent. The sorbents having such selective sorbency are generally of the inorganic type, such as specially activated carbons, prepared for example, by carbonization of acid sludges, specially activated alumina, and a class of zeolite-type sorbents comprising metal aluminosilicates, particularly the dehydrated zeolitic alkali metal and alkaline earth metal aluminosilicates, which upon dehydration

contain pores of from 4 to 5 Angström units in diameter and which have a high sorbent capacity for polar molecules and normal or straight chain compounds containing at least 3 carbon atoms but which reject branched and cyclic compounds because said pores do not permit entry of compounds having larger molecular diameters than the straight chain compounds. The activated carbons and aluminas are also capable of selectively sorbing straight chain compounds, particularly hydrocarbons, while rejecting branched chain and cyclic compounds having molecular diameters greater than can be accommodated by the internal pores of the sorbent.

In all of these processes, however, the sorbent gradually becomes deactivated during use as a result of the sorption of polar compounds which contaminate the feed stock or as a result of the sorption of higher molecular weight compounds which are retained by the sorbent with greater tenacity than the selectively sorbed component of the feed stock. Thus, in the use of alkaline earth metal aluminosilicates, such as a calcium aluminosilicate, containing pores of from 4 to 5 Angstrom units in diameter for the separation of straight chain hydrocarbons from their branched chain isomers and cyclic analogs, the capacity of the sorbent tends to decline after several days of continued use. Examination of the deactivated molecular sieves indicates that several types of compounds are responsible for the deactivation. One class of material which produces an effect essentially similar to a deactivation of the sorbent is the high molecular weight, straight chain contaminants of the feed stock for which the molecular sieve sorbent has a greater preferential sorptiveness than for the lower molecular weight homologs present in the feed stock. Another class

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of substances which tends to deactivate the sorbent with respect to hydrocarbon feed stocks is the class referred to as polar compounds (namely organic compounds containing a polar radical, e.g. hydroxyl, carbonyl, nitro, sulfhydryl, amino which, because of their electrophilic nature, tend to be retained by the sorbent with greater tenacity than the straight chain hydrocarbon components of the feed back. Thus, a molecular sieve sorbent, such as an activated carbon or a metal alumino-silicate, when utilized for treating a hydrocarbon feed stock contaminated with a small amount of an alcohol, a ketone, an amine, an aldehyde, a carboxylic acid, or other polar compound will gradually, after each sorption-desorption cycle, evidence a decline in sorptive capacity as the pores of the sorbent become progressively filled with the polar contaminant, thereby blocking off the inlet of such pores and preventing the entry of the desired component of the feed stock into the pores. The deactivation increases with time as a greater proportion of the pore openings become clogged with the polar contaminant because the desorption stage of the cycle cannot completely dislodge the more tenaciously held deactivating compound. Similarly, in the separation of straight chain hydrocarbons from branched chain and cyclic hydrocarbons, the hydrocarbon feed stock mixture generally contains a small but significant amount of higher molecular weight straight chain hydrocarbon components which are also retained by the sorbent with greater tenacity than their lower molecular weight homologs. Because of their preferential retentiveness on the sorbent and the inability of the desorbent to dislodge completely such contaminants from the sorbent, these higher molecular weight straight chain contaminants of the feed stock gradually accumulate in the pores of the sorbent until the quantity of the more tenaciously held longer chain or higher molecular weight contaminant is sufficient to block a major proportion of the pores and the sorbent becomes progressively less capable of sorbing the desired straight chain hydrocarbons of the feed stock, evidencing the characteristics of deactivation.

Methods heretofore employed for reactivating molecular sieve sorbents which have become deactivated as a result of the sorption of higher molecular weight compounds or polar contaminants within the porous structure of the sieves have involved heating the reactivated sorbent to a temperature above 400° C., generally up to 500° C., in an attempt to remove the deactivating component by vaporization, oxidation, or decomposition of the deactivating substance. It has been consistently observed, however, that in such attempted

means of reactivation, the high molecular weight contaminant present within the porous structure of the sorbent tends to crack and carbonize at such temperatures or, if the contaminant is a polar compound, the residue within the pores of the sorbent tends to resinify or undergo various condensation reactions which also tend to fill the pores of the absorbent with permanently deactivating material. In fact, such methods of reactivation result in the deposition of refractory materials within the pores of the sorbent, thereby tending to cause a permanent deactivation which progressively reduces the activity of the sorbent by gradually increasing accumulation of irremovable contaminants which clog the pores of the sorbent and occupy space normally required for sorption of the straight chain component of the feed stock. Thermal methods of reactivation also cause the sorbed deactivating substance to crack into branched chain and olefinic residues. Once inside of the pore of the sorbent, the branched chain molecules formed via cracking cannot escape because the size of the pore opening is only sufficient to permit the passage of straight chain molecules. Similarly, the olefin formed inside of the pore is held more strongly than the normal paraffin component of the feed stock (because of its greater relative polarity) and cannot be displaced therefrom by thermal reactivation. In addition, the olefin tends to undergo polymerization with other olefins, forming a molecule much too large to be vacated from inside of the pore. Ultimately through successive reactivation-sorption cycles the pores of the sorbent are more or less completely filled and the sorbent thus substantially permanently deactivated.

In accordance with the present invention a process is provided for the reactivation of thermally stable inorganic sorbents of the group of activated carbons, activated alumina and zeolite type sorbents used in the separation of organic compounds from mixtures thereof and which have become deactivated by the retention of organic contaminants after repeated sorption-desorption cycles which comprises passing through the deactivated sorbent a hydrocarbon purge stream containing a normal paraffin having from 3 to 8 carbon atoms per molecule at a temperature below 250° C. and at substantially atmospheric or superatmospheric pressure thereafter hydrating said sorbent by contact with a water- or steam-containing stream and subsequently dehydrating the hydrated sorbent by heating to a temperature of from 250° to 375° C.

In the purging step of the present process higher molecular weight hydrocarbons or other organic, selectively sorbed components of the feed stock mixture are stripped from



the sorbent by passing a low molecular weight straight chain hydrocarbon, such as normal butane, preferably in liquid state, through the sorbent at a temperature substantially below 250° C., preferably in the range of from 10° to 150° C., and more advantageously at 50° to 150° C., to thereby remove a major proportion of the deactivating contaminant. In the second step of the process the sorbent is contacted with a water-containing stream, preferably a water-saturated stream of the same low molecular weight straight chain hydrocarbon used in the purging step. The second step is preferably applied at about the same temperature as the preceding purging or stripping operation, for a time sufficient to bring the sorbent to its maximum state of hydration, the water displacing any organic material which may have been retained by the sorbent. Such displaced organic material is carried away in the flowing stream of low molecular weight hydrocarbon passing through the bed of the sorbent and is ultimately removed from the process flow. The sorbent, in its hydrated condition, is thereafter heated to a temperature of from 250° to 375° C. to remove the water of hydration and reactivative the sorbent to substantially its initial sorbent capacity. During such heating operation the flush stream of low molecular weight hydrocarbon is preferably continued through the bed of sorbent to thereby sweep the vaporized water of hydration out of contact with the resulting dehydrated sorbent.

Depending upon the particular deactivating substance present within the pores of the sorbent, the procedure herein provided for reactivating the sorbent varies from a single purging step to one embodying multiple purges at varying temperatures, the number of purges required, in general, being dependent upon the relative difficulty of removing the deactivating component from the pores of the sorbent. Advantageously the purge stream is largely composed of a normal paraffinic hydrocarbon containing from 3 to 8 carbon atoms per molecule, which purges by virtue of the normal paraffin ability to replace the sorbed deactivating component in the pores of the sorbent. The ability of the purge stream normal paraffin to replace the deactivating component sorbed in the internal pores of the sorbent is dependent upon several factors, including, the relative sorbabilities of the purge stream normal paraffin and the sorbed deactivating component, as well as the molar ratio in the sorption zone of the purge stream normal paraffin to the sorbed reactivating component. The relative sorbability of normal paraffin to the sorbed deactivating compounds is directly proportional to the number of carbon atoms in the respective com-

pounds. Thus, normal hexane will replace sorbed normal butane, even if no more than an equimolar ratio of hexane to butane exists in the sorption zone. On the other hand, normal butane will replace sorbed normal hexane from the sorbent if the quantity of purge stream normal butane supplied to the sorption zone containing the normal hexane-sorbent complex in place is sufficient to provide a molar ratio of *n*-butane to *n*-hexane greater than 1 to 1, and preferably, from 1.5 to 1, up to ratios of 10:1. In general, when the molecular weight of the deactivating component present in the pores of the sorbent is substantially greater than the molecular weight of the purge stream normal paraffin the proportion of purge stream normal paraffin to reactivating substances in the sorption zone on a molar ratio basis must be substantially greater than 1 to 1 in order to provide the necessary driving force for displacing deactivating substance. The preferred reactivation procedure in the present process utilizes as purge stream a *n*-paraffin of lower molecular weight than that of the sorbed deactivating contaminant, and the passage of the purge stream through the deactivated sorbent is continued until the quantity of purge stream of deactivating component exceeds a molar ratio of 1 to 1. Because of its low viscosity and high degree of effectiveness, normal butane alone, or admixed with a lesser amount of isobutane, constitutes the preferred purge stream for use in the present process.

The sorbent is hydrated to its theoretical maximum during the hydration stage of the present process by passing the moist purge stream through the sorbent until the quantity of moisture thus charged into the sorbent equals at least the theoretical maximum required to effect substantially complete hydration of the sorbent. A convenient means of thus introducing the water to hydration comprises injecting steam into the purge stream as the latter is charged into and passes through the bed of sorbent. A preferred method is to saturate the liquid purge material with water at approximately the temperature to be employed in the purging operation. The quantity of moisture required varies with the type of sorbent to be reactivated. Thus, the quantity of water to be charged into the sorbent is directly proportional to the number of mols of water required to saturate the sorbent to its highest state of hydration.

Following the hydration step of the reactivation procedure hereof in which the quantity of water is sufficient to effect practically complete hydration of the sorbent, a dry stream, for example the same normal paraffin of 3 to 8 carbon atoms as used for the purging and hydrating steps, is passed through the sorbent at a temperature within



Individuals in the same class of organic

deactivating substances

the range of from 250° to 375° C., which is sufficient generally to restore the sorbent to its dehydrated, active sorbent state. Adequate dehydration will usually be effected within a period of from 1 to 5 hours. When dehydration of the sorbent has proceeded to the desired degree, the sorbent is cooled to the operating temperature of the sorption cycle of the process, preferably while the dry dehydrating stream continues to flow through the sorbent. When, for example, normal butane is used, the sorbent pores become filled with the short butane molecules. The latter is readily displaceable from the pores of the sorbent by the feed stock normal compound (sorbate) and may thus be readily removed from the sorbent and recovered, if necessary, for reuse in the reactivation cycle.

Although the entire reactivation may be conducted at substantially atmospheric pressure, it is generally preferred to effect the purging stages of the process at pressure at least equal to the sorption pressure and more preferably at a pressure sufficient to maintain the purge stream in substantially liquid phase and to operate the dehydration stage of the process at subatmospheric pressure which assists in the removal of the water of hydration at a more rapid rate and with consummate finality. During the final purging stage, the purge stream is charged at a pressure preferably equal to the on-stream pressure of the sorption phase of the process, thereby eliminating any readjustment of pressure when the stream charged into the process is changed to feed stock.

The present invention is further illustrated by the comparative tests of the following example.

In the following runs two separate columns packed with fixed beds of calcium alumino-silicate molecular sieves were utilized to process a mixture of normal and isoparaffins recovered from a gasoline-boiling range reformat fraction having an end boiling point of 200° C., and containing normal, branched chain and cyclic paraffins as well as aromatics. Each molecular sieve column contained approximately 70.8 liters of the calcium alumino-silicate molecular sieves and each received the same feed stock and was used in the same manner insofar as the sorption-desorption cycles of the separation process are concerned. In each case, the column received the foregoing feed stock in liquid phase at a temperature of 93° C., and at a superatmospheric pressure of 13.6 atmospheres. A continuous system of analysis was maintained on the effluent product streams. When normal paraffins began to appear in the non-sorbed effluent from the column (isoparaffinic and cyclic hydrocarbons), the flow of feed stock into the

column was discontinued and the sorbed *n*-paraffins were desorbed from the "spent" sieves by passing liquid *n*-butane at 93° C., and at 13.6 atmospheres into the column, collecting the desorbed effluent (a mixture of *n*-butane and feed stock *n*-paraffins) at the bottom outlet of each column. When analysis of the desorbent effluent indicated that it contained nothing but *n*-butane, the flow of desorbent was discontinued and feed stock was again charged in liquid phase into the column. The above sorption-desorption cycles were continued on a continuous basis until the total volume of feed stock charged into each column was 4542 liters. During the processing period it was noted that the total capacity of each column for feed stock *n*-paraffins gradually declined. After a total feed stock volume of 1514 liters had been processed, the capacity of the sieves was approximately 82% of their initial capacity. After processing 2271 liters of feed, the capacity of the sieves had declined to 73% of their initial capacity and to 51% after processing 4542 liters of feed stock.

Residual hydrocarbon liquid was withdrawn from each bed and the sieves thereafter subjected to a reactivation treatment. Each column was flushed with liquid *n*-butane at 100° C., for 2 hours to ensure removal of feed stock normal paraffins from the sieve particles. One column was thereafter purged with nitrogen heated to a temperature of 400° C. for 2 hours, followed by passing oxygen through the sieve bed at 450° C. for 2 hours. The sieves regenerated in this manner were then cooled and their capacity for liquid *n*-paraffin measured. The sieves retained a slight coloration following the treatment with oxygen and when regenerated in this manner, recovered approximately 84% of their initial capacity (that is, they sorbed 84% by volume of the *n*-hexane sorbed by the freshly prepared calcium alumino-silicate molecular sieves).

In the method of regeneration in accordance with the procedure provided by the present invention, the deactivated sieves of the other separation column were purged with liquid *n*-butane at 100° C. for a further 2 hours. Thereafter, the liquid *n*-butane was saturated with water at 110° C., and the resulting "wet" *n*-butane was passed through the sieves until enough water had been added to the sieves to equal their total sorbate volume. The *n*-butane effluent from the column, containing the desorbed material removed from the "spent" sieves was collected, the *n*-butane was distilled overhead from the residue and the latter was analyzed by Mass Spectrographic means. The material recovered boiled over a temperature range of from 152° to 256° C. and consisted of the following classes of hydrocarbons:—



Product

	Mass Spectrographic Analysis	Vol. %
	Paraffins	3.1
	Naphthenes, monocyclic	1.5
	Naphthenes, bicyclic	0.2
5	Naphthenes (tricyclic) or cyclo-olefins	1.0
	Alkylbenzenes	82.8
	Indanes and Tetralins	5.6
	Alkyl naphthalenes	5.8
10	Tricyclic aromatics	Trace

Following the treatment of the sieves with wet *n*-butane, nitrogen was passed through the sieves for 4 hours at 116° C. and atmospheric pressure. Thereafter, nitrogen at a temperature of 288° to 316° C. was passed through the sieves for 4 days at atmospheric pressure, followed by cooling to 116° C. and treatment of the sieves first with vaporized *n*-butane, and then at 93° C. and 13.6 atmospheres with liquid *n*-butane. The sieves reactivated as indicated above were restored substantially to their initial capacity.

WHAT WE CLAIM IS:—

- 25 1. Process for reactivating thermally stable inorganic sorbents of the group of activated carbons, activated alumina and zeolite type sorbents used in the separation of organic compounds from mixtures thereof and which have become deactivated by the retention of organic contaminants after repeated sorption-desorption cycles, characterized by the steps of passing through the deactivated sorbent a hydrocarbon purge stream containing a normal paraffin having from 3 to 8 carbon atoms per molecule, at a temperature below 250° C. and at substantially atmospheric or superatmospheric pressure, thereafter hydrating said sorbent by contact with a water-containing stream and subsequently dehydrating the hydrated sorbent by heating to a temperature of from 250° to 375° C.

2. Process as claimed in Claim 1, characterized in that each of the hydrocarbon purge stream and the water-containing stream is maintained in substantially liquid phase at an elevated temperature below 250° C. during its passage through the deactivated sorbent and said sorbent is dehydrated during the subsequent heating at a substantially lower pressure than the pressure maintained during the contact thereof with said purge stream and said water-containing stream.

3. Process as claimed in Claim 1 or 2, characterized in that the sorbent is substantially hydrated during contact with the water- or steam-containing stream and the sorbent is contacted during the subsequent heating with a gaseous stream of the group consisting of nitrogen and normally gaseous paraffins.

4. Process according to any of the Claims 1 to 3 wherein the normal paraffin comprises normal butane in liquid state.

5. Process according to any of the Claims 1 to 4, wherein the sorbent is hydrated by contact with liquid normal butane which is saturated with water.

6. Process according to any of the Claims 1 to 5, wherein the sorbent comprises a metal-alumino-silicate.

7. Process according to Claim 6, wherein the sorbent comprises a calcium alumino-silicate having pores of from 4 to about 5 Angstrom units in diameter.

8. Process for reactivating thermally stable inorganic sorbents by treatment with a hydrocarbon purge stream and a water-containing stream and by subsequent heating substantially as described.

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	Mass Spectrographic Analysis	Vol. %
	Paraffins	3.1
	Naphthenes, monocyclic	1.5
	Naphthenes, bicyclic	0.2
5	Naphthenes (tricyclic) or cyclo-olefins	1.0
	Alkylbenzenes	82.8
	Indanes and Tetralins	5.6
	Alkyl-naphthalenes	5.8
10	Tricyclic aromatics	Trace

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