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COMPLETE SPECIFICATION

DRAWINGS ATTACHED

Selective Conversion of Normal Paraffins

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, 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:—

The present invention relates to the upgrading of hydrocarbon oils, and more particularly relates to an improved process for reducing the normal paraffin content of hydrocarbon oils in which such paraffins are present in admixture with other hydrocarbons. The process according to the invention comprises contacting such oils with a metallic alumino-silicate having uniform pore spaces of about 5 Angstrom units under conditions such that normal paraffins are continuously adsorbed into the alumino-silicate and continuously converted to olefins which are recovered with the non-adsorbed constituents of the oil.

Because of their low octane value in gasolines and their adverse effect upon the pour point and cloud point of hydrocarbon oils generally, normal paraffins are undesirable in high octane gasolines, aviation turbo-jet fuels, kerosenes, heating oils, lubricating oils and other premium quality petroleum products. Recognition of this fact has spurred efforts to develop processes which will permit the removal of normal paraffins from oils intended for use in the manufacture of such products. One of the most promising methods proposed for separating normal paraffins from branched chain and cyclic compounds developed to date involves the use of adsorbents which are selective for the normal paraffin molecules. These adsorbents, generally referred to as molecular sieves, are crystalline metallic alumino-silicates containing a large number of submicroscopic cavities interconnected by many smaller pores or channels which are extremely uniform in size. Molecules having affinity for the alumino-silicate and small enough to enter the pores or channels are readily adsorbed, while those of greater size or lacking such affinity are rejected. By employing alumino-silicates having uniform pore spaces of about 5 Angstrom units in diameter, excellent separations between normal paraffins and other hydrocarbons present in hydrocarbon oils can be made.

The scientific and patent literature contains numerous references to the composition and adsorbing action of metallic alumino-silicates. In general these are crystalline zeolites containing an alkali or alkaline earth metal, aluminum, silicon and oxygen. They may be either natural or synthetic in origin and may have uniform pore spaces generally in the range of from 3 to 15 Angstrom units, depending upon their composition and the conditions under which they were formed. As mentioned above, those having pores of about 5 Angstroms are useful for separating normal paraffins from branched chain and cyclic compounds. Among the natural zeolites having molecular sieve properties may be mentioned analcite, $NaAlSi_2O_6.H_2O$, and chabasite $CaAl_2Si_4O_{12}.6H_2O$. Synthetic zeolites having similar properties have been described in the chemical and patent literature.

Despite the excellent selective adsorption properties of molecular sieves, certain difficulties have been encountered in attempting to apply them to the large scale removal of normal paraffin hydrocarbons from branched chain and cyclic hydrocarbons. In using such adsorbents, it is necessary to employ a two-step cyclic process. The normal paraffins must first be selectively adsorbed upon the molecular sieve. Usually this is accomplished by contacting the oil with the adsorbent at temperatures in the range of from 100° to 600°F. and at pressures of from atmospheric to 100 psig. Following this adsorption step, the molecular sieve must next be reactivated by a desorption step before it can be used for adsorption again. The desorption step is usually carried out by steaming the used adsorbent, evacuating it, or displacing the adsorbed compounds by means of a gas which is not itself adsorbed by the sieve. The capacity of molecular sieve adsorbents when used in this manner is very low and therefore such cyclic processes are relatively expensive because of the frequency with which the sieve must be desorbed. The desorption methods available are only partially effective and the selectivity and capacity of the sieve rapidly decline as it is used. A further difficulty is that carbonaceous deposits rapidly build up on the surface of the sieve. Regeneration of the sieve at frequent intervals by heating it to very high temperatures or by employing other regenerative techniques alleviates this latter difficulty to some extent but very frequent regeneration shortens the active life of the sieve. Because of these difficulties, the cost of effecting separations between hydrocarbons by means of molecular sieves is inordinately high.

The present invention provides a new and improved method for eliminating normal paraffins from hydrocarbon oils by means of molecular sieves which is free from many of the disadvantages associated with molecular sieve processes employed in the past. The process differs from prior processes in that molecular sieves are employed to effect chemical conversion of the normal paraffins upon a selective basis, rather than merely a mechanical separation. It has been found that normal paraffins present in a hydrocarbon oil can be selectively converted to olefins by contacting the oil with a molecular sieve having pore diameters of about 5 Å under critical conditions. It is believed that the explanation for this selective conversion phenomenon lies in the fact that gas phase configurations are not possible in the pores of molecular sieves. It is impossible for a normal paraffin molecule to rotate in the 5 Angstrom pores of a molecular sieve except on its longitudinal axis and therefore the rotations corresponding to the three main moments of inertia of the molecule become vibrations as the molecule is occluded in the sieve. This results in a high loss in energy of the molecule over an extremely short period of time. By providing the molecule with a sufficiently high initial energy, it is possible to use this energy loss to effect rupture of bonds in the molecule and convert the normal paraffins into lower molecular weight olefins before complete occlusion takes place. The olefins are not retained by the sieve but instead are recovered with the non-adsorbed isoparaffins and cyclic compounds in the oil.

Regardless of the theoretical explanation for the phenomenon which takes place, the process of the invention has numerous advantages over processes which have been proposed for the removal of normal paraffins from hydrocarbon oils by means of molecular sieves in the past. Since the normal paraffins which would otherwise be occluded by the sieve are continuously converted to olefins which are not retained on the sieve, the pores of the sieve remain relatively free of hydrocarbons. No desorption step is necessary and the difficulties encountered in desorbing the sieve in prior processes are thus avoided. Olefins formed in the process can readily be separated from saturated constituents in the oil and form a valuable by-product. The simplified procedure and equipment employed make the process considerably more attractive from an economic standpoint than processes utilized heretofore.

Molecular sieve adsorbents suitable for use in the process of the invention are available commercially and may be produced in a number of ways. One suitable process for preparing such adsorbents involves the mixing of sodium silicate, preferably sodium metasilicate, with sodium aluminate, under carefully controlled conditions. The sodium silicate employed should be one having a ratio of soda to silica between 0.8 to 1 and 2 to 1. Water glass and other sodium silicate solutions having lower soda to silica ratios do not produce the selective absorbent crystals unless they are subjected to extended heat soaking or crystallization periods. Sodium aluminate solutions having a ratio of soda to alumina in the range of from 1 to 1 to 3 to 1 may be employed. High soda to alumina ratios are preferred and sodium aluminate solutions having soda to alumina ratios of about 1.5 to 1 have been found to be eminently satisfactory. The amounts of the sodium silicate and sodium aluminate solutions employed should be such that the ratio of silica to alumina in the final mixture ranges from 0.8 to 1 to 3 to 1 and preferably from 1 to 1 to 2 to 1.

These reactants are mixed in a manner to produce a precipitate having a uniform composition. A preferred method for combining them is to add the aluminate to the silicate at ambient temperatures using rapid and efficient agitation to produce a homogeneous mixture. The mixture is then heated to a temperature of from 180° to 215°F. and held at that temperature for a period of from 0.5 to 3 hours or longer. The crystals may be formed at lower temperatures but in that case longer reaction periods are required. At temperatures above 250°F. a crystalline composition having the requisite uniform size pore openings is not obtained. During the crystallization step, the pH of the solution should be maintained on the alkaline side, at 12 or higher. At lower pH levels, crystals having the desired properties are not as readily formed.

The crystals prepared as described above have pore diameters of about 4 Angstrom units. To convert these to crystals having 5 Angstrom pores, it is necessary to employ a base exchange reaction for the replacement of some of the sodium by calcium, magnesium, cobalt, nickel, iron or a similar metal. Magnesium, cobalt, nickel and iron have greater cracking activity than does calcium and therefore it will often be preferred to employ solutions of these metals for replacement purposes.

The base exchange reaction may be carried out by water washing the sodium alumino-silicate crystals and adding them to a solution containing the desired replacement ions. An aqueous solution of magnesium chloride of about 20% concentration, for example, may be used for preparation of the magnesium form of the 5 Angstrom sieve. After a contact time which may range from 5 minutes to an hour, the 5 Angstrom product is filtered from solution and washed free of the exchange liquid. 50 to 75% of the sodium in the crystals is normally replaced during the base exchange reaction.

The crystals thus prepared are in a finely divided state and are usually pelleted with a suitable binder material before they are calcined in order to activate them. Any of a number of binder agents used in the manufacture of catalysts may be employed for this purpose. A binder consisting of bentonite, sodium silicate and water, for example, has been found satisfactory. In using this binder, the constituents should be mixed so that the product contains from 5 to 10% bentonite, 5 to 15% sodium silicate and 75 to 90% of the crystals on a dry basis and that the total mixture contains 25 to 35% water. This mixture may then be extruded into pellets or otherwise shaped and subsequently dried and calcined. Calcination temperatures of from 700° to 900°F. or higher are satisfactory.

In carrying out the process of the invention, the feed stream is contacted with the molecular sieve adsorbent in vapor phase at a temperature of from 800° to 1100°F. At temperatures below 800°F. little conversion takes place and therefore removal of normal paraffins from the oil is low. At temperatures above 1000°F. some thermal cracking, and above 1100°F. considerable thermal cracking, of isoparaffinic and cyclic constituents of the oil takes place and hence much of the selectivity of the process disappears. Contacting temperatures of from 800° to 900°F. are most effective and a temperature of about 850°F. is particularly preferred.

The pressures employed in contacting the oil with the adsorbent may range, for example, from 50 mm. of mercury to 10 atmospheres. Generally it is preferable to carry out the contacting step at about atmospheric pressure. The feed rate employed may range, for example, from 0.1 to 3 pounds of oil per pound of molecular sieve per hour. Preferred rates range between 0.1 and 1.0 pounds per pound per hour. Under these conditions, normal paraffins present in the oil will be selectively converted to lower boiling olefins which are not retained upon the sieve and instead are discharged with the product oil. These olefins may be readily separated from the oil and constitute a valuable by-product of the process.

The invention in a preferred embodiment is a process for lowering the pour point of a middle distillate, boiling between 300° and 650°F., by treating it in the vapor phase with a 5A alumina-silicate at a temperature between 800° and 900°F. and at a space velocity of 0.3 to 1.2 lb./lb., removing any by-product boiling below 300°F. and recondensing the vaporized product.

Although the olefins formed by the selective conversion of normal paraffins in the process are not retained upon the sieve, deposits gradually build up on the sieve surface, probably due to polymerization of the olefins. Sulfur compounds, water and other contaminating materials present in the feed may also contribute to the gradual accumulation of such deposits. In order to remove these deposits and maintain the activity of the adsorbent at a high level, the sieve is regenerated at suitable intervals. Although steam and other regeneration procedures heretofore disclosed may be employed in this step of the process, it is normally preferred to regenerate the sieve by passing a stream of oxygen-containing gas through the sieve bed at high temperatures. In the presence of the oxygen, the deposits are burned from the surface of the sieve and the sieve activity is restored. The quantity of oxygen required for this burning step is small, since the total amount of foreign matter on the sieve is small, and therefore gas streams containing as little as

5% oxygen may be used. It is preferred, however, to employ air for this purpose. The air or other gas stream used in the regenerative step may be preheated to a temperature of from 500° to 800°F. before contacting it with the sieve. The high temperature zone formed by combustion of the deposits upon the sieve surface proceeds through the adsorbent mass rapidly and exists at any one spot for only a brief instant. It has been found that the sieve crystals are not appreciably impaired by this regenerative treatment.

In order to further minimize deposit formation and reduce the frequency of regeneration, it is often advantageous to contact the feed stream with a guard bed of alumina, silica gel or a similar adsorbent prior to introducing it into the treating zone. Polar contaminants in the feed are removed by the guard bed and hence the formation of deposits within the treating zone is reduced. The guard bed may be regenerated by burning or other conventional techniques.

In order to further reduce deposit formation within the treating zone, it is preferred to carry out the process in the presence of added hydrogen, nitrogen, carbon dioxide or a similar gas having a molecular diameter smaller than the pore diameter of the sieve. The presence of such a gas serves to purge hydrocarbon fragments from the pores of the molecular sieve and prevent the reaction of such fragments to form carbon and polymeric deposits. Hydrogen is particularly preferred for this purpose because it may also result in saturation of some of the olefins produced and thus further reduce deposit formation. The use of hydrogen is particularly effective in the presence of metallic alumino-silicate adsorbents which have some hydrogenation properties. The nickel form of 5A molecular sieve, for example, tends to cause hydrogenation of the olefin to a greater degree than does the calcium form and therefore deposit formation is reduced. The gas employed may be introduced with the feed at a rate such that its concentration in the reactor ranges from 5 to 95 mole percent.

The oils adapted for treatment in accordance with the process of the invention are preferably hydrocarbon oils boiling in the range between 100° and 750°F. and especially between 320° and 650°F. Such oils include naphthas, kerosene (boiling between 320° and 555°F.) and middle distillates and are widely used for the production of gasolines, jet fuels, diesel fuels, heating oils and similar products wherein the content of normal paraffins must be limited to control undesirable effects such as solidification in storage at low temperature. The process of the invention is particularly effective for removing wax and similar normal paraffinic constituents from middle distillate petroleum fuels in order to reduce their pour point, cloud point and haze point, and it is in this area that the process of the invention will find widest application.

The process described above is particularly effective in extending the time between adsorption and desorption when wax-containing feeds are treated. The chemical conversion of wax by the sieve rather than its retention within the sieve pores greatly extends the scope and capacity of such a bed. Nonetheless, after a period on the adsorptive cycle, the sieve gradually loses capacity, and this is reflected by a gradual increase in the pour point of the dewaxed oil. However, pour points cannot be quickly determined on the oil, and thus their determination is not a suitable means for controlling the sorptive cycle. Were the wax sorbed without cracking or thermal conversion, the gradual saturation of the bed could be readily followed by measuring the temperature rise in each section of the bed as the adsorption front moves through it. However, when selective wax conversion occurs, during adsorption, there is no temperature rise in any section of the sieve bed.

It is a further feature of the present invention that the rate of saturation of the sieve bed under selective wax cracking conditions can readily be followed by measuring the rate of hydrocarbon "make" gas. It has been found that as the pour point reduction of the treated oil decreased, the amount of hydrocarbon gas make also decreases. When the gas make rate has leveled off, there is likewise no further reduction in pour point, i.e. the sieve has become saturated, and the desorptive regeneration part of the cycle now is employed.

The exact nature and objects of the invention may be more readily understood by referring to the following detailed description of a preferred embodiment of the process, to the examples set forth hereafter, and to the attached drawings in which:

Figure 1 depicts a flow diagram of a preferred embodiment of the process of the invention;

Figure 2 is a graphical representation of data showing the effect of contacting temperature upon the reduction in pour point of a gas oil treated in accordance with the invention; and

Figure 3 is a graphical representation of data illustrating the effect of contacting temperature upon sieve capacity in the treatment of a gas oil in accordance with the invention;

Figure 4 is a graphical representation of data relating the pour point reduction of a treated oil with the rate of hydrocarbon make gas production;

Figure 5 is a graphical representation of data illustrating the effect of contacting time upon the rate of hydrocarbon make gas production; and

Figures 6 and 7 are graphical illustrations of the data in Examples 10 and 11 relating the gas make rate with sorption time of 5 Angstrom molecular sieves (Figure 6) and hydrogen chloride modified 5 Angstrom sieves (Figure 7).

Referring now to Figure 1 a hydrocarbon oil containing normal paraffins as well as iso-paraffinic and cyclic compounds, a gas oil boiling in the range of from 450° to 700°F., for example, is introduced through line 1 into furnace 2 where it is preheated to a temperature of about 850°F. The preheated feed, now in vapor phase, is passed through line 3 and valve 4 into contacting zone 5. Hydrogen or a similar gas having a molecular diameter less than 5 Angstrom Units may be introduced with the vaporized feed into zone 5. The contacting zone has disposed therein a bed of molecular sieve having uniform pore diameters of 5 Angstrom units. The contacting zone may be fitted with suitable jacketing, heat coils or similar means for controlling temperature within the bed. The feed stream passes upwardly through the adsorbent bed and in so doing, normal paraffins present therein are selectively converted to lower molecular weight olefins. Some light gases are also formed. The vapor stream after contact with the adsorbent is removed overhead from contacting zone 5 through line 6 containing valve 7 and is passed to condenser 8. In the condenser, hydrocarbons boiling above 100°F. are condensed and taken off as a bottoms product through line 9. Uncondensed gases are removed overhead through line 10. The product oil recovered through line 9 may be further fractionated to remove constituents boiling below the feed boiling point if desired. The overhead gas stream may be passed to a light ends plant for separation and recovery of the individual gaseous constituents.

The contacting procedure described above is continued until the concentration of normal paraffins in the product stream withdrawn through line 9 reaches an unacceptable level. This concentration may readily be determined by ultraviolet analysis, infra red analysis, refractive index determination or the like. Preferably, the contacting procedure described above is continued until the rate of light hydrocarbon gas formation, as determined by analysis of product stream withdrawn through line 10, has become substantially zero or has leveled off at a very low rate of about 10 to 50 cc/min. At this point, the sieve has now become saturated with wax and other carbonaceous deposits, and the desorptive regeneration part of the cycle follows.

Introduction of the feed stream is therefore halted and following nitrogen or other inert gas, air or other oxygen containing gas is introduced into the bottom of contacting zone 5 through line 11 containing valve 12. The gas stream should be preheated to a temperature of from 500° to 800°F. This may be accomplished in a suitable furnace, not shown. Under the temperature conditions prevailing within the sieve bed, oxygen in the gas stream combines with the deposits on the sieve surface and the deposits are burned off. The combustion takes place within a narrow zone which moves from the bottom of the bed to the top of the bed. At any instant the temperature within the combustion zone may range from 1000° to 1500°F. but because of the short time during which these temperatures prevail at any level in the bed, crystallinity of the sieve is not materially affected. Gases are removed overhead from the contacting zone through line 13 containing valve 14. Upon completion of the regenerating step of the process, valves 12 and 14 may be closed and valves 4 and 7 opened to permit resumption of the contacting step. Although only one contacting vessel is shown in Figure 1, it will be understood that in most cases it will be advantageous to employ two or more vessels suitably connected in parallel to permit regeneration of the spent sieve without interruption of the process. The arrangement of such vessels will be obvious to those skilled in the art.

The process of the invention is further illustrated by the following examples.

EXAMPLE 1

A petroleum middle distillate boiling between 326°F. and 680°F. was contacted with a calcium form molecular sieve having uniform pore diameters of 5 Angstrom units by passing the feed stream downflow through a fixed bed containing 500 grams of the sieve. The contacting temperature was 850°F. and the pressure was about 760 mm. of mercury. The feed rate averaged 1 pound of oil per pound of sieve per hour. This contacting was continued until about 750 grams of the oil had been passed through the sieve bed. At this point the operation was discontinued and the product collected was analyzed. A similar run was then made in which the feed stream was contacted with the sieve at a temperature of 390°F. and at a pressure of 0.2 mm. of mercury. Again the product recovered from the contacting zone was collected and analyzed. Inspections of the feed stream and the products from these two operations are shown in Table I below.

TABLE I

INSPECTIONS OF FEED AND PRODUCTS

ASTM D-158 Distillation	*Feed*	*850°F. Product*	*390°F. Product*
I.B.P.	326	108	328
5%	369	180	362
10%	385	320	378
20%	415	352	406
30%	440	418	430
40%	472	456	456
50%	504	502	488
60%	533	534	520
70%	562	560	552
80%	592	579	584
90%	623	592	620
95%	642	598	654
F.B.P.	680	652	676
Pour Point, °F.	+5	−55*	−40
Cloud Point, °F.	+16	−55*	−32
R.I. at 20°C.	1.4630	1.4737*	1.4662
Bromine No.	0.4	17.1	0.5

* 850°F. product adjusted to 325°F. initial boiling point.

From the distillation data set forth in the above table it can be seen that an appreciable quantity of low boiling material was formed in the run carried out at 850°F., while essentially none was formed during the low temperature run. The initial 10% of the product collected in the 850°F. run had an extremely high bromine number, indicating that this fraction consisted largely of olefins. The pour point and cloud point data found in the table show that normal paraffins present in the feed stream were reduced to a much greater extent in the high temperature run than in the 390°F. run. This was true even after material boiling below 325°F. was removed from the 850°F. product. In the low temperature run it was found that the sieve bed rapidly became saturated with normal paraffins. In the high temperature run the sieve was inspected at the end of the run and there was no evidence of any hydrocarbons on the sieve. It therefore appears that normal paraffins present in the feed stream were adsorbed upon the sieve in both runs but that in the high temperature run the adsorbed compounds were continuously selectively converted to olefins which were not retained by the sieve.

EXAMPLE 2

A mixed blend gas oil boiling between 575° and 658°F. was passed through a bed containing 850 grams of a 5A calcium molecular sieve at temperatures of from 600° to 1010°F. Data collected in these runs are shown in Table II below.

TABLE II

PRODUCT DISTRIBUTION AT SIEVE SATURATION(1)

Contacting Temp. °F.	600	755	850	900	1010
Pressure, mm Hg			750		
Rate, W/W/Hr.			0.5		
Feed Treated, g/100 g sieves	83	80	195	190	190
Total Product, g/100 g sieves	70	70	170	158	118
wt. % on feed	84.0	87.0	85.7	83.4	61.9
Material retained on sieve, g/100 g. sieves	—	7.3	7.8	7.6	10.6
Material Distribution, wt. % on feed:—					
Gas (C_4 and lighter)	Nil	<0.5	5.4	6.1	15.6
Naphtha (C_5-325°F.V.T.)	Nil	≃1.0	1.9	6.3	7.3
Product (325-575°F.V.T.)	Nil	12.0	23.7	29.3	27.5
(575°F. +)	84.0	75.0	62.0	54.1	34.4
Material retained on sieves	—	9.1	4.0	4.0	5.6
Material Balance	—	97.6	97.0	99.8	90.4(2)

(1) Sieves were considered saturated when products boiling above 575°F. showed no improvement in pour point compared to fresh feed.

(2) Poor material balance believed to be caused by loss of gas.

In order to differentiate between the benefits due to selective conversion of normal paraffins and benefits which might be due to cracking, only material boiling above 575°F. was considered in determining the saturation or exhaustion point. The data show that the amount of feed which can be treated before saturation occurs is considerably greater at temperatures of 850°F. and higher. A temperature of 850°F. showed the most favorable results. At that temperature the total product yield was about 86%, based on the feed. With increasing temperatures, this value decreased appreciably with a corresponding increase in the production of gases. This indicates that a non-selective cracking occurs when too high a temperature is used. Material retained on the sieve at a temperature of 1010°F. was greater than that retained at any of the lower temperatures. This again appeared due largely to non-selective cracking but may also be attributable to increased polymerization of olefins at the higher temperature.

The products obtained in the runs described in Example 2 were analysed and their inspections are set forth in Table III below.

TABLE III

PRODUCT INSPECTIONS

Mixed Blend Gas Oil Treated With 5A Molecular Sieves

Contacting Temp. °F.	— (feed-stock)	600	755	850	900	1010
Liquid Product						
Bromine No.	2	4	6	6	7	11
Mercaptan No.	4.2	0.5	0.4	Nil	0.2	0.1
Total S. Wt. %	0.42	0.44	0.44	0.40	0.48	0.51
Visc. 100°F. SUS	47.6	47.0	45.2	—	46.0	41.2
Aniline Pt. °F.	172			156		
R.I. at 68°F.	1.4778	1.4813		1.4855		
% Gas on Feed	—	Nil	<0.15	5.4	6.1	15.6
Total Gas						
Hydrogen, mol. %				21.7		22.8
Methane		Essentially No Gas Produced		11.3		29.0
Ethylene					6.1	9.8
Ethane					15.2	17.5
Propylene					22.1	15.7
Propane					14.4	
Butene-1					2.5	
Butene-2					2.9	5.2
Isobutane					1.5	
n-butane					2.3	
Gas Gravity					1.01	0.79

The inspections in the above table show that the bromine number of the product increased with increases in contacting temperature. The change in bromine number with a change in contacting temperature of from 755° to 900°F. was not appreciable. Increasing the temperature to 1010°F., however, brought about a large increase in bromine number. This indicates that at the lower temperatures, the process was largely limited to selective conversion of the normal paraffins and that at the higher temperature non-selective cracking was taking place.

Samples of the product obtained at intervals during the runs described in Example 2 were tested to determine their pour points. These samples had been "flashed" to an initial boiling point of 575°F., approximately the initial boiling point of the feed, in order to avoid distortion of the results that would otherwise have been caused by the presence of the low boiling cracked materials, which naturally have low pour points. These pour point data are shown in Figure 2 of the drawing. From the figure it can be seen that greater quantities of considerably lower pour point product can be obtained by contacting the feed at temperatures of 850° to 900°F. than can be obtained by treating the feed at higher or lower temperatures. At the lower temperatures the sieve rapidly becomes saturated and little further improvement in pour point results. At high temperatures above about 1000°F. non-selective cracking takes place and the pour point is not improved as much.

Based on data obtained in the runs set forth in Example 2, sieve capacity at various temperatures for a 0°F. pour point product was determined. The results of these determinations are shown in Figure 3. The data thus presented illustrate the critical effect of the contacting temperature upon sieve capacity. At a temperature of about 850°F. capacities in excess of 100 grams per 100 grams of sieve are obtained. At temperatures higher than 950°F., or lower than 800°F. capacity rapidly falls off.

EXAMPLE 3

In order to determine the effect of contacting pressure upon the selective conversion of normal paraffins, a gas oil was contacted with a 5A molecular sieve at a temperature of 980°F. and 750 mm of mercury. A sample of the same gas oil was then tested under similar conditions except that the pressure was reduced to 200 mm of mercury. It was found that the reduction in pressure improved the selective conversion of normal paraffins somewhat. This improvement, however, did not increase the yield of accumulative product in excess of that obtained at 850°F. and 750 mm of mercury. Operation under the latter conditions is therefore to be preferred.

EXAMPLE 4

A number of runs were also conducted at a feed rate of 1.5 W/W/Hr. and the results obtained were compared with those obtained in earlier runs carried out at 0.5 W/W/Hr. It was found that increasing the feed rate from 0.5 to 1.5 W/W/Hr. without changing the temperature gave a lower yield of good product. By increasing the temperature to 950°F., however, it was possible to operate at the higher feed rate without any significant reduction in sieve capacity over that obtained at 850°F. with the lower feed rate.

EXAMPLE 5

In order to further demonstrate the effect of temperature and pressure upon the process of the invention, a C_6 naphtha was processed with a 5A molecular sieve at a temperature of 1100°F. and a pressure of 100 psig. The feed rate was 1 V/V/Hr. At this temperature and pressure it was found that a substantial amount of the naphtha was thermally cracked to form low boiling gases. Despite this thermal cracking, however, a considerable amount of selective conversion, nevertheless, took place as shown by the following data.

TABLE IV
TREATMENT OF C_6 NAPHTHA
1100°F., 100 psig

Liquid Product Components, Vol. %	*Feed*	*Product*
n-Hexane	52.3	36.1
C_6 Isoparaffins	30.4	30.3
C_6 Naphthenes	11.3	9.0
Other type Hydrocarbons	6.0	24.6
Ratio n-Hexane to Isop. + Naphthenes	1.25	0.92

From the above table it can be seen that the ratio of normal hexane to isoparaffins and naphthenes decreased from 1.25 to 0.92, indicating that normal paraffins were converted in the presence of the molecular sieve, in preference to isoparaffins and naphthenes. Under the conditions which have been found necessary for carrying out the process of the invention, thermal cracking does not occur to a significant extent and therefore the improvement in the ratio of straight chain compounds to isoparaffins and naphthenes would be considerably higher.

EXAMPLE 6

Samples of a mixed blend heavy atmospheric gas oil having an ASTM boiling range between 560 and 658°F. and a pour point of +40°F. were contacted with a 5 Å molecular sieve in the presence and in the absence of added hydrogen in order to demonstrate the effect of a gas having a molecular diameter less than that of the sieve upon the process of the invention. The contacting temperature employed was 850°F. Pressure within the contacting zone was held at 750 mm of mercury. The feed rate in both cases was 0.1 pounds of feed per hour of sieve per hour. In the first run no hydrogen was used and in the second hydrogen was introduced with the feed at a rate such that the hydrogen concentration in the reactor was 90 mole percent. The results obtained in these two parallel runs are shown in Table V below.

TABLE V
EFFECT OF ADDED HYDROGEN UPON CONVERSION OF NORMAL PARAFFINS

Run	A	B
Contacting Temp., °F.	850	850
Contacting Pressure, mm Hg.	750	750
Feed Rate, W/W/Hr.	0.1	0.1
H_2 Conc. in Reactor, Mole %	0	90
0°F. Pour Point Product, g/100 g. Sieve	173	242
Wt. % Yield on Feed	79	84
−30°F. Pour Point Product, g./100 g. Sieve*	123	177
Wt. % Yield on Feed	77	82
Bromine No. of Product	6.5	5.7

* Product adjusted to 325°F. initial vapor temperature.

Referring to Table V, it can be seen that the presence of the added hydrogen in Run B resulted in an increase in sieve capacity of about 40 to 45% and an increase in yield, based upon feed, of about 5% over the values obtained in Run A. This improvement is shown with respect to both the 0° and the −30°F. product. The bromine numbers of the two products indicate that the improvement was primarily due to the purging of the gas, rather than hydrogenation of olefins, although some hydrogenation did occur. From this it can be seen that the improvement obtained is not limited to the use of hydrogen and that other gases, nitrogen for example, may be used as purging agents during the contacting step of the process. The improvement due to the use of such a purging agent is a significant one and for this reason it is preferred to employ such an agent.

EXAMPLE 7

A 560/658°F. boiling range gas oil from Western Canadian crude, having a +40°F. pour point, was dewaxed by passing the feed through 850 g. of 5Å sieves packed in a bench scale apparatus similar to that shown in Figure 1. Sorption conditions were 850°F., atmospheric pressure, and 0.5 W/W/Hr. feed rate. By measuring the hydrocarbon gas make with a wet test meter or some other type of flowmeter, sufficient data were obtained to relate the rate of hydrocarbon gas formation with sorption time (shown in Figure 5). When the gas make had levelled off to a low rate (in this case, approximately 25 cc/min.) the sieves were considered saturated and the desorptive regenerative part of the cycle commenced.

EXAMPLE 8

A 545/660°F. virgin gas oil from Pembina crude showing a +40°F. pour point and a hydrogen gas stream were simultaneously passed through 850 g. of 5Å sieves. Sorption conditions were 858°F., atmospheric pressure, and 0.5 W/W/Hr. feed rate. Hydrogen gas rate was maintained at 1250 std. cc/min. so that the concentration was 65 mole percent in the reactor at the designated sorption conditions. By measuring the hydrocarbon gas make rate (in this case, total gas make rate minus 1250 ml. H_2/min.) at periodic sorption time, a similar plot as shown in Example 7, relating gas make rate with sorption time was obtained (Figure 6). When the hydrocarbon gas make rate levelled off at about 20 cc/min., the sorption part of the cycle was stopped and regeneration commenced.

Under the sorption conditions employed in Examples 7 and 8, the waxy n-paraffins were cracked upon sorption to lower boiling hydrocarbons. As described earlier, this selective wax cracking phenomenon permitted an appreciable increase in sieve capacity. However, as the sieve cavities became fouled with polymers and other contaminants, the sorbability of the sieves decreased, and consequently the pour point reduction of the treated oil gradually approached zero (Figure 4). The rate of hydrocarbon gas make followed a similar trend as the reduction in pour point. At the early stages of the sorption cycle, considerable waxy n-paraffins were sorbed, and under the sorption conditions employed they were converted to low boiling hydrocarbons. Consequently, the rate of hydrocarbon gas make was high. Typical analyses of the make gas were H_2 21.7 mole %, CH_4 11.3, C_2H_4 6.1, C_2H_6 15.2, C_3H_6 22.1 C_3H_8 14.4, C_4H_8 5.4, C_4H_{10} 3.8. As the sieves became fouled, less n-paraffins were sorbed, resulting in a smaller quantity of light hydrocarbons formed and a lower hydrocarbon gas make rate. When the sieves approached saturation, the rate of gas formation levelled off to a very low rate, which is a measure of the small amount of non-selective cracking of the feed that was occurring during sorption at 850°F.

Comparative data on treating the 560/658°F. virgin gas oil with a hydrogen chloride modified 5Å sieves are shown in Figure 7. Treating conditions were 908°F., atmospheric pressure and 0.6 W/W/Hr. feed rate. The 5Å sieves were modified by initially saturating the sieve cavities with anhydrous hydrogen chloride at 700°F. (11 g/100 g sieves) before passing the gas oil feed. Thus, with the sieve cavities filled, any gas formation must be due entirely to non-selective cracking of the feed. As can be seen from the data the sieves were essentially ineffective for sorbing n-paraffins. The 5°F. reduction in pour point was due to non-selective cracking of the feed. The hydrocarbon gas make rate curve did not exhibit a maximum that was evident in Examples 7 and 8. Instead, it was a linear relationship; the hydrocarbon gas rate decreasing slowly as the cracking activity of the sieves dropped. If an 850°F. treating temperature were employed instead of 908°F., non-selective cracking of the feed would be reduced considerably. In the absence of selective wax cracking; the hydrocarbon gas make relationship should be similar to that shown in Figure 6 but displaced to a much lower value.

WHAT WE CLAIM IS:—

1. A process for reducing the normal paraffin content of a hydrocarbon oil characterized by contacting said oil in vapor phase at a temperature of from 800 to 1100°F. with a crystalline metallic aluminosilicate having uniform pore spaces of about 5 Angstrom units in a contacting zone, and withdrawing from said zone a vapor stream having a reduced normal paraffin content and an increased olefin and light hydrocarbon content.

2. A process according to claim 1 further characterized in that said hydrocarbon oil boils in the range of from 100 to 750°F.

3. A process according to claim 1 or claim 2 further characterized by condensing the hydrocarbons boiling above 100°F. from said withdrawn vapor stream, separating the uncondensed gases, maintaining said contacting until the rate of said light hydrocarbon gas formation is less than 50 cc per minute and thereafter regenerating said metallic aluminosilicate with an oxygen containing gas.

4. A process according to claim 1 or claim 2 further characterized by continuing said contacting until vapor is withdrawn having an undesirably high normal paraffin content and thereafter regenerating said metallic aluminosilicate with an oxygen containing gas.

5. A process according to any of claims 1-4 further characterized in that said hydrocarbon oil is contacted in said vapor phase with said aluminosilicate at a pressure of from 50 millimeters of mercury to 10 Atmospheres.

6. A process according to any of claims 1-5 further characterized in that said hydrocarbon oil is contacted in said vapor phase with said aluminosilicate at a rate of from 0.1 to 3.0 lbs. of oil per lb. of aluminosilicate per hour.

7. A process according to any of claims 1-6 further characterized in that said hydrocarbon oil is contacted with said aluminosilicate in the presence of a gas selected from the group consisting of hydrogen, nitrogen, carbon dioxide and an inert gas, said gas having a molecular diameter less than 5 Angstroms.

8. A process according to claim 7 further characterized in that said hydrocarbon oil is contacted with said aluminosilicate in the

presence of from 5 to 95 mole percent of said gas having a molecular diameter of less than 5 Angstrom units.

9. A process according to any of claims 1-8 further characterized in that said n-paraffins comprise waxy hydrocarbons.

10. A process according to claim 1 substantially as hereinbefore described with particular reference to the examples and accompanying drawings.

11. A hydrocarbon oil whose normal paraffin content has been reduced by a process according to any preceding claim.

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960,026 COMPLETE SPECIFICATION
3 SHEETS *This drawing is a reproduction of the Original on a reduced scale.*
SHEET 1

FIG.1.

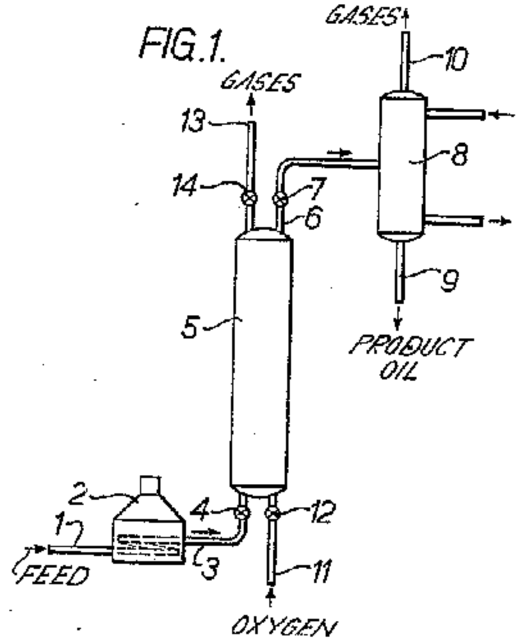
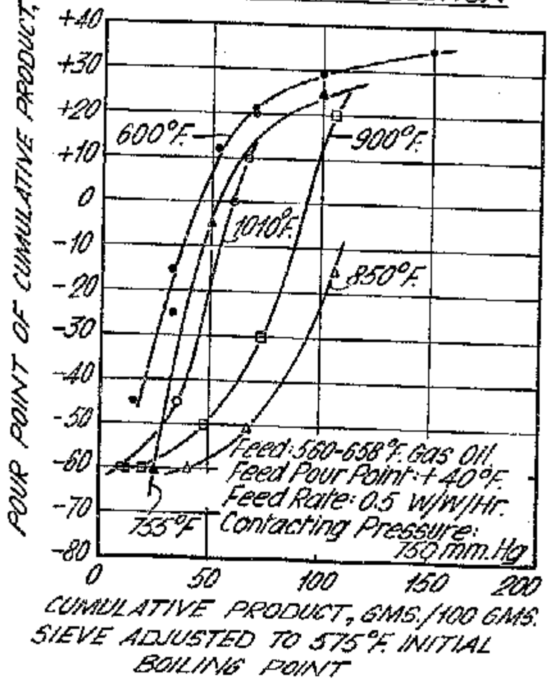


FIG.2.

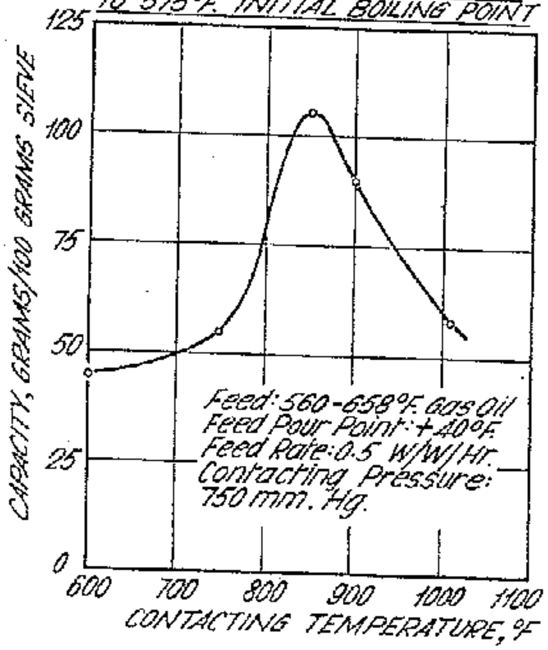
EFFECT OF CONTACTING TEMPERATURE UPON POUR POINT REDUCTION



EFFECT OF CONTACTING TEMPERATURE UPON SIEVE CAPACITY

FIG. 3.

0°F. POUR POINT PRODUCT ADJUSTED TO 575°F. INITIAL BOILING POINT



Feed: 560-658°F. Gas Oil
Feed Pour Point: +40°F.
Feed Rate: 0.5 W/W/Hr.
Contacting Pressure: 750 mm. Hg.

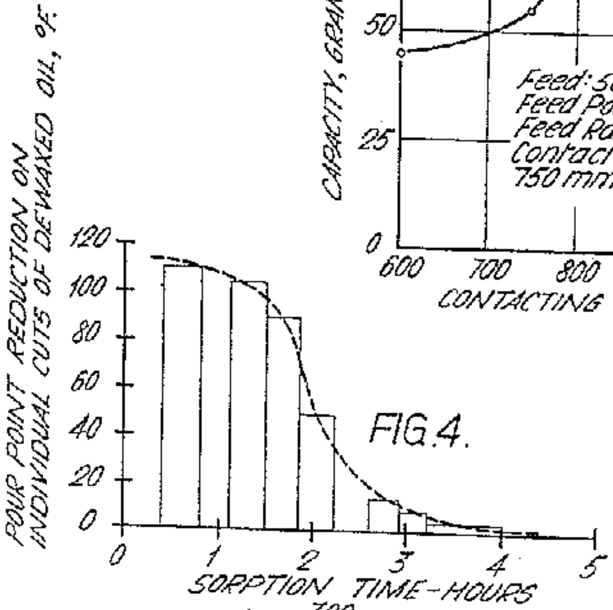


FIG. 4.

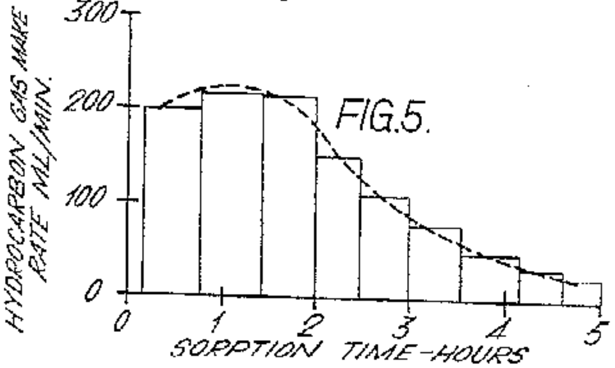


FIG. 5.

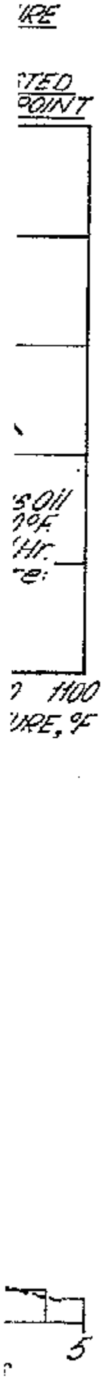

IRE
TED
POINT
s Oil
°F
Hr.
e:
1100
IRE, °F
5

FIG.6.

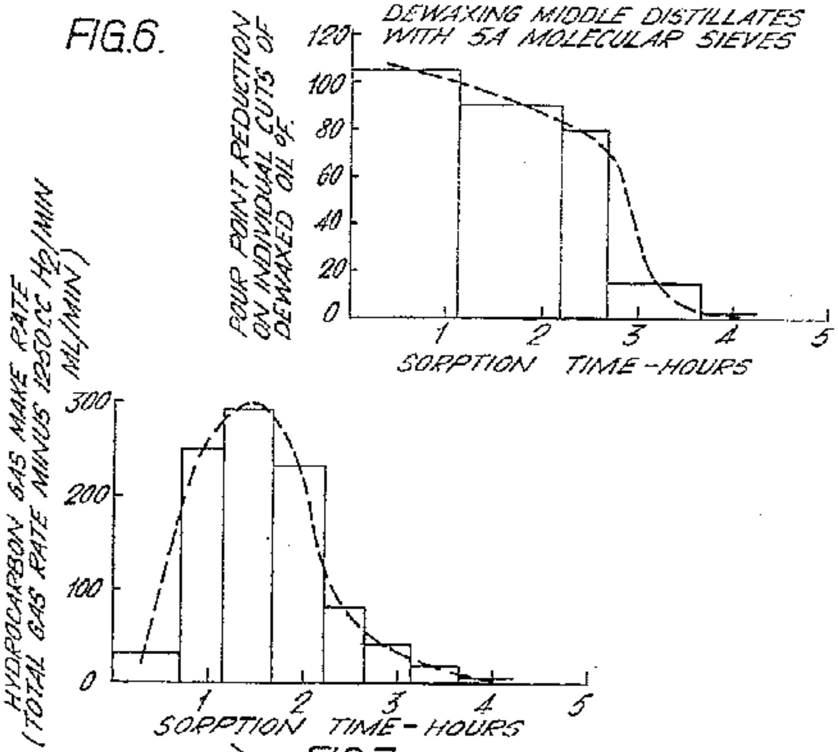
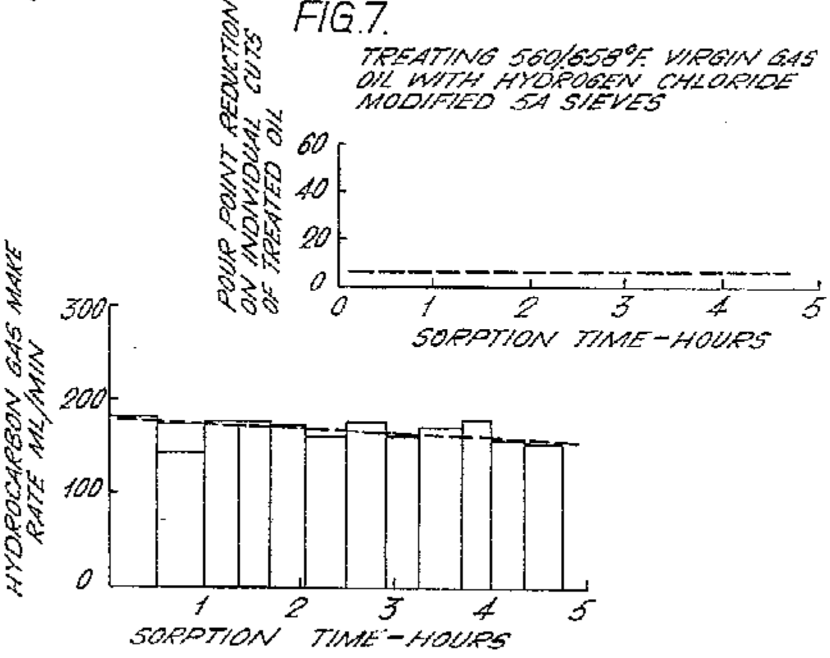

DEWAXING MIDDLE DISTILLATES WITH 5A MOLECULAR SIEVES
POUR POINT REDUCTION ON INDIVIDUAL CUTS OF DEWAXED OIL °F.
120
100
80
60
40
20
0
1
2
3
4
5
SORPTION TIME-HOURS
HYDROCARBON GAS MAKE RATE (TOTAL GAS RATE MINUS 1250 CC H2/MIN ML/MIN)
300
200
100
0
1
2
3
4
5
SORPTION TIME-HOURS

FIG.7.


TREATING 560/658°F. VIRGIN GAS OIL WITH HYDROGEN CHLORIDE MODIFIED 5A SIEVES
POUR POINT REDUCTION ON INDIVIDUAL CUTS OF TREATED OIL
60
40
20
0
0
1
2
3
4
5
SORPTION TIME-HOURS
HYDROCARBON GAS MAKE RATE ML/MIN
300
200
100
0
1
2
3
4
5
SORPTION TIME-HOURS

960,026 COMPLETE SPECIFICATION
3 SHEETS This drawing is a reproduction of the Original on a reduced scale.
SHEETS 2 & 3

FIG.3. EFFECT OF CONTACTING TEMPERATURE UPON SIEVE CAPACITY
0°F POUR POINT PRODUCT ADJUSTED TO 575°F INITIAL BOILING POINT

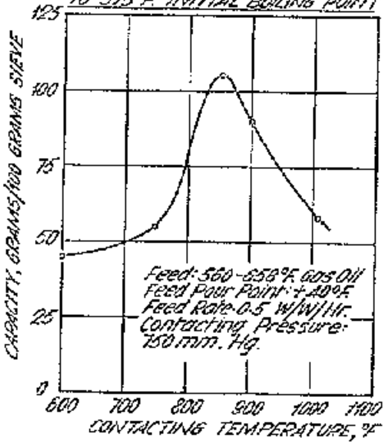


FIG.4.

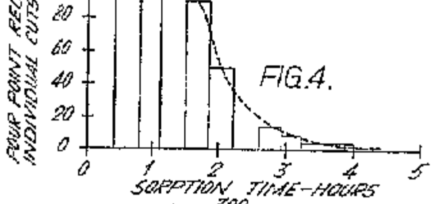


FIG.5.

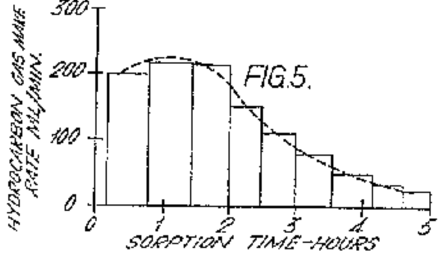


FIG.6.

DEWAXING MIDDLE DISTILLATES WITH 5A MOLECULAR SIEVES

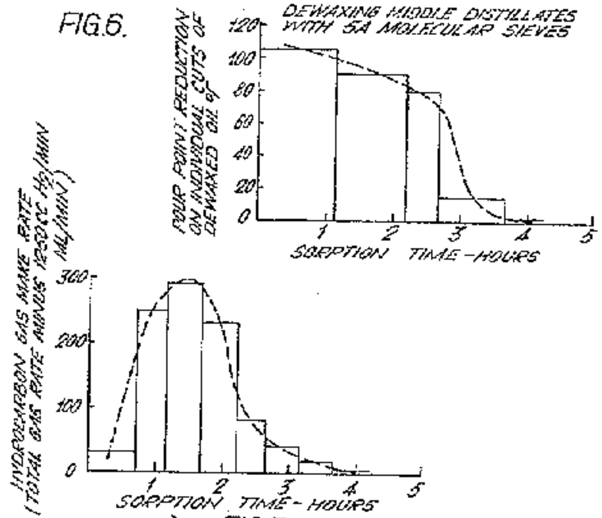


FIG.7.

TREATING 560/658°F. VIRGIN GAS OIL WITH HYDROGEN CHLORIDE MODIFIED 5A SIEVES