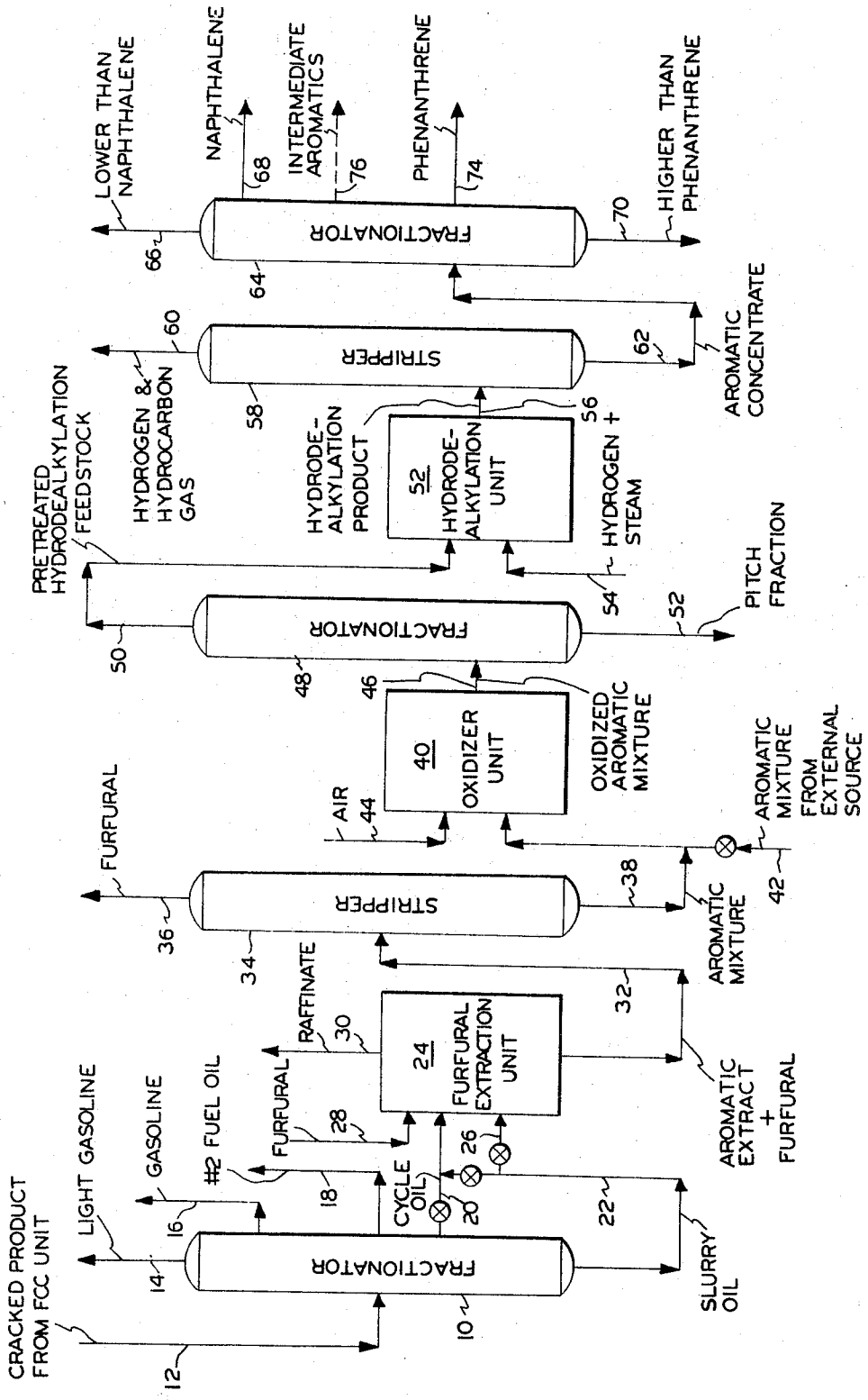
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POLYCYCLIC AROMATICS FOR HYDRODEALKYLATION

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POLYCYCLIC AROMATICS FOR HYDRODEALKYLATION

Charles D. Hoertz, Jr., Ashland, Ky., and William Sidney Green, Huntington, W. Va., assignors to Ashland Oil & Refining Company, Houston, Tex., a corporation of Kentucky

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The present invention relates to the preparation of a feed stock for the dealkylation of hydrocarbons, a method of dealkylating this feed stock, a novel asphaltic product, a novel hydrodealkylation feed stock and a novel aromatic product. In a more specific aspect, the present invention relates to a process for preparing a feed stock for the hydrodealkylation of aromatic hydrocarbons, the hydrodealkylation of this feed stock, a novel asphaltic product of the feed stock preparation, a novel hydrodealkylation feed stock, and a novel aromatic product of hydrodealkylation.

In the prior art it has been well known to obtain mononuclear and polynuclear aromatic hydrocarbons from various sources. One such source of aromatics is a coal tar fraction. The coal tar fraction contains some aromatics which are unsubstituted and, therefore, useful as such, if they can be adequately separated from impurities, such as, carbazole and sulfur containing compounds, and substituted aromatics having substituent groups, such as, methyl and ethyl groups. It is also known that the alkyl substituted aromatics may be dealkylated to improve the product yield. Other sources of aromatics, in addition to coal tar distillates, include tar sands, shale oil, bone oils, wood tar and other naturally occurring materials. Still another source of aromatics is the various products resulting from processes for refining liquid petroleum oils. Since liquid petroleum oils are basically made up of the same components as tar sands, shale oils and the like, except for quantities of components and the form of the crude product, large amounts of aromatics occur in petroleum oils, depending upon their origin, and, as a result, large amounts of impure aromatics and aromatic precursors are obtained as products of various processes for refining petroleum oil to produce the usual ultimate product—gasoline. As indicated, most refinery streams containing substantial amounts of aromatics are impure streams and the aromatics must be separated from paraffinic, naphthenic and other types of hydrocarbons. One method of making this separation involves the use of aromatic selective solvents, such as, furfural and the like. Such selective solvents, however, also separate alkylated aromatics, which were previously referred to as aromatic precursors. As is the case with coal tar distillate fractions, the alkylated aromatics in petroleum oil streams include both mononuclear and polynuclear alkyl substituted materials. In addition, the substituent groups include one or more methyl groups, ethyl groups and the like. Accordingly, in order to produce aromatics in commercial yields, it is necessary to convert the alkylated aromatics to unsubstituted products. This conversion is generally carried out by dealkylating the substituted aromatics generally by what is known as a hydrodealkylation operation. In such hydrodealkylation methods, the feed stock is treated at high temperatures with hydrogen or hydrogen producing compounds in the presence of a catalyst in order to selectively split off the alkyl group or groups. This process is especially well suited for the dealkylation, of mononuclear and binuclear aromatics. Such hydrodealkylation operations may be carried out at temperatures between 800° and 1500° F. Higher yields can generally be obtained by operating at or near the upper temperature

limits. These upper temperature limits are also advantageous when operating on comparatively high boiling feed stock materials. The major difficulty, however, in all hydrodealkylation processes, even at low temperatures, is in the formation of carbon and coke during the reaction. This carbon and coke formation is generally considered to be the result of scission or rupturing of aromatic rings at high temperatures or under severe conditions to form tar or coke precursors, as well as from the tar and coke precursors present in the feed stock itself. Again, higher boiling feed stocks will generally contain much higher quantities of coke and tar precursors. This formation of tar and coke in the hydrodealkylation process results in a rapid plugging and deactivation of the catalyst and the frequent necessity of shutting down the operation to clear the catalyst and regenerate it. This frequent and time-consuming shutdown, clean up and regeneration obviously results in an expensive and a highly inefficient overall operation.

Polynuclear aromatic materials higher than naphthalene, e.g. phenanthrene, have been difficult to produce by prior art techniques in substantially pure form. Up to the present time the principal source of phenanthrene has been a coal tar distillate or anthracene oil (green oil) fraction, usually boiling between 300 and 360° C. Phenanthrene is used in making dyes, is a stabilizer for explosives and smokeless powder and has been used in the synthesis of pharmaceuticals, drugs and organic intermediates. As previously indicated, prior art techniques for recovery of phenanthrene have included selective solvent extraction with furfural, carbon disulfide and the like, as well as selective crystallization and selective absorption. However, the separated products have at best been in poor yields of marginally poor products.

It is therefore an object of the present invention to provide an improved technique for the preparation of a hydrodealkylation feed stock. A further object of the present invention is to provide an improved technique for the removal of tar and coke precursors from hydrodealkylation feed stock. Another and further object of the present invention is to provide an improved technique for the preparation of a hydrodealkylation feed stock from high boiling catalytic cracking products. Yet another object of the present invention is to provide an improved technique for the preparation of a hydrodealkylation feed stock from a catalytically cracked slurry oil. A further object of the present invention is to provide an improved technique for the preparation of a hydrodealkylation feed stock from a catalytically cracked cycle oil. Yet another object of the present invention is to provide an improved technique for the preparation of a hydrodealkylation feed stock from a mixture of catalytically cracked cycle oil and slurry oil. Another and further object of the present invention is to provide an improved technique for the preparation of a hydrodealkylation feed stock wherein a hydrocarbon fraction containing aromatic precursors is oxidized at an elevated temperature. Still another object of the present invention is to provide an improved technique for the preparation of a hydrodealkylation feed stock wherein a hydrocarbon fraction containing aromatic precursors is treated with an aromatic selective solvent and the extracted aromatics are thereafter oxidized at an elevated temperature. Another object of the present invention is to provide an improved hydrodealkylation process in which a selectively treated feed stock is employed. A further object of the present invention is to provide an improved hydrodealkylation process in which a highly selective catalyst is employed. A still further object of the present invention is to provide an improved hydrodealkylation process in which a selectively treated feed stock is hydrodealkylated in the presence of a catalyst of improved effectiveness. Yet another object of the present

invention is to provide an improved hydrodealkylation process in which a high boiling catalytically cracked fraction is selectively treated prior to the hydrodealkylation process. A further object of the present invention is to provide an improved hydrodealkylation process in which a catalytically cracked slurry oil is pretreated prior to the hydroealkylation process. Another object of the present invention is to provide an improved hydrodealkylation process in which catalytically cracked cycle oil is selectively pretreated prior to hydrodealkylation reaction. A still further object of the present invention is to provide an improved hydrodealkylation process in which a mixture of catalytically cracked cycle oil and slurry oil is selectively pretreated prior to the hydrodealkylation process. Another object of the present invention is to provide an improved hydrodealkylation process in which a mixture of catalytically cracked cycle oil and slurry oil is selectively pretreated prior to the hydrodealkylation process and a highly effective catalyst is employed in the reaction. Another object of the present invention is to provide an improved hydrodealkylation feed stock. A further object of the present invention is to provide a novel tar product. Another object of the present invention is to provide an improved unsubstituted aromatic composition. Another and further object of the present invention is to provide an improved aromatic product including naphthalene and higher boiling aromatics. Still another object of the present invention is to provide a polynuclear aromatic product of improved purity. Yet another object of the present invention is to provide an improved aromatic product rich in phenanthrene and fluorene. A further object of the present invention is to provide a phenanthrene product of high purity. These and other objects and advantages of the present invention will be apparent from the following detailed description when read in conjunction with the accompanying drawing. The drawing is a flow diagram of the preferred technique for preparation of a hydrodealkylation feed stock, hydrodealkylation of the feed stock and the production of a substantially pure unsubstituted aromatic product.

The present invention is applicable to any hydrocarbon product of petroleum or coal tar origin, containing significant amounts of aromatics, specifically, mononuclear and polynuclear compounds having substiuent alkyl groups and, particularly the higher boiling mononuclear and polynuclear materials, such as, dimethylphenanthrenes, methylphenanthrenes, alkyl fluorenes and alkylnaphthalenes. While alkyl benzenes can be treated in accordance with the present invention, it has found its most effective use in the production of phenanthrene, anthracene, fluorene and naphthalene. Accordingly, the present invention is most useful in treating hydrocarbon materials boiling above about 550° F.

One source of mixtures of these materials has been product streams from petroleum refining operations, such as, catalytic reforming, hydroforming, cracking, etc. Such processes yield large amounts of alkylated aromatics. While such alkylated aromatics may be utilized in motor fuels and other products as such, greater demand for these products exists in the pure chemical field where a highly purified material is desired for use as solvents and chemical intermediates. By way of specific example, product streams obtained by fractionating the liquid product of a fluid catalytic cracking process produce feed stocks which benefit most significantly by the use of the present invention.

Referring specifically to the drawing, a cracked product from a fluid catalytic cracking unit is fed to fractionator **10** through line **12**. In fractionator **10** the fluid catalytic cracking product is separated into a light gasoline fraction which is discharged through line **14**, a gasoline product discharged through line **16** and a #2 fuel oil product discharged through line **18**. These three materials, of course, have direct uses in industry and further reference thereto is unnecessary. In addition to the above, the remaining or bottoms of the fractionation operation is split into what is called a cycle oil, normally having a boiling point of about 600 to 700° F. and a higher boiling slurry oil, normally having a boiling range of about 650° to 850° F. The cycle oil is discharged from fractionator **10** through line **20** and the slurry oil through line **22**. Both of these materials are rich in alkyl aromatics, such as, alkyl phenanthrenes and alkyl fluorenes and, by the same token, because of their high boiling point, also contain substantial amounts of coke precursors of generally unknown composition. Speculatively, these coke precursors include indene and the like and, to a great extent, act like olefins and polymerize readily. Preferably, the slurry oil is clarified, as by settling, distillation or other means. However, this conventional operation is not shown so that the drawing will not be unduly complicated.

The slurry oil and/or the cycle oil are fed to furfural extraction unit **24** through the continuation of cycle oil line **20**, or, if slurry oil alone is utilized, through slurry oil branch line **26**. Furfural is fed to extraction unit **24** through line **28**. This extraction operation selectively removes aromatics from paraffinic, naphthenic and other non-aromatic components. The solvent-to-oil volume ratio utilized should be in the neighborhood of 0.2:1 to 2:1. This, of course, can be readily selected by one skilled in the art. While furfural has been given as a specific example and is the preferred aromatic selective solvent, other suitable solvents include phenol, methanol, acetonitrile, dimethylformamide, etc. From extraction unit **24**, byproduct raffinate is discharged through line **30**. The mixture of aromatic extract, plus furfural, passes through line **32** to stripper **34**. In stripper **34** the furfural is removed by distillation and discharged through line **36**.

A highly concentrated aromatic mixture is discharged through line **38**. This mixture will normally have a boiling point of about 600° to 850° F., or more or less, depending of course upon the original starting material.

The concentrated aromatic mixture passing from stripper **34** through line **38** is fed to oxidizer unit **40**. While the specific example pertains to the treatment of cycle oils and slurry oils, it should also be recognized that any aromatic concentrate of petroleum origin can be utilized. In some cases, as with highly aromatic petroleum mixtures, such as reformer bottoms, the previously discussed fractionation, extraction and stripping operations would be unnecessary and the aromatic mixture could be fed directly to oxidizer unit **40** through line **42**. Oxidizer unit **40** is supplied with air, oxygen or oxygen-containing material through line **44**. In oxidizer unit **40** the aromatic mixture is subjected to air-blowing or oxidizing conditions, such as those normally used for air-blowing or oxidizing asphaltic materials. Illustrative conditions for use in the oxidation unit include a temperature of about 475° to 500° F., a pressure from atmospheric pressure to about 100 p.s.i.g., and an air velocity of approximately 0.1 to 0.5 cubic feet per minute per gallon of aromatic mixture. The oxidation is carried out to a softening point of at least about 50 to about 300° F. and preferably about 50 to about 150° F. Measurements of softening point, and its significance as a measurement of the degree of oxidation of asphalt, are well-known to those skilled in the art. It should be recognized, however, that the higher the softening point above about 150° F., the more difficult it becomes to process the oxidized aromatic mixture. At present, it is thought most desirable to oxidize until the aromatic mixture has a softening point in the range of about 50 to about 100° F. in order that the coke precursors may be substantially removed while producing a useable tar pitch. During such oxidation the aromatics of the character of alkyl- and unsubstituted-phenanthrene remain relatively stable whereas the coke precursors tend to condense and polymerize to products of substantially higher boiling points.

Oxidized aromatic mixture from oxidizing unit **40** is discharged through line **46** to fractionator **48** where it is

fractionated or stripped to remove the above-mentioned higher boiling coke precursors. Specifically, vacuum distillation is preferred. The oxidized aromatic mixture is fractionated or stripped in fractionator **48** to produce a pretreated hydrodealkylation feed stock which is discharged through line **50**. The hydrodealkylation feed stock is substantially free of materials boiling above about 740° F. and preferably the hydrodealkylation feed stock has an end point falling in the range of about 690° to 740° F. The heavier fraction or higher boiling pitch fraction is discharged through line **51**. This pitch fraction, as well as the hydrodealkylation feed stock which is a primary stream, has been found to have highly desirable properties when derived from petroleum fractions, as indicated. The pitch fraction obtained, from petroleum based aromatic mixtures has been found to have characteristics and properties very closely resembling or surpassing those of pitch fractions obtained from coal tar and, as such, has numerous industrial uses.

The hydrodealkylation feed stock may, at this point, be subjected to a desulfurization operation under conditions well known to those skilled in the art. Again, to simplify the drawing and facilitate the description of the present invention, this conventional operation is not shown in the drawing. Hydrodealkylation feed stock from line **50** is fed to hydrodealkylation unit **52**. Hydrodealkylation unit **52** is also supplied with hydrogen through line **54**. It is also desirable to inject water (steam) along with or separately from the hydrogen. The injected steam appears to reduce the temperature necessary for a given degree of conversion.

Hydrodealkylation unit **52** may be any conventional apparatus adapted for contacting gases and liquids with solids. For example, fixed, circulating and fluid bed contactors having single or multiple beds may be employed. Such contactors may be operated according to various modes, such as batch, cyclical or continuous. In a continuous operation, a catalyst in granular, powdered or pelleted form is contacted for countercurrently or concurrently while flowing through the reactor ordinarily by gravity flow, with restricted streams of reactant gases and liquids. Heat may be supplied by suitable preheating of the catalyst or by internal or external heating of reactor itself and/or by preheating the feed fluids. Contact time and heat supplied may be regulated by suitably adjusting the flow rate of catalyst and feed materials. In a cyclic operation a plurality of stationary beds of catalyst are ordinarily employed, whereby some of the units may be maintained on stream at all times, while others are undergoing regeneration or cleaning. Heat is ordinarily supplied externally or by internal heating elements, and the operation may be conducted at atmospheric pressure or above. In accordance with the preferred embodiment of the invention, a single fixed bed reactor unit is employed. Fresh or regenerated catalyst is held stationary in the reactor and the feed is passed downwardly through the bed under pressure on a continuous basis. If coke or carbon builds up in the bed, the pressure drop across the bed increases. When the pressure drop and carbon content of the bed reach levels which are either inconvenient or impossible to contend with, the bed is no longer usable and the reactor is shut down. Then, the catalyst is either regenerated in the reactor or is removed and replaced with fresh catalyst. Because the invention has the effect of minimizing the production of carbon in the catalyst bed, the above described mode of operation is quite simple and eminently practical because the reactor requires only infrequent shutdowns on account of carbon formation in the catalyst bed and such shutdowns do not constitute a serious interruption of production, considering their infrequency.

The reaction conditions generally employed in accordance with the invention may include temperatures ranging from about 800° to about 1500° F. However, in the present operation, this range will normally be between 1100° and 1400° F. and preferably between 1235° to 1350° F. A weight-hourly space velocity suitable, for use in accordance with the present invention includes 0.2 to 2 and preferably 0.5 to 1.0. The ratio of hydrogen to hydrodealkylation feed stock can range from 5 to as high as 30 moles per mole of feed material. In the present operation the normal operating range will be 10:1 to 30:1 and preferably 15:1 to 20:1. Operating pressures may vary anywhere from atmospheric to as high as 1500 p.s.i.g. The range to be used herein is atmospheric to 1000 p.s.i.g. and preferably 400 to 800 p.s.i.g.

The catalysts employed in accordance with the present invention may include any of the well-known hydrodealkylation catalysts. Catalysts of this type generally comprise, as a primary or sole ingredient, an active metal catalyst or compound thereof, which metal may be any of the heavy metals, that is, those having atomic weights of about 22 or above. A preferred class of metals includes those belonging to groups VI–B and VIII of the Periodic Table. These metals are chromium, molybdenum, tungsten, uranium, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum. The metals are preferably employed in the form of their oxides, but the free metals in finely divided form may be employed, or other compounds thereof, such as the sulfides or phosphides, and phosphates or sulfates may be employed. Molybdenum in the form of molybdic trioxide, either alone or supported on a suitable carrier, is a highly effective catalyst, especially when this material is promoted with other metals or metal oxide, such as, cobalt oxide, nickel oxide, iron oxide and chromia. It has been indicated in the literature that the molybdic trioxide in such a catalyst should not be chemically combined with any of the added promoters. Similarly, it has been indicated that a molybdic oxide and cobalt oxide-containing catalyst prepared by alternately impregnating with molybdenum and cobalt salts, in such manner that the oxides are not combined, is more active than cobalt molybdate catalyst prepared by coimpregnation or coprecipitation, wherein the molybdenum is more or less chemically combined with the cobalt. Catalysts which have been found highly useful in accordance with the present invention have the following analyses and properties.

	Weight percent
Chemical, dry basis:	
Volatile at 1200° F.	2.4
Al_2O_3	20.3
MoO_3	12.1
CoO	3.77
Na_2O	.049
SO_4	.22
Fe	.038
SiO_2	By difference
Physical:	
Surface area, M.²/g.	270
Pore volume, cm.³/g.	.45
Pore diameter, A.	67
ABD, g./cc.	.53
Strength, lbs. crush	8.5

This catalyst is called "Nalcoden" by its manufacturer Nalco Chemical Company. While heavy metal catalysts of the type described give best results, it is possible to use conventional synthetic silica-alumina catalysts, such as "Houdry S–65" manufactured by the Houdry Process Corporation. This particular catalyst has the following properties.

Chemical:	
Al_2O_3 wt. percent	12.4
SiO_2 wt. percent	87.3
Physical:	
Surface area, m.²/g.	375–400
Bulk density, kg./l.	0.54

Physical:	Weight percent
Pellet density, kg./l.	0.86
Porosity, vol. percent	60
Absorption, wt. percent	65
Average pore size, A.	80

Hydrodealkylation product from hydrodealkylation unit **52** is passed through line **56** to stripper **58**. In stripper **58** the hydrodealkylation product is separated into a liquid and a gaseous fraction. The gaseous fraction including hydrogen and hydrocarbon gases, principally, methane is discharged through line **60**. The liquid aromatic concentrate is passed through line **62** to fractionator **64**. In fractionator **64** the aromatic concentrate is separated into its individual components or groups of components as desired for end use. For example, a fraction having a boiling point below naphthalene can be discharged through line **66** and a naphthalene fraction through line **68**. Also, materials boiling above phenanthrene may be discharged through line **70** and a relatively pure phenanthrene through line **74**. If desired, the phenanthrene may then be purified by conventional techniques which are known to persons skilled in the art and which form no part of the present invention. Materials boiling between phenanthrene and naphthalene may be removed as a bulk product or, as shown in the drawing, as individual components. These intermediate products are shown in the drawing by a single discharge line **76** representing a plurality of cuts or individual fractions.

The following specific examples will show the highly advantageous results obtained and the highly desirable products produced in accordance with the present invention.

EXAMPLE I

A feed stock comprising about 75% clarified slurry oil and 25% cycle oil from a fluid catalytic cracking operation was extracted with furfural to produce an aromatic mixture. This aromatic mixture was then oxidized by air-blowing to a softening point of about 125° F. The oxidized aromatic mixture was then fractionated to produce a pretreated hydrodealkylation feed stock having a nominal boiling range of 610° to 720° and an A.P.I. gravity at 60° F. of 9.0. The boiling point analysis of this material was as follows:

	° F.
I.B.P.	578
Percent over:	
5	601
10	612
20	623
30	637
40	648
50	660
60	669
70	681
80	694
90	718
95	738
E.B.P	772

This hydrodealkylation feed stock was then fed to a hydrodealkylation unit. The reactor itself was a 2" diameter chamber of Schedule 80 stainless steel pipe. The previously described Nalcoden catalyst was placed in the reactor to a bed depth of approximately 15". During the course of the hydrodealkylation reaction the temperature was maintained at about 1275° to 1300° F., the weight-hourly space velocity about 0.6, the pressure about 800 p.s.i., the hydrogen to hydrocarbon mole ratio about 15:1 and the residence time about 0.4 minute. A liquid product yield of about 69% was obtained, based on the weight of liquid feed to the hydrogenation unit. This product was charged to a batch still for distillation and the following table lists the analysis of the product and the percentage of each component obtained.

Component:	Weight percent
<Naphthalene	3.19
Naphthalene	9.32
Naphthalene-betamethylnaphthalene	0.03
Betamethylnaphthalene	2.94
Alphamethylnaphthalene	1.00
Alphamethylnaphthalene-biphenyl	0.40
Biphenyl	0.96
Biphenyl-acenapthene	2.23
Acenaphthene	0.81
Acenaphthene-Fluorene	1.12
Fluorene	6.94
Fluorene-phenanthrene	6.88
Phenanthrene, Anthracene (trace quantities)	26.50
>Anthracene	38.13

After operating the hydrodealkylation unit on this pretreated hydrodealkylation feed stock for over 350 hours, the reactor was still operating satisfactorily, thus indicating that the catalyst bed was substantially free of coke deposits.

EXAMPLE II

Another portion of the same mixture of slurry oil and cycle oil was subjected to the same type of furfural extraction, followed by stripping and oxidation in the same manner as in Example I. Thereafter, this oxidized aromatic mixture was fractionated to produce a pretreated hydrodealkylation feed stock having a nominal boiling range of about 570 to 720° F., an A.P.I. gravity at 60° of 10.6 and the following specific boiling point analysis:

	° F.
I.B.P.	550
Percent over:	
5	568
10	577
20	586
30	597
40	606
50	615
60	623
70	632
80	643
90	662
95	677
E.B.P.	705

This pretreated hydrodealkylation feed stock was fed to a hydrodealkylation unit comprising a ¾" diameter chamber of Schedule 80 stainless steel. The reactor was filled to a bed depth of about 8½" with the previously described Houdry S–65 catalyst. During the course of the hydrodealkylation the temperature was maintained at 1290° to 1315° F., a weight-hourly space velocity of 1.18 to 1.41 was employed, the pressure was 400 p.s.i., the hydrogen to hydrocarbon mole ratio was 15:1 and the residence time was about 0.36 minute. The liquid product yield was found to be about 72% based on the weight of liquid feed. This product had the following typical chromatographic analysis:

Component:	Weight percent
<Naphthalene	5.2
Naphthalene	11.2
Intermediate oils boiling between naphthalene and acenaphthene	13.8
Acenaphthene	2.1
Intermediate oils boiling between acenaphthene and fluorene	1.5
Fluorene	9.2
Intermediate oils boiling between fluorene on the one hand and phenanthrene and anthracene on the other hand	7.5
Phenanthrene (at least)	15.7

Component:	Weight percent
Anthracene (no more than)	0.8
Material boiling above phenanthrene and anthracene	33.0

After the catalyst had been utilized to process a total of 1.3 barrels of liquid feed per pound of catalyst, the reactor was still operating normally and, thus, insufficient coke to detrimentally affect the unit had been formed up to this point.

While specific examples have been utilized herein, it is to be understood that such examples are given by way of illustration and the present invention is to be limited only in accordance with the appended claims.

We claim:

1. A method for dealkylation of a liquid hydrocarbon fraction, comprising: extracting aromatics from a liquid hydrocarbon fraction boiling between about 550° and 850° F. and containing alkylated aromatics with an aromatic selective solvent; oxidizing said extracted aromatic mixture at an elevated temperature until said oxidized aromatic mixture has a softening point between about 50 and 300° F. is obtained; separating a hydrodealkylation feed stock boiling below about 740° F. from a higher boiling fraction containing coke precursors; and subjecting said hydrodealkylation feed stock to a hydrodealkylation reaction, in the presence of a hydrodealkylation catalyst containing molybdic trioxide and cobalt oxide as active ingredients and, under the following conditions: a temperature between 1100 and 1400° F., a weight-hourly space velocity of 0.2 to 2, a hydrogen to hydrocarbon ratio of 10:1 to 30:1, a pressure between atmospheric and 1000 p.s.i.

2. A method for dealkylation of a liquid hydrocarbon fraction, comprising: extracting aromatics from a liquid hydrocarbon fraction boiling between about 550° and 850° F. containing alkylated aromatics; oxidizing said extracted aromatic mixture at an elevated temperature until said oxidized aromatic mixture has a softening point between about 50° and 300° F.; separating a hydrodealkylation feed stock boiling below about 740° F. from a higher boiling fraction containing coke precursors; and subjecting said hydrodealkylation feed stock to a hydrodealkylation reaction in the presence of hydrogen and a hydrodealkylation catalyst.

3. A method of preparing a hydrodealkylation feed stock, comprising: oxidizing a liquid hydrocarbon fraction boiling between about 550° and 850° F. containing alkylated aromatics at an elevated temperature until said oxidized hydrocarbon fraction has a softening point between about 50° and 300° F. and separating a low boiling hydrodealkylation feed stock boiling below about 740° F. from a higher boiling fraction containing coke precursors.

4. A method in accordance with claim 3 wherein the liquid hydrocarbon fraction is a coal tar product.

5. A method in accordance with claim 3 wherein the liquid hydrocarbon fraction is a slurry oil from a catalytic cracking operation.

6. A method in accordance with claim 3 wherein the liquid hydrocarbon fraction is a heavy cycle oil from a catalytic cracking operation.

7. A method in accordance with claim 3 wherein the oxidation is carried out by air-blowing at an elevated temperature.

8. A method in accordance with claim 3 wherein the oxidation is carried out at an elevated temperature not exceeding about 500° F.

9. A method in accordance with claim 3 wherein the oxidation is carried out at a temperature between about 475° and 500° F.

10. A method in accordance with claim 3 wherein the oxidation is carried out for a time sufficient to produce a product having a softening point between about 50° and 150° F.

11. A method in accordance with claim 3 wherein a hydrodealkylation feed stock having an end point between about 690° and 740° F. is separated from the higher boiling fraction.

12. A method of preparing a hydrodealkylation feed stock comprising: extracting aromatics from a liquid hydrocarbon fraction boiling between about 550° and 850° F. containing alkylated aromatics; oxidizing said extracted aromatic mixture at an elevated temperature until said oxidized aromatic mixture has a softening point between about 50° and 300° F.; and separating a low boiling hydrodealkylation feed stock boiling below about 740° F. from a higher boiling fraction containing coke precursors.

13. A method in accordance with claim 12 wherein the aromatics are extracted by a solvent selective for aromatics.

14. A method in accordance with claim 12 wherein the extraction is carried out with furfural as a solvent for the aromatics.

15. A method in accordance with claim 12 wherein the extraction is carried out with a solvent selective for aromatics and a solvent to liquid hydrocarbon volume ratio of 0.2:1 to 2:1 is employed.

16. A method in accordance with claim 12 wherein fraction, comprising: oxidizing a liquid hydrocarbon fraction boiling between about 550° and 850° F. containing alkylated aromatics at an elevated temperature until said oxidized hydrocarbon fraction has a softening point between about 50° and 300° F.; separating a low boiling hydrodealkylation feed stock boiling below about 740° F. from a higher boiling fraction containing coke precursors; and subjecting said hydrodealkylation feed stock to a hydrodealkylation reaction in the presence of hydrogen and a hydrodealkylation catalyst.

17. A method in accordance with claim 16 wherein the catalyst contains molybdic trioxide.

18. A method in accordance with claim 16 wherein the catalyst contains cobalt oxide.

19. A method in accordance with claim 16 wherein the catalyst contains molybdic trioxide and cobalt oxide.

20. A method in accordance with claim 16 wherein the catalyst is molybdic trioxide on a silica-alumina carrier.

21. A method in accordance with claim 16 wherein the catalyst is cobalt oxide on a silica-alumina carrier.

22. A method in accordance with claim 16 wherein the catalyst contains molybdic trioxide and cobalt oxide. silica-alumina carrier.

23. A method in accordance with claim 16 wherein the hydrodealkylation reaction is carried out at a temperature between 1100 and 1400° F.

24. A method in accordance with claim 16 wherein the hydrodealkylation reaction is carried out at a temperature between 1275 and 1350° F.

25. A method in accordance with claim 16 wherein the hydrodealkylation reaction is carried out at a weight-hourly space velocity of 0.2 to 2.

26. A method in accordance with claim 16 wherein the hydrodealkylation reaction is carried out at a weight-hourly space velocity of 0.5 to 1.

27. A method in accordance with claim 16 wherein the hydrogen to hydrodealkylation feed stock mole ratio is from 10:1 to 30:1.

28. A method in accordance with claim 16 wherein the hydrogen to hydrodealkylation feed stock mole ratio is 15:1 to 20:1.

29. A method in accordance with claim 16 wherein the hydrodealkylation reaction is carried out at a pressure between atmospheric pressure and 1000 p.s.i.

30. A method in accordance with claim 16 wherein the hydrodealkylation reaction is carried out at a pressure between 400 and 800 p.s.i.

31. A hydrodealkylation feed stock obtained by: oxidizing a liquid hydrocarbon fraction boiling between about 550° and 850° F. containing alkylated aromatics at an elevated temperature until said oxidized hydrocarbon fraction has a softening point between about 50°

and 300° F. and separating a low boiling hydrodealkylation feed stock boiling below about 740° F. from a higher boiling fraction containing coke precursors.

32. A hydrodealkylation feed stock obtained by: extracting aromatics from a liquid hydrocarbon fraction boiling between about 550° and 850° F. containing alkylated aromatics; oxidizing said extracted aromatic mixture at an elevated temperature until said oxidized aromatic mixture has a softening point between about 50° and 300° F.; and separating a low boiling hydrodealkylation feed stock boiling below about 740° F. from a higher boiling fraction containing coke precursors.

33. An aromatic mixture, containing substantial amounts of unsubstituted aromatics, obtained by: extracting aromatics from a liquid hydrocarbon fraction boiling between about 550° and 850° F. and containing alkylated aromatics with an aromatic selective solvent; oxidizing said extracted aromatic mixture at an elevated temperature until said oxidized aromatic mixture has a softening point between about 50° and 150° F. is obtained; separating a hydrodealkylation feed stock boiling below about 740° F. from a higher boiling fraction containing coke precursors; and subjecting said hydrodealkylation feed stock to a hydrodealkylation reaction, in the presence of a hydrodealkylation catalyst containing molybdic trioxide and cobalt oxide as active ingredients and, under the following conditions: a temperature between 1100 and 1400° F., a weight-hourly space velocity of 0.2 to 2, a hydrogen to hydrocarbon ratio of 10:1 to 30:1, a pressure between atmospheric and 1000 p.s.i.

34. An aromatic mixture, containing substantial amounts of unsubstituted aromatics, obtained by: extracting aromatics from a liquid hydrocarbon fraction boiling between about 550° and 850° F. containing alkylated aromatics; oxidizing said extracted aromatic mixture at an elevated temperature until said oxidized aromatic mixture has a softening point between about 50° and 300° F.; separating a hydrodealkylation feed stock boiling below about 740° F. from a higher boiling fraction containing coke precursors; and subjecting said hydrodealkylation feed stock to a hydrodealkylation reaction in the presence of hydrogen and a hydrodealkylation catalyst.

35. An aromatic mixture, containing substantial amounts of unsubstituted aromatics, obtained by: oxidizing a liquid hydrocarbon fraction boiling between about 550° and 850° F. containing alkylated aromatics at an elveated temperature until said oxidized hydrocarbon fraction has a softening point between about 50° and 300° F.; separating a low boiling hydrodealkylation feed stock boiling below about 740° F. from a higher boiling fraction containing coke precursors; and subjecting said hydrodealkylation feed stock to a hydrodealkylation reaction in the presence of hydrogen and a hydrodealkylation catalyst.

36. An asphaltic product obtained by: extracting aromatics from a petroleum-base, liquid hydrocarbon fraction boiling between about 550° and 850° F. and containing alkylated aromatics; oxidizing said extracted aromatic mixture at an elevated temperature until said oxidized aromatic mixture has a softening point between about 50° and 300° F.; and separating said asphaltic product from a lower boiling liquid hydrocarbon material having an end point between about 690° and 740° F.

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DELBERT E. GANTZ, *Primary Examiner.*

G. E. SCHMITKONS, *Assistant Examiner.*