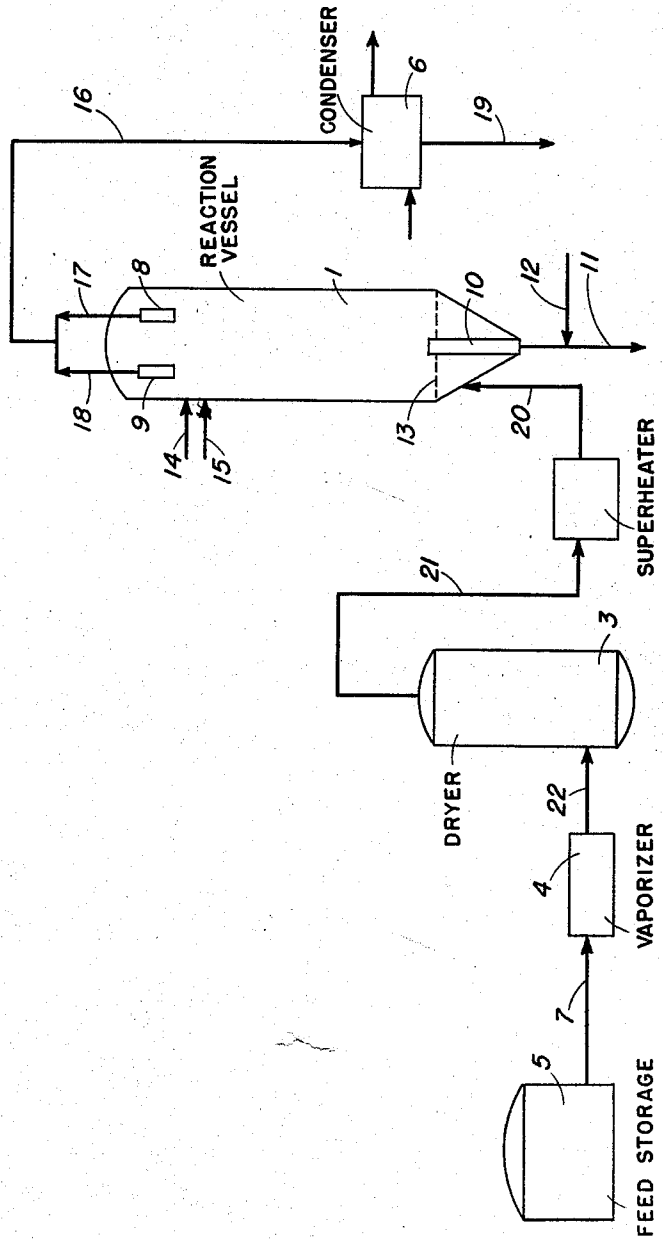
Nov. 15, 1960 J. F. NOBIS ET AL 2,960,546

DESULFURIZATION OF AROMATIC HYDROCARBONS

Filed March 11, 1957



DESULFURIZATION OF AROMATIC HYDROCARBONS

J. F. NOBIS
L. M. WATSON
INVENTORS

BY Lawrence Rosen
ATTORNEY

United States Patent Office 2,960,546
Patented Nov. 15, 1960

2,960,546

DESULFURIZATION OF AROMATIC HYDROCARBONS

John F. Nobis and Lloyd M. Watson, Cincinnati, Ohio, assignors to National Distillers and Chemical Corporation, New York, N.Y., a corporation of Virginia

Filed Mar. 11, 1957, Ser. No. 645,035
8 Claims. (Cl. 260—674)

This invention relates to a method for desulfurizing aromatic hydrocarbons. More particularly, the invention pertains to a process for obtaining nitration grade aromatic hydrocarbons which are substantially free of thiophene and other impurities.

One important commercial source of aromatic hydrocarbons is the light oil produced as a by-product in coke oven operations. The coke oven light oil, known as BTX, comprises a mixture of benzene, toluene, and xylene. Though this synthetically produced mixture of aromatic hydrocarbons or its individual aromatic constituents have many uses, recent industrial demands have been for higher quality aromatic hydrocarbons than presently available. Coke plant benzene, for example, is not advantageously employed for synthetic fiber production because of its objectional thiophene content. In many other uses of aromatic hydrocarbons, removal of the paraffin as well as the thiophene impurities is required. The prior art acid and caustic wash purification processes do not purify the aromatic hydrocarbons to a low enough thiophene content; and, furthermore, they present serious acid sludge disposal problems. Recently, a purification process has been proposed which involves hydrogenating the coke oven light oils to convert the sulfur compounds to hydrogen sulfide, and the subsequent selective solvent extraction of the aromatics from the paraffins. One serious drawback to this process is the loss of aromatics resulting from hydrogenation during the desulfurization operation. This process also has the disadvantage of requiring readily available hydrogen gas. Furthermore, high pressures are required for the hydrogenation of the sulfur compounds and relatively large installations are needed for economic operation.

It is one object of this invention to provide a simplified continuous process for the direct purification of aromatic hydrocarbons. Another object of the invention is the substantial removal of thiophene from coke oven light oil or the aromatic constituents thereof. Other objects will become apparent from the ensuing description of the invention.

In accordance with the present invention, it has now been found that coke oven light oil as well as the individual aromatic hydrocarbon constituents thereof can be effectively and economically desulfurized by treatment with high surface metallic sodium on an inert solid inorganic carrier in a highly agitated solids mass system which ensures intimate contact. The preferred method of this invention comprises passing aromatic hydrocarbons in vapor form up through a fluidized bed of metallic sodium dispersed on an inert, finely divided, solid carrier medium. In the so-called 'fluidized bed" system a solid-in-gas dispersion is maintained. As noted above, the solid phase in this invention is high surface metallic sodium coated on finely divided inert carrier material. The sodium coated solid material is dispersed in an upflowing stream of the aromatic hydrocarbon vapors under controlled gas velocity conditions so that a fluidized bed is maintained in the reaction vessel. By operating in this manner, it has been found that the metallic sodium, which is in the form of a substantially monoatomic film on the finely divided carrier material, will react with the sulfur compounds in the aromatic hydrocarbon feed and thereby effect their removal.

This aspect of the invention will be best understood by reference to the accompanying drawing which is a diagrammatic illustration of suitable apparatus consisting of a fluidized reactor and auxiliary equipment. In operation, a stream of coke oven light oil is passed from feed storage 5 via line 7 to vaporizer 4, wherein it is heated to a temperature of about 165° to 300° F. Conventional heating means such as steam coils may be employed in vaporizer 4 to achieve the desired temperature. The vaporized coke oven light oil is next passed via line 22 to dryer 3 for dehydration. Examples of suitable drying agents which may be employed in dryer 3 are activated alumina, silica gel, calcium chloride, molecular sieves, etc. Molecular sieves are preferred, since they have the added advantage of removing straight chain paraffins in addition to water. Synthetic molecular sieves composed of soda, lime, alumina and silica with the atoms arranged in a definite crystalline pattern are particularly useful. Examples of operable synthetic molecular sieves include Linde's Type 4A and Type 5A, which have pore openings which permit only molecules smaller than about 4 angstroms and up to about 5 angstroms, respectively, to enter the cavities and be absorbed.

The anhydrous, vaporized coke oven light oil is withdrawn from the top of dryer 3 and passed via line 21 to superheater 2 wherein it is heated to a temperature within the range of about 250° to 600° F. As in vaporizer 4, conventional heating means may be employed for superheating the coke oven light oil vapors. The superheated coke oven light oil vapors are then passed via line 20 to the bottom of reaction vessel 1, which contains a suspension of high surface metallic sodium coated on a finely divided inert carrier medium such as sand positioned above perforated grid plate 13. The coke oven light oil vapors are preferably passed into reaction vessel 1 at a point of entry below perforated grid plate 13.

The velocity of the coke oven light oil vapors are maintained at about 0.2 to 2.0, preferably about 0.3 to 0.7 foot per second, which is sufficient to segregate the sodium-coated carrier material into a dense turbulent layer, characteristic of a fluidized bed, in the lower portion of reaction vessel 1. The desulfurization treatment is carried out at a temperature of about 250° to 600° F., preferably about 450° to 525° F., and at a pressure of about 1 to 50 p.s.i.g., preferably about 1 to 5 p.s.i.g. The contact time of the coke oven light oil vapors with the high surface metallic sodium will vary from about 1 to 10 seconds, preferably about 2 to 5 seconds. It will be understood, however, that longer contact times may be employed and that contact time will vary in accordance with the degree of sulfur removal desired and the amount of sulfur present in the particular feed material employed.

The treated coke oven light oil vapors are removed from the upper portion of reaction vessel 1 via lines 17 and 18. However, before leaving the reaction vessel, the treated oil vapors are passed through micrometallic filters 8 and 9 to ensure the removal of solid fines from the vapor stream. As hereinafter described, the maintenance of the solid fines in the fluidized bed is an important feature of this invention and contributes substantially to an effective and efficient desulfurization operation. The micrometallic filters useful for the present purpose are made of porous stainless steel. Though in reaction vessel 1 only two micrometallic filters are shown, it will be understood that no limitation is intended thereby and any number of such filters may be employed. Furthermore, the filters 8 and 9 may be operated alternately and cleaned on the off cycle by blow back with nitrogen.

The desulfurized light oil vapors withdrawn via lines 17 and 18 are passed via line 16 to condenser 6, which is maintained at a temperature sufficient to condense the

light oil vapors. The condensed, desulfurized coke oven light oil is withdrawn from condenser **6** via line **19**.

Returning to reaction vessel **1**, make-up sodium and inert solid carrier are added via lines **14** and **15**, respectively. In accordance with another feature of the present invention, minor amounts of certain metal salts of high molecular weight aliphatic carboxylic acids having from about 16 to 24 carbon atoms per molecule or colloidal carbon are added along with the metallic sodium to ensure the coating of the sodium on the finely divided carrier material. Examples of such salts include aluminum stearate, calcium stearate, zinc stearate, sodium oleate, copper oleate, metal salt of dimer acid, etc. In general, about 0.1 to 5.0% of the high molecular weight carboxylic acid salt, based on sodium will be employed. The use of the dispersing aid is important, since it was found that in its absence a recoating of the carrier with high surface sodium was difficult.

The lower portion of reaction vessel **1** may also be provided with a vertical tubular conduit **10** for continuously withdrawing spent carrier material or contaminant desulfurization by-products from the fluidized bed. Tubular conduit **10** connects with vertical line **11** for removing the withdrawn material from reaction vessel **1**. As is well known in the art of standpipe design for fluidized bed operations, a small amount of an inert aerating gas such as nitrogen is introduced into vertical line **11** via line **12** for mixture with the materials being withdrawn to maintain them in a fluid condition capable of developing a fluid pressure. It is also within the scope of this invention to employ an inert gas such as nitrogen for starting up purposes.

Though not shown in the accompanying drawing, it is also contemplated that the desulfurized aromatic hydrocarbon feed stream withdrawn from condenser **6** via line **19** may be further treated. For example, if coke oven light oil is employed as the feed material, the recovered desulfurized light oil may be fractionated to separate the benzene, xylene and toluene fractions.

Synthetic or naturally occurring aromatic hydrocarbons of the benzene series are the preferred feed stocks, which can be desulfurized in accordance with the inventive process. Coke oven light oil containing about 55 to 76 wt. percent benzene, 12 to 20 wt. percent toluene and 5 to 10 wt. percent mixed xylenes is especially useful as the feed material. The coke oven light oil may also be separated into benzene, toluene and xylene fractions either prior to or subsequent to desulfurization with high surface sodium.

The aromatic hydrocarbon feed may be pretreated for concentration or purification purposes by distillation, solvent extraction, acid washing, clay treatment or a combination of these and other operations. In accordance with one particular embodiment of this invention, the feed is extracted with a mineral acid such as sulfuric acid to remove undesirable unsaturated organic compounds which tend to be gum formers.

Finely divided sand is the preferred inert solid carrier medium for the metallic sodium. Other carriers which may be utilized are soda ash, fuller's earth, carbon, salt, calcium carbonate, alumina, etc. However, when compared to sand, the soda ash had relatively poor fluidization characteristics, while the fuller's earth resulted in less efficient desulfurization with higher sodium consumption. It has also been determined that the inert carrier must be coated with at least about 1.0% sodium, preferably about 1.5 to 10% by weight, sodium based on the weight of the carrier, in order to obtain effective desulfurization in a fluidized system. In general, the total amount of sodium employed will be at least stoichiometrically sufficient to substantially remove the undesirable sulfur contaminants from the feed material. It will be understood, however, that the sodium may be employed in amounts ranging from about 30 to 50% over the stoichiometric amount. It has also been found that in order to obtain effective desulfurization a definite particle size distribution of the sodium-coated carrier material must be maintained in the gas fluidized bed. More particularly, it has been found that about 30 to 90% preferably about 40 to 85%, of the carrier material should have a mesh size within the range of about 200 to 400. The following table represents the particle size distribution maintained in reaction vessel **1**:

Mesh size:	Percent
40 to 200	15 to 60
200 to 400	40 to 85

It will be noted that an essential feature of the present invention is the maintenance in the fluidized bed of carrier particles, which are generally classified as fines and which are usually removed in the conventional fluidized bed operation. By this method sodium efficiency has been increased in some runs from 15 to 33%.

The invention will be more fully understood by reference to the following illustrative examples:

EXAMPLE I

In the following runs a high surface sodium bed was prepared by coating the sand with sodium in a ribbon blender under a nitrogen atmosphere and at a temperature of about 300° F. The reaction apparatus was purged with nitrogen, the fluid bed reactor was charged with the high surface sodium bed. Nitrogen was heated by passage through the vaporizer and superheater and passed through the high surface sodium bed to bring it up to a temperature of about 200° F. The benzene feed was then passed through a silica gel drying bed, vaporizer, superheater and fluid bed reactor until the desired reaction temperature was reached. At this point, the benzene feed rate was adjusted to the desired amount. The operating conditions and the results achieved in the runs are set forth below in Table A. Any solid particles in the reaction vapors leaving the fluid bed reactor were recovered by the micrometallic filters, and the thus treated benzene was then condensed and collected.

Table A

Run	Feed	Carrier	Percent Na on Carrier	Bed Temp., ° F.	Bed Depth (Inches)	Flow Rate, lbs./hr.	Contact Time (secs.)	Velocity (ft./sec.)	P.p.m. Thiophene		Percent Recovery
									Feed	Product	
1	Benzene	Sand, 50%, 200 to 300 mesh; 50%, 80 to 140 mesh.	2.0	500	9.5	14.1	2.0	0.38	415	0.0	97.0
2	do	do	2.0	440–455	7.25	10.1	2.2	0.27	415	0.0	97.0
3	do	Sand, 80%, 200 to 400 mesh.	2.1	450–460	18.0	13.2	4.6	0.33	170	0.0	[1] 98.0
4	do	Sand, 60%, 100 to 140 mesh; 40%, 200 mesh.	9.1	435–465	10.0	20.5	1.6	0.51	462	0.8	----------
5	do	do	8.0	450–455	9.5	18.9	1.7	0.48	80.5	0.0	----------

[1] Sodium efficiency—33.2%.

EXAMPLE II

In the following runs the desulfurization procedure

employed was similar to that in Example I with the exception that a two stage bed was used in the fluid bed reactor. The operating conditions and results for each run are set forth in Table B.

EXAMPLE III

BTX was run through a single stage reactor using the same procedure as in Example I with a sand bed containing 2% sodium at a BTX rate of 14.0 pounds per hour, a bed depth of 15.0 inches, a temperature of 465° F., a contact time of 3.5 seconds, and a vapor velocity of 0.36 foot per second. The thiophene content was reduced from 400 in the feed to zero in the product.

EXAMPLE IV

Using the procedure described in Example I three pounds of 100–140 mesh sand and two pounds of 200–300 mesh sand were added to the fluid bed reactor along with ten grams of aluminum stearate. The bed was then fluidized with benzene at fourteen pounds per hour and a temperature of 250° F. Sodium was added dropwise until 9% had been added. Uniform coating of the sand particles was evident after 30 minutes' benzene flow. Complete benzene desulfurization took place when the temperature was raised to 450° F. After seven hours' operation an additional 4% sodium was added to the 450° F. bed. This sodium dispersed immediately into small droplets which disappeared as benzene treatment proceeded.

An attempt to coat a similar sand bed with sodium but without using aluminum stearate was not successful.

Table B

Run	Feed	Carrier	Percent Na on Carrier	Bed Temp., ° F.	Bed Depth (Inches)		Flow Rate, lbs./hr.	Contact Time (secs.)	Velocity (ft./sec.)	P.p.m. Thiophene		Percent Recovery
					Lower	Upper				Feed	Product	
1	Benzene	Sand [1]	2.17	465	10.0	3.0	13.3	3.0	0.37	440	0.0	96.2
2	do	do	2.87	425	5.5	5.7	12.7	4.9–3.7	0.24–0.34	440	0.0	97.4
3	do	Sand [2]	2.61	520	10.5	7.5	13.2	3.9–5.5	0.28–0.39	440	0.0	
4	do	do	3.0	485	11.2	8.5	14.9	3.9–4.7	0.35–0.42	440	0.0	93.9
5	do	do	4.0	403–475	12.0	7.5	15.8	3.7–4.0	0.41–0.44	462	0.0	96.7

[1] Runs 1 and 2—83% 200–300 mesh; 17% 80–200 mesh.
[2] Runs 3 to 5—70% 200–300 mesh; 30% 80–200 mesh.

In accordance with another aspect of this invention, the high order of agitation or turbulence required to effectively desulfurize the aromatic hydrocarbons with high surface sodium dispersed on an inert, solid carrier medium may be accomplished mechanically. Certain commerically available propeller-type mixers can be used to provide the necessary agitated solids mass. An example of a suitable mixer is the ribbon blender, where the mixing action is produced by revolving helical blades. For the present purposes, agitation speeds of at least 60 r.p.m. are required. Though agitation speeds of 120 r.p.m. or higher have been employed, it was found that the same order of desulfurization was accomplished at 60 r.p.m. as at the higher speeds. One advantage of operating at the lower speeds is that less attrition is encountered.

When mechanically agitated beds are employed certain operating conditions are different than those used in a gas fluidized solids system. For example, the desulfurization temperature will ordinarily be about 400° to 600° F., though temperatures within the range of about 450° to 550° F. are preferred when reduction to less than one part per million of thiophene is desired. An important difference in the fluidized solids bed and the mechanically agitated bed operations is the particle size of the inert, solid carrier. As previously described, in a gas fluidized bed it is essential that at least about 30 to 90% of the solid carriers have a particle size of about 200 to 400 mesh. In a mechanically agitated bed, however, it is essential that about 70 to 95%, preferably about 80 to 90%, of the solid carriers have a particle size of about 30 to 100 mesh. Furthermore, it is preferred that no more than about 1% of the carriers should have a particle size of 200 mesh. The contact time will vary from about 1 to 20 seconds or longer depending on the feed material, degree of desulfurization sought etc.

This aspect of the invention will be more fully understood by reference to the following example.

EXAMPLE V

In the following runs a 6 inch diameter, 19.5 inches long, jacketed ribbon blender containing a close fitting ribbon agitator which gave end to end mixing was employed. The aromatic hydrocarbon feed material in vapor form was fed through a one inch line into the top at one end of the blender and discharged through a one inch line at the other end of the reactor. The treated aromatic hydrocarbon vapors were then condensed in a water cooled condenser.

In more detail, silica sand containing 95% particles of 20 to 60 mesh and 5% particles of less than 60 mesh was charged to the heated ribbon blender and dried under a blanket of dry nitrogen. Molten sodium was then charged to the blender together with some aluminum stearate (about 15 to 20 grams) to ensure coating. The resulting bed was then agitated for about 1 to 2 hours until it appeared to be well coated with the sodium. An impure benzene feed was then heated to the specified temperatures and passed through the ribbon blender and condenser. Operating conditions and the results achieved are set forth below.

Table C

Run	Percent Na on Carrier	Temp. of Feed, ° F.	Temp. of Vapors leaving blender, ° F.	Feed Rate (lb./hr.)	Feed Velocity (ft./sec.)	Contact Time (secs.)	R.p.m.	Thiophene, p.p.m.	
								Feed	Product
1	1.5	590–630	435	5	0.087	18.5	120	176	1.80
2	1.5	570–585	450	5	0.088	18.0	120	176	0.20
3	1.5	515–530	400	5	0.083	19.5	120	176	1.50
4	1.0	575–580	455–465	5	0.089	18.0	120	176	0.13
5	1.5	575–590	460–475	5	0.089	18.0	120	176	0.16
6	1.5	575–595	460–490	5	0.118	13.5	120	176	0.05
7	1.5	580–620	455–465	5	0.115	14.0	120	265	0.02
8	1.5	590–610	465–475	5	0.090	17.5	60	265	0.0
9	1.5	595–615	450–500	5	0.117	13.5	60	265	0.32
10	1.5	565–585	470–495	7.5	0.178	9.0	60	128	0.02
11	1.5		450	7.5	0.171	9.5	60	128	0.05
12	1.5		375	7.5	0.157	10.0	60	128	1.20

It will be understood that the reactants and operating conditions set forth in the foregoing specific embodiments may be varied within the limits indicated in the more general description of the invention and in the appended claims.

What is claimed is:

1. A process for reducing the thiophene content of aromatic hydrocarbons containing more than one part per million, said aromatic hydrocarbons being selected from the group consisting of benzene, toluene, xylene, and mixtures thereof, which consists of passing said aromatic hydrocarbon feed in vapor form through an agitated bed in turbulent state comprising metallic sodium dispersed on a finely divided, solid, inert carrier medium, said carrier being coated with at least 1% by weight of sodium, at a temperature within the range of about 400° to 600° F. in a reaction zone, and recovering therefrom said aromatic hydrocarbons having a thiophene content of less than one part per million.

2. The process of claim 1 wherein said aromatic hydrocarbon feed is benzene.

3. The process of claim 1 wherein said aromatic hydrocarbon feed is a mixture of benzene, toluene, and xylene.

4. The process of claim 1 wherein said aromatic hydrocarbon feed is substantially anhydrous.

5. The process of claim 1 wherein said bed is mechanically agitated, and said carrier is sand particles of which about 70 to 95% have an average particle size within the range of about 30 to 100 mesh.

6. The process of claim 1 wherein said bed is gas fluidized, and said carrier is sand particles of which about 30 to 90% have an average particle size within the range of about 200 to 400 mesh.

7. A method for coating finely divided inert solid carrier particles with sodium in a fluidized mass, which comprises adding metallic sodium to said fluidized mass along with an amount of a metal salt of a high molecular weight aliphatic carboxylic acid having from about 6 to 24 carbon atoms per molecule.

8. The method of claim 7 wherein said metal salt is aluminum stearate.

References Cited in the file of this patent

UNITED STATES PATENTS

1,729,943	Hofsass	Oct. 1, 1929
1,865,235	Cross	June 28, 1932
1,938,672	Ruthruff	Dec. 12, 1933
2,058,131	Carlisle	Oct. 20, 1936
2,818,350	Kavanagh	Dec. 31, 1957

OTHER REFERENCES

Altieri's "Gas Chemist's Book of Standards For Light Oils and Light Oil Products," 1943, American Gas Assoc. Inc., New York, New York, pages 4 and 5.