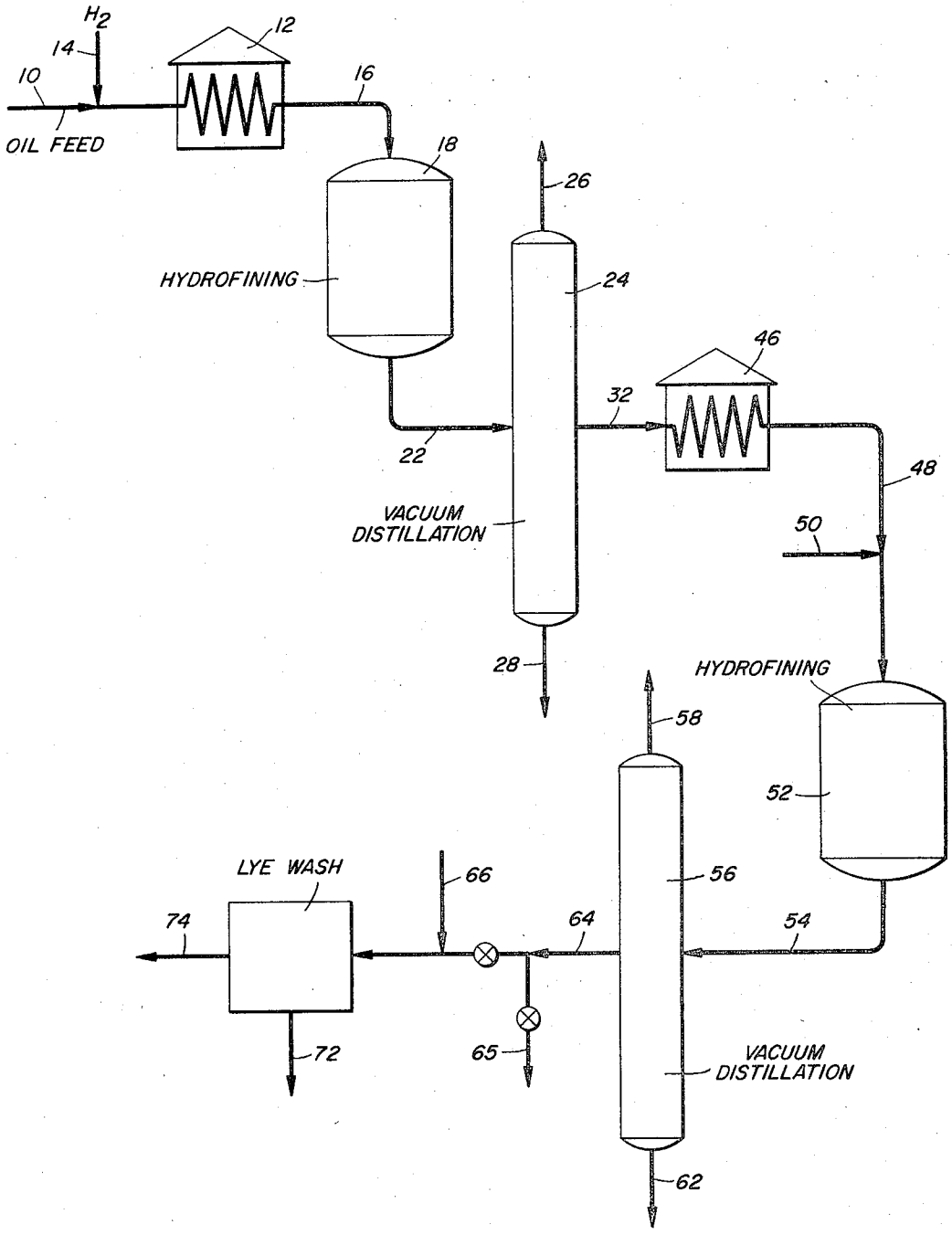
Feb. 20, 1968 L. F. KING 3,370,001

PROCESS FOR MANUFACTURE OF AROMATIC SOLVENTS

Filed July 23, 1965



LAURENCE F. KING INVENTOR

BY George J. Silberg

PATENT ATTORNEY

United States Patent Office 3,370,001 Patented Feb. 20, 1968

3,370,001

PROCESS FOR MANUFACTURE OF AROMATIC SOLVENTS

Laurence F. King, Mooretown, Ontario, Canada, assignor to Esso Research and Engineering Company, a corporation of Delaware

Filed July 23, 1965, Ser. No. 474,312
7 Claims. (Cl. 208—264)

This invention relates to a process for the manufacture of aromatic solvents and more particularly to a process for upgrading aromatic solvents for color and color stability.

Various processes are known for the production of aromatic solvents such as solvent extractin of an aromatic-rich feed followed by acid treating and caustic neutralization and then distillation. These previous processes give large yield losses. Clay treating is an alternative to acid treating. It is also known to hydrofine an aromatic feedstock and then vacuum re-run the product. This latter product is generally satisfactory but the color and color stability can be greatly improved by the process of this invention. The color degradation is associated with oxidation since little or no color change occurs under nitrogen.

According to the present invention an aromatic hydrocarbon oil boiling between about 150° F. and 600° F. such as steam cracked heavy naphtha or raw gas oil separated from steam cracked products is the feedstock which is to be treated to produce an improved aromatic solvent. The heavy naphtha is hydrofined and then solvent extracted to concentrate the aromatics. The aromatic oils to be treated according to the present invention contain at least 70% by volume of aromatic hydrocarbons and preferably 90% by volume. For steam cracked products it is generally unsatisfactory to use solvent extraction as the first step because of the great variety of unsaturates present in the feed. After mild hydrofining, solvent extraction will concentrate the aromatics satisfactorily.

The present invention is preferred for maximum utilization of stocks from steam cracking, such as gas oils and naphthas, which normally contain "extraneous" materials, such as diolefins, phenols, cresols, aromatics with unsaturated side chains etc., and these are notoriously poor as feedstocks for purified aromatics production.

In the present invention the process for improving color stability of aromatic solvents includes a first mild hydrofining treatment to reduce sulfur and to hydrogenate the unsaturates such as olefins and diolefins, solvent extraction to concentrate the aromatics, if necessary, and then a further treatment of the hydrofined oil or solvent extract using a sulfided nickel catalyst preferably on a support to improve the color and color hold of the aromatic solvent. Monoolefins are present only in small amounts in raw gas oil and are apparently sterically hindered because they are not materially reduced by hydrofining. The bromine number shows a big decrease, however. Lighter distillates of steam cracked naphtha have larger amounts of olefins which are susceptible to hydrofining.

The first hydrofining step reduces the sulfur content to the desired low range of 0–0.37. Not much color improvement is noticeable at this point but the first mild or prehydrofining step is necessary to remove some color-forming bodies which cannot be removed later by the nickel sulfide catalyst alone.

The sulfided or "spent" catalyst used in the second or hydrofinishing step comprises nickel sulfide on kieselguhr or other support such as alumina, alumina-silica, silica, activated carbon, molecular sieves, and contains 40–70% by weight of nickel calculated as the metal. The preferred amount of nickel is 43% by weight. The nickel metal catalyst is deactivated when it has been treated for a period with a sulfur-containing material and when the

catalyst contains 0.5 to 2%, generally about 1%, by weight of sulfur. The sulfided or spent catalyst is used in the hydrofinishing step.

With the particular combination of steps of the present invention the color of the aromatic solvent is improved with each treating step but the aromatic hydrocarbons are retained without conversion to naphthenes in the aromatic solvent. The presence of these aromatic hydrocarbons in the aromatic solvent gives high solvency power. Conversion of even a minor proportion of aromatics to naphthenes reduces solvency markedly.

In some cases where necessary or desirable, a solvent extraction step may be used after hydrofining to concentrate aromatics, but this step is usually not necessary for treating steam cracked products such as gas oil as feed for aromatic solvent manufacture. Then the hydrofined product is distilled to remove light and heavy ends and to obtain some improvement in color. Then the distilled product is hydrofinished over sulfided nickel catalyst on a support, which catalyst is preferably a sulfided or spent supported nickel catalyst.

This hydrofinishing step is the one mainly responsible for the greatly improved color stability of the treated aromatic solvent product obtained. No aromatic hydrocarbons are removed or converted in this hydrofinishing step and only minor amounts (not more than 0.1% at the highest temperature used) of sulfur are removed so that the mechanism for color upgrading is not known. Many heavy aromatic solvents on the market are deficient in color hold or stability. Severe hydrofining with cobalt molybdate on alumina catalyst in the hydrofining step results in higher desulfurization but is less effective in improving color hold than the conventional commercial mild hydrofining treatment or the first hydrofining step above referred and so would not eliminate the hydrofinishing step.

The deactivated or sulfided nickel catalyst is useful for removing color bodies and improving color stability oxidation resistance of the aromatic feed without hydrogenating or removing aromatic hydrocarbons so that the high solvency properties of the aromatic feed are preserved. The spent or deactivated nickel catalyst has no dearomatization activity.

As a final step the hydrofinished product may be vacuum distilled to about 95–98% overhead, which leaves 2–5% as bottoms.

In the drawing, the figure is a diagrammatical representation of apparatus adapted to carry out the process of the present invention.

Referring now to the drawing, the reference character **10** designates a line for passing a hydrocarbon oil feedstock through a furnace **12**. Hydrogen is added to the feed in line **10** through line **14**. The hydrogen may be pure hydroven or a recycle gas comtaining between about 70 and 95% hydrogen recovered from a hydroforming unit. The hydrocarbon oil feed in line **10** may be a steam cracked gas oil or a steam cracked heavy naphtha.

Steam cracking is a well known process and is known to produce aromatic products. The oil feed for a steam cracking process is preferably a gas oil having a boiling range between about 400° F. and 825° F. The temperature of cracking may be between about 1200° F. and 1450° F. Steam in an amount between about 60 and 85 mole percent of the feed may be used. The gas oil product recovered from steam cracking has a boiling range between 350° F. and 600° F. and has an aromatic content between about 80 and 95 volume percent.

Where a steam cracked naphtha is used rather than a steam cracked gas oil, the boiling range of the steam cracked naphtha is between about 150° F. and 350° F.

The steam cracked oil to be treated according to the present invention is passed through line **10** and after

heating in the furnace 12 has a temperature between about 540° F. and 560° F. The heated oil is then passed through line 16 and introduced into the top of the catalyst chamber 18 which contains a conventional hydrofining catalyst such as cobalt molybdate on alumina comprising about 3% cobalt oxide and 10–15% molybdenum oxide on alumina. Other hydrofining catalysts such as nickel oxide (0.3% Ni), cobalt oxide (2% Co) and molybdenum oxide (10% Mo) on alumina or kieselguhr may be used in the catalyst chamber 18 instead of the cobalt molybdate.

The oil passing through the catalyst chamber 18 is hydrofined at a temperature between about 450° F. and 700° F., preferably 500–600° F., the amount of hydrogen is between about 500 and 2000 s.c.f./bbl. (standard cubic feet per barrel of oil feed), the pressure is between about 150 and 500 p.s.i.g. and the space velocity is between 0.5 and 2 v./v./hr. (volume of oil as liquid per volume of catalyst per hour).

The hydrofined oil stream is removed from the catalyst chamber 18 through line 22 which conducts the hydrofined material from the bottom of the catalyst chamber and introduces it into the vacuum distillation tower 24 which is diagrammatically shown in the drawing. More than one vacuum tower may be used in series. The tower 24 is maintained under pressure between about 10 and 100 mm. of mercury. Gases including hydrogen, H_2S, and light hydrocarbons pass overhead through line 26 from the vacuum distillation tower 24. Where more than one vacuum tower is used, the gaseous fraction passes overhead from the first tower and the desired product passes overhead from the second tower. A bottoms fraction (highly colored) boiling above 550 to 650° F. approximately is withdrawn from the bottom of the tower 24 through line 28 (or the second tower) and is discarded because it contains high molecular weight compounds formed during hydrofining.

The re-running or distillation of the first hydrofining step is done under reduced pressure such as vacuum distillation to strip out 1–5% front or light ends (which are formed by splitting of sulfur compounds and perhaps hydrocarbons during hydrofining), take a heart-cut fraction and leave the 90–98%+ material as still bottoms. The heart-cut fraction is of improved color but is still unstable in storage. Oxidation inhibitors have no effect on color hold of the heart-cut fraction at this stage.

An aromatic heart-cut fraction boiling between about 370° F. and 550° F. is withdrawn from the tower 24 through line 32 and passed to a furnace 46 where it is heated to a temperature between about 400° and 600° F. The heated oil leaves furnace 46 through line 48. Hydrogen is introduced into line 48 through line 50. Preferably, the heated oil is passed through line 48 into the top of catalyst chamber 52 which contains a sulfided or spent nickel catalyst containing sulfur. The catalyst may be a nickel sulfide catalyst on a support such as kieselguhr, alumina, silica-alumina, silica, activated carbon, etc.

The nickel sulfide catalyst is preferably a supported sulfided catalyst and may be produced by treating a nickel metal catalyst on kieselguhr with sulfur-containing gas or sulfur-containing oil in any conventional manner. Or the catalyst may have been already used to treat sulfur-containing oils for conversion of aromatics to naphthenes or for the removal of traces of sulfur from the oil and in this way the catalyst is sulfided. It is to be noted that the sulfided catalyst used in the hydrofinishing step is substantially completely spent as far as the conversion of aromatics to naphthenes is concerned but is still active in removing color bodies and sulfur from the oil under suitable conditions.

The supported sulfided nickel catalyst used in the present invention contains about 0.5 to 2% by weight of sulfur (based on catalyst) combined with the nickel. The support forms about 25 to 75% by weight of the catalyst.

The nickel as metal forms about 40 to 70 weight percent of the catalyst.

The nickel catalyst as received from the manufacturer, is usually in the oxide form on a carrier such as kieselguhr (43% Ni) and this is treated with hydrogen at 600–700° F., 800 p.s.i.g., 3000 s.c.f./bbl. of hydrogen for about 12 hours to reduce the oxide to nickel metal. The nickel is then sulfided by using a sulfur-containing gas oil or naphtha which is hydrogenated and dearomatized by passing over the nickel catalyst which becomes quickly sulfided. This sulfide form of nickel catalyst is the one preferably used in the catalyst chamber 52.

In the preferred form of the invention, reduced nickel or nickel metal on kieselguhr is used as the catalyst for hydrogenating hydrofined virgin naphtha to produce low odor solvents by conversion of aromatics to naphthenes in a blocked operation. The hydrofined virgin naphtha has a boiling range of about 280° to 420° F. which is then re-run or distilled under vacuum of about 10 to 100 mm. of mercury to give separate fractions boiling between (1) 310° F. and 350° F., (2) 310° and 390° F., and (3) 360° to 410° F. These fractions contain a maximum sulfur content of about 10 p.p.m. to minimize poisoning of the nickel catalyst. Instead of fractions, the entire naphtha fraction may be hydrofined and fractionation carried out as a second step.

These fractions are then separately hydrogenated in blocked operation over reduced nickel or kieselguhr catalyst which converts aromatics to naphthenes. The catalyst contains 10 to 70% nickel by weight on kieselguhr. Operating conditions for this step are as follows: temperature, 400–550° F.; pressure of 800 p.s.i.g.; space velocity or feed rate of 5 to 15 v./v./hr.; and a hydrogen rate of 1500 to 2000 s.c.f./b.

During this operation, the nickel catalyst is gradually spent by the combined effect of heat and sulfur in the naphtha feed. The nickel catalyst is deactivated or completely inactive for the conversion of aromatics to naphthenes when between about 0.5 and 2% sulfur has been combined with the catalyst. This inactivation of the catalyst may require anywhere from 10 days to several weeks depending on the naphtha feeds used. No dearomatization is obtained with the deactivated or spent nickel catalyst.

Normally the spent nickel catalyst is returned to the supplier who reactivates the catalyst, but in the present invention, this spent catalyst has found use in improving the color of hydrofined steam cracked gas oil or in the naphtha hydrofinishing step. After the catalyst has been used in the catalyst chamber 52 for several weeks, it is returned to the supplier who reactivates the spent nickel catalyst.

In the catalyst chamber 52, the partially hydrofined oil is at a temperature between about 250° F. and 500° F., a pressure between about 200 and 1000 p.s.i.g. and the feed rate or space velocity is between about 0.5 and 10 v./v./hr. About 200 to 3000 s.c.f./b. of hydrogen are used in the catalyst chamber 52.

The furter treated oil is removed from the bottom of the catalyst chamber 52 through line 54 and is passed to a second vacuum distillation zone shown diagrammatically at 56, where the pressure is between about 10 and 100 mm. of mercury. A gaseous fraction containing traces of H_2S, mercaptans and light hydrocarbons is taken overhead through line 58. A bottom fraction comprising about 3 to 5% of the oil feed in line 54 and containing highly colored hydrocarbons boiling above 550° F. is withdrawn from the bottom of distillation tower 56 through line 62.

The aromatic product of improved color and color stability is withdrawn from the tower 56 through line 64 and may be washed to insure color and color stability of the aromatic product or may be withdrawn as product through line 65. When highest product quality (color and colorhold) is desired, the product should be re-run and preferably lye washed as a finishing step. The

effect of oxidation inhibitors is enhanced when the product is vacuum re-run a second time.

The aromatic fraction in line 64 is mixed with a lye or an aqueous sodium hydroxide solution introduced into line 64 through line 66. The lye solution may be of a concentration between about 5 and 25% by weight. About 0.1 to 0.3 gallon of lye solution per gallon of oil feed in line 64 is used. The mixture of oil and lye is introduced into the treating chamber 68 where the lye functions to wash the vacuum distilled oil and to remove traces of hydrogen sulfide, mercaptans and other acidic sulfur compounds. Lye washing is used mainly for odor improvement. Water contaminated with dissolved sulfur compounds is withdrawan from the bottom of the lye washing chamber 68 through line 72 and discarded from the system. The lye washed aromatic fraction product is withdrawn from chamber 68 through line 74.

With the present invention yields of 85–88% of aromatic product are obtainable, whereas the prior art treating using acid treating etc. may give yields of only 60–80%.

In cases where it is desired to concentrate the aromatics in the oil feed to be passed through line 10, the oil may be subjected to a conventional solvent extraction step and this may be done by using sulfur dioxide, liquid ammonia, sulfolane, Udex, etc., depending on the feedstock used. With steam cracked oils, particularly heavy naphtha, hydrofining should be carried out before solvent extraction.

A pilot plant hydrogenation run was made with a sulfided nickel catalyst. The catalyst was made as follows: a reduced nickel or nickel metal on kieselguhr was produced by starting with nickel oxide on kieselguhr (43% as nickel metal) and the nickel oxide was reduced to metallic nickel with hydrogen using 3000 s.c.f. of hydrogen per barrel of hydrogen, a temperature of 650° F., a pressure of 800 p.s.i.g. for about 12 hours.

The reduced nickel on kieselguhr catalyst was then purposely inactivated for aromatics conversion by passing a hydrofined aromatic gas oil solvent having a boiling range of 370° F. to 546° F. and containing 0.45% sulfur over the catalyst at a temperature of about 250° F. The temperature was then raised stepwise to about 500° F. The catalyst became sulfided quickly during the run. The pressure during the run was 800 p.s.i.g., feed rate of 5 v./v./hr. and 2000 s.c.f. H_2/b. were used. The extent of desulfurization was not appreciable except at the beginning at the lower temperature before the catalyst was sulfided and near the end of the run at the highest temperatures of 475° F. and 500° F. The saturated hydrocarbons increased by not more than 1% indicating that at most only traces of aromatics were converted to naphthenes because there was also saturation of olefins. Diolefins were removed in the first hydrofining step when the aromatic gas oil solvent was hydrofined.

Improvement in color was evident at the 375° F. reaction temperature and higher, with the best results being obtained at 450° F.–500° F. The Robinson number at the temperatures between 375° and 500° F. was between 12 and 17.

Table I shows the effect of temperature on the rehydrofining or hydrofinishing of an aromatic gas oil solvent containing 0.45% sulfur. The aromatic solvent had a boiling range of about 350° F. to 550° F. The data shown are for different temperatures while holding the pressure, space velocity and hydrogen rates constant. The best product was obtained at 475° F. and after this product was redistilled under a vacuum of about 10–20 mm. of mercury, the resulting product was a distillate whose storage stability is shown in the last two columns under V of Table IV. The hydrofinished aromatic solvent had a boiling range of 365° F. to 542° F.

TABLE I.—REHYDROFINING OR HYDROFINISHING HYDROFINED STEAM CRACKED GAS OIL OVER NICKEL SULFIDE CATALYST [1]

[Pressure, 800 p.s.i.g.; space velocity, 5 v./v./hr.; hydrogen rate, 2,000 s.c.f./b.]

Reactor Temperature, ° F.	Robinson Color	Sulfur, wt. percent	Aromatics, vol. percent
Feed	11.5	0.45	90
		Desulfurization, percent	Aromatics Conversion, p ercent
250	10.5	nil	
275	10.5	nil	
300	9.5	nil	
325	9.5	nil	
350	10	8	
375	12	15	nil
400	13		
425	14	18	
450	15	18	
475	16.5	30	
500	16	30	

[1] Reduced nickel deactivated by sulfur contained in feed hydrofined over cobalt molybdate catalyst. Sulfur content initially is 0.5% minimum. The catalyst is completely deactivated for dearomatization. The run in Table I used the cobalt molybdate hydrofined steam cracked gas oil to deactivate the catalyst in the initial stages of the run and then the run was continued with the same feed.

The product taken at 475° F. was re-run or distilled under a vacuum of about 10–20 mm. of mercury, at a maximum bottoms temperature of about 300° F. and 98% overhead and the color (+8 Saybolt) of the distillate was well beyond the Tag Robinson Scale. A description of the Tag Robinson Scale is given at page 83 of Fisher/Tag Manual, 28th edition (1954). The Saybolt scale is described in A.S.T.M. D156–53T (23T Robinson=Minus 8 Saybolt). The data are included in Table II in which the catalyst used is as above described where the nickel metal catalyst was sulfided by using a high sulfur aromatic gas oil fraction. Table II also includes the inspection of the feedstock. The bromine number is also further reduced which is highly desirable in a solvent.

TABLE II.—INSPECTIONS OF HEAVY AROMATIC SOLVENT

	Aromatic Gas Oil	
	As is—Plant Product (hydrofined and re-run)	Re-hydrofined over sulfided Ni catalyst and re-run at 475° F.
Gravity, °API	17.5	
Flash Point, ° F	160	
Color:		
Tag Rob	[1] 12.5	
Saybolt		+8
Sulfur, wt. percent	0.45	0.31
Kauri Butanol Value	100+	
Mixed Aniline Pt., ° F.	76.5	79
FIA: [2]		
Aromatics, vol. percent	88	88
Olefins, vol. percent	5	4
Saturates, vol. percent	7	8
Bromine No. ASTM	2.9	1.5
ASTM Distillation, ° F.:		
IBP	370	
5%	403	
10%	414	
50%	456	
90%	507	
95%	520	
FBP	546	

[1] After 6 months plant storage. Originally it was 18 but color degraded quickly in storage.
[2] Fluorescent Indicator Adsorption, ASTM D 1319–61T.

Color hold tests at 110° F. were carried out using the 475° F. product (see Table II) with no oxidation inhibitor and with inhibitor Parabar 441, du Pont Metal Deactivator and Primene 81R. Parabar 441 is a trade name for 2,6-di-tertiary butyl, 4-methyl phenol. Other suitable inhibitors may be used instead of the ones mentioned. The inhibitor is used in the amount of 5 pounds per thousand barrels of oil.

Parabar 441 was the best inhibitor with the du Pont Metal Deactivator almost as good. Both of these inhibitors gave times in excess of 10 weeks at 110° F. before 18

Robinson color was obtained. The uninhibited aromatic oil after the hydrofining step lasted only about 1½ weeks at 110° F. in reaching the Robinson number of 18.

The aromatic gas oil of Table II inhibited with Parabar 441, but without the stabilizing treatment with nickel sulfide catalyst, lasted only about 2 days under these conditions. From this it will be seen that the best oxidation inhibitors are relatively ineffective in retarding color degradation unless the aromatic hydrocarbon solvent oil is treated with a hydrofinishing step using a suitable sulfided nickel catalyst.

Table IV includes data to show the improvement in color hold by accelerated storage tests at 110° F. in the presence of air. The coils were tested by putting 200 cc. of oil in a quart can and sealing (air present in can when sealed). Table IV also shows the phenomenal improvement in color stability especially where an inhibitor is added to the hydrofinished oil. See the last two columns under V.

TABLE IV.—ACCELERATED STORAGE STABILITY OF STEAM CRACKED GAS OILS

[In quart cans at 110° F. (air not removed)]

	Designation				
	I	III		V	
	As produced	Hydrofined (Co Molybdate Cat.) plus Vacuum Re-run		Rehydrofined (Ni Sulfide Cat.) plus Vacuum Re-run	
Inhibitor,[1] lb./1,000 barrels	None	None	5	None	5
Initial Color:					
Tag Robinson	<1	23	23	Above 23	Above 23
Saybolt				+8	+8
Time (days) required to reach color indicated:					
18 Tag Robinson		<2	2	12	70+
10 Tag Robinson		4	10	28	[2] ∞

[1] 2,6-di-tertiary butyl, 4-methyl phenol.
[2] Curve approaches 18 color asymptotically.

Table III shows inspections of the raw gas oil from steam cracking and after successive stages of hydrofining, vacuum re-running, hydrofinishing over sulfided nickel catalyst and vacuum distillation a second time. It will be seen that the aromatic hydrocarbons retained in the solvent form about 90% of the total so there is no loss or conversion of hydrocarbons.

The hydrofining was carried out at 525° F., 250 p.s.i.g., and 1.0 v./v./hr. and 750 s.c.f. H_2/barrel of feed. The catalyst was conventional cobalt molybdate on alumina.

The first vacuum re-run (col. III) was made at 10–100 mm. of mercury. The light overhead was sent to the gasoline pool. The bottoms fraction was added to a middle distillate pool.

The sulfided nickel catalyst contained 43% Ni and 1.5% sulfur and was supported on kieselguhr.

The second vacuum distillation was made at 10–100 mm. of mercury. In this step there were no light or front ends to discard because of mild treatment with no cracked products formed.

In a specific example, an aromatic gas oil fraction having a boiling point range of 375° to 550° F. from a steam cracking process at a temperature of about 1410° F. is separately hydrofined with cobalt molybdate catalyst in chamber **18**. The cobalt molybdate catalyst contains 3% cobalt oxide and 12% mloybdenum oxide on alumina. The temperature during hydrofining is about 475° F., 200 p.s.i.g., the amount of hydrogen used is about 750 s.c.f./b. and the space velocity is about 1.5 v./v./hr.

The effluent from the hydrofining step is vacuum distilled in tower **24** to give a 5–95% heart-cut fraction. The vacuum distillation is carried out at a pressure which varies during the run decreasing from 30 mm. of mercury to 10 mm. of mercury as the boiling points of the oil increases to keep the bottoms temperature below 300° F.

The effluent aromatic fraction is then withdrawn through line **32**, is heated in heater **46** to a temperature of about 475° F., mixed with hydrogen and then passed over nickel sulfide or spent nickel catalyst on kieselguhr in catalyst chamber or vessel **52**. The spent catalyst was obtained as will be hereinafter specifically described. In

TABLE III.—TREATMENT OF STEAM CRACKED GAS OIL

	Designation				
	I	II	III	IV	V
	As Produced	Hydrofined (Cobalt Molybdate Cat)		Rehydrofined (Hydrofinished) Sulfided Nickel Cat.[2]	
		As is	Vacuum Re-run [1]	As is	Vacuum Re-run [3]
Gravity, ° API	15	17.5	17.5	18	19
Flash, ° F	170	150	160		165
Color:					
Tag Robinson	<1	10	[4] 10–23	16.5	23+
Saybolt					+8
Sulfur, wt. percent	1.0	0.55	0.45	0.37	0.31
FIA:					
Aromatics, vol. percent	90	88	88	88	90
Olefins	5	5	5	4	4
Saturates	5	7	7	8	8
Odor	Disagreeable	Mild	Mild	Very mild	Very mild
ASTM Distillation, ° F.:					
IBP	385	326	370	355	365
5%	424	386	403	395	396
10%	436	406	414	408	407
50%	480	456	456	450	450
90%	530	518	507	516	515
95%	560	542	520	540	532
FBP	cracks	580	546	550	542
Bromine No	38	4	3	1.5	1.5
Mixed Aniline Pt., ° F	77	78	77	78	79

[1] Nominal 5%, 565° F. cut, usually 5–95 vol. percent overhead.
[2] At 475° F., 800 p.s.i.g., 5 v./v./hr., 2,000 s.c.f. Hydrogen/b.
[3] 0–98% overhead fraction.
[4] 23 Tag Robinson color when produced, rapidly degrades in storage to 10.

the catalyst chamber **52**, the aromatic fraction is maintained at a temperature of about 475° F., a pressure of about 800 p.s.i.g. and in the presence of about 2000 s.c.f. hydrogen per barrel of oil fed to the chamber **52**. The space velocity was about 5 v./v./hr. The effluent from the catalyst chamber **52** is passed through line **54** and vacuum distilled under a pressure which varies between about 10–30 mm. of mercury as above explained in connection with tower **24** to give a final aromatic product of improved color and color stability which is withdrawn through lines **64** and **65**. Starting with 100 barrels of feed, about 88 barrels of final product are obtained.

Or the aromatic product in line **64** may be cooled to a temperature of 125° F. and washed with lye in chamber **68** using an aqueous lye solution containing about 15% by weight of sodium hydroxide and using about 0.15 gallons of the lye solution per gallon of gas oil effluent introduced into line **64** from line **66** and the mixture passed to the chamber **68**.

The spent nickel catalyst above referred to in this example is obtained after a nickel catalyst has become spent in the hydrogenation of virgin naphtha to convert or partially convert aromatics to naphthenes. Virgin naphtha having a boiling range of about 280° F. to 420° F. is heated to 600° F. and treated with cobalt molybdate on alumina catalyst in a hydrofining step to remove sulfur. The catalyst is substantially the same type of cobalt molybdate catalyst above described in connection with the gas oil treatment in chamber **18**. The temperature during hydrofining is 600° F., the pressure is 250 p.s.i.g., the space velocity is 2 v./v./hr. and the amount of hydrogen is 500 s.c.f./b. of feed.

The hydrofined naphtha is vacuum distilled into three fractions, 310°–350° F., 310°–390° F. and 360°–410° F. The hydrofined naphtha fractions are then heated and passed over a reduced nickel catalyst which contains 43% by weight nickel metal on kieselguhr. The temperature is 400° F. for the first fraction, 425° F. for the second fraction and 450° F. for the third fraction, the pressure is 800 p.s.i.g., the space velocity is 10 v./v./hr., with 2000 s.c.f. of hydrogen per barrel of feed until the catalyst becomes substantially inactive for the conversion of aromatics which is determined by analyzing for sulfur in the catalyst which must be at least 0.5% to about 1% sulfur. This spent nickel catalyst is the one used in the hydrofinishing step of the aromatic gas oil above described in this specific example.

What is claimed is:

1. A process for improving the color stability of aromatic solvents which comprises catalytically hydrofining a hydrocarbon oil boiling between about 150° F. and 600° F. containing at least about 80% by volume of aromatic hydrocarbons, said hydrofining being carried out without conversion of said aromatic hydrocarbons to naphthenes, vacuum distilling the hydrofined oil to recover an aromatic heart-cut fraction boiling between about 200° F. and 500° F., contacting said aromatic heart-cut fraction and hydrogen with a supported sulfided nickel catalyst at a temperature ranging between about 250° F. and 500° F., said contacting being carried out without conversion of said heart-cut fraction to naphthenes, vacuum distilling the treated heart-cut fraction to recover an aromatic solvent and lye washing said aromatic solvent to obtain an aromatic solvent characterized by improved color stability and an aromatic hydrocarbon content of at least about 80% by volume.

2. A process according to claim **1** wherein the catalyst in said hydrofining step is cobalt molybdate on alumina.

3. A process for improving the color stability of aromatic solvents containing at least about 70% by volume of aromatic hydrocarbons, which comprises heating a steam cracked aromatic hydrocarbon gas oil containing at least about 80% of aromatic hydrocarbons and hydrogen and passing the heated mixture in contact with a hydrofining catalyst under a pressure between about 250 and 1000 p.s.i.g., a temperature between about 500° F. and 700° F., at a space velocity between about 0.5 and 3.0 v./v./hr. in the presence of hydrogen between about 200 and 1000 s.c.f. hydrogen per barrel of oil feed, removing hydrofined oil and passing it to a vacuum distillation zone to recover a hydrofined aromatic hydrocarbon heart-cut oil boiling between about 370° F. and 550° F., hydrofinishing said aromatic heart-cut oil by mixing it with hydrogen and contacting the mixture with a nickel sulfide on kieselguhr catalyst containing between about 40% and 70% by weight of nickel as metal and between about 0.5% and 2% by weight of sulfur, at a temperature between 400° F. and 600° F., a pressure between 200 and 1000 p.s.i.g., at a space velocity between 0.5 and 10 v./v./hr. in the presence of 200–3000 s.c.f. of hydrogen/bbl. of the aromatic heart-cut oil, then vacuum distilling the hydrofinished effluent at a pressure not above about 30 mm. of mercury to recover a color stable aromatic hydrocarbon oil solvent and then lye washing the aromatic hydrocarbon solvent to improve its stability.

4. A process for improving the color stability of aromatic hydrocarbon oil solvents containing at least about 80% by volume of aromatic hydrocarbons and selected from the group consisting of steam cracked gas oil and steam cracked heavy naphtha, which comprises heating the hydrocarbon oil and hydrogen and passing the heated mixture in contact with a hydrofining catalyst in a hydrofining zone under a pressure between about 250 and 1000 p.s.i.g., a temperature between about 500° F. and 700° F., at a space velocity between about 0.5 and 3.0 v./v./hr. in the presence of hydrogen between about 200 and 1000 s.c.f. per barrel of hydrocarbon oil feed, recovering hydrofined hydrocarbon oil and vacuum distilling it to recover a hydrofined aromatic hydrocarbon heart-cut oil boiling between about 350° F. and 550° F., hydrofinishing said aromatic heart-cut oil by mixing it with hydrogen and contacting the mixture with a nickel sulfide on kieselguhr catalyst containing about 43% by weight of nickel as metal and about 1.5% by weight of sulfur, at a temperature between 400° F. and 600° F., a pressure between 200 and 3000 p.s.i.g., at a space velocity between 0.5 and 10 v./v./hr. in the presence of 200–1000 s.c.f. of hydrogen per barrel of the aromatic heart-cut oil and then vacuum distilling the hydrofinished effluent to recover a color stable steam cracked aromatic hydrocarbon oil solvent.

5. A process according to claim **4** wherein said hydrofinishing catalyst is a spent sulfided nickel catalyst discarded from a catalytic dearomatizing zone for treating naphtha and which catalyst has no dearomatization activity in said hydrofinishing step.

6. A process for improving the color stability of steam cracked aromatic hydrocarbon solvent oils containing at least about 90% by volume of aromatic hydrocarbons, which comprises heating steam cracked aromatic hydrocarbon gas oil and hydrogen and passing the heated mixture into a hydrofining zone for contact with a hydrofining catalyst under a pressure between about 250 and 1000 p.s.i.g., a temperature between about 500° F. and 700° F. at a space velocity between about 0.5 and 3.0 v./v./hr. in the presence of hydrogen between about 200 and 1000 s.c.f. hydrogen per barrel of aromatic hydrocarbon gas oil feed, removing hydrofined oil from said hydrofining zone, vacuum distilling the hydrofined oil to recover a hydrofined aromatic hydrocarbon heart-cut oil boiling between about 350° F. and 550° F., hydrofinishing said aromatic heart-cut oil by mixing it with hydrogen and contacting the mixture with a nickel sulfide on kieselguhr catalyst removed from a reaction zone as spent catalyst after having been used in the dearomatization of naphtha and which spent catalyst contains about 43% by weight of nickel as metal and about 1.5% by weight of sulfur and has no dearomatization activity in the hydrofinishing

step at a temperature between 400° F. and 600° F., a pressure between 200 and 1000 p.s.i.g., at a space velocity between 0.5 and 10 v./v./hr. in the presence of 200–1000 s.c.f. of hydrogen/bbl. of the aromatic heart-cut oil, and then vacuum distilling the hydrofinished oil effluent to recover a color stable aromatic hydrocarbon oil solvent having substantially the same aromatic hydrocarbon content as the aromatic hydrocarbon solvent oil feed.

7. A process according to claim 6 wherein said hydrofinished color stable aromatic hydrocarbon oil solvent is lye washed.

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