

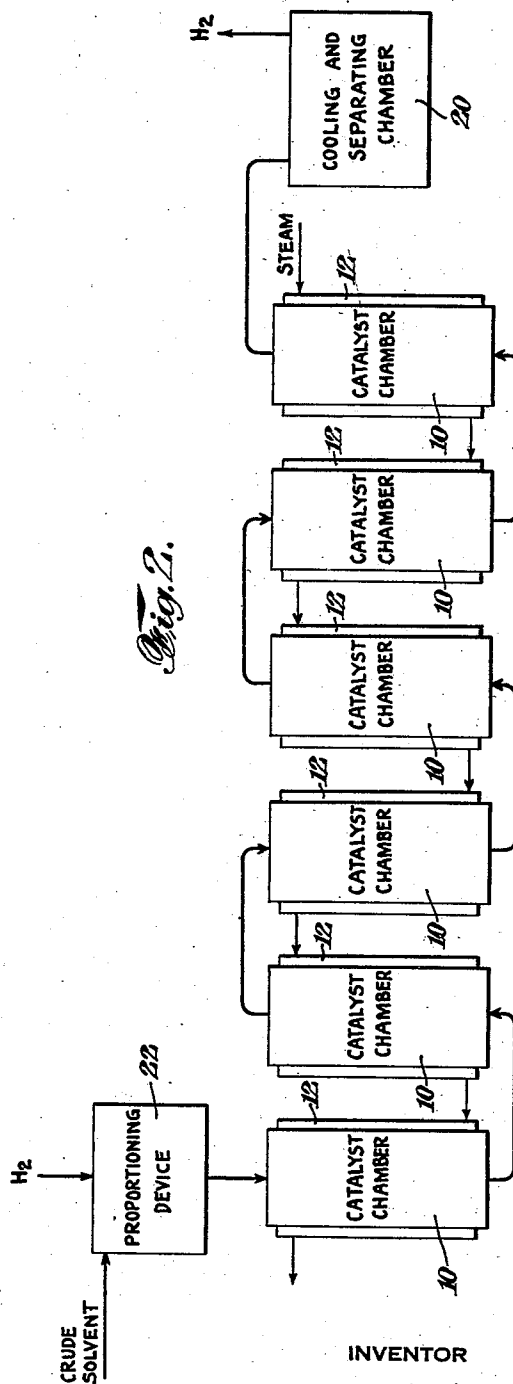
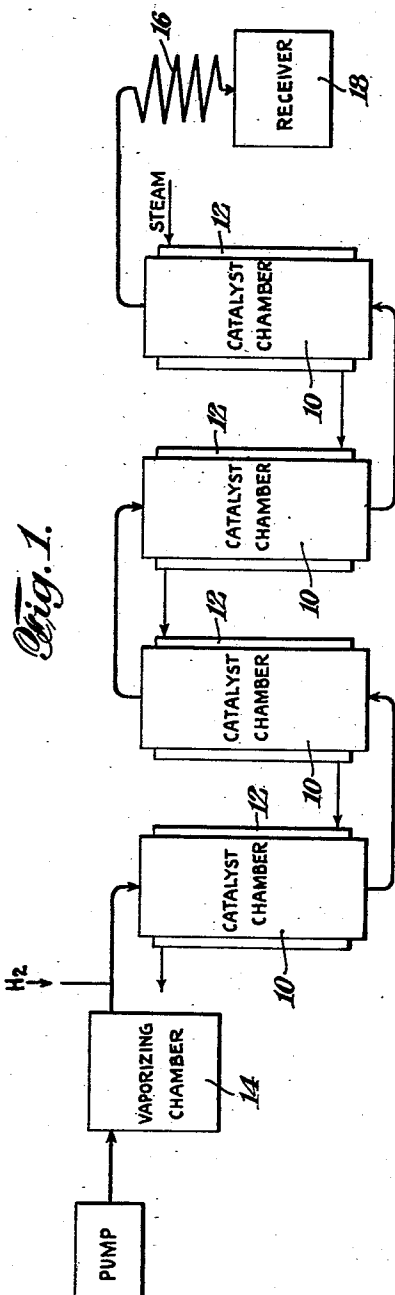
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METHOD OF CATALYTIC HYDROGENATION OF CRUDE BENZENE DERIVATIVES

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METHOD OF CATALYTIC HYDROGENATION
OF CRUDE BENZENE DERIVATIVES

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This invention relates to a process for producing a new type of aromatic solvent by a new process of hydrogenating crude solvent naphthas recovered as by-products of the coking of coal, or of hydrogenating and refining chemically similar liquids from other sources, and the product thereof.

The essential portion of the invention comprises an economic procedure for the selective and non-destructive catalytic hydrogenation, generally without pre-purifications, of these crudes, with catalysts of medium activity.

Catalysts of greater activity have been heretofore used, generally after an extensive purification of the material to be treated, involving the removal of naphthalene, tar acids and sulphur components. In no case has such procedure been found necessary, although it may be desirable in isolated instances to partially remove thio compounds and even tar acids. If the crude material contains oxygen heterocycles, tar acids may be formed by hydrogenation and may be removed after.

Moreover, whenever lower temperature catalysts, hereinafter termed medium activity catalysts, have been used, the conditions employed were highly uneconomic either of catalyst or time, generally the former. To obtain the best results during hydrogenation, interadjustment and interregulation of catalysts, temperatures and pressures are needed. Heretofore, these factors have been given as constant, or where a range was specified, it was understood that a single temperature or pressure was to have been selected from within that range. By the new process herein disclosed, new hydrogenated products are obtained without loss of yield containing new and useful compounds in substantial quantities.

One object of this invention is the provision of a method of partial hydrogenation preferably in the vapor phase and without pre-purification of the crude starting product. This is defined as a hydrofining operation, as hydrogenating to refine, in contrast to the usual prerequisite refining before hydrogenation.

If it is desirable to produce highly stable and water white solvents, this vapor phase hydrogenation may be followed by a finishing stabilization consisting of a liquid phase hydrogenation.

In the drawing I have diagrammatically shown two forms of apparatus adapted for use with my invention, in which

Fig. 1 represents a four-stage treatment; and Fig. 2 represents a six-stage treatment.

As an example, the raw materials used in this process may distill between 120 and 240° C., and include light and heavy solvent naphthas recovered from the coking of coal, drip oil from carburetted water gas, carboilic oil, crude high

flash naphtha, and other similar materials whether naturally produced or synthetically derived. It is preferred to use those most commonly and abundantly produced. They are crude light solvent naphtha, which distills mainly between 120 and 180° C., and crude heavy solvent naphtha, which distills mainly between 140 and 240° C. In both cases closer fractions are used, such as the following, but it is to be understood that fractions having the above ranges may be used and mixtures thereof may be used. My crude mixtures contain reactive polymerizable compounds having an unsaturated side chain or unsaturated side ring, the compounds containing 11 carbon atoms or less.

	Light	Heavy
Index of refraction at 20° C.-----	1.502	1.544
Specific gravity at 15° C.-----	0.873	0.958
Distillation initial-----	130° C.	166° C.
Distillation end-----	165° C.	193° C.
Major saturated components-----	Dimethyl Benzenes	Trimethyl Tetramethyl Benzenes

Major unsaturated components i. e., the principal reactants in my process-----	Styrene	Cumarone Indene Naphthalene
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The hydrogenation is carried out in the presence of catalysts. If used in the form of powders, the catalysts may be variously prepared by the many methods well known in the art, preferably suspended on porous and comparatively indifferent bases such as kieselguhr, fuller's earth or carborundum. One form of catalyst which may be used is the permanent type of catalyst which may be said to be suspended on itself. The preparation and activation of such a catalyst is described in U. S. Patent #1,519,035, and others.

The preferred catalyst is of the nickel type, such as, nickel oxide with or without the oxides of copper, chromium, or molybdenum, the whole completely or in part reduced with hydrogen at the usual temperatures. Copper oxide, with or without chromium, cobalt or silver oxides, with or without reduction may be used. However, the invention is not to be limited to these alone, as catalysts of lower activity, such as the sulfides and oxides of molybdenum, chromium, tungsten or manganese, especially when promoted with the oxides or sulfides of cadmium, silver, cobalt, zinc, copper, tin and magnesium; and even the completely or partially reduced metals, cobalt, cadmium, silver and tin, may be used, always,

however, with increased temperatures and pressures involving more expensive equipment, cracked products, and lessened yields. If it is desired to transform coumarone and coumarone homologs to phenols, or when dealing with high sulphur crudes or fractions, such catalysts may find limited use especially in the first stages of isothermal hydrogenation over 200° C. The above are medium activity catalysts. Low activity catalyst like aluminum chloride, carbon or iron are excluded on account of their destructiveness, incompleteness, high temperature and pressure requirements, and the noble metal catalysts, such as, palladium, platinum, etc. are excluded on account of their cost and susceptibility to poisoning.

When a plurality of catalysts is used in a plurality of chambers, it is preferable to use different degrees of freshness in the same metal, the freshest in the last portion of the hydrogenation. However, different metal catalysts having different activities may be used in the chambers instead of the same metal catalyst.

The temperatures used in this process may be varied although each activity of catalyst has its corresponding optimum range. For the following catalysts the range is approximately as follows: nickel type 100-160° C.; copper 190-230° C.; cobalt, silver and cadmium 260-340° C., but these temperatures may be reduced 20° C. with a highly active or fresh form of the catalyst and increased 20 or 30° C. with the low active or spent form. It was found that by using the lower temperatures, which is very unusual, during the very early stages of the hydrogenation, and the higher temperatures during the later stages that the catalyst lasted much longer. The acceleration of this ascending gradient of temperature is preferably negative.

In vapor phase work, it is best to maintain the pressures substantially constant.

In liquid phase work, pressures can be raised in an ascending gradient, whose acceleration is preferably positive, to counteract a falling rate of hydrogenation and keep the rate uniform or constant. However, the rate of hydrogen absorption may also be maintained uniform or constant with more or fresher catalyst and/or higher temperatures.

While hydrogenation can be effected in one step, it is advantageous to do so in stages, as a means of better control and of continuous hydrogenation. When hydrogenating in stages, the method may be operated continuously by by-passing and reactivating individual chambers of catalyst, as they become spent, while continuing the hydrogenation through the unexhausted chambers and through fresh ones, held in reserve. While not limiting the invention to any single method of applying heat to the chambers, the use of a counter-current flow of the heating medium through jackets about the chambers, or the use of controlled electric current are given as examples.

By using less active catalyst and/or lower temperature in the early stages, the poisoning effect of the unsaturated and sulfur compounds in the crude material is minimized. For instance, in the vapor phase the less active catalyst was found the better, but while working in the liquid phase the less active catalyst and lower temperature together were found preferable. Furthermore, while either phase may be used singly with nickel and the heavy crude fraction heretofore described, it was distinctly advantageous to add the major portion of the hydrogen in the vapor state at 155

±20° C. and the final smaller portion in the liquid state, with the temperature grading sharply up and toward 175° C. Nearly spent nickel can be used at higher temperatures and pressures, but it is then in the class of low active catalysts, being unusually sub-normal. The 155° C. may be said to apply to a normal nickel catalyst. While it is possible to use higher temperatures with nickel, the results are detrimental to the catalyst and product.

The corresponding pressures, however, cannot be defined so closely. In the vapor phase with a nickel catalyst, little advantage is gained at pressures of more than three atmospheres. In the liquid phase the corresponding pressure is twenty atmospheres, the chromite type of catalyst requiring greater pressures for practical outputs. Actually, considerably lower pressures than three and twenty atmospheres, respectively, have been used very effectively in the vapor phase even sub-atmospheric pressures. On the other hand, the liquid phase pressure may be increased tenfold or greater if the activity or the quantity of the catalyst, or the temperatures, become very low. While the crude liquids may be volatilized for the vapor phase by any of the methods known to the art, a vaporizer of the carburetor type is preferred to minimize the loss of solvent by heat polymerization. A nickel catalyst is used where it is undesirable that the side rings be opened and, in general, for more selective hydrogenation, especially at low temperatures (namely, below 175° C.) and in the liquid phase.

Hydrogenation with nickel at 178° C., in the vapor phase at four atmospheres, produced appreciable quantities of cyclohexane derivatives, hydrogen having gone into the benzene ring. This is prejudicial to solvent strength and uses excessive hydrogen.

With the crude heavy solvent as a starting product, a high degree of selectivity was attained. One example will now be given using four catalyst units, the catalysts in this example being of substantially the same composition. A closed vessel is divided into four chambers holding separate nickel catalyst units and these are connected in series and jacket heated by steam. The jackets are so connected that the last receives the fresh steam first and the first receives comparatively cold steam. The nickel was prepared as described in U. S. Patent 1,519,035, reduced at 250° C. Liquid is continuously pumped into a hot (190° C.) vaporizing chamber. At the outlet of this chamber, the vapors are mixed with an excess of hydrogen and the mixtures led over the first catalyst whose temperature is 115° C., thence over the second catalyst at 130° C., over the third catalyst at 140° C., and over the last catalyst at 145° C. These temperatures are raised 5°, 10°, and 20° as the catalyst becomes spent. The pressure on the system is about 1½ atmospheres, although pressures less than atmosphere (vacuum) may be used. The vapors are passed through a condenser and the excess hydrogen is separated. The condensed product needs a finishing treatment to make a water-white solvent. In Fig. 1 the catalyst chambers 10, having jackets 12 are shown connected together, the first chamber being connected with a vaporizing chamber 14 into which is pumped the liquid to be treated. At the outlet of the vaporizing chamber the vapors are mixed with hydrogen and the mixture led through the catalyst chambers 10. Steam is used for heating the chambers as shown in the drawing, and the steam enters the jacket 12 of

the last chamber so that the steam flows in a direction opposite to the direction of the vapors being treated. A condenser 16 is used to condense the treated vapors and the condensate is collected in a receiver 18.

The velocity of the vapors is sufficient to carry the supersaturated mixture into the warmer tubes with practically no precipitation. When the final outlet catalyst was fresh the temperatures were kept at about 150° C. When it had been in use some time, the temperature was raised to 160° C. The specific gravity of the heavy crude starting product was reduced .04, the refractive index was less than .03 and the polymerizable bodies decreased more than fifteen fold by this hydrogenation.

The same results may be obtained in a single reaction chamber in which the temperature may be substantially constant or may be varied. It is simple to heat such a vessel countercurrently.

An even higher degree of selectivity, i. e., where the great bulk of the hydrogen is added to the side chains or side linkages rather than the benzene nucleus, was obtained in a six stage continuous operation heated in the same manner as the four stage equipment and with the catalyst prepared in the same way. A cooler and a separating chamber for the hydrogen excess, but not a condenser, are needed at the outlet. The liquid solvent was fed with a proportioning device into the first reaction chamber with hydrogen gas under 140 pounds pressure. The successive chambers were at 50°, 70°, 85°, 100°, 115°, and 125° C. These temperatures may be lowered and it is to be expressly understood that the temperatures given are not to be taken as invariable. These temperatures were elevated to 70°, 90°, 110°, 130°, 145°, and 155° C., when the activity of the catalyst as measured by its production, fell 25%. Alternately the pressure could have been increased to 200 lbs. The continuously produced hydrofined solvent had absorbed 0.75% hydrogen, its specific gravity had been reduced by 0.03, its refractive index reduced by more than 0.02. The apparatus shown in Fig. 2 for carrying out the six-stage operation is similar to the one shown for the four-stage in that jacketed catalyst chambers are used. However, a condenser is not needed but a cooler and separating chamber 20 is used. Also a known proportioning device 22 is used for feeding the liquid solvent and hydrogen into the first catalyst chamber.

The product of the hydrofinement described in the liquid phase multistage run, as compared to the original crude aromatic material, contains a higher proportion of hydrogen, has increased solvent strength as measured by the aniline point method, is less dense, and has a lower boiling range. Two examples of the resulting product compared to the crude follows:

	Crude	Hydrofined
Index of refraction at 20° C.	1.544	1.52
Specific gravity at 15° C.	0.958	0.928
Distillation initial	166° C.	163° C.
Distillation end	193° C.	183° C.
Polymerizable content	60%	5%
Aniline point	23° C.	21° C.
Index of refraction	1.502	1.493
Specific gravity	0.873	0.865
Distillation initial	130° C.	128° C.
Distillation end	165° C.	160° C.
Polymerizable content	25%	2%

To the hydrogenated product as much as an equal volume of such compatible liquids as petroleum, benzine, mineral spirits, xylol, refined solvent naphtha or refined high flash naphtha, may be added depending on the distillation range and rate of evaporation desired.

An anti-oxidant such as 1/20 of 1% hydroquinone may also be added to retard the slow yellowing, especially when the hydrofined product has not been further treated.

To obtain a purer product the vapor phase product resulting from the vapor phase process above given, may be subjected to the liquid phase hydrogenating treatment described in the six stage run or a product only partially hydrogenated may then be run through a six stage liquid phase treatment similar to that above given but using temperatures of 95°, 115°, 130°, 140°, 145° and 150° C. respectively instead of those given in the above example. This is given as one example only as it is within the contemplation of the invention to subject the product obtained by the vapor phase method to a liquid phase treatment in which a four stage process or any other number of stages may be used. After condensing the treated vapor, it may be caustic washed before being subjected to the liquid phase hydrogenation. The caustic wash comprises a dilute sodium hydroxide solution.

Instead of using only one catalyst a plurality of different catalysts of slightly different activity may be used in several stages, all working at the same pressure and approximately the same temperature. To make the catalyst for one chamber, mix equimolar portions of cobalt, nitrate, nitric acid, and ammonium chromate; evaporate to a paste, and gently ignite. Fill the first catalyst chamber with the lumps after an extraction with very weak acetic acid. To make the catalyst for the second chamber follow the above procedure substituting cadmium nitrate for the cobalt. The second chamber is then filled with the second catalyst. Alone, the first would act most efficiently at an average of 260° C. and the latter near 230° C. The corresponding pressures for these catalysts are of quite wide range, but of the order of eighty atmospheres and sixty atmospheres respectively. The crude liquid can then be pumped through these chambers, starting at 230° C. and about sixty atmospheres as a mean operating pressure and quickly working up to seventy atmospheres and a temperature of 240° C. which can be raised when the cadmium is nearly spent.

In like manner, three stages might be used, or ammonium molybdate could be substituted for part or all of the chromate in the above method of preparing the catalyst, and the nitrates by those of other metals such as silver and copper.

With the use of such catalysts and hydrogenating in the liquid phase, but preferably hydrogenating with a metallic catalyst in the vapor phase, oxygen heterocycles may be hydrogenated so as to produce substituted phenols, such as ortho ethyl phenol from cumarone. Whenever this is done the resulting tar acids are preferably separated before a finishing liquid phase hydrogenation.

The hydrogen used in this process may be pure hydrogen or hydrogen rich gasses essentially free from carbon oxysulfide, carbon disulfide and like impurities.

At present, there is a rapidly increasing production of synthetic resins and use of them as protective coatings. Coal tar solvents have a

marked superiority as vehicles in such coatings, particularly with resins of the glyptal type, because of their solvent power and evaporation rate. This invention makes possible the production of large quantities of refined solvent adapted for this purpose. The product herein described is made more usable by refinement to a permanent water-white color, by the reduction of onion-like odor, by the elimination of bodies that precipitate in the cold, by improvement of solvent power, and by reduction in the speed of evaporation.

Heretofore, the important method for refining crude solvent naphthas, and to a lesser extent, crude toluols from coal tar has been washing with 66° Bé. sulfuric acid which resinifies the highly unsaturated components. This washing is followed, after separation of the acid sludge, by a caustic wash and a distillation, from which the resin remains in the still.

In the past, this resin formation has been the only known means of refining, although it has always meant a loss of solvent. In a lower boiling range, distilling between 130 and 180° C., the yield of refined solvent, chiefly dimethyl benzenes, more commonly known as xylenes, has been about 75% of the crude solvent naphtha. The loss is chiefly styrene. In the next higher fraction, distilling approximately between 150 and 200° C., the yield varies. It falls as low as 35% of the solvent naphtha. The loss is chiefly coumarone and indene, which are removed as resin, but which, by the herein disclosed process, are converted into stable and useful solvents. The unchanged components consist chiefly of tri and tetra methyl benzenes.

The formation of undesired resin is eliminated by hydrogenating those bonds at which polymerization occurs. By controlling the degree and selectivity of hydrogenation it is possible to control the quantity and quality of resin produced.

As one result of the hydrogenation is a lowering in distillation range, the range of the crude solvent is extended upward. At the same time, the higher boiling fractions, which are solid when chilled and are otherwise undesirable, are converted by hydrogenation into stable liquids with useful solvent properties. For example, when naphthalene is present in the crude solvent, it is converted by hydrogenation from a deleterious solid into tetra-hydro naphthalene, a liquid closely related chemically and compatible with the refined solvent.

As the polymerizable constituents of crude heavy solvent naphtha, for example, range from 30 to 65% in different samples, the degree of hydrogenation of the final product varies with the source of the crude material. As the proportion of indene in the total polymerizable constituents of this crude material ranges from one-fifth to four-fifths, the composition of the final product will vary accordingly. For example, and depending on the crude material hydrogenated, the ratio of hydrindene to dihydrocoumarone in the final product may be as high as 5 to 1, or as low as 1 to 5. Similarly with crude light solvent naphtha, practically all the styrene that in the past has been lost is hydrogenated to the useful stable solvent, ethyl benzene.

Heretofore, the only benzene derivatives that have been hydrogenated (without secondary reaction) and in an economic manner, have been highly purified prior to hydrogenation. Not only have the numerous difficulties involved in hydrogenating crude benzene derivatives been over-

come, but new and useful constituents in substantial quantities, have been added and new products created.

While it has not been necessary to use special treatments of the crude mixtures before hydrogenation, pre-treatments with substances like metallic sodium, or with metallic hydrogenating catalysts before or after reduction may be used on very low grade crudes or extremes of fractions.

If the original crude product contains tar acids, or if it is expedient to form tar acids during hydrogenation, such tar acids may be removed by washing the hydrogenated product with dilute aqueous sodium hydroxide with or without the usual recovery with a strong acid such as sulfuric acid.

When hydrofining has not, for reasons of economy, been carried to complete saturation of the bonds at which polymerization occurs, the unchanged polymerizable bodies may be removed by any of the polymerizing agents known to the art and commonly used in refining. Such agents and 66° Bé. sulfuric acid and commercially anhydrous aluminum trichloride. To obtain the maximum yield of desirable solvent, it is necessary to remove the remaining polymerizable product with a reagent which will not react with the desirable solvent itself. As the hydrogenated bodies of the type formed are easily sulfonated, the use of 66° Bé. sulfuric acid is attended by considerable losses. Refining may be completed without sulfonating loss by using in the customary way such agents as aluminum, antimony or stannic chlorides; phosphoric with or without sulfuric acid; micro-porous siliceous compounds, such as fuller's earth with or without hydrofluoric acid treatment, silicates in which the aluminum is easily extracted with sulfuric acid, or silica gels.

What I claim is:

1. In the art of hydrogenating polymethyl benzenes mixed with crude unsaturated compounds, a method of saturating the unsaturated unpurified compounds without vaporization which comprises subjecting the crude mixture and hydrogen to the action of a nickel type catalyst at a relatively low temperature and pressure to hydrogenate the unsaturated crude compounds, raising the temperature gradually so that the average for the whole operation is about 125° C. while increasing the pressure sufficiently to maintain the rate of absorption of hydrogen substantially constant.

2. A method of the character described, which comprises, vaporizing a crude unpurified mixture containing hydrocarbon benzene derivatives, mixing an excess of hydrogen therewith, passing the mixture in contact with a series of nickel type catalysts while maintaining the temperatures under an ascending gradient such that the temperature at the first catalyst portion is less than the temperature at the last catalyst portion to hydrogenate the hydrocarbon benzene derivatives of the crude unpurified mixture, the method being carried out at a relatively low substantially constant pressure, the average temperature being substantially 145° C. while maintaining a partial pressure of hydrocarbon vapors less than three atmospheres.

3. A method for producing high yields of stable refined solvent which comprises, passing a mixture of hydrogen and the vapors of an unpurified crude mixture of hydrocarbon benzene compounds having unsaturated side chains or

rings continuously over a reduced nickel catalyst at a temperature of about 150° C. and at a pressure of about 1½ atmospheres such that the major portion of the hydrogen necessary to
5 saturate the side rings or chains is added, then condensing the vapors, then adding the final portion of hydrogen necessary to substantially saturate the side rings or chains in the presence of an active nickel catalyst at a temperature of
10 about 150° C. at a relatively low pressure.

4. In the art of stabilizing crude, unpurified mixtures of essentially hydrocarbon benzene compounds having unsaturated side chains or unsaturated side rings, the method which com-
15 prises passing the vapors of the crude unpurified

compounds with an excess of hydrogen through a confined space and subjecting the vapor mixture to the action of a metal base nickel catalyst at a temperature of about 115° C., then passing
5 such mixture over a second nickel catalyst in the presence of hydrogen at about 130° C. then passing such mixture over a third nickel catalyst at about 140° C. in the presence of hydrogen, and then passing such mixture over a fourth
10 nickel catalyst at about 145° C. in the presence of hydrogen, the pressure in the stages of the method being substantially constant and being about 1½ atmospheres.

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