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CHEMICAL PROCESS AND PRODUCT

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This application is a continuation-in-part of my copending application Serial Number 264,591, filed March 28, 1939.

The present invention relates to the production of aryl substituted phenols. More particularly, it relates to the production of aryl substituted phenols by reacting phenols with unsaturated aromatic hydrocarbons including unsaturated aromatic hydrocarbons boiling in the range of from 150° to 167° C. and obtained from light oil from the pyrolysis of petroleum oil.

The lower boiling condensate and the distillate from the tar produced in the manufacture of carburetted water gas, oil gas, and the like, which involve the pyrolysis of petroleum, is termed light oil. The higher boiling portion of the light oil contains a variety of unsaturated aromatic hydrocarbons mixed with saturated aromatic hydrocarbons of neighboring boiling points.

For instance, the higher boiling portion of a light oil produced in the manufacture of oil gas may contain styrene, ortho, para, and meta methyl styrene, indene, and other unsaturated aromatic hydrocarbons in admixture with the xylenes, cumene, pseudo-cumene, durenene, and possibly other saturated aromatic hydrocarbons. These unsaturated hydrocarbons may be concentrated by further fractionation of the higher boiling portion of the light oil. For instance, a light oil produced in the manufacture of oil gas has been fractionated as follows to concentrate the following unsaturated aromatic hydrocarbons:

	Cut points, °C.
Styrene forerunnings.....	135 to 140
Styrene	140 to 150
Unsaturates A ₁	150 to 160
Unsaturates A ₂	160 to 167
Methyl styrene group 1.....	167 to 172
Methyl styrene group 2.....	172 to 175
Indene group.....	175 to 183
Unsaturates B ₁	183 to 190
Unsaturates B ₂	190 to 200

The letters A₁, A₂, B₁, and B₂ refer to unsaturated aromatic hydrocarbons or mixtures of such unsaturates, not definitely identified.

According to the present invention, unsaturated aromatic hydrocarbons including unsaturated aromatic hydrocarbons boiling in the range from 150° to 167° C. obtained from light oil from the pyrolysis of petroleum oil, are reacted with phenols in the presence of a mineral acid catalyst, under controlled temperature conditions to produce aryl substituted phenols.

The entire portion of the light oil containing

aromatic unsaturated hydrocarbons and including unsaturated aromatic hydrocarbons boiling in the range from 150° to 167° C., may be reacted with phenols to give mixed aryl substituted phenols corresponding to the various aromatic unsaturates contained therein, or preferably the light oil may be fractionated to concentrate the unsaturated aromatic hydrocarbons boiling in the range from 150° to 167° C. individually or in groups and phenols reacted with the unsaturated aromatics in such fractions to give substituted phenols or groups of substituted phenols of greater or lesser purity.

For example, prior to reaction with a phenol, the light oil of the class described may be fractionated to yield a fraction having the preponderant portion of its unsaturation in the form of unsaturated aromatic hydrocarbon material boiling in the range from 150° to 167° C. The concentration may be such as to yield a fraction having its 10% and 90% boiling points within the recited range or the concentration may be such as to yield a fraction boiling substantially completely within the recited range.

The unsaturation contained in the light oil and boiling within the range from 150° to 167° C. may be subdivided, if desired, and the divisions separately reacted with a phenol. For example, it may be advantageous to react with a phenol a light oil fraction having the preponderant part of its unsaturation in the form of unsaturated aromatic hydrocarbon material boiling in the range from 150° to 160° C. The concentration may be such, that the 10% and 90% boiling points of the fraction fall between 150 and 160° C., or substantially the entire fraction may boil between 150° and 160° C. Likewise a phenol may be reacted with a light oil fraction having the preponderant portion of its unsaturation in the form of unsaturated aromatic hydrocarbon material boiling in the range from 160° to 167° C., or having its 10% and 90% boiling points within that range, or boiling substantially completely within that range.

It may be desirable in the case of highly concentrated individual unsaturates or groups, to add an inert solvent such as a saturated hydrocarbon prior to reaction with the phenol.

By phenols, I intend to mean the mono- and polyhydroxy derivatives of benzene and its homologues, such as for instance, phenol, cresol, resorcinol, pyrogallol, hydroquinone, pyrocatechol, naphthols, and the like, and substitution products of such compounds. As examples of acids suitable as catalysts for the reaction, sulphuric acid and phosphoric acid may be mentioned.

I have found that the aryl substituted phenols produced in the performance of my invention may be reacted with aldehydes to form resins which are soluble in drying oils, such as linseed oil and tung oil. This characteristic gives them great value for use in varnishes and lacquers in which the usual phenol aldehyde condensation products cannot be used due to their incompatibility with linseed oil and tung oil.

By aldehydes, it is intended to mean the aldehydes customarily employed in the production of phenol aldehyde condensation products of which, for example, formaldehyde and furfural may be preferred because of their relative cheapness.

I have found that in the performance of my invention, in addition to producing valuable aryl substituted phenols, the saturated aromatic hydrocarbons contained in such light oil fractions from the pyrolysis of petroleum may be recovered in a state of purity which requires little or no washing and, therefore, obviates the large wash losses which arise in the washing of these saturated aromatic hydrocarbons in the presence of the unsaturates.

I have further found that by controlling the concentration of the phenol with respect to the unsaturated aromatic hydrocarbons contained in such light oil fractions, the proportion of the mono substituted aryl phenols with respect to di- and tri-substituted phenols may be controlled, increasing excesses of phenol giving higher proportions of mono substituted products.

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

EXAMPLE 1

Twelve mols of phenol (1128 grams) were weighed into a 3 necked flask equipped with a stirring device, a dropping funnel and a thermometer. To this was added 1.2 cc. of 96% H_2SO_4 . To this were added 1684 grams of a light oil hydrocarbon fraction obtained during a fractional distillation of light oil produced in the manufacture of oil gas by taking a cut over the temperature range 150–160° C. This hydrocarbon fraction contained 28.0% of unsaturated materials by bromine analysis (the unsaturated material being arbitrarily calculated as monoolefine and having an average molecular weight of 118) and the weight used contained 4 mols of reactive hydrocarbon material. This addition was performed dropwise with vigorous agitation. To facilitate agitation at the start of the reaction, the phenol was melted by heating it on a water bath to about 42° C.

By variation of the rate of addition of the hydrocarbon fraction, the temperature was maintained at approximately 45° C. during the entire time the hydrocarbon was being added to the phenol catalyst mixture. The time required for this addition of hydrocarbon material was 3–4 hours.

When addition of the hydrocarbon fraction had been completed, heat was applied. The material was kept at a temperature of 130–160° C. for 2 hours. After cooling to 100° C., the sulfuric acid in the mixture was neutralized by adding the calculated quantity of Na_2CO_3 dissolved in a few cc. of water.

The purification of the desired condensation product and the recovery of the excess phenol and saturated hydrocarbon was accomplished as follows:

Without further washing or other treatment the reaction mixture was distilled. After collect-

ing about 2263 grams of unreacted phenol and saturated hydrocarbons, a fraction was taken distilling over in the range 140–200° C. at 2–5 mm. absolute pressure, which weighed 494 grams (58.7%) of theory. This fraction was a viscous, oily liquid, phenolic in nature as shown by subsequent tests. A solid residue remained in the distillation flask, amounting to 95.5 grams.

Data are available indicating that the hydrocarbon material which is non-reactive in nature may be separated from the excess phenol by simply conducting the distillation under a fractionating column.

The material distilling over from 140° C. to 200° C. at 5 mm. absolute, pressure, had the following physical properties:

Color (Gardner Holt)	64
Sp. gr. D 20/4	1.0798
N 20/D	1.5860
Mol. weight	178.6
Zerewitinoff value	per cent. 90.8

This phenolic material evidently comprises a mixture of aryl substituted phenols produced by reaction of the phenol with the aromatic unsaturates contained in this light oil cut.

EXAMPLE 2

6.6 mols of phenol (620 grams) were weighed into a 3 necked flask equipped with a stirring device, a dropping funnel and a thermometer. To this was added 0.66 cc. H_2SO_4 . To this were then added dropwise 880 grams of a light oil hydrocarbon fraction obtained during a fractional distillation of light oil produced in the manufacture of oil gas by taking a cut over the temperature range 160–187° C. This hydrocarbon fraction contained 29.8% by weight of unsaturated materials according to bromine analysis (the unsaturated material being arbitrarily calculated as monoolefine and having an average molecular weight of 118) and the weight used therefor contained about 2.2 mols of reactive hydrocarbon material. To facilitate agitation at the start of the reaction, the phenol was melted by heating it on a water bath to about 42° C.

By variation of the rate of addition of the hydrocarbon fraction, the temperature was maintained at approximately 45° C. during the entire time the hydrocarbon was being added to the phenol-catalyst mixture. The time required for this addition of hydrocarbon material was about 3 hours.

When addition of the hydrocarbon fraction had been completed heat was applied. The material was kept at a temperature of 130–160° C. for 2 hours. After cooling to 100° C., the H_2SO_4 in the mixture was neutralized by adding the calculated quantity of Na_2CO_3 dissolved in a few cc. of water.

The purification of the desired condensation product and the recovery of the excess phenol and saturated hydrocarbon was accomplished as follows:

Without washing or other treatment the reaction mixture was distilled. After collecting about 979 grams of unreacted phenol and saturated hydrocarbons, a fraction was taken distilling over in the range 140–196° C. at 2–3 mm. absolute pressure, which weighed 360 grams (about 77% theory). This fraction was a viscous, oily liquid, light amber in color and phenolic in nature as shown by subsequent tests. A solid residue remained in the distillation flask amounting to 84 grams. This solid residue need not be

considered a waste as it has interesting properties indicative of industrial value.

The hydrocarbon and the unused phenol can each be recovered in a relatively pure state by simply conducting the distillation under a fractionating column.

The material distilling in the range 140–196° C. at 2–3 mm. absolute, pressure, had the following physical properties:

Color (Gardner Holt)	5
Sp. gr. D 20/4	1.0901
N 20/D	1.5915
Mol. weight	194.5
Zerewitinoff value	percent 86.5

The phenolic material evidently comprises a mixture of aryl substituted phenols, produced by reaction of the phenol with the aromatic unsaturates contained in the light oil cut.

Referring to Examples 1 and 2, the following table gives properties of the distillation residues produced therein.

Table

Example	Description of unsaturates	Grams residue per mol.	2-5 mm. absolute pressure initial distillation point	Properties
1.....	A-1	24	°C. 200	Dark, resinous, tacky,
2.....	A-2	38	196	solid. Do.

Distillation of these residues gives very viscous semi-solid liquids of deep amber color constituting di-substituted phenols.

As before stated, the proportion of mono-substituted phenols to di-substituted and tri-substituted phenols produced in the reaction may be controlled by controlling the proportion of phenol to the unsaturated aromatic hydrocarbons, a molar excess of phenol having been found desirable when the desired products are mono substituted phenols. However, the excess of phenol may be limited by practical considerations and it may be desirable to employ proportions resulting in the production of considerable proportions of both mono and di-substituted products.

For example, a molar ratio of phenol to fraction unsaturation (considered arbitrarily for purposes of calculation as monoolefinic material of average molecular weight of 118) of 5 to 1 may result in the production of mono-substituted and di-substituted product respectively in a ratio of the order of 10 to 1 whereas a molar ratio of phenol to fraction unsaturation of 1 to 1 (calculated as above) may produce a ratio of mono-substituted product to di-substituted product of less than 2 to 1.

Thus varying proportions of mono and di-substituted phenols may be secured by varying the ratio of the reactants to each other.

EXAMPLE 3

To two mols of phenol containing 0.2% by weight of H_2SO_4 are added slowly a quantity of a cut taken from 150° to 160° C. of a light oil obtained in the manufacture of oil gas, said quantity containing 1 mol. of unsaturation (arbitrarily calculated as monoolefinic and having a molecular weight of 118). The temperature is kept below 50° C. by regulation of the rate of addition. When the light oil cut is all added the mass is heated to 120–150° C. for 2 hours

with agitation. After neutralization of the H_2SO_4 with the calculated amount of Na_2CO_3 solution, the product is fractionally distilled. The fraction distilling above 200° C. at 2–5 mm. will be found to be principally the disubstituted product.

EXAMPLE 4

Following the same procedure as in Example 3, but employing a light oil cut taken from 160° to 167° C. in sufficient quantity to provide 1 mol of unsaturation (arbitrarily calculated as monoolefinic and having an average molecular weight of 118), the distillation of the product will yield a fraction boiling above 196° C. at 2–5 mm. and containing principally the disubstituted product.

It will be seen from the examples given above, that the process of the invention provides a simple and inexpensive separation of the products of the reaction.

After neutralization of the small quantity of acid, it is only necessary to distill the products to recover separately the unreacted hydrocarbons and water, the unreacted phenol, and to separate the mono aryl phenol from di-aryl phenols and any higher substitution products, which are less valuable products. It is not necessary to wash out the acid catalyst prior to distillation because of the small quantity employed.

The procedure permits the recovery of the saturated aromatic hydrocarbons of the light oil fractions boiling in the range from 150° to 167° C. and obtained in the pyrolysis of petroleum, which contain considerable concentrations of aromatic unsaturates without the large wash losses incident to washing out the aromatic unsaturates and further provides for recovering the aromatic unsaturates as valuable aryl phenols.

For example, in the production of substituted phenols from the light oil unsaturation in the boiling range of from 150° to 167° C., recoveries of saturated aromatic hydrocarbons containing little olefinic contamination are possible by fractional distillation of the product. The yield of saturated hydrocarbons may be as high as 75% or more of the light oil fraction employed.

As stated before, the aryl phenols produced in accordance with the present invention may be reacted with aldehydes to produce substituted phenol-aldehyde resins which are compatible with drying oils, such as linseed oil and tung oil.

EXAMPLE 5

Approximately 318 grams of the mono-substituted product of Example 1 (corresponding to 1½ mols of the mono-substituted phenol on the basis of the assumed average molecular weight of 118 for the original unsaturates) are used in a specific preparation of a varnish resin. A wide boiling cut made from about 140 to 200° C. at approximately 2–5 mm. pressure is used. The above quantity is reacted with three mols (90 grams) of formaldehyde in the form of an approximately 37% solution and three grams of oxalic acid with agitation on a steam bath for 24 hours. The reaction is carried out in a flask provided with a reflux condenser. In order to compensate for the loss of formaldehyde by vaporization during the long heating period, the formaldehyde solution is added stepwise: 50% being added initially, 25% after 8 hours and 25% after 16 hours. After the heating period, the reflux condenser is changed to a take-off condenser, the temperature is raised to about 200° C., the system is evacuated to about 50 mm. pressure and the resin is steamed for two hours. The flask is

cooled somewhat and the resin is poured out while still molten.

The hardened resin is crushed and sieved. It will be found compatible with linseed and tung oil and may be cooked with these oils to form varnishes.

The compatibility of these resins with the usually employed drying oils, linseed oil and tung oil, is an extremely valuable characteristic. It opens the door to the employment of phenol aldehyde condensation products in coating compositions, such as drying oil varnishes, and affords a new utilization of the unsaturated aromatic hydrocarbons contained in light oil from petroleum pyrolysis, of which there is an extremely large potential supply.

The process herein described also affords a more economical method of recovering the saturated aromatic hydrocarbons accompanying the unsaturated aromatic hydrocarbons in such light oil.

It is to be understood that the above particular description is by way of illustration and that changes, omissions, additions, substitutions, and/or modifications may be made within the scope of the claims without departing from the spirit of the invention which is intended to be limited only as required by the prior art.

I claim:

1. A process comprising reacting a phenol with a light oil fraction containing unsaturated hydrocarbon material boiling within the range from 150° to 167° C., said reaction taking place in the presence of a condensation catalyst, and said light oil having been obtained from products of pyrolysis of petroleum oil.

2. A process comprising condensing a phenol in the presence of a mineral acid catalyst with a light oil fraction containing unsaturated aromatic hydrocarbon material which boils in the range from 150° to 167° C., said light oil having been obtained from products of pyrolysis produced in the manufacture of combustible gas by a process involving the thermal decomposition of petroleum oil.

3. A process for producing aryl substituted phenol material comprising reacting a phenol in the presence of a mineral acid catalyst with a light oil fraction boiling preponderantly in the range from 150° to 167° C. and containing unsaturated aromatic hydrocarbon material boiling within said range, said light oil having been separated from products of pyrolysis obtained in combustible gas manufacture involving the thermal decomposition of petroleum oil.

4. A process for producing aryl substituted phenol material comprising reacting phenol in the presence of a mineral acid catalyst with a light oil fraction having 10% and 90% boiling points within the range from 150° to 167° C. and containing aromatic unsaturation boiling within said range, said light oil having been recovered from petroleum pyrolysis products.

5. A process for producing aryl phenol material comprising condensing a phenol in the presence of a mineral acid catalyst with a light oil fraction boiling preponderantly within the range from 150° to 160° C. and containing aromatic unsaturation boiling in said range, said light oil having been obtained from products of petroleum oil pyrolysis.

6. A process for producing aryl phenol material comprising condensing a phenol with a light oil fraction the preponderant part of which boils in the range 160° to 167° C. and which contains aromatic unsaturation which boils within said range, said light oil having been obtained from products of pyrolysis of petroleum oil.

7. A process for producing aryl phenol material comprising condensing phenol in the presence of sulfuric acid as a catalyst with a fraction of a light oil obtained from petroleum oil pyrolysis products, said fraction containing unsaturated aromatic hydrocarbon material which boils within the range from 150° to 167° C., said condensation being effected under temperature conditions of from approximately 120° C. to approximately 160° C.

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