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TAR REMOVAL IN PHENOL PROCESS

Leendert Blom, Sittard, and Johannes L. F. M. Zwinkels,
Geleen, Netherlands, assignors to Stamicarbon N.V.,
Heerlen, Netherlands

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1 Claim. (Cl. 260-621)

The present invention relates to the preparation of phenols from monocarboxylic acids of the benzene series or from the salts, esters or anhydrides of such acids.

It is known that phenols can be prepared by pyrolytic oxidation and decarboxylation in the liquid phase of monocarboxylic acids of the benzene series or of the salts, esters or anhydrides of such acid, in the presence of a copper compound and at a temperature at which the compound is present in the dissolved state. This reaction is carried out with the aid of molecular oxygen in the presence of water vapor, e.g., steam.

At least part of the copper compound used as the catalyst in this reaction consists of the copper salt of the treated carboxylic acid of the benzene series. This copper salt can either be preformed or else it can be formed in the reaction zone by introducing another copper compound, e.g., cupric salicylate, cupric oxide, cuprous oxide or even metallic copper.

The reaction can be carried out by introducing molecular oxygen, e.g., in the form of air, and steam into the molten carboxylic acid of the benzene series or the salt, ester or anhydride thereof. Alternatively, the carboxylic acid or derivative thereof can be dissolved in an inert solvent, such as water. The copper salt is dissolved in the liquefied carboxylic acid prior to dissolving the latter in water. Air and steam are also introduced into the solution of the carboxylic acid in inert solvent.

Besides the desired phenol this reaction yields, as a by-product, a tarry, highly viscous product which, during the reaction, remains in solution in the liquid carboxylic acid or derivative. To recover non-converted carboxylic or derivative this tarry by-product must be removed from the reaction mixture and the carboxylic acid must be extracted. While much of the carboxylic acid or derivative and the catalyst is dissolved by the extraction liquids normally used, such as water, alcohols, e.g., methanol, ethanol, isopropanol, butanol, cyclohexanol and hexanol, aliphatic hydrocarbons, such as hexane, heptane, octane and cyclohexane, aromatic hydrocarbons, e.g., benzene, toluene, xylene, biphenyl, substituted hydrocarbons, e.g., chlorobenzene, trichloroethylene, and diphenyl oxide, unfortunately the tarry by-product is obtained as a viscous, semi-solid mass which is difficult to extract, seriously fouls the extraction apparatus and is difficult to remove therefrom. The result is not only that heavy losses of carboxylic acid occur, but also that the extraction apparatus is soon put out of operation.

Accordingly, it is an object of the present invention to eliminate the losses of unreacted carboxylic acid and derivatives thereof in the copper salt catalyzed formation of phenols from carboxylic acids and derivatives thereof.

Another object is to separate the tarry by-product from the unreacted carboxylic acid or derivative in such a process.

Still further objects and the entire scope of applicability

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of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

It has now been found that these objects can be attained and the tarry by-product loses its high viscosity if it is mixed with aromatic hydrocarbons, the molecule of which contains a condensed, unsaturated hydrocarbon ring system. After such admixture, the tar can be extracted with water and easily removed.

According to the invention, after the phenols are prepared by pyrolytic oxidation and decarboxylation in the presence of molecular oxygen, e.g., air, and water vapor, e.g., steam, in the liquid phase of monocarboxylic acids of the benzene series, or the salts, esters or anhydrides of such acids, in the presence of a copper compound which is in the dissolved state at the reaction temperature, the tarry by-product formed is separated off, as indicated, with an aromatic hydrocarbon, or substituted aromatic hydrocarbon containing a condensed unsaturated hydrocarbon ring.

As the catalyst there can be used copper or any of the copper compounds set forth below, e.g., cupric benzoate, cupric o-toluate, cupric m-toluate, cupric m-nitrobenzoate, cupric p-toluate, cupric p-nitrobenzoic acid, cupric p-chlorobenzoic acid, cupric p-methoxybenzoic acid, cupric p-phenylbenzoic acid, cupric 2,4-dimethyl benzoic acid, cupric salicylate, cupric oxide, cuprous oxide, metallic copper, cupric chloride, cuprous chloride, cupric sulfate, cupric nitrate.

Illustrations of phenols which can be obtained using benzoic acid and ring-substituted benzoic acids, according to the invention, using the copper salt catalysts, are given in Table 1.

TABLE 1

Starting material:	Product
Benzoic acid -----	Phenol.
o-Toluic acid -----	m-Cresol.
m-Toluic acid -----	o-Cresol and p-cresol.
p-Toluic acid -----	m-Cresol.
m-Nitrobenzoic acid -----	p-Nitrophenol.
p-Nitrobenzoic -----	m-Nitrophenol.
p-Chlorobenzoic acid -----	m-Chlorophenol and
p-Methoxybenzoic acid ----	phenol.
2,4-dimethylbenzoic acid --	m-Methoxyphenol and
	phenol.
p-Phenylbenzoic acid -----	2,5-dimethylphenol.
	m-Phenylphenol.

As the starting material in place of the free benzoic acid or free-substituted benzoic acid there can be used salts, esters and anhydrides, as previously indicated. Illustrative of such starting materials are magnesium benzoate, sodium benzoate, calcium benzoate, potassium benzoate, barium benzoate, methyl benzoate, ethyl benzoate, magnesium o-toluate, propyl p-toluate, sodium m-nitrobenzoate, methyl p-nitrobenzoate, benzoic anhydride, toluic anhydride, m-nitrobenzoic anhydride, ethyl p-methoxybenzoate, p-phenylbenzoic anhydride, ethyl 2,4-dimethylbenzoate.

Examples of aromatic hydrocarbons and derivatives thereof containing a condensed unsaturated hydrocarbon

ring system which can be used to separate off the tarry by-product, include aromatic hydrocarbons (including alkyl and other hydrocarbon substituted aromatic hydrocarbons), naphthalene, anthracene, phenanthrene, fluorene, pyrene, α -methyl naphthalene, β -methyl naphthalene, dimethyl naphthalene, methyl anthracene, acenaphthene, fluoranthene, chrysene, carboxylic acids, such as α -naphthoic acid, β -naphthoic acid and anthracene carboxylic acid, chloro derivatives, such as α -chloronaphthalene, β -chloronaphthalene, α -bromonaphthalene, and dichloronaphthalene, phenols, e.g., α -naphthol, β -naphthol, and hydroxyanthracene, tetrahydronaphthyl naphthalene.

Furthermore, there can be used aromatic oils predominating in aromatic hydrocarbons containing a condensed unsaturated hydrocarbon ring system including coal tar oils, such as anthracene oil and creosote oil and high-boiling aromatic hydrocarbon residues obtained in the refining of mineral oil, and preferably boiling above 200° C.

The tarry by-product can be mixed with the condensed ring aromatic hydrocarbon after the phenol produced has been separated from the product of the reaction between oxygen and the carboxylic acid or derivative of the benzene series. The tarry by-product is thus converted to the form of a thin liquid which can be subjected to an extraction with a solvent in which the carboxylic acid can be dissolved. The preferred solvent for the purpose of recovering the carboxylic acid from the tar is water. However, other solvents can be used, such as alcohols, e.g., methanol, ethanol, isopropanol, butanol, hexanol, isooctanol and cyclohexanol, aliphatic hydrocarbons, such as hexane, heptane, decane and cyclohexane, aromatic hydrocarbons, such as benzene, toluene, xylene, biphenyl, mesitylene, cymene and cumene, substituted hydrocarbons, e.g., ethers, such as diphenyl oxide and halo hydrocarbons, such as chlorobenzene, bromobenzene, trichloroethylene, tetrachloroethylene, dichloroethylene, ethylene dichloride, acetylene tetrachloride and carbon tetrachloride.

The amount of aromatic hydrocarbon or derivative containing a condensed unsaturated hydrocarbon ring system can be varied within wide limits. The amount is generally smaller in the case of nonsubstituted higher aromatic hydrocarbons than in the case of alkyl or other substituted aromatics, such as dimethylnaphthalene. In most cases the amount of the aromatic hydrocarbon or derivative need not exceed 300% by weight of the tarry by-product. Preferably, 35% to 100% of the aromatic hydrocarbon or derivative is used, based on the weight of the tar. If smaller amounts of the condensed ring extractant are used, the tar becomes more flowable, but nevertheless retains such a high viscosity that considerable energy is required to pump it.

Unless otherwise indicated, all parts and percentages are by weight.

EXAMPLE 1

In a 3 liter cylindrical reaction vessel 200 grams of cupric benzoate and 175 grams of magnesium benzoate were dissolved in 2.5 kilograms of benzoic acid at a temperature of 230° C. Then 250 liters of air and 200 liters of steam (both calculated at 0° C. and 1 atm., STP) per hour were continuously introduced into the solution at atmospheric pressure while the temperature was maintained at 230° C. to 235° C. The gas-vapor mixture discharged from the reaction vessel was passed into a fractionating column from the top of which a mixture of phenol and water was discharged. The benzoic acid discharged from the bottom of the column was returned to the reaction vessel. Additionally, 180 grams of benzoic acid were supplied per hour. After 50 hours the reaction was stopped. 4.2 kilograms of phenol were recovered, which corresponded to a yield of 80% with respect to the amount of benzoic acid converted.

During the reaction a tarry by-product formed which was mixed with the benzoic acid in the reaction vessel. To prevent accumulation of the tar, 60 grams of liquid reac-

tion mixture was discharged from the reaction vessel per hour and fed to a storage tank.

3 kilograms of the reaction mixture were taken from the storage tank and mixed with 0.45 kilogram of creosote oil. This mixture was then introduced into an extraction apparatus, where, at a temperature of 150° C. and a pressure of 6 atm. it was extracted in four steps, with 9 kilograms of water passed through in counter-current flow. From the resulting aqueous benzoic acid solution, which also contained copper benzoate and magnesium benzoate, the starting material was recovered by evaporation of the water. The oil phase, 1 kilogram, remaining after the aqueous extraction of the benzoic acid contained 0.55 kilogram of tarry by-product. This oil phase had a viscosity of 33 centipoises at 150° C. and was discharged from the reaction vessel by means of a pump. It was useful as a fuel oil.

EXAMPLE 2

After a stock of tar mixed with non-converted benzoic acid was obtained in the storage tank by repeating the preparation of phenol described in Example 1, continuous extraction was applied.

Per hour, 650 grams of the tar mixture, together with 75 grams of creosote oil, were introduced into a continuously operating rotating disc extractor and extracted with water passed at a rate of 2 kilograms per hour in counter-current flow at a temperature of 150° C. and a pressure of 6 atm.

The oil phase having a viscosity of 107 centipoises was separated off continuously at 150° C.

EXAMPLE 3

2.7 kilograms of the tar mixture from the storage tank of Example 2 was mixed with 0.48 kilogram of aromatic hydrocarbon residue boiling above 200° C. and obtained in the refining of mineral oil. The resulting mixture was then extracted with 8.1 kilograms of water in the manner described in Example 1 to recover the benzoic acid.

The oil phase separated off contained 52% by weight of tarry by-product and had a viscosity of 700 centipoises at 150° C.

EXAMPLE 4

The procedure of Example 1 for preparing phenol was repeated except that 50 grams of anthracene oil per hour were charged into the reaction vessel and 110 grams of liquid reaction mixture per hour (rather than 60 grams per hour) were discharged from the reaction vessel and introduced into the storage tank.

To recover non-converted benzoic acid 4.3 kilograms of the reaction mixture was taken from the storage tank and extracted with 12 kilograms of water at 150° C. and a pressure of 6 atm. No creosote oil was used in this extraction since anthracene oil was already present.

The benzoic acid was recovered from the aqueous extract. The oil phase separated off amounted to 1 kilogram and contained 0.7 kilogram of tarry by-product and had a viscosity of 700 centipoises at 150° C.

We claim:

In a process for preparing a phenol by pyrolytic oxidation and decarboxylation in the liquid phase of a carboxyl compound of the group consisting of monocarboxylic acids of the benzene series and salts, esters and anhydrides of such acids in the presence of a copper compound catalyst dissolved in said liquid phase and in the presence of molecular oxygen and water vapor and in which process a tarry by-product is formed and separated off, the improvement comprising mixing said tarry by-product with a condensed ring compound of the group consisting of aromatic hydrocarbons containing a condensed unsaturated hydrocarbon ring system and halo, hydroxyl and carboxyl substituted derivatives of said aromatic hydrocarbons and extracting said mixture with an extraction liquid which is

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a solvent for said carboxylic acid wherein the condensed ring compound is added to the tarry by-product as it is being formed and the oxidation and decarboxylation are carried out in the presence of the condensed ring compound.

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10 H. M. HELFER, *Assistant Examiner.*