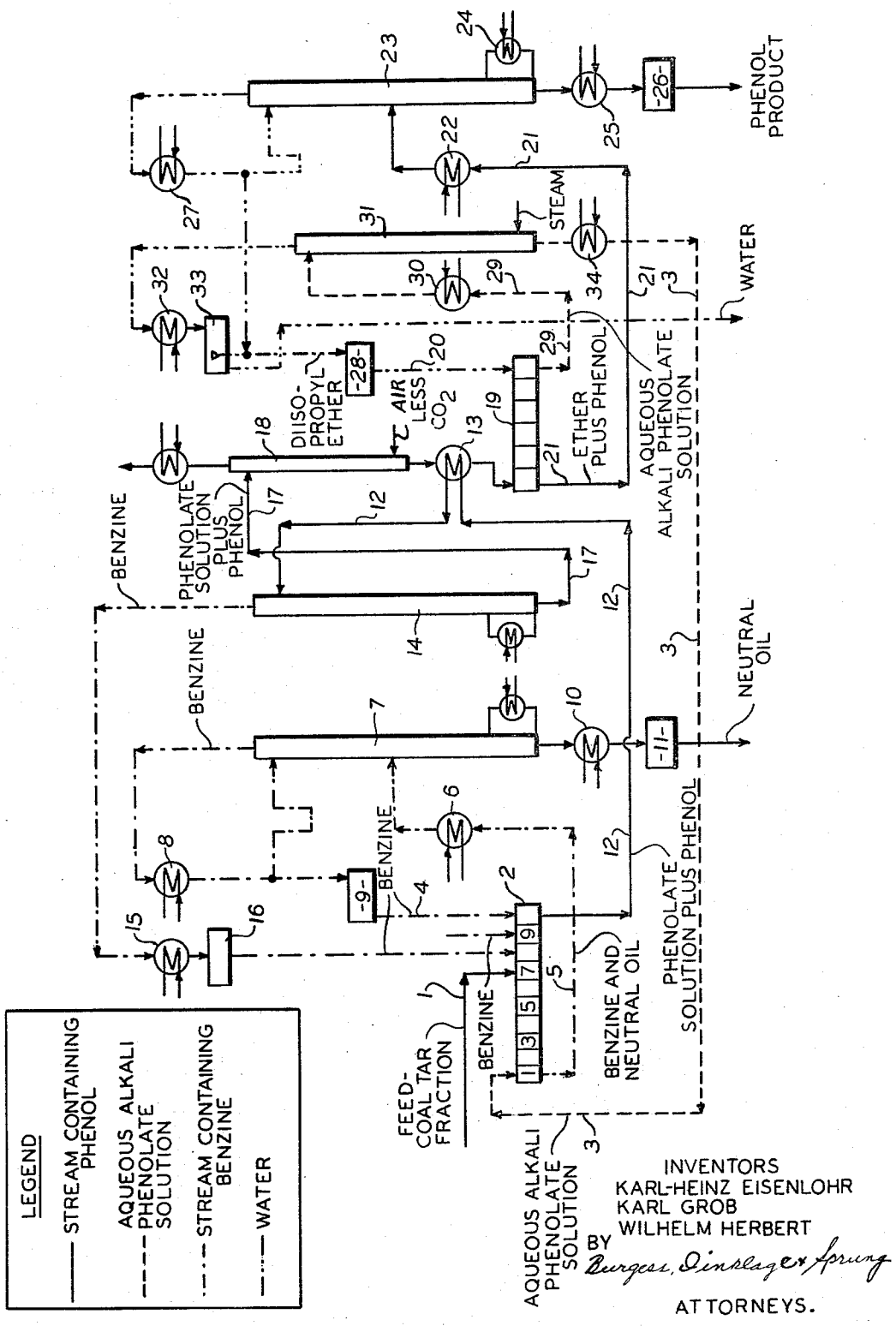
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PROCESS FOR PRODUCING PURE PHENOLS FROM THEIR MIXTURES WITH NEUTRAL OILS

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This application is a continuation of part of application Serial No. 702,950, filed December 16, 1957, based on German applications filed December 21, 1956, and July 24, 1957. The disclosure of the said prior applications is incorporated herein by reference. Said application Serial No. 702,950 has been abandoned.

The present invention relates to a process for the production of pure phenols being photostable and free from neutral oils, from their mixtures with neutral oils.

Such mixtures of phenols and neutral oils are, for instance, the tars or tar fractions obtained as by-products in low-temperature carbonization, in high-temperature carbonization and in the gasification of solid fuels, in particular of mineral coal and brown coal.

Neutral oils are also contained in crude phenols obtained in the purification of phenol-containing waste waters by extraction with organic solvents, as for instance benzene or butyl acetate. Such waste waters result in coal refining plants and in works in which phenols are treated. Fractions containing small quantities of phenols can also arise in the refining of crude oils.

Such mixtures of phenols and neutral oils arising in technical refining plants for fuels often still contain as accompanying constituents organic sulfur compounds, in particular mercaptans, neutral organic oxygen compounds and organic nitrogen compounds which are basic Among the latter ones are especially mentioned pyridine and its derivatives.

The numerous known processes for the separation of neutral oils, in particular for the separation of the hydrocarbons from acid oils, preferably the phenols and acid sulfur compounds, either serve for purifying a neutral oil, for instance, a petroleum fraction, by separating the acid constituents in order to use the neutral oil as a motor fuel or for recovering the acid constituents, preferably the phenols, from a mixture of acid and neutral oils.

The first case, for instance, relates to fractions of mineral oil having a relatively small phenol content, of about 5%, which has to be completely removed from the neutral oil.

The second case applies, for instance, to tar oils having a relatively high phenol content of about 30–40%. These phenols are to be recovered possibly free from neutral oils, whereby residual contents of about 2–3% of phenols can be accepted in the remaining neutral oil.

Most of the processes for separating phenols from their mixtures with neutral oils are based on the fact that the phenols can be extracted from such mixtures by means of aqueous solutions of alkali hydroxide and alkali carbonate.

A neutral oil free from phenol and an aqueous alkali hydroxide solution containing alkali phenolate are obtained when a phenol-containing oil is washed in countercurrent with an aqueous alkali hydroxide solution. In case a quantitative washing out of the phenols from the mixture is to be performed, the alkali hydroxide is then employed in considerable excess of the stoichiometrical requirement. If in the recovering process of the lower, unmistakably acid phenols some higher, slightly acid

phenols are allowed to remain in the neutral oil, it is then possible to employ a smaller proportion of alkali in excess of the stoichiometrical requirement.

In most of the cases the thus obtained aqueous alkali phenolate solution, possibly containing free alkali, also contains small quantities of neutral oils and organic bases. These equally dissolved neutral or basic accompanying substances can be expelled by the introduction of vapor, distilled off or removed from the solution through an extraction with a low-boiling benzine, or possibly destroyed through a treatment with oxidizing agents, as for instance air at increased temperature.

The alkali phenolates can be extracted from the alkali phenolate solution by means of suitable solvents, as for instance amyl alcohol. They can be isolated as a substance by distilling off the alcohol and be decomposed into free phenols and alkali sufate by means of mineral acids, as for instance sulfuric acid. However, it is also possible to decompose them already in the alcoholic solution.

In most cases, however, the aqueous alkali phenolate solution is directly decomposed by mineral acids. The phenols are thereby separated as an oily layer and can be eliminated from the aqueous layer containing alkali salts. Said aqueous phase containing alkali salts still contains dissolved phenols which must be recovered by extraction with an organic solvent, for instance benzene, toluene, diisopropyl ether, butyl acetate or the like. But also thereafter an alkali sulfate solution, for instance, still remains an undesired waste water in which the initial alkali hyroxide gets lost.

For this reason carbon dioxide is used under pressure for decomposing the aqueous alkali phenolate solution. The alkali carbonate solution separated from the oily phenolic phase is then converted by means of calcium hydroxide into an alkali hydroxide solution and calcium carbonate after having first been purified by means of an extraction with organic solvents. The alkali hydroxide solution is anew employed for extracting the phenols from the initial substance. The calcium carbonate is calcinated whereby calcium oxide and carbon dioxide are obtained both of which are returned into the process. Although this conversion process of alkali carbonate into alkali hydroxide, known as the calcination of soda, theoretically does not cause a loss in chemicals, it consumes a high amount of energy during the calcination of the calcium carbonate and requires very voluminous auxiliary installations.

According to another known process the phenols are separated from their mixtures with neutral oils by treating the latter ones with a solution of alkali carbonates at an increased temperature and an increased pressure. Thereby the phenols are likewise dissolved into alkali phenolate from which the neutral oils are separated as an insoluble layer, whereas the gaseous carbon dioxide escapes.

Also in this process the alkali phenolate solution is purified from neutral or basic accompanying substances by means of evaporation, distillation or extraction, as described above, and then converted again into alkali carbonate and free phenols by means of carbon dioxide. Since in this process the higher, only slightly acid phenols cannot be completely separated, the resulting oil, which is made poor in phenols, is subjected in most of the cases to a further washing with alkali hydroxide, if necessary. The thereby resulting alkaline phenolate solution is subsequently treated together with that obtained from the alkali carbonate solution. Also in this process the recovering of alkali hydroxide from alkali carbonate is necessary, however, the consumption of energy and the dimensions of the auxiliary installations are substantially smaller.

No organic solvents are known which, possibly diluted with water, are capable of extracting phenols from their

mixtures with neutral oils. Although by employing methanol or water-containing methanol an enrichment in phenols is obtained as compared with the neutral oil, but the obtained extract still contains so much neutral oil that it cannot be dispensed with another separation process in which alkalies are employed.

Contrary thereto, aqueous solutions of alkali phenolates have good and specific dissolving properties for phenols. For instance, in case a phenol-containing tar fraction is extracted by means of an aqueous solution containing of from 10 to 40% of alkali phenolate, a supersaturated phenolate solution is then obtained as an extract. Said solution contains the phenols taken up from the phenol-containing tar fraction in a physically dissolved state, and they can be re-extracted from it with suitable organic solvents, in particular ethers or ketones, and preferably diisopropyl ether or methyl isopropyl ketone.

By "supersaturated phenolate solution" or "oversaturated phenolate solution" is meant a phenolate solution containing free phenol.

Such a saturated aqueous alkali phenolate solution does not only absorb the phenols from the oil mixture to be decomposed, but also small quantities of neutral oils as well as organic nitrogen, sulfur and oxygen compounds. For the purpose of carrying through a selective extraction and of finally obtaining pure phenols, i.e., phenols free from foreign substances, from the supersaturated aqueous alkali phenolate solution, the latter one is washed prior to the extraction of the pure phenols with a low-boiling aliphatic benzine (in the boiling range of from 50–70° C.), which absorbs the hydrocarbons from the aqueous alkali phenolate solution. The organic nitrogen compounds which have an alkali reaction are separated from the extract obtained with isopropyl ether by washing them out by means of an aqueous sulfuric acid prior to the distillation of the isopropyl ether and residues of the low boiling benzine from the pure phenols.

It is also possible to extract simultaneously the hydrocarbons and the organic nitrogen compounds from the supersaturated aqueous alkali phenolate solution by means of a cycloparaffinic benzine. Thereby the benzine, which remains in the aqueous alkali phenolate solution and which is then absorbed, together with the pure phenols by the isopropyl ether, must be separated from the ether, which is very difficult. A cycloparaffinic benzine absorbs also phenols from the supersaturated phenolate lye which have to be recovered from the extract. After the benzine is distilled off, the extract is in most of the cases added to the oil mixture to be treated.

The possibilities of purifying the phenols dissolved in the aqueous alkali phenolate solution by means of a refining are limited. Chemical methods, as for instance the employment of acids, cannot be applied, because they would more or less rapidly destroy the aqueous alkali phenolate solution which is circulated as a physically acting solvent without loss through the extractor of the phenols from the initial mixture, the purification stages and the re-extraction stage of the pure phenols from the phenolate lye.

For this reason, also the oxidation treatments which proved to be successful with phenolate lyes containing free alkali and with impure phenol concentrates, are applicable in an alkaline medium only, if no carboxylic acids are formed thereby through the oxidation of alcohols, aldehydes, ethers, and the like. Such carboxylic acids would slowly destroy the phenolate lye by forming free phenols and carboxylic acid alkali salts.

The phenols contained in solution in the aqueous alkali phenolate solution are freed from the also dissolved accompanying substances, the hydrocarbons, the organic bases and the non-acid organic oxygen compounds through their extraction by means of a low-boiling benzine. The boiling point of said benzine is to be lower than those of the simplest phenol, i.e., C_6H_5OH, and of the organic oxygen-containing solvent being used for extracting the pure phenols from the purified aqueous alkali phenolate solution, so that the portion of said benzine remaining after the extraction in the supersaturated aqueous alkali phenolate solution can be separated from the phenols as well as from the oxygen-containing solvent. It is also possible to expel this portion of the extraction benzine remaining in the aqueous alkali phenolate solution by introducing direct vapor. However, phenols are also volatilized thereby and come into the aqueous condensate of said water steam distillation which may cause an additional waste water problem.

Only small, unessential quantities of phenols are volatilized in the evaporation of alkali phenolate lyes which still contain free alkali and in which the phenols are chemically combined.

In the reprocessing of tars or tar fractions from the dry distillation or from the gasification of brown coal or mineral coal into pure phenols the extraction of the phenols from their mixtures with other organic substances by means of an aqueous alkali phenolate solution is very advantageous insofar as only small quantities of chemicals are consumed and only small quantities of waste water accrue.

It proved, however, that the purification alone of the supersaturated aqueous alkali phenolate solution by extraction with a benzine prior to the re-extraction of the phenols with an organic oxygen-containing solvent does not suffice to obtain pure phenols, stable to light, of the kind as they are in particular required by the plastics industry.

It is neither an advantage to obtain a phenol concentrate according to the said method and to process and purify that concentrate according to the previously described known methods. These methods are based on the conversion of the phenols into phenolates and would then require a high consumption of chemicals and produce great quantities of waste water, both of which effects are to be avoided.

It has now been found that the phenols dissolved in the aqueous alkali phenolate solution can be refined to their complete purity and light stability if the aqueous aklali phenolate solution containing phenol is extracted in a countercurrent with benzene, toluene, xylene or a mixture of the same or with a benzine containing at least 25% of said aromatic hydrocarbons, subsequently distilled and finally subjected to an oxidation treatment.

The extraction of the aqueous alkali phenolate solution containing phenols with the hydrocarbon mixture containing at least 25% of aromatics results in an extract containing such quantities of neutral oils and oxygen compounds as well as of nitrogen and sulfur compounds that have also been dissolved by the aqueous alkali phenolate solution, but containing also a portion of the phenols.

After a mixture of hydrocarbons containing aromatics is distilled off, the extract is added again to the initial mixture to be processed.

This portion of phenols re-extracted together with the accompanying substances may amount to more than 10% of the phenols contained in the aqueous alkali phenolate solution. This is the reason why it has been avoided hitherto to employ aromatic hydrocarbons for purifying supersaturated alkali phenolate solutions. The portion of phenols contained in said circulation is decreased according to the invention by charging the aqueous alkali phenolate solution at the extraction of the phenol containing initial substance to such an extent that the solution contains at the utmost 0.6 mole, preferably from 0.3 to 0.5 mole of phenols per 1 mole of alkali phenolate. This corresponds in case of 28 weight percent of phenols in the initial substance and an alkali phenolate solution of 40 weight percent to a ratio of 1 weight part initial substance to from 1.7 to 2.7 parts of alkali phenolate solution.

Under these conditions, less than 6%, in general only about 3%, of the phenols pass over from the phenol-containing alkali phenolate solution into the benzine containing aromatics.

The accompanying substances are absorbed by the benzine containing aromatics through the extraction of the phenol-containing alkali phenolate solution. The portion of the aromatic-containing benzine remaining in the phenol-containing alkali phenolate solution is expelled by means of a water steam distillation, whereby also phenols are passing over. The condensed distillate is separated into two phases. The non-aqueous phase contains the benzine with the aromatics and the greatest portion of the phenols passed over from the phenol-containing alkali phenolate solution. Also the aqueous phase still contains phenols which can be recovered in an installation for the purification of phenol-containing waste waters. However, the distillation of the phenol-containing alkali phenolate solution by means of water steam is preferably carried out in an indirect heating and without a direct introduction of steam, whereby the steam is produced in the solution itself. The alkali phenolate solution becomes thereby more concentrated. Since the total quantity of the condensate from this water steam distillation is added again to the phenol-containing alkali phenolate solution prior to the extraction with the aromate-containing benzine, said increase in concentration is compensated thereby. The benzine, the phenols and the evaporated water are thereby recirculated into the process, so that no waste water results and the concentration of the aqueous alkali phenolate solution is re-established.

The phenol-containing alkali phenolate solution treated by means of the extraction with the aromatic-containing benzine and the distillation is then subjected to an oxidation in a treatment with air free from carbon dioxide at increased temperature or by the action of hydrogen peroxide or sodium peroxide. These oxidizing agents are consumed in the phenol-containing alkali phenolate solution without leaving disturbing residues. After oxygen-containing neutral organic compounds being oxidizable up to carboxylic acids have been removed through the extraction with the benzine containing aromatics, only amino phenols and oxidizable diphenols are converted now into higher molecular substances by the formation of quinoidal systems, which substances remain in the distillation residue at the fractionizing distillation of the pure phenols. By this oxidation treatment in particular the color-changing accompanying substances are rendered harmless, but also some sulfur compounds through the oxidation of the mercaptan type to the disulfide type.

The pure phenols are then extracted in a known manner with diisopropyl ether from the thus refined phenol-containing alkali phenolate solution and obtained as a pure mixture after the ether has been distilled off from the extract. The extract, which still contains ether, may suitably be washed with a diluted sulfuric acid in order to remove completely the last residues of organic bases. This security measure is particularly advisable in case the obtained phenols are to be processed to light-colored synthetic resins.

It is the object of the present invention to devise a method of obtaining phenols free from neutral oils and stable to light from tar fractions or crude phenols from coal by extracting the phenol-containing oil or the crude phenols in countercurrent with an aqueous alkali phenolate solution, extracting the obtained alkali phenolate solution supersaturated with phenols with an oxygen-containing organic solvent and distilling the solvent out of the phenol-containing extract.

The process according to the invention is characterized in that the phenol-containing oils or crude phenols are extracted simultaneously in countercurrent with the aqueous alkali phenolate solution and with an aromatic hydrocarbon mixture or a mixture containing at least 25% of aromatics, in a boiling range of from 75 to 145° C., and in that subsequently the proportions of these hydrocarbons remaining dissolved in the alkali phenolate solution supersaturated with phenols are distilled off from said lye which is then treated by an oxidizing agent at normal or increased temperature, prior to the extraction with the organic, oxygen-containing solvent.

The simultaneous extraction of the phenol-containing oils or the crude phenols with an alkali phenolates solution and an aromatic or aromatic-containing hydrocarbon mixture is so carried out that the alkali phenolate solution is introduced on one side of the extractor, whereas on the other side the aromatic-containing hydrocarbon mixture is introduced and in one of the median stages the oil fraction to be dephenolated.

The extraction of the phenol-containing oil or of the crude phenols with the alkali phenolate solution can be carried out at increased temperature and under pressure. According to the invention the aqueous alkali phenolate solution is supersaturated by the extraction of the phenols from the phenol-containing oils only to such an extent that it contains one mole of alkali phenolate per 0.6 mole of phenols.

In carrying out the process according to the invention it is important that the countercurrent extraction of the phenol-containing crude oil is performed simultaneously with the aqueous alkali phenolate solution and the aromatic-containing hydrocarbons, that the supersaturation in phenols of the phenolate lye does not exceed thereby the molar ratio of 1:0.6 and that the other operational steps, namely, the distillation of the aromatic extraction agent from the alkali phenolate solution and the oxidation are subsequently performed in the mentioned sequence. If the simultaneous countercurrent extraction of the phenol-containing crude oil by means of the alkali phenolate solution and the aromatic-containing extracting agent is so carried out that the latter ones are conducted in countercurrent with respect to each other through a column or a multistage extractor and that the phenol-containing crude oil is introduced at a point positioned laterally between the ends of the column or into one of the median stages of the extractor, the neutral and basic accompanying substances which have also been dissolved by the alkali phenolate solution are then forced out in a particularly effective way into the portion of neutral oil.

Those portions of the aromatic extracting agent which remain dissolved in the alkali phenolate solution are distilled off. After said distillation the alkali phenolate solution supersaturated in phenols only contains easily water-soluble accompanying substances, in particular thiophenols, sulfurous phenol compounds and aminophenols to be converted by the subsequent oxidation into disulfides or quinoidal substances of a higher molecular weight, which accompanying substances remain in the residue from the distillation of the last fractionating distillation of the pure phenols. Such an oxidation treatment is also essential for the purpose of preventing the alkali phenolate lye from being enriched with resinifying foreign substances. A precondition therefor is the previous elimination of substances, which can easily be oxidized to carboxylic acids, from the alkali phenolate solution. These neutral oxygen compounds containing the oxygen in alcoholic hydroxyl groups, in aldehyde groups or in ether groups are forced out into the remaining neutral oil by the simultaneous extraction according to the invention of the phenolated crude oil with the alkali phenolate solution and the aromatic extracting agent.

The flow diagram of an installation for carrying out the process according to the invention is illustrated in the drawing by way of example.

An oil fraction of a mineral coal tar boiling in the range of from 150 to 230° C. is introduced through conduit 1 into the seventh stage of a ten-stage-extractor 2, into the first stage of which an aqueous sodium phenolate solution is introduced through conduit 3 and into the tenth stage of which toluene is introduced through conduit 4. The toluene, which has absorbed the neutral oils

and bases contained in the tar oil fraction, passes through conduit **5** via a preheater **6** into the distillation column **7** in which the toluene is distilled off and conducted via the condenser **8** into the storage tank **9**. The neutral oil remaining as a distillation residue in the sump of column **7** is conducted into a refrigerator **10** and thereafter stored for further use in the tank **11**. The aqueous alkali phenolate solution enriched with phenols is discharged from the extractor **2** via conduit **12** and is conducted via the heat exchanger **13** into the distillation column **14**. In the latter distillation column the toluene dissolved in the alkali phenolate solution is distilled off by indirect heating, whereby also water and some phenols are passed over. The distillate passes via condenser **15** into the storage tank **16** from where it is conducted into the eighth stage of the extractor.

The clear-distilled alkali phenolate solution passes through the conduit **17** into the aerating tower **18** in which it is treated with air free of carbon dioxide. Thereafter it is conducted through the heat exchanger **13** into the second, six-stage extractor **19**, in which it is freed from the absorbed physically dissolved phenol mixture by means of an oxygen-containing solvent, for instance, diisopropyl ether, which is introduced in a countercurrent. The diisopropyl ether is introduced into the extractor **19** through conduit **20** and flows, charged with the phenols from the extractor **19**, through conduit **21** via the preheater **22** into the distillation column **23**. The latter distillation column in which diisopropyl ether is distilled off from the pure phenols, is indirectly heated with steam at **24**. The refined phenols pass from the sump of column **23** via refrigerator **25** into the storage tank **26**, from where they are taken for fractionating or for further use. The solvent distilled off in column **23** is condensed in condenser **27** and reconducted via the storage tank **28** through conduit **20** into the extractor **19**. The alkali phenolate solution which is freed from the dissolved phenols is introduced via conduit **29** and preheater **30** into the upper part of the distilling column **31**, in which the dissolved ether is distilled by means of steam, condensed in condenser **32** and also conducted into the storage tank **28** after separation of the water in the separator **33**. In the refrigerator **34** the aqueous alkali phenolate solution free from ether is cooled down to the temperature desired for the extraction and then recirculated into the extractor **2** through conduit **3**.

Example 1

Coal-tar oil having a boiling range of from 170 to 225° C. and a phenol content of 37.0% by weight is introduced at a ratio of 1000 kg. per hour into the seventh stage of an eleven-stage countercurrent extractor, whereas into its first stage a 25% sodium phenolate solution is introduced at a ratio of 3000 kg. per hour, and into its eleventh stage benzine having a boiling range of from 70 to 110° C. and a content of aromatics at 25% at a ratio of 600 kg. per hour. The benzine absorbs 8.5 kg. of phenols which remain in the neutral oil after the distillation. The sodium phenolate solution which is supersaturated with phenols, has absorbed 361.5 kg. of phenols and 90 kg. of benzine. The benzine is distilled off. The water-containing distillate is recirculated into the extractor. The sodium phenolate solution was supersaturated with phenol in a ratio of 0.58 mole of phenols per 1 mole of sodium phenolate. Air free of carbon dioxide is then blown into the sodium phenolate solution being free from benzine and having a temperature of 80° C. whereafter it is extracted in six stages of a second extractor in countercurrent with 900 kg. of isopropyl ether. After the latter one is distilled off, 361 kg. of a phenol mixture are obtained. After the fractionation of the mixture the following phenols are obtained.

	Percent
182 kg. of phenol, clearly soluble in aqueous solution of sodium hydroxide, pyridine content	0
42 kg. of orthocresol, clearly soluble in aqueous solution of NaOH, pyridine content	0
108 kg. of a mixture of meta- and paracresol, clearly soluble in aqueous solution of NaOH, pyridine content	0
29 kg. of xylenols, clearly soluble in aqueous solution of NaOH, pyridine content	0.03

Example 2

1000 kg. of a lignite tar oil having a boiling range of from 150 to 230° C. and containing 200 kg. of phenols are introduced per hour into a ten-stage extractor, in which they are treated with 3500 kg. of a 20% potassium phenolate solution and with 500 kg. of a light oil having a boiling range of from 75 to 145° C. and a content of aromatics of 30%. The oil is introduced into the fourth stage, whereas the potassium phenolate solution is introduced into the first stage and the light oil into the last stage. Into the ninth stage of the extractor are introduced 50 kg. of phenols having been recovered from the waste water of the low-temperature carbonizing installation by extraction. Besides the neutral oil the light oil also absorbs 9.2 kg. of phenols, it is then distilled off from these higher boiling constituents and recirculated into the tenth stage of the extractor. From the potassium phenolate solution supersaturated with phenols in a ratio of 0.55 mole phenol per 1 mole of potassium phenolate 50 kg. light oil are distilled off, whereby also water is distilled. The distillate is conducted into the eighth stage of the extractor. To the potassium phenolate solution free from benzine and supersaturated with phenols are added 0.2 kg. of a 30% hydrogen peroxide per hour, whereafter it is extracted with 650 kg. of methyl isobutyl ether. After the methyl isobutyl ether is distilled off, 330 kg. of refined phenols remain, from which are obtained after their fractionation products which are stable to light and free from neutral oils and which have the following composition:

	Percent
138 kg. of phenols, clearly soluble in aqueous NaOH, pyridine content	0
26 kg. of orthocresol, clearly soluble in aqueous NaOH, pyridine content	0
98 kg. of a mixture from meta- and paracresols, clearly soluble in aqueous NaOH, pyridine content	0.1
68 kg. of xylenols, clearly soluble in aqueous NaOH, pyridine content	0.3

Example 3

Coal-tar oil in the boiling range of from 150–230° C. having been separated in the known manner from naphthalene and having a phenol content of 26% by weight is introduced approximately in the median zone of an extraction tower at a ratio of 100 kg./h. At the lower end of the tower a mixture of benzene and toluene (boiling range of from 80 to 110° C.) is introduced at a ratio of 30 kg./h. An aqueous alkali phenolate solution containing 45% by weight of potassium phenolate trickles down from above at a ratio of 200 kg. per hour towards the mixture of oil, toluene and benzene. A temperature of 130° C. is maintained in the tower and care is taken for a proper heat utilization by heat exchange in a manner known per se between the supplied and the discharged products. During the extraction a pressure of about 2 to 2.5 atmospheres absolute arises of itself. The mixture of neutral oil, benzene and toluene discharged from the tower still contains 0.8 kg. of phenols, substantially xylenols, and is separated from the latter ones in a distilling column for the purpose of recovering the benzene and toluene. The hot potassium phenolate solution supersaturated with phenols being discharged from the bottom of the extraction tower has absorbed 25.2 kg. of phenols. The potas-

sium phenolate solution supersaturated with phenols is expanded and heated in a distillation column for removing the dissolved benzene and toluene. The distillate is added to the phenolate solution recirculated into the extraction tower.

The purified potassium phenolate solution supersaturated with phenols is subsequently treated with air at 90° C. in a packed colum and thereafter extracted with isopropyl ether at a ratio of 60 kg./h. After the isopropyl ether is distilled off from the extract, there remain 24.7 kg. of a phenol mixture, from which after its fractionation the following fractions free from neutral oil are obtained, which contain less than 0.05% by weight of nitrogen bases and remain water-white even after several weeks:

	Kg.
Carboxylic acid	8.1
Orthocresol	2.5
A mixture of meta- and paracresol	10.8

Example 4

Coal-tar oil in the boiling range of from 170 to 220° C. is treated at a ratio of 100 kg. per hour at 100° C. in countercurrent with 240 kg. of a 28% aqueous potassium phenolate solution in a horizontal, ten-stage extractor consisting of mixers and separators. The phenolate lye is thereby introduced into the first and tar-oil into the sixth stage. Xylene is introduced into the tenth stage of the extractor at a ratio of 45 kg./h. The treated oil still contains 0.5 kg. of phenols. The phenol-containing alkali phenolate solution has a ratio of supersaturation of 0.39 mole phenols per mole of potassium phenolate. The xylene is distilled off from the neutral oil and recirculated into the extractor. The dissolved xylene is distilled from the alkali phenolate solution supersaturated with phenols. The distillate which also contains water and phenols is recirculated into the eighth stage of the extractor. The supersaturated alkali phenolate solution is subsequently treated with air free of CO_2 in a packed column. The further treatment corresponds to that indicated in Example 3. The following final products are obtained:

7.8 kg. of phenols 2.5 kg. of orthocresols 10.8 kg. of a mixture from meta- and paracresols 2.5 kg. of xylenols 0.7 kg. of residue	Clearly soluble in aqueous NaOH, water-white, stable to light, pyridine content 0.

What is claimed is:

1. In a process for recovery of phenols from a mixture thereof with neutral oils by extraction of the mixture with an aqueous alkali phenolate solution of about 10–50% concentration to dissolve phenols in the aqueous alkali phenolate solution and thereby extract phenols from the neutral oil and form an aqueous alkali phenolate solution containing free phenol, contacting the aqueous alkali phenolate solution containing free phenol with a low boiling hydrocarbon solvent to separate therefrom by extraction neutral oil retained thereby and provide neutral oil-free, aqueous alkali phenolate solution containing free phenol, contacting the neutral oil-free aqueous alkali phenolate solution containing free phenol with an oxygen-containing organic solvent to separate therefrom by extraction phenols by dissolving of phenols in the oxygen-containing solvent and provide aqueous alkali phenolate solution depleted in phenol, recycling the aqueous alkali phenolate solution depleted in phenol to extraction of the mixture of phenols and neutral oils, and separating phenols from the solution thereof in the oxygen-containing organic solvent, the improvement which comprises simultaneously extracting the said mixture with the aqueous alkali phenolate solution and the low boiling hydrocarbon solvent, said low boiling hydrocarbon solvent consisting essentially of hydrocarbons in the boiling range of about 75–145° C. and containing at least 25% of aromatic hydrocarbons, distilling the neutral oil-free, aqueous alkali phenolate solution containing free phenol to separate therefrom low boiling hydrocarbon retained thereby, and prior to the contacting of the neutral oil-free, aqueous alkali phenolate solution containing free phenol with an oxygen-containing organic solvent, contacting the neutral oil-free, aqueous alkali phenolate solution containing free phenol with an oxidizing agent for oxidation of amino phenols and diphenols to high boiling quinoidal compounds.

2. Process according to claim 1, wherein said simultaneous contacting is carried out by multi-stage contacting including a first stage, and last stage, the alkali phenolate solution being introduced into the first stage and passed to the last stage, said low boiling hydrocarbon solvent being introduced into the last stage and passed through the stages countercurrent to the alkali phenolate solution, the mixture of phenols with neutral oils being introduced intermediate said first and last stages and passed through the stages countercurrent to the alkali phenolate solution, said neutral oil-free, aqueous alkali phenolate solution containing free phenol being withdrawn from the last stage, withdrawing the low boiling hydrocarbon solvent containing neutral oil and basic ingredients dissolved from the said mixture from the first stage, the separated low boiling hydrocarbon solvent resulting from the distillation of the neutral oil-free aqueous alkali phenolate solution containing free phenol being introduced into the multi-stage contacting intermediate said last stage and the point of introduction of said mixture of phenol and neutral oils.

3. Process according to claim 1, wherein the aromatic hydrocarbon in said low boiling mixture of hydrocarbons is mononuclear aromatic hydrocarbon selected from the groups consisting of benzene, toluene, xylene, and mixtures thereof.

4. Process according to claim 3, said aromatic hydrocarbon being benzene.

5. Process according to claim 3, said aromatic hydrocarbon being toluene.

6. Process according to claim 3, said aromatic hydrocarbon being xylene.

7. Process according to claim 1, the oxidizing agent being air.

8. Process according to claim 1, the oxidizing agent being hydrogen peroxide.

9. Process according to claim 1, the oxidizing agent being sodium peroxide (Na_2O_2).

10. Process according to claim 7, the air being at about 80° C.

11. Process according to claim 1, wherein the aqueous alkali phenolate solution containing free phenol contains less than about 0.6 mols of phenols per mol of alkali phenolate.

12. Process according to claim 1, wherein the aqueous alkali phenolate solution containing free phenol contains about 0.3–0.6 mols of phenols per mol of alkali phenolate.

13. In a process for recovery of phenols from a mixture thereof with neutral oils by extraction of the mixture with an aqueous alkali phenolate solution of about 10–50% concentration to dissolve phenols in the aqueous alkali penolate solution and thereby extract phenols from the neutral oil and form an aqueous alkali phenolate solution containing free phenol, contacting the aqueous alkali phenolate solution containing free phenol with a low boiling hydrocarbon solvent to separate therefrom by extraction neutral oil retained thereby and provide neutral oil-free, aqueous alkali phenolate solution containing free phenol, contacting the neutral oil-free, aqueous alkali phenolate solution containing free phenol with an oxygen-containing organic solvent to separate therefrom by extraction phenols by dissolving the phenols in the oxygen-containing solvent and provide aqueous alkali phenolate solution depleted in phenol, recycling the aqueous alkali phenolate solution depleted in phenol to extraction of the mixture of phenols and neutral oils, and separat-

ing phenols from the solution thereof in the oxygen-containing organic solvent, the improvement which comprises using as the low boiling hydrocarbon solvent such a solvent consisting essentially of hydrocarbons in the boiling range of about 75–145° C. and containing at least 25% of aromatic hydrocarbon, distilling the neutral oil-free, aqueous alkali phenolate solution containing free phenol to separate therefrom low boiling hydrocarbons retained thereby, and prior to said contacting of the neutral oil-free, aqueous alkali phenolate solution containing free phenol with an oxygen-containing organic solvent, contacting the neutral oil-free, aqueous alkali phenolate solution containing free phenol with an oxidizing agent for oxidation of amino phenols and diphenols to high boiling quinoidal compounds.

14. Process according to claim **13**, wherein the aqueous alkali phenolate solution containing free phenol contains less than about 0.6 mols of phenols per mol of alkali phenolate.

15. The method of claim **13**, wherein extraction with

the alkali phenolate solution and extraction with the low boiling hydrocarbon solvent is performed simultaneously and the aqueous alkali phenolate solution containing free phenol resulting from the simultaneous contacting is contacted with the low boiling hydrocarbon solvent for countercurrent extraction of the aqueous alkali phenolate solution containing free phenol with the low boiling hydrocarbon solvent, and the low boiling hydrocarbon solvent after such countercurrent contacting is utilized for the simultaneous contacting.

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