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PROCESS FOR THE SEPARATION OF MIXTURES OF ALKYL PHENOLS THROUGH SELECTIVE ALKYLATION

Daniel B. Luten, Jr., and Aldo De Benedictis, Berkeley, Calif., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

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10 Claims. (Cl. 260—621)

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This invention relates to a process for separating a distillable mixture of differently substituted alkyl phenols which have approximately the same boiling temperatures. More particularly, it comprises a method in which the mixture is alkylated with a limited amount of an alkylating compound to form higher substituted phenols which may readily be separated by fractional distillation.

Alkyl phenols such as cresols, xylenols, trialkylphenols, etc., are commonly obtained from coal tar or petroleum. Certain alkyl phenol fractions obtainable from either of the above sources often contain alkyl phenols which boil at approximately the same temperature and which sometimes are as high as 90% or more of meta and para substituted isomeric alkyl phenols. Since these alkyl phenols are not separable by conventional fractional distillation methods, these mixtures are usually utilized without further treatment.

Generally, it is a purpose of this invention to separate and recover in a simple, direct and economical manner pure substituted alkyl phenols from mixtures containing them. Specifically, it is a purpose to provide a method of utilizing mixtures of meta. ortho and para substituted alkyl phenols as a source of para substituted alkyl phenols in the production of higher alkylated para substituted alkyl phenols. It is still another purpose to provide such higher alkylated para substituted alkyl phenols substantially free from meta substituted alkyl phenols, the former being useful as oxidation inhibitors.

The term "alkyl phenols" herein signifies those hydroxy aromatic compounds, particularly monohydroxy benzenes, having at least one hydrogen of the aromatic nucleus replaced by an alkyl radical.

Mixtures of such alkyl phenols having approximately the same boiling temperature, that is within less than 5° C. of each other and preferably less than 3° C., must contain at least one alkyl phenol which has at least one vacant position in said aromatic nucleus that is ortho or para to the hydroxyl group and is not ortho to an alkyl radical. Examples of such mixtures of some alkyl phenols which are included within the scope of the above-defined group and which occur in phenol fractions obtained commercially are listed in tables presented hereinafter.

When phenols are alkylated, the alkyl substitution proceeds predominantly in "available" ortho and para positions to the hydroxyl radical, the rate of substitution in the meta position being vastly lower. At the ortho or para positions to the hydroxyl radical the rates of substitution are approximately identical, provided there is no hindrance due to an alkyl radical ortho to the position sought to be alkylated. Thus, for example, when alkylating a 2-methyl phenol the 4- and 6-positions alkylate at approximately the same rates. However, when alkylating a 3-alkyl phenol, the 2-position will alkylate at a materially lower rate than the 6-position, because of the difference in influence of the alkyl radical on these two positions. By the term "available positions," as used herein, is meant unsubstituted positions which are ortho or para to the hydroxyl radical and are not ortho to an alkyl radical.

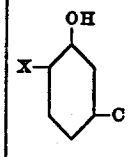
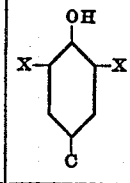
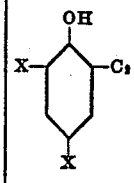
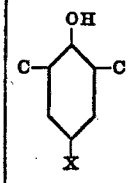
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In carrying out the process of this invention, the mixture is alkylated with a limited amount (defined later) of an alkylating compound under conventional alkylating conditions to alkylate only the "available," i. e. more reactive, positions in the aromatic nucleus. When thus alkylated, alkyl radicals are introduced predominantly in those positions which are ortho or para to the hydroxyl radical and which are not at the same time ortho to an alkyl radical. By limiting the amount of an alkylating compound, only the easily substituted ortho and para vacant positions are alkylated to produce new substituted alkyl phenols having substantially different boiling temperatures, that is more than about 3° C. apart. For example, in the particular case of a mixture of meta and para cresols which have approximately the same boiling temperature, a reaction product of the para isomer is obtained having one more alkyl group than is contained in the corresponding product of the meta isomer. Because of this difference in the number of alkyl radicals the respective products boil at widely different temperatures. The resulting mixture is then fractionally distilled, yielding an overhead fraction of the meta-substituted compound and leaving as the distillation residue predominantly the para-substituted reaction product with but a small proportion of the meta-substituted compounds, if any.

To further illustrate the above, several groups of alkyl phenols having boiling ranges within about 3° C. of each other are listed in separate tables below. In the structure of each alkyl phe-

nol presented in each table, X marks the vacant ortho and para positions that are not ortho to an alkyl radical and which are "available" and therefore may be readily alkylated. The figures shown below each alkyl phenol represent its approximate boiling temperature in degrees centigrade, both before and after alkylation, wherein the added alkyl group X comprises C_1, C_2 and in some cases tertiary C_4 alkyl radicals. In the first column opposite the temperatures is shown the number of carbon atoms contained in each added alkyl radical.

Table I

	Group A, boiling between 201° C. and 203° C.			
	m-Cresol	p-cresol	2-ethyl phenol	2,6-dimethyl phenol
				
X=0	202.8	201.1	202.5-203	201
X=C_1	211.5	221	228	221
X=C_2	219.8-220.8	229-230	244-246	228-230
X=C_4	240	[1] 264 (267)	[1] 274	[1] 251

[1] Estimated boiling temperatures.

A mixture of all the alkyl phenols in group A may be separated by methylation or ethylation into three separate fractions consisting of (*a*) meta-cresol, (*b*) 2-ethyl phenol, and (*c*) para cresol and 2,6-dimethyl phenol. However, a mixture of all the alkyl phenols in group A may be separated into each of its four constituents by butylation. A mixture of meta- and para-cresol and 2-ethyl phenol may be separated by alkylation into its three components, as can a mixture of meta-cresol, 2-ethyl phenol and 2,6-dimethyl phenol. In such cases alkylation with a larger alkyl radical further increases the boiling temperatures of these compounds, as may be seen from Table I above.

The next three groups (groups B, C and D) of alkyl phenols presented overlap to a certain degree in that it is not always possible by fractional distillation alone to separate those of group B from group C, or of group C from group D. However, it is always possible to separate those of group B from those of group D. Accordingly, groups B and C will be taken together and groups C and D will be taken together.

Table II

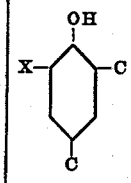
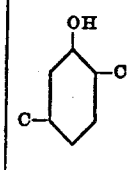
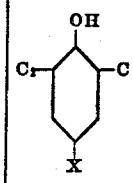
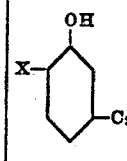
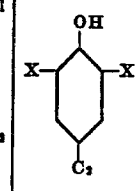
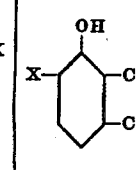
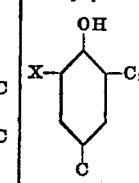
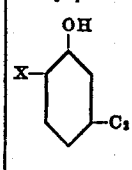
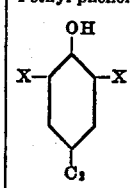
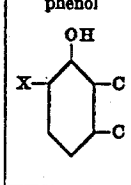
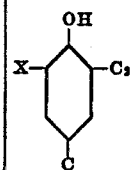
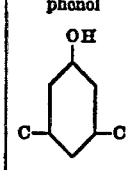
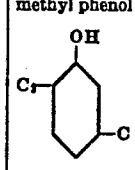
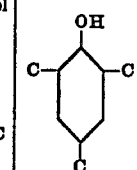
	Group B, boiling at 211-214° C.			Group C, boiling at 216-217.1° C.			
	2,4-dimethyl phenol	2,5-dimethyl phenol	2-methyl-6-ethyl phenol	3-ethyl phenol	4-ethyl phenol	2,3-dimethyl phenol	2-ethyl-4-methyl phenol
							
X=0	211.5	211.5	212-214	216-216.5	216.5-217	217.1	217
X=C_1	221	----------	228	226	228-230	226.7	228
X=C_2	228	----------	234-236	[1] 229	244-246	[1] 232	229-230

Table III

	Group C, boiling at 216-217.1° C.				Group D, boiling at 219.5-221° C.		
	3-ethyl phenol	4-ethyl phenol	2,3-dimethyl phenol	2-ethyl-4-methyl phenol	3,5-dimethyl phenol	2-ethyl-5-methyl phenol	2,4,6-trimethyl phenol
							
X=0	216-216.5	216.5-217	217.1	217	219.5	219.8-220.8	221
X=C_1	226	228-230	226.7	228		No available position	
X=C_2	[1] 229	244-246	[1] 232	229-230			

[1] Estimated boiling temperature.

The alkyl phenols in group D do not contain any available positions and therefore are only separable from those alkyl phenols in group C which may be readily alkylated. This also applies to 2,5-dimethyl phenol in group B with respect to the other alkyl phenols in group B and those in group C.

Tables II and III show that those alkyl phenols which have the same number of "available" positions in the same relation to the hydroxyl radical are as a rule not separable from each other by alkylation, but are separable only from other alkyl phenols having "different available positions," i. e. whose available positions differ in number and/or their relation to the hydroxyl radical. By way of illustration, the particular alkyl phenols in Table II which upon alkylation do not change substantially in boiling temperatures with respect to each other are: 2,4-dimethyl phenol, 3-ethyl-phenol, 2,3-dimethyl phenol and 2-ethyl-4-methyl phenol. This means that these alkyl phenols may be separated from the other alkyl phenols in groups B, C and D, but they are very difficulty separable from each other by alkylation followed by fractional distillation.

Of the alkyl phenols in Table V only three (3-methyl-4-ethyl, 3-ethyl-4-methyl and 2-3-4-trimethyl) contain "available" positions which may be readily alkylated. As a result these alkyl phenols may be separated from the others in group F. However, since these available positions are the same and not "different," the alkylated compounds cannot be separated from each other by distillation.

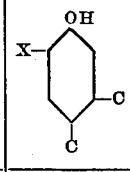
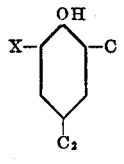
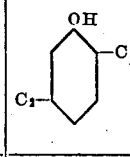
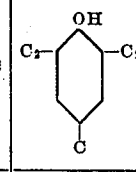
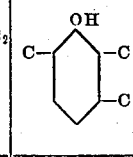
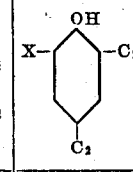
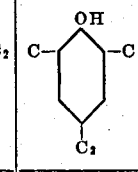
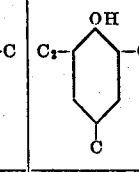
A mixture of alkyl phenols which may be separated by the process of this invention may consist of any two or more alkyl phenols from any one group, provided at least one alkyl phenol has an available position which is different from the available position of at least one other alkyl phenol in the mixture.

The number of carbon atoms in the different alkyl phenols belonging to one group is not always the same. Differences in the position of the alkyl radicals relative to the hydroxyl radical or each other may have more effect on the boiling temperatures than small differences in the number of carbon atoms.

As previously stated, in certain instances alkylation with one particular alkylating radical, say a methyl radical, may not produce a sufficient difference in the boiling temperatures of the several products to permit easy separation by fractional distillation. This difficulty may be overcome by introducing an alkylating radical of a greater number of carbon atoms such as an ethyl or still higher radical, for example butyl or higher. A greater difference in boiling temperatures will result to make possible a separation of the resulting alkyl phenols by simple fractional distillation.

Alkylation may be carried out by using as alkylating compounds olefins such as ethylene,

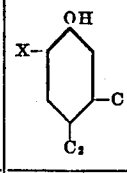
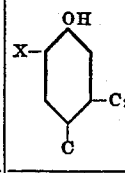
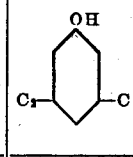
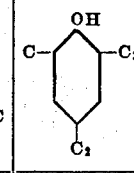
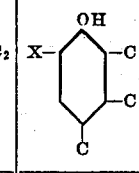
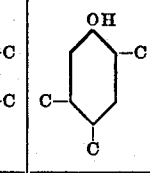
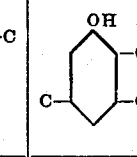
Table IV

	Group E, boiling between 225° C. and 230° C.							
	3,4-dimethyl phenol 	2-methyl-4-ethyl phenol 	2-methyl-5-ethyl phenol 	2,6-diethyl-4-methyl phenol 	2,3,6-trimethyl phenol 	2,4-diethyl phenol 	2,6-dimethyl-4-ethyl phenol 	2,4-dimethyl-6-ethyl phenol 
X=0	225	225. 5–226	226	229–230	226. 7	228–230	228–230	228
X=C_1	232	228–230				234–236		
X=C_2	[1] 238	234–236				244–246		

[1] Estimated boiling temperature.

Of the phenols in Table IV 3,4-dimethyl phenol, 2-methyl-4-ethyl phenol and 2-4-diethyl phenol have "available" positions which may be readily alkylated. These three alkyl phenols may therefore be separated from the other alkyl phenols in group E. As will be noted, the three mentioned alkyl phenols of this group have the same available positions and therefore should not be separated from each other according to the rule laid down before. As a matter of fact, 3,4-dimethyl phenol and 2-methyl-4-ethyl phenol are not separable in this manner. 2,4-diethyl phenol, however, is an exception and can be separated.

Table V

	Group F, boiling between 232 and 237° C.						
	3-methyl-4-ethyl phenol 	3-ethyl-4-methyl phenol 	3-methyl-5-ethyl phenol 	2,4-diethyl-6-methyl phenol 	2,3,4-trimethyl phenol 	2,4,5-trimethyl phenol 	2,3,5-trimethyl phenol 
X=0	234–235	235	233	234–236	235–237	232	235. 5
X=C_1	245	242–244			248+		
X=C_2	247–249	[1] 247–249			250–252		

[1] Estimated boiling temperature.

propylene, butylene, isobutylene, amylenes, diisobutylene, etc.; alkyl chlorides such as methyl chloride, ethyl chloride, normal propyl and isopropyl chloride, primary, secondary or tertiary butyl chlorides, amyl chlorides, etc.; alcohols such as methyl alcohol, ethyl alcohol, isopropyl alcohol, butyl alcohols, amyl alcohols, n-hexyl alcohol, secondary hexyl alcohol, tertiary hexyl alcohol, cyclohexanol, etc.; ethers such as diethyl ether, di-isopropyl ether, ethyl butyl ethers, etc. However, in no event should the alkylating compound have so many carbon atoms that it produces an alkylated product which is not distillable.

Catalysts or condensing agents useful in alkylating phenolic compounds are the inorganic poly-oxy acids such as sulfuric acid, sulfonic acids, phosphoric acids, P_2O_5, etc.; Friedel-Crafts catalysts such as zinc chloride acid zinc sulfate, aluminum chloride, tin tetrachloride, antimony trichloride, ferric chloride, boron trichloride, boron fluoride, hydrogen fluoride, etc.; complex compounds of Friedel-Crafts catalysts such as halides of aluminum, boron, iron, tin, antimony and tungsten with inactive halide salts as NaCl, $HgCl_2$, AgCl, etc., or with organic polar liquids such as nitrobenzene, acetone, acetophenone, benzophenone, benzoyl chloride, diethyl sulfone, ethyl phenyl sulfone, diphenyl sulfone, di-isopropyl sulfate, ethyl benzol sulfonic acid ester, etc.; acidic clays, silica gel, etc., and combinations of the above. Those familiar with the art know the proper catalysts to use with each of the alkylating compounds mentioned above.

If desired, the reaction may be carried out in dilution of inert solvents for the alkyl phenols such as low boiling paraffins free of reactive tertiary atoms, carbon disulfide, nitrobenzene, etc.

Temperatures suitable for our alkylations may vary with the catalysts but usually are between about 0° C. and 100° C. and the quantities of catalyst may vary from very small amounts to those equalling or slightly exceeding the amount of alkyl phenols present.

The reaction time should be sufficient to permit substantially all the available positions to be alkylated, but should not be prolonged unnecessarily so that rearrangement of the alkyl radicals on the aromatic ring will take place.

The amount of alkylating compound used is computed by multiplying the mol quantity of each alkyl phenol in the mixture with its number of available positions. Thus:

(Mols of alklating agent) $=\Sigma$(mols of each alkyl phenol) $\times$ (its available positions)

For example, in the case of a mixture of three mols of metal-cresol and one mol of 2-ethyl phenol it would require five mols of alkylating agent to fill the available positions of these two compounds, meta-cresol having one and 2-ethyl phenol two available positions. The number of such available positions for one alkyl phenol in a mixture may be either 0, 1 or 2, but at least one alkyl phenol must have an available position of not less than one.

A slight excess, that is up to about 10% and preferably about 7%, of the alkylating compound over the required amount for alkylating all available positions in any one mixture is permissible since that excess quantity causes only a negligible amount of alkylation in the positions of lesser reactivity while at the same time permitting a substantially complete alkylation of available positions of higher reactivity.

The alkylating compound may be added to the mixture of alkyl phenols all at once; or it may be added slowly as it is absorbed; or as in the case of alkylation with a gas it may be bubbled through until the required amount has been absorbed. For example, when alkylating with isobutylene the required amount may be liquefied and added all at once; or the same amount may be bubbled slowly through the mixture at a rate which permits substantially complete absorption or at a faster rate and recycled until all absorbed; or a larger amount may be bubbled rapidly through the mixture until the difference between the intake and exhaust gas equals the amount required to be absorbed. However, in any case, the amount absorbed must be limited by the above stated amount, regardless of how the alkylating agent is added to the mixture.

After completed reaction and prior to the distillation of the reaction product, the catalyst may have to be removed. Thus, when acids are used as condensing agents it is usually necessary to neutralize the mixture by washing it with dilute caustic alkali or soda ash solution. Other catalysts may be washed out with warm water or be eliminated by other conventional means.

Example I

A xylenol fraction boiling at 211° C. and containing approximately 315 gms. (17.5%) of 2,5-dimethyl phenol and 1485 gms. of 2,4-dimethyl phenol was divided into three equal portions. To each portion was added 350 gms. of tertiary butyl chloride, 80 gms. of ferric chloride and 1500 cc. of carbon disulfide. The mixtures were refluxed for 8 hours. The carbon disulfide was removed under vacuum. The high boiling residue was dissolved in benzene and the resulting solution was washed with water to remove the ferric chloride. The benzene was distilled off under vacuum, and thereafter a high boiling distillate was taken overhead which was refractionated at atmospheric pressure to distill unreacted 2,5-dimethyl phenol and to recover 2,4-dimethyl-6-tertiary butyl phenol as the bottom product. The amount of unreacted 2,5-dimethyl phenol recovered from the unreacted xylenols was 85% of the amount contained in the original mixture.

Example II

A portion of 207 grams of a xylenol fraction having an A. S. T. M. distillation as follows: 5% at 210° C., 50% at 211° C. and 95% at 211.5° C., which contained 65% of 2,4-dimethyl phenol, 25% of 2,5-dimethyl phenol, and 10% of unidentified alkyl phenols was butylated by contacting with vaporized butane-butylene fraction from a cracking unit, containing about 17% isobutylene, in the presence of 1% of concentrated sulfuric acid until an amount of isobutylene equivalent to 90% of the 2,4-dimethyl phenol and unidentified alkyl phenols had been absorbed. The resulting product was neutralized, washed and fractionally distilled to separate butylated from unbutylated alkyl phenols. The unreacted material (77.3 grams) contained 52% 2,5-dimethyl phenol (40.2 grams=79% of the charged 2,5-dimethyl phenol) and 48% (37.1 grams) of the unidentified alkyl phenols including some 2,4-dimethyl phenol.

Example III

To a commercial coal tar mixture of 30 parts of para cresol and 70 parts of meta cresol in a vessel were added 1 part of 96% sulfuric acid as the catalyst and 68 parts of liquid isobutylene. The resulting mixture was then maintained at a

temperature of 90° C. for 12 minutes. At the end of this time substantially all of the isobutylene had been absorbed in the cresol mixture. The resulting mixture was then neutralized with 9 parts of 10% sodium hydroxide solution. The neutralized mixture was then flash vacuum distilled to separate water salts from the alkyl phenols. The latter were then fractionally distilled at atmospheric pressure to yield 3 fractions, shown in the table below.

Fraction		Meta Cresol		Para Cresol	
Composition	Parts of Original Mixture	Parts of Original Mixture	Per Cent of Fraction	Parts of Original Mixture	Per Cent of Fraction
Unalkylated cresols	9.2	6.2	67	3	33
Monobutylated cresols	73	60	82	13	18
Dibutylated cresols	17.8	3.8	21	14	79
Total Original Mixture	100	70	----------	30	----------

Many of the alkylated para-substituted alkyl phenols obtained by the reaction of this process, such as the trimethyl phenols, 2,4-dimethyl-6-ethyl phenol, 2,4-dimethyl-6-tertiary butyl phenol, 2,4-diethyl-6-tertiary butyl phenol, 2-ethyl-4-methyl-6-tertiary butyl phenol, etc., are useful as oxidation inhibitors when incorporated in cracked gasoline and other petroleum products. In contrast, most meta alkyl phenols have little if any anti-oxidant value and if present in active anti-oxidant mixtures, their role is normally little more than that of an inert diluent.

This application is a continuation-in-part of our co-pending application Serial No. 386,372, filed April 1, 1941.

We claim as our invention:

1. The process of producing a 2,4-dimethyl-6-alkyl substituted phenol of high anti-oxidant power from a mixture of 2,4- and 2,5-dimethyl phenols, comprising alkylating the mixture with an alkylating compound in an amount approximately equal to one mol of alkylating compound per mol of 2,4-dimethyl phenol contained in the mixture, and fractionally distilling the reaction product to produce a residue comprising predominantly the 2,4-dimethyl-6-alkyl phenol and being substantially free from 2,5-dimethyl phenols.

2. The process of separating 2,5-dimethyl phenol from a mixture of 2,5- and 2,4-dimethyl phenols comprising alkylating the mixture with an olefin alkylating compound in an amount not more than 10% more than one mol of alkylating compound per mol of 2,4-dimethyl phenol contained in said mixture, and fractionally distilling the reaction product to produce an overhead fraction containing the unreacted 2,5-dimethyl phenol and a residue comprising predominantly 2,4,6-trialkyl phenol.

3. The process of separating 2,5-dimethyl phenol from a mixture of 2,5- and 2,4-dimethyl phenols comprising: contacting said mixture under alkylating conditions with an amount of an alkylating compound and thereby effecting alkylation of said mixture, and stopping said alkylation before not more than about 90% of said amount of alkylating compound has thus reacted and within the minimum period of time required for a molar amount of said alkylating compound not more than 10% more than the number of mols of 2,4-dimethyl phenol contained in said mixture to thus react under said alkylating conditions; and fractionally distilling the reaction product to produce an overhead fraction containing the unreacted 2,5-dimethyl phenol and a residue comprising predominantly 2,4-dimethyl 6-alkyl phenol.

4. The process of claim 3 wherein the alkylating catalyst is sulfuric acid.

5. The process of claim 3 wherein said alkylating catalyst is an acid catalyst and said spent catalyst is separated from said reaction mixture by washing and neutralizing with dilute aqueous alkali solution.

6. The process of separating meta cresol from a mixture of meta and para cresols comprising: contacting the mixture under alkylating conditions with an amount of an alkylating compound and thereby effecting alkylation of said mixture, and stopping said alkylation before not more than about 90% of said amount of alkylating compound has thus reacted and within the minimum period of time required for an amount approximately equal to 2 mols per mol of para cresol plus one mol per mol of meta cresol of said alkylating compound to thus react under such alkylating conditions; and fractionally distilling the reaction product to produce an overhead fraction containing the resulting mono-alkylated derivative of the meta cresol and a residue comprising predominantly the resulting di-alkylated derivative of said para cresol.

7. The process of separating 2,5-dialkyl phenol from a mixture of 2,5- and 2,4-dialkyl phenols having approximately the same boiling temperatures, which comprises: contacting the mixture under alkylating conditions with an amount of an olefin alkylating compound and thereby effecting alkylation of said mixture, and stopping said alkylation before not more than about 90% of said amount of said olefin alkylating compound has thus reacted and within the minimum period of time required for an amount not more than about 10% more than one mol of alkylating compound per mol of 2,4-dialkyl phenol contained in said mixture to thus react under said alkylating conditions, said alkylating compound having a sufficient number of carbon atoms to produce as the reaction product a second more highly alkylated mixture which contains at least two alkylated phenols boiling at substantially different temperatures, and thereby producing such a second more highly alkylated mixture; and fractionally distilling the reaction product to produce an overhead fraction containing unreacted 2,5-dialkyl phenol and a residue comprising predominantly 2,4,6-trialkyl phenol.

8. The process of separating 2,5-dialkyl phenol from a mixture of 2,5- and 2,4-dialkyl phenols having approximately the same boiling temperatures, which comprises: contacting the mixture under alkylating conditions with an amount of an alkylating compound and thereby effecting alkylation of said mixture, and stopping said alkylation before not more than about 90% of said amount of said alkylating compound has thus reacted and within the minimum period of time required for an amount not more than about 10% more than one mol of alkylating compound per mol of 2,4-dialkyl phenol contained in said mixture to thus react under said alkylating conditions, said alkylating compound having a sufficient number of carbon atoms to produce as the reaction product a second more highly alkylated mixture which contains at least two alkylated phenols boiling at substantially different temperatures, and thereby producing such a second more highly alkylated mixture; and frac-

tionally distilling the reaction product to produce an overhead fraction containing unreacted 2,5-dialkyl phenol and a residue comprising predominantly 2,4,6-trialkyl phenol.

9. The process of claim 8 wherein the alkyl groups of the 2,5- and 2,4-dialkyl phenols are limited to alkyl groups of one and two carbon atoms per group and the alkylating compound is butyl chloride.

10. The process of separating a dialkyl phenol having the general formula $R_1R_2C_6H_3OH$, wherein R_1 and R_2 are alkyl groups the positions of which on the aromatic nucleus ($=C_6H_3-$) are such that there is no non-substituted position of the aromatic nucleus thereof which is ortho or para to the hydroxyl group and is not ortho to at least one of the R_1 and R_2 groups, from a mixture of said dialkyl phenol $R_1R_2C_6H_3OH$ and a different dialkyl phenol having the general formula $R_3R_4C_6H_3OH$, wherein R_3 and R_4 are alkyl groups the positions of which on the aromatic nucleus ($=C_6H_3-$) are such that there is one non-substituted position of the aromatic nucleus thereof which is ortho or para to the hydroxyl group and is not ortho to either of the alky groups R_3 and R_4, said dialkyl phenols having approximately the same boiling temperatures, which process comprises: contacting the mixture under alkylating conditions with an amount of an alkylating compound and thereby effecting alkylation of said mixture, and stopping said alkylation before

not more than about 90% of said amount of said alkylating compound has thus reacted and within the minimum period of time required for an amount not more than about 10% more than one mole of alkylating compound per mol of said different dialkyl phenol $R_3R_4C_6H_3OH$ contained in said mixture to thus react under said alkylating conditions, said alkylating compound having a sufficient number of carbon atoms to produce as the reaction product a second more highly alkylated mixture which contains at least two alkylated phenols boiling at substantially different temperatures, and thereby producing such a second more highly alkylated mixture; and fractionally distilling the reaction product to produce an overhead fraction containing unreacted dialkyl phenol $R_1R_2C_6H_3OH$ and a residue comprising predominantly an alkylated product of said dialkyl phenol $R_3R_4C_6H_3OH$.

DANIEL B. LUTEN, JR.
ALDO DE BENEDICTIS.

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