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MANUFACTURE OF PHENOLS.

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The presence of phenol in the air-oxidation products of benzene obtained by means of palladium-hydrogen sponge was first reported in 1879 by Hoppe-Seyler (Ber. 12, 1552). Radziszewski (Ann. 203, 305 (1880)) and also Nencki (J. f. prakt. Chem. (2) 23, 96 (1881)) demonstrated that inorganic bases activated the oxygen molecule to such an extent that aromatic hydrocarbons can be made to yield traces of phenolic compounds by air oxidation. Cross, Bevan and Heiberg (Ber. 33, 2015 (1900)) were able to oxidize appreciable quantities of benzene by means of hydrogen peroxide in the presence of ferrous sulfate at a temperature of 45° C., but the reaction product, consisting chiefly of pyrocatechol, contains still other compounds in addition to a small quantity of phenol.

I have now discovered that the presence of certain metallic oxides in a hot aerated benzene-caustic soda emulsion constitutes an admirable agency for mono-hydroxylization of this benzene without the appearance of undesirable polyhydric phenols and the tarry products usually obtained in these direct oxidation processes. Accordingly, even though the portion of the benzene that is oxidized to phenol may not be large, the benzene remains as pure benzene and when withdrawn from the system, together with the phenate, may be easily separated from the latter and then used over again without intervening steps for its purification.

To the accomplishment of my improved method of direct oxidation of benzene for the manufacture of phenol I accordingly employ the steps hereinafter fully described and particularly pointed out in the claims, the following description setting forth but one of the various ways in which the principle of the invention may be used.

It may be stated first that the production of a monohydric phenol from benzene is apparently dependent upon the concentration of alkali as well as upon the selection of the metallic oxide or oxides employed as the catalytic agent. It is also desirable that the operation be carried on at a relatively high temperature and under a correspondingly high pressure in order to avoid too prolonged heating. A caustic soda solution of from 20 to 25 per cent concentration has been found to serve satisfactorily in the process. Caustic potash of course works somewhat better while the hydroxides of alkaline earth metals do not prove so efficient, although the reaction will occur where they are used. The last remark also applies to the carbonates of the alkali earth metals which serve only to fair advantage. As the catalytic agent certain oxides of the fifth and sixth groups of the periodic system have proved to be most effective, viz, the oxides of vanadium, molybdenum, tungsten, and uranium. As at present advised, the oxides of uranium, there being several such oxides, apparently give the best results. As an illustration of the practical procedure in carrying out my improved process, I give the following example:—

An autoclave is one-third filled with a 20 per cent. solution of caustic soda containing a small amount of an oxide of uranium, with or without varying small portions of the oxides of vanadium, molybdenum or tungsten. An equal volume of benzene is then added and the contents of the autoclave heated quickly to a temperature in excess of 300° C., and preferably ranging from 320° to 400° C. and under a correspondingly high pressure, i. e., under a pressure greater than the vapor tension of the reacting substances, such pressure for the temperature range in question being approximately 3,000 pounds per square inch. After heating under these conditions for approximately one hour, the clear mixture is discharged from the autoclave and the benzene which has not been acted upon is removed by simple distillation. It is then ready for use over again in the next operation. The residual aqueous liquor which contains the hydrolytic oxidation product of the reaction, e. g. sodium phenate in the particular case in hand, is thereupon acidified for the liberation of phenol and the latter removed by distillation. The salt layer remaining may be discarded or worked over for the recovery of the oxides of the rare earth metals used in the process.

It will be understood that the space left over in the autoclave after introducing the ingredients named above will be occupied by atmospheric air (or equivalent oxygen containing gas), to which the reaction mixture is exposed while the autoclave is being heated.

Other modes of applying the principle of my invention may be employed instead of the one explained, change being made as re-

gards the method herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

I therefore particularly point out and distinctly claim as my invention:—

1. In a method of hydrolyzing a benzene hydrocarbon to form a uni-valent phenol, the step which consists in heating a mixture of such hydrocarbon and caustic alkali solution in the presence of an oxide of a metal of Groups V and VI of the periodic system at a temperature of from approximately 300° to 400° C. and a pressure greater than the vapor tension of the reacting substances at such temperature.

2. In a method of hydrolyzing a benzene hydrocarbon to form a uni-valent phenol, the step which consists in heating a mixture of such hydrocarbon and caustic alkali solution in the presence of an oxide of uranium at a temperature of from approximately 300° to 400° C. and a pressure greater than the vapor tension of the reacting substances at such temperature.

3. In a method of hydrolyzing benzene to form a uni-valent phenol, the step which consists in heating an aerated emulsion of the benzene and caustic soda solution to a temperature of from approximately 300° to 400° C. and under a corresponding high pressure in the presence of an oxide of a metal of Groups V and VI of the periodic system.

4. In a method of hydrolyzing benzene to form a uni-valent phenol, the step which consists in heating an aerated emulsion of the benzene and caustic soda solution to a temperature of from approximately 300° to 400° C. and under a corresponding high pressure in the presence of an oxide of uranium.

Signed by me this 4th day of January, 1924.

WILLIAM J. HALE.