UNITED STATES PATENT OFFICE.

JOHN M. WEISS, OF NEW YORK, N. Y., AND CHARLES R. DOWNS, OF CLIFFSIDE, NEW JERSEY, ASSIGNORS TO THE BARRETT COMPANY, A CORPORATION OF NEW JERSEY.

PRODUCTION OF QUINONE.

1,318,631. Specification of Letters Patent. Patented Oct. 14, 1919.

No Drawing. Application filed May 27, 1918. Serial No. 236,899.

To all whom it may concern:

Be it known that we, (1) JOHN M. WEISS and (2) CHARLES R. DOWNS, citizens of the United States, residing at (1) 210 West 110th street, and (2) Cliffside, in the counties of (1) New York and (2) Bergen and States of (1) New York and (2) New Jersey, have invented certain new and useful Improvements in the Production of Quinone, of which the following is a specification.

This invention relates to the selective oxidation of hydrocarbons of the benzene series or their derivatives, and has particular references to the production of quinone from benzene by the partial oxidation of the latter.

It is well known that naphthalene or amino-naphthol or other di-substitution products of naphthalene can be converted into naphtho-quinone by oxidation of the same. It is also known that anthraquinone can be obtained by the direct oxidation of anthracene, and that quinone can be obtained by oxidizing hydroquinone and some other derivatives of benzene in which the substituting groups occupy the para position relatively to each other.

Prior to our invention, however, it has been considered impossible to oxidize benzene to produce quinone by subjecting mixtures of benzene and oxygen in the vapor phase to the action of a catalyzer. It has formerly been customary, in order to produce quinone from benzene, to first replace the corresponding hydrogen atoms by substitution and then to oxidize the derivatives, or to oxidize the benzene in the liquid phase by means of an electric current.

This present invention relates to a modification of our prior process set forth in application, Serial No. 210,554, filed January 5, 1918, in that we have found that we can influence the degree of oxidation of the benzene thereby obtaining benzoquinone and maleic acid in varying proportions, or a mixture of quinone and other products such as maleic acid and formaldehyde.

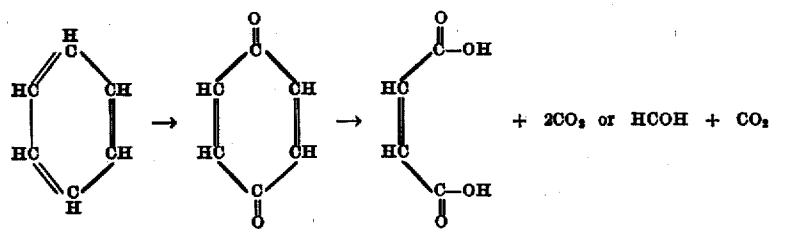
Our invention may be carried out with a variety of compounds which contain a benzene ring having two CH groups in the para position, but our process will be more particularly described with reference to benzene (benzol C_6H_6) and the production of quinone therefrom.

A mixture of benzene and air, for example, is passed through a heated space in which is contained a suitable catalyzer, such as vanadium, vanadium oxid, or other compounds containing vanadium, at such a rate, and under such conditions of temperature and pressure that there will occur a partial oxidation of benzene short of complete combustion, and even short of conversion into maleic acid or compounds of the straight chain or alipathic series as set forth in our prior application above referred to. While we have thus far obtained the most satisfactory results with vanadium oxid as the catalyzer, it is to be understood that the invention is not restricted to the use of vanadium or its compounds, as we have succeeded in carrying out the invention and have secured satisfactory results with a large number of other substances as catalyzers, for instance, such as molybdenum, tungsten, gold, ruthenium, cobalt and oxids of copper, manganese, cobalt, lead, chromium, antimony, cadmium and thorium.

As a specific example of carrying out our invention we may pass a mixture of oxygen and benzene, preferably in the form of a vapor or spray, through a tube containing pumice impregnated with vanadium oxid, and heated between about 300° C. and 700° C. The proporations of benzene and oxygen may vary widely and the oxygen may be pure oxygen, or oxygen in air, or the oxygen may be mixed with diluent gases such as nitrogen or other neutral gases which may have a blanketing effect on the oxidation as will be more fully indicated below. A certain proportion of benzene will pass through unchanged. This benzene may, of course, be recovered and passed through again with another quantity of oxygen for further partial oxidation. We have found that when the speed at which the mixture is passed through the heated space containing the catalyzer is increased, a correspondingly large amount of quinone is produced within certain limits although a considerable portion of the benzene may be more highly oxidized to maleic acid. The process may be carried out throughout a wide range of pressure varying from a partial vacuum to a pressure far above atmospheric.

While we do not wish to confine ourselves to any theory as to what chemical reactions

take place, we believe, from the results which we have obtained, that the direct oxidation of benzene to maleic acid passes through an intermediate step as indicated in the following:



If this theory be correct, it is evident that by controlling the extent of the oxidation the amount of the quinone may be increased. This may be done in various ways, such, for example, as by passing the mixture of benzene and oxygen through more rapidly as already stated, or by blanketing the oxygen with diluent gases, or by regulating the fineness of the pumice, or by regulating the temperature, or by varying the dimensions of the heated space through which the benzene and oxygen pass, etc.

We have found in practice that ordinarily after the mixture has passed through the treating chamber and is condensed, there is found in the condensate some excess benzene, maleic acid, quinone, water, and other by-products. The maleic acid can be removed from the condensate in any convenient manner such as permitting it to crystallize or shaking the solution with water. The quinone may also be removed by any of the well known or convenient methods. For example, after the maleic acid has been removed the benzene solution may be concentrated by distillation to a small volume when the quinone will crystallize out in a substantially pure state and can be recovered and used for various purposes. Or it may be reduced to hydroquinone which is so widely used in photography as a "developer".

By varying the conditions under which this process is operated when using vanadium oxid as the catalyzer, various proportions of quinone to maleic acid may be obtained. If a larger amount of quinone is produced than is desired, or commercial conditions warrant, the excess benzene solution of the condensate containing the quinone, after the maleic acid has been removed, may be again passed through the treating chamber so that the quinone is probably further oxidized into maleic acid and some of the benzene is partially oxidized to an equal amount of quinone. We have found that quinone is not formed in constantly increasing amounts when the condensed benzene and quinone from which maleic acid has been extracted is returned to the process without the extraction of quinone. Under fixed conditions for carrying out the process there seems to be a substantially fixed proportion of quinone to maleic acid in the condensate, which proportion does not seem to be materially altered by introducing some quinone with the benzene.

What we claim is:

1. The herein described process of treating benzene which comprises subjecting it in the vapor phase to an oxygen containing gas at such a temperature and in the presence of such a catalyzer that benzoquinone is produced, and recovering benzoquinone from the products of reaction.

2. The herein described process of treating benzene which comprises subjecting it in the vapor phase to an oxygen containing gas at such a temperature and in the presence of metallic oxid as a catalyzer so that benzoquinone is produced, and recovering benzoquinone from the products of reaction.

3. The herein described process of treating benzene which comprises subjecting it in the vapor phase to an oxygen containing gas at such a temperature and in the presence of vanadium oxid as a catalyzer so that benzoquinone is produced, and recovering benzoquinone from the products of reaction.

4. The herein described process of treating benzene which comprises subjecting it in the vapor phase to an oxygen containing gas at a temperature between 300° C. and 700° C. and in the presence of such a catalyzer that benzoquinone is produced, and recovering benzoquinone from the products of reaction.

5. The herein described process of treating benzene which comprises subjecting it in the vapor phase to an oxygen containing gas at a temperature between 300° C. and 700° C. and in the presence of metallic oxid as a catalyzer so that benzoquinone is produced, and recovering benzoquinone from the products of reaction.

6. The herein described process of treating benzene which comprises subjecting it in the vapor phase to an oxygen containing gas at a temperature between 300° C. and 700° C. and in the presence of vanadium oxid as a catalyzer so that benzoquinone is produced, and recovering benzoquinone from the products of reaction.

7. The herein described process which comprises oxidizing benzene in the vapor phase in the presence of such a catalyzer and at such a temperature that quinone and maleic acid are produced and recovering quinone and maleic acid from the products of reaction.

8. The herein described process which comprises oxidizing benzene in the vapor phase in the presence of vanadium oxid as a catalyzer and at such a temperature that quinone and maleic acid are produced, and recovering quinone and maleic acid from the products of reaction.

9. The process of producing quinone and maleic acid which comprises the steps of partially oxidizing benzene in the presence of vanadium oxid as a catalyzer at a temperature of about 300° C. to 700° C. condensing the resulting products, extracting the maleic acid from the condensate, concentrating the residue and removing the quinone therefrom.

In testimony whereof we affix our signatures.

JOHN M. WEISS.
CHARLES R. DOWNS.