UNITED STATES PATENT OFFICE.

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CATALYTIC OXIDATION OF NAPHTHALENE.

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To all whom it may concern:

Be it known that I, CHARLES R. DOWNS, a citizen of the United States, residing at Cliffside, in the county of Bergen and State of New Jersey, have invented certain new and useful Improvements in Catalytic Oxidation of Naphthalene, of which the following is a specification.

This invention relates to the catalytic oxidation of napthalene and to the production of products of partial oxidation therefrom. It comprises a partial or selective oxidation of naphthalene by means of an oxygen-containing gas, either alone or mixed with diluents in the presence of aluminium oxid as a catalyzer to form phthalic acid anhydrid, benzoic acid and naphthaquinone, or one or more of these products. The term "phthalic acid anhydrid." is intended to include both the acid and the anhydrid. Products other than those enumerated may also be formed in small amounts during the reaction. The invention is based upon the discovery that by subjecting naphthalene to oxidation in the presence of aluminium oxid as a catalyzer and at an appropriate temperature, a selective or partial oxidation of the naphthalene takes place with the formation of an oxidation product or oxidation products, short of complete combustion. It has been found that under proper conditions of operation, the naphthalene may be changed to products that are more valuable without effecting the complete combustion of a very large proportion of the material treated. The invention may be practised by subjecting the naphthalene in the vapor phase mixed with air or with oxygen, either alone or admixed with other diluent gases, or with certain oxygen containing gases, to a suitable temperature in the presence of aluminium oxid as a catalyzer. Diluent gases, such as carbon dioxid, nitrogen, or steam, etc., may be used with the reaction mixture, if desired, to aid in controlling the reaction.

By suitably regulating the conditions, such as temperature, pressure, and presence of diluents, etc., the degree of oxidation can be controlled whereby the naphthalene is oxidized in a particular manner to produce valuable oxidation products short of what is commonly known as complete combustion.

The invention will be explained in connection with the following example, which is given for illustrative purposes. It is not intended to limit the procedure to the details given as the process can be varied throughout wide limits without departing from the spirit or scope of the invention.

The mixture of naphthalene and air in the vapor phase may be passed through tubes having aluminium oxid therein, while the aluminium oxid is maintained at a temperature between 350° C. and 700° C. with the result that the products of partial oxidation are produced. Instead of introducing oxygen as oxygen of the air, oxygen gas may be used either alone or diluted with steam or other inert gas; the proportion of oxygen to naphthalene may be varied; the aluminium oxid may be deposited on crushed pumice or other suitable powdered granulated or fibrous material, which has no destructive action on the desired products, and acts merely as a catalyst carrier or mechanical distributer; the rate at which the mixture is passed through the tubes may be regulated to suit the needs; the tubes may be varied in length or diameter or confined spaces other than tubes may be used in which to place the catalyzer. It is essential that naphthalene in the vapor phase shall come into contact with the aluminium oxid as a catalyzer in the presence of oxygen for the proper reaction to take place. The introduction of a diluent gas is a convenient way to assist in regulation of the reaction. It has been found that the pressure may be varied throughout quite wide ranges, say slightly below atmospheric up to considerably above atmospheric, with satisfactory results.

As a further specific example, it may be mentioned that when 100 parts of naphthalene is passed together with air in the proportion of one part of naphthalene to 16 parts of air by weight, through a tube containing aluminium oxid maintained at about 450° C., and the time of contact with the aluminium oxid maintained for about 0.4 of a second, there has been produced about 12½ parts by weight of phthalic anhydrid and about 5 parts of naphthaquinone together with small amounts of other by-products. The separation of various prod-

ucts of oxidation may be accomplished by the usual chemical procedures or by fractional condensation or other convenient methods.

Where considerable excess of naphthalene is used over and above that which enters into the reaction, the remaining naphthalene will in part pass through practically unchanged, and the reaction gases will be correspondingly diluted by the excess naphthalene present during the reaction.

The naphthalene used should preferably be of high purity, or if admixed with impurities, it should be substantially free from impurities of such character as would prejudice the desired selective or partial catalytic oxidation.

Various types of apparatus may be used for carrying out the present invention, and for bringing about the necessary contact of the reacting gases of the catalyst and for maintaining the proper temperature for the catalytic reaction. Accordingly, it is not deemed desirable to describe in further detail such types of apparatus.

The various conditions of the reaction are capable of variation. Among these conditions may be mentioned the temperature and pressure at which the reaction is carried out, the time of contact of the reactive gases with the catalyst, the proportion of catalyst to the reacting gases, and the relative proportions of naphthalene and oxygen and of diluent gases such as nitrogen, steam or carbon dioxid. The oxidizing effect can be modified by further diluting the reacting gases as by returning the air, impoverished in oxygen by the reaction, to dilute the reacting gases in the further carrying out of the process or by mixing oxygen with the air to increase the oxygen content thereof, or by using oxygen alone without other diluent or by using oxygen in admixture with other gases than those contained in air, etc.

The time of contact of the reacting gases with the catalyst can be varied by increasing the catalytic mass or by decreasing the speed at which the reacting gases pass through or in contact with the catalyst. These and other variations will correspondingly modify and affect the catalytic oxidation. The various conditions of the reaction speed (or velocity of the gases) ratio of naphthalene to oxygen, proportion of diluent, and temperature are manifestly interdependent, *e. g.*, if a higher catalyst temperature is employed, a faster speed of vapors or a different ratio or different quantity of diluents might be used to secure the desired oxidation which would take place at a lower temperature and a different ratio or speed. Similarly, by lengthening the catalyst layer and thus securing more time of contact for the reaction vapors, a lower catalyst temperature to secure a given reaction might be employed than with a shorter catalyst layer. In a similar way, more or less vigor of oxidation may be secured by changing one or more of the running conditions. As a general rule, the conditions which cause a more rapid oxidation to take place will result in a correspondingly larger proportion of the naphthalene being oxidized to complete combustion. Therefore, it is quite difficult to state definitely the optimum conditions for the best conversion of naphthalene to the desired products, as the governing factors of operation may be so varied that a number of different running conditions would achieve practically the same result. The specific example that has already been given is sufficient to illustrate the invention so that others may practise the process.

The valuable products mentioned are apparently intermediate products of the incomplete oxidation of naphthalene. In the operation of this process under proper conditions, there has been found to be very little complete combustion, thus indicating that practically all of the naphthalene which is oxidized is changed to more valuable products. Any of the naphthalene which passes through the process unchanged may be separated from the other products by sublimation, crystallization, distillation, etc., and may be passed through the reaction zone mixed with oxygen or mixed with a sufficient supply of naphthalene and oxygen, if desired, and more will be oxidized.

I claim:

1. The method of partially oxidizing naphthalene which comprises subjecting it in the vapor phase to the action of an oxygen containing gas in the presence of aluminium oxid as a catalyst.

2. The method of partially oxidizing naphthalene which comprises subjecting it in the vapor phase to the action of an oxygen containing gas in the presence of aluminium oxid as a catalyst, at a temperature between 350° C. and 700° C.

3. The method of partially oxidizing naphthalene which comprises subjecting it in the vapor phase to the action of an oxygen containing gas in the presence of aluminium oxid as a catalyst at a temperature about 450° C.

4. The method of producing phthalic anhydrid and naphthaquinone which comprises subjecting naphthalene in the vapor phase to the action of air in the presence of aluminium oxid as a catalyst at a temperature between 350° C. and 700° C.

5. The method of producing phthalic anhydrid and naphthaquinone which comprises subjecting naphthalene in the vapor phase to the action of an oxygen containing gas in the presence of aluminium oxid as a catalyst, separating the reaction products

from any unchanged naphthalene and returning the naphthalene for similar oxidizing treatment.

6. The method of producing phthalic anhydrid and naphthaquinone which comprises subjecting naphthalene in the vapor phase to the action of an oxygen containing gas in the presence of aluminium oxid as a catalyst at a temperature between 350° C. and 700° C., separating the reaction products from any unchanged naphthalene and returning the naphthalene for similar oxidizing treatment.

In testimony whereof I affix my signature.

CHARLES R. DOWNS.