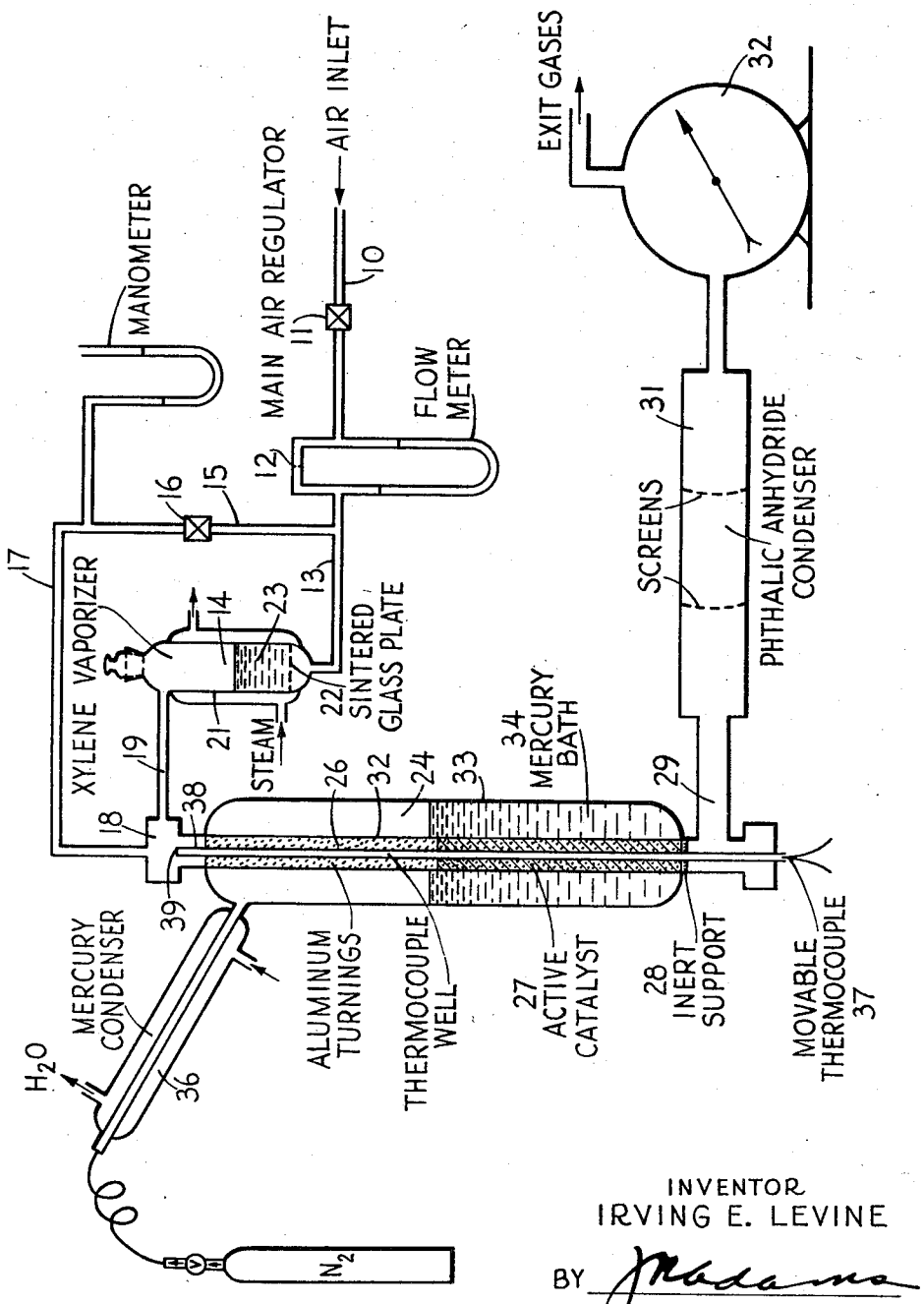
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PRODUCTION OF DICARBOXYLIC ACIDS OR ANHYDRIDES THEREOF

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PRODUCTION OF DICARBOXYLIC ACIDS OR ANHYDRIDES THEREOF

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This invention relates to a process for producing phthalic anhydride or phthalic acid from a mixture of aliphatic substituted benzenes.

More particularly, the invention is directed to a process for producing phthalic anhydride or acid from a mixture of polyalkyl benzenes containing a predominant or major proportion of ortho dialkyl benzenes, but also substantial amounts of meta or para polyalkyl benzenes. The invention provides a process of producing relatively pure phthalic anhydride in good yields from relatively impure ortho di-alkyl benzenes as a xylene mixture containing 5–30% of meta and para xylenes in admixture with ortho xylene.

An object of the invention is to provide a new and improved process for partially oxidizing mixtures of alkyl benzenes and for facilitating separation of the oxidation products so produced to obtain phthalic anhydride or phthalic acid.

Another object of the invention is to produce phthalic anhydride from mixed xylenes containing a major proportion of ortho xylene and to eliminate the meta and para xylenes by selectively rupturing the ring by chemical oxidation.

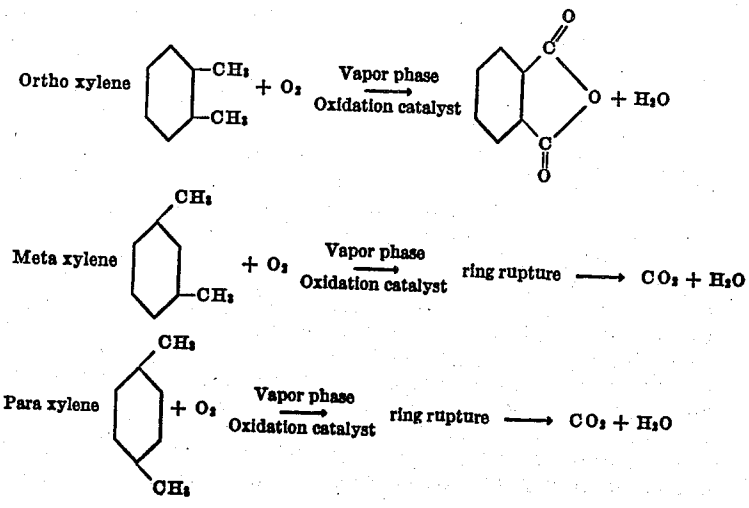
Other objects and advantages of the invention will be apparent from the following disclosure.

The alkyl benzenes from which phthalic anhydride is produced according to the present invention are exemplified by a mixture of ortho, meta and para xylenes containing more than 50%, desirably from about 70% to 95% by weight, and preferably approximately 80 to 90% of ortho xylene. Other mixtures of vaporizable aliphatic

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substituted benzenes may be utilized, provided that the vapors therefrom contain a major proportion of an ortho di-alkyl benzene. For example, mixtures of di-alkyl benzenes in which the alkyl groups may be ethyl, normal propyl or isopropyl, or mixtures of these alkyl benzenes with each other or of methyl, ethyl and propyl substituents, or of any of the foregoing with dimethyl substituted benzenes may be utilized where a content of more than 50%, and preferably 70% to 95% of ortho di-alkyl benzenes is obtained in vapors therefrom. Small amounts of paraffinic or naphthenic hydrocarbons or mono-alkyl benzenes in mixtures such as the foregoing are not precluded.

It has been discovered that phthalic anhydride can be produced from mixtures of alkyl benzenes because such as the foregoing by partially oxidizing the ortho substituted aliphatic benzenes to phthalic anhydride and preferentially removing the non-ortho alkyl benzenes by simultaneously selectively over-oxidizing these constituents at least to the point of ring rupture and preferably substantially to carbon dioxide and water. The partially oxidized ortho alkyl benzenes are then separated from the mixture of combustion products by condensing the phthalic anhydride and separating, in the form of a gas, oxidation products from the other alkyl benzenes. Thus, the present invention, in its preferred embodiment, involves simultaneous oxidation of the three xylenes, as follows:



It will be observed that ortho xylene in the xylene mixture is only partially oxidized according to the present invention, and the reaction is stopped short of ring rupture and substantially at the phthalic anhydride stage. However, in the same reaction zone the meta and para xylenes are selectively over-oxidized at least to the point of ring rupture and preferably to carbon dioxide and water. The meta and para xylenes, which might otherwise yield aromatic oxidation products sufficiently similar to the phthalic anhydride from ortho xylene to make separation and purification extremely difficult, are thus preferentially eliminated from the reaction mixture by over-oxidation and maintaining the combustion products thereof in a gaseous phase. The phthalic anhydride is then easily recovered by selective condensation or other suitable processes.

It is known that ortho xylene may be partially oxidized to yield various reaction products, including phthalic anhydride. However, the selective over-oxidation of meta and para alkyl benzenes to eliminate these components from mixtures with ortho alkyl benzenes while only partially oxidizing the ortho alkyl benzenes to phthalic anhydride is believed new and unobvious. For example, it has been shown that aromatic hydrocarbons with side chains are oxidized from 1,000 to 6,000 times faster than benzene (Catalytic Oxidation of Organic Compounds in Vapor Phase, by Marek and Hahn, page 395); yet by the present invention the aliphatic side chains of the meta and para alkyl benzenes can be substantially completely oxidized and the benzene ring ruptured, while oxidation of the ortho alkyl benzenes is preferentially stopped without breaking the bond between the ortho alkyl carbon atoms and the benzene ring. Further, Burgoyne (Proceedings of the Royal Society, volume A–174, page 379, 1939) concluded that in an oxidation under pressure "the order of increasing reactivity is para, meta, ortho," suggesting that as between these three components the more reactive ortho, if any, would be selectively over-oxidized. Accordingly, the discovery that (even though alkyl benzenes may be more easily oxidized than benzene, and despite the report that ortho alkyl benzenes are more reactive than meta and para alkyl benzenes in oxidation under pressure) the meta and para alkyl benzenes may be selectively over-oxidized to the point of ring rupture, and even to carbon dioxide and water, in the presence of a predominant proportion of ortho alkyl benzene without a corresponding destruction of the ring or of its bond to ortho alkyl carbon atoms directly attached thereto, is believed unobvious.

Briefly described, the process of the invention comprises vaporizing a mixture of aliphatic substituted benzenes of which a major proportion has two aliphatic groups positioned ortho to each other on the benzene ring and a substantial proportion of the hydrocarbon mixture comprises aliphatic benzene hydrocarbons other than ortho aliphatic substituted benzenes, partially oxidizing the ortho-substituted aliphatic benzene vapors to phthalic anhydride, simultaneously selectively over-oxidizing the other aliphatic benzene vapors in the mixture, at least to the point of ring rupture, to produce over-oxidized combustion products readily separable from the phthalic anhydride, and separating phthalic anhydride from the combustion mixture.

The foregoing partial oxidation and selective over-oxidation are carried out in accordance with this invention preferably by mixing the vaporized alkyl benzene vapors with an excess of an oxygen-containing gas, such as air, and contacting the vapor-oxygen mixture at elevated temperatures with a metal oxide which is an oxidation catalyst, such as a vanadium oxide catalyst. The reaction is exothermic and heat is removed by any suitable means to control temperature of the reaction. Catalyst temperature preferably is maintained in the zone of red heat. Such relatively high temperatures, together with a large excess of the oxygen-containing gas, serve to form the phthalic anhydride quickly and to carry the oxidation of the meta and para alkyl benzenes not only to the point of ring rupture, but at least in major part to carbon dioxide and water. Since the selective over-oxidation may be carried only to the point of ring rupture, catalyst temperatures as low as about 800° F. are operable. However, a catalyst temperature in the dark red heat range is desirable and from a dark blood red to a dark cherry red, as indicated in Marks' Mechanical Engineers' Handbook (2nd ed., page 297) is preferred (i. e., 990° F. to 1175° F.). It should be clear that the entire catalyst bed need not be maintained at this high temperature level. Only a relatively short zone, sufficient to insure selective over-oxidation at least to ring rupture and preferably substantially completely to carbon dioxide and water, need be in the dark red heat range (e. g., 1/3–1/6 of the catalyst bed). Likewise, it is to be understood that temperatures referred to above are catalyst temperatures as measured by a thermocouple in the catalyst bed.

A large molar excess of oxidizing gas is utilized in the process. Air is preferred, although mixtures of oxygen or air with nitrogen, carbon dioxide or other inert or non-oxidizing gases may be utilized. Desirably, the molar ratio of air to hydrocarbon should be at least about 50 to 1, and preferably from 50:1 to 150:1. A still higher ratio of air to hydrocarbon (300:1 or more) may be utilized with an adequate system for recovering the product in the resulting more dilute gaseous mixture. In general, corresponding ratios of other oxygen-containing gases are utilized. The oxygen-containing gas should be in an amount sufficient to reduce the concentration of hydrocarbon vapors below the explosive range.

The selective over-oxidation of meta and para alkyl benzenes in the above described process converts these compounds into combustion products which, for the most part at least, are separable with relative ease from the phthalic anhydride contained in the combustion gases. Thus, when a xylene feed stock containing about 85 parts ortho xylene and 15 parts meta and para xylenes in 100 to 110 parts hydrocarbon is utilized and the meta and para xylenes, together with other hydrocarbon impurities, are selectively over-oxidized mainly to carbon dioxide and water, these impurities are eliminated and phthalic anhydride may be easily separated by mere cooling and condensation to yield a product containing no more than about 2% and even less than 1% aromatic impurities. For example, the hydrocarbon combustion mixture may be passed from the oxidation zone to relatively large air cooled chambers where the temperature of the gaseous mixture is reduced to below the phthalic anhydride frost point (i. e., the temperature at which phthalic anhydride condenses as a solid) whereby the phthalic anhydride solidifies as crystals in the cooling chamber. These crystals are collected in the cooling

chambers and separate from the over-oxidized products of meta and para alkyl benzenes, as well as from the other combustion products.

In those operations where the oxidation of aromatic hydrocarbons other than ortho alkyl substituted benzenes is carried to the point of ring rupture but a substantial portion is not completely oxidized to carbon dioxide and water, small amounts of the residues of the ruptured rings, as well as other impurities, may be precipitated in the cooling chambers with the phthalic anhydride, thereby generally decreasing the purity level of the crude condensate. However, even in this type of operation the main impurities are non-aromatic and differ in chemical kind from phthalic anhydride by reason of the selective over-oxidation and ring rupture. Any suitable method may be utilized for further purifying the crude condensate, e. g., fractional crystallization from a solvent, such as mixed xylenes, or fractionation by distillation.

The initial recovery of phthalic anhydride from the combustion gases and separation from the over-oxidation products of meta and para xylenes may be accomplished in various ways, including washing the mixture of gases with a suitable solvent or chemical extractants or by proper selective absorption. However, the best method at present appears to be cooling and condensation as above described. The gaseous mixture is preferably cooled to a point within the range between the phthalic anhydride frost point and the water dew point. The "phthalic anhydride frost point" may be defined as that temperature at which phthalic anhydride first begins to separate out as a solid phase. The water dew point is that temperature at which moisture first begins to condense as a liquid phase. Where there is no objection to the formation of phthalic acid in the condensate, or, if this should be desired (e. g., to increase the ultimate recovery of desired product), the gaseous reaction product may be cooled below the dew point with the consequent precipitation of water and reaction thereof with anhydride to form phthalic acid.

The phthalic anhydride frost point varies with the phthalic anhydride content of the gaseous mixture, which in turn is a function of other process variables, such as air-hydrocarbon ratio, ortho xylene content of the original hydrocarbon mixture, etc. Likewise, the water dew point is a function of such variables, as well as of the humidity of the original oxidizing gas. Determination of these two points (phthalic anhydride frost and water dew points) for any given operating condition is readily determined by those skilled in the art and it is believed unnecessary to here designate specific temperature. However, cooling to temperatures lower than prevailing atmospheric temperatures is usually unwarranted, and an upper temperature limit for the gases leaving the final stage of a cooling and condensing system is at present found to be from about 100 to 150° F.

Various forms of apparatus may be used for carrying out the foregoing process. One which has been found suitable is shown somewhat diagrammatically in the drawing. The apparatus comprises three principal units or sections; namely, an air feed and hydrocarbon vaporization unit which vaporizes the hydrocarbon feed and mixes the vapors with air to form a reaction mixture; a temperature regulated catalyst chamber in which the desired conversion of the foregoing reaction mixture is effected; and a phthalic anhydride condenser for separating the reaction products.

More specifically, air is admitted to the vaporization unit through inlet 10 controlled by a main regulator 11, flows through a calibrated orifice 12 for determining volume of air fed, and is then divided into a primary and a secondary air stream. The primary air stream flows through conduit 13 and vaporizer 14 where the hydrocarbon feed stock is vaporized into the primary air. Secondary air from metered orifice 12 flows by way of conduit 15, secondary air regulator 16, and line 17 to chamber 18 which also receives, by way of conduit 19, the air-hydrocarbon mixture from vaporizer 14. The two air streams are blended and mixed with the hydrocarbon vapors in chamber 18.

As here shown, hydrocarbon vaporizer 14 comprises a steam jacketed liquid hydrocarbon container 21 provided with a sintered glass plate 22 at its lower end serving as a bottom for container 21 partially filled with alkyl benzenes 23. The primary air thus is dispersed into fine bubbles or streams by the sintered glass plate 22 and flows through the liquid phase alkyl benzenes 23, forming the air-hydrocarbon mixture which is finally diluted and mixed with secondary air in chamber 18.

Catalyst chamber 24 is provided with a preheating bed of aluminum turnings 26 further to mix the gases and bring them to desired temperature prior to entering catalyst bed 27 wherein the desired reactions are effected. Any suitable foraminous means 28 for supporting the catalyst bed 27 may be provided at the lower end thereof in the bottom of chamber 24. The gaseous reaction mixture flows from mixing chamber 18 through preheating bed 26 into the catalyst bed and is discharged from the catalyst chamber through conduit 29 to an air cooled condenser 31 where the temperature of the gases is lowered sufficiently to cause phthalic anhydride to precipitate as needle-like crystals. The remaining components of the reaction mixture are discharged from condenser 31 and may be passed through a suitable meter 32.

Catalyst chamber 24, as here illustrated, comprises an inner catalyst tube 32 surrounded by an outer sealed container 33 for a liquid mercury temperature regulating bath 34 which only partially fills the container but preferably is maintained at a level as high as the catalyst bed. This mercury bath serves to remove heat of reaction from the catalyst bed 27 and, in so doing, boils and is vaporized. The rising mercury vapors of partially filled container 33 heat the bed of aluminum turnings 26 and bring the hydrocarbon vapor feed at least up to reaction temperature and usually approximately to the mercury bath temperature. Since the reaction is highly exothermic, excess heat must be removed from the system, and this is here accomplished by providing a condenser 36 for mercury vapors from cooling bath 34. Water, steam or any suitable fluid may be utilized for condensing the mercury vapors and carrying off the excess heat of reaction by indirect heat exchange. The mercury bath also serves as a heat reservoir to regulate temperature by distributing heat throughout the length of the catalyst bed and by maintaining temperature at a desired minimum value.

The boiling point of the mercury, and hence the temperature of the catalyst bed, are here controlled by maintaining the mercury system under an atmosphere of nitrogen at a predetermined pressure. The boiling temperature of the

mercury bath may thus be raised by increasing the nitrogen pressure, and likewise may be lowered by reducing the nitrogen pressure. The temperature of the catalyst bath can thus be measured either directly or determined by the existing pressure in the boiling mercury system. Suitable means for directly measuring the temperature of the beds in the catalyst tube 32 is preferably provided and is here shown as a thermocouple 37 which is slidable longitudinally through a tube 38 sealed at its inner end 39 and passing centrally through catalyst bed 27.

Any suitable means (not shown) for bringing the catalyst chamber up to reaction temperature may be provided. One convenient device comprises electric strip heaters mounted on sealed container 33.

To illustrate in detail the process of this invention and to guide those skilled in the art in the practice thereof, the following illustrative data and examples of processes, which may be carried out in the foregoing apparatus, are submitted.

Example 1

A xylene feed stock having a boiling range of about 288–296° F., a specific gravity of about .8825, containing approximately 85% by volume of ortho xylene and about 15% by volume of mixed meta and para xylenes is passed in vapor phase through a catalyst tube containing vanadium oxide on aluminum granules, at the rate of .12 mols per hour. The xylene vapors are mixed with 4,950 cc. per minute of air (12.4 mols of air per hour) and the hottest portion of the catalyst bed is maintained at about 1000° F. Air-hydrocarbon ratio is thus approximately 103 mols of air per mol of hydrocarbon, and this mixture was passed through about 51 cc. of catalyst having about 48% voids to obtain a contact time of approximately .12 seconds in the catalyst bed (contact time is here based on volume of gas and volume of voids in the catalyst bed). A yield of approximately 94% phthalic anhydride was obtained, and the meta and para xylenes were selectively over-oxidized and removed as gases composed, for the most part, of carbon dioxide and water.

Example 2

Utilizing the same mixed xylene stock with a feed rate of .063 mol per hour and an air rate of 7.0 mols per hour, catalyst temperature was regulated at about 980° F. by a boiling mercury bath at approximately 950° F. Air-hydrocarbon ratio (molecular) was about 111 and contact time about .17 seconds. A yield of approximately 87% phthalic anhydride resulted.

Example 3

An additional run, utilizing a feed stock and process conditions substantially like those of Example 2, except that the hydrocarbon feed rate was .066 mol per hour, yielded 82% phthalic anhydride.

Example 4

With a boiling mercury bath temperature of 950° F., a catalyst hot zone temperature of 1080° F., and a contact time of approximately .07 seconds, an 86% yield of phthalic anhydride was obtained from a mixed xylene feed stock of substantially the same composition as in Examples 1 and 3.

Example 5

Vapors of naphthalene and the foregoing xylene feed stock are mixed (e. g., equal parts), diluted with air and oxidized in vapor phase substantially as disclosed in Example 1. A good yield of phthalic anhydride and selective over-oxidation of meta and para xylenes are obtained.

The yields in the foregoing examples are based on the amount of phthalic anhydride as it is actually condensed from the combustion mixture. Yield is based on the weight of this product and is calculated as per cent of the weight of ortho xylene in the feed.

Despite the fact that the original feed stock in the above example contains about 15% of hydrocarbons which are here regarded as impurities, the phthalic anhydride recovered by the foregoing processes has been found to be relatively low in organic impurities. Most of these impurities are products of ring rupture, and not more than about 1% of aromatic impurities is found in the phthalic anhydride crude condensate, thereby indicating that the meta and para xylenes are substantially entirely over-oxidized at least to the point of ring rupture, while the partial oxidation of the ortho xylene is preferentially stopped at the phthalic anhydride stage to give good yields of this desired product.

It should be observed that maintenance and control of reaction temperature is facilitated by selectively over-oxidizing the meta and para components of the reaction mixture to thereby provide a relatively large positive heat input to the reaction chamber without the necessity of supplying this extra heat at the cost of ortho xylene with resulting loss of phthalic anhydride product. This heat input serves to minimize minor variations in heat formation or heat transfer rates which might otherwise occur, as well as to maintain the hot spot in the relatively high temperature range presently preferred. This extra heat also may be derived in part from other hydrocarbon impurities, such as ethyl benzene or paraffins boiling in the same range as the xylenes. Thus, the feed stock may consist of: 100 parts of xylenes in which o-, m-, and p-xylene are present in the range of proportions previously disclosed, from 1 to 5 parts ethyl benzene and 0 to 5 parts paraffins.

The catalyst used in Example 1 was prepared by evaporating an aqueous paste of chemically pure ammonium meta vanadate on 20 mesh granular aluminum and igniting at 1200° F. to liberate ammonia and form vanadium oxide which fuses in a coherent mass. The fused mass was broken and screened to pass 14 mesh and be retained on a 30 mesh screen. This screened product yielded a catalyst bed with about 48% voids. The catalyst utilized in Examples 2 to 4 was prepared in a similar manner, but the final oxide coating was composed of approximately 60% vanadium oxide, 30% molybdenum oxide and 5% manganese oxide on 20 mesh aluminum. Other metal oxide catalysts for vapor phase oxidation may be utilized within the spirit of this invention, since the catalysts per se are not a part of this invention and various catalysts of this type are well known. Likewise, other catalyst supports may be substituted for the aluminum, for example, silicon carbide, or other inert high melting oxidation resistant granular materials.

Non-porous catalysts are preferred in order that the control of the selective over-oxidation

featured by this invention may be facilitated. By "non-porous catalyst" as here used it is intended to designate those catalysts in which the effective catalyst area is limited essentially to the outer surface portion of the catalyst granule; i. e., a catalyst in which the catalytic action takes place in or on the outer surface region, not in the deeper interior portion of a macroscopic catalyst granule or the like. Porous catalysts, though not precluded, have been found less selective and tend to increase over-oxidation of the ortho xylene together with the meta and para xylenes. To the extent this occurs, one primary advantage of this invention is diminshed.

In this specification and claims the term "over-oxidation," as applied to the oxidation of alkyl substituted aromatic hydrocarbons, is utilized to designate the oxidation of these materials, at least to the point of ring rupture. "Selective over-oxidation" designates an over-oxidation of minor hydrocarbon components which appears not to conform to the law of mass action; that is, meta and para di-alkyl substituted benzenes are selectively over-oxidized when the ratio of mols of the meta and para compounds over-oxidized, to mols of ortho di-alkyl benzene over-oxidized, is greater than the ratio of the molar concentration of meta and para constituents in the vapor to the molar concentration of ortho alkyl benzene therein. Stated mathematically, selective over-oxidation of meta and para xylene occurs when

$$\frac{\text{mol. m- \& p-xylene over-oxidized}}{\text{mol. o-xylene over-oxidized}} > \frac{\text{molar conc. m- \& p-xylene in vapor}}{\text{molar conc. o-xylene in vapor}} < 1$$

As previously noted herein, the invention embraces selective oxidation of mixed alkyl benzenes other than xylenes. Likewise, selective over-oxidation of meta and para xylenes or other alkyl benzenes in admixture with naphthalene vapors, ortho di-alkyl benzenes, and air may be effected as here disclosed. In such a process, the ortho alkyl component should be the major constituent of the alkyl benzenes present and preferably the molar quantity of alkyl benzenes should at least equal that of the naphthalene in the hydrocarbon vapors.

Although this invention has been illustrated with specific embodiments and preferred process conditions have been described, various alterations utilizing the principles thereof will occur to those skilled in the art, and it is to be understood that the invention may be otherwise embodied or practiced within the scope of the appended claims.

I claim:

1. A process of manufacturing a benzene ortho dicarboxylic acid anhydride by oxidation in vapor phase of a mixture of aliphatic substituted benzenes having aliphatic radicals of 1 to 3 carbon atoms, a major proportion of said aliphatic substituted benzenes having two aliphatic groups positioned ortho to each other on the benzene ring and a minor but substantial proportion having meta and para aliphatic substituents, said process comprising the steps of oxidizing the ortho aliphatic substituted benzenes to a benzene ortho dicarboxylic acid anhydride and simultaneously selectively over-oxidizing said meta and para aliphatic substituted benzenes at least to the point of ring rupture by passing said mixture in vapor phase over a vanadium oxide catalyst at a catalyst temperature of from about 990 to about 1175° F., and separating said benzene ortho dicarboxylic acid anhydride from said oxidized gases.

2. A process of producing phthalic anhydride which comprises vaporizing a mixture of xylenes containing a major proportion of ortho xylene and a minor but substantial proportion of alkyl benzenes selected from the group consisting of meta and para xylenes, converting ortho xylene in said vapors to phthalic anhydride by oxidation of the ortho alkyl groups with a vanadium oxide catalyst at a temperature of from about 800° F. to about 1175° F., concurrently rupturing the ring of said meta and para xylenes by selective over-oxidation of their vapors with a vanadium oxide catalyst at a temperature of from about 800° F. to about 1175° F., said concurrent oxidation reactions being effected with a molar excess of air in the ratio of from about 50 to about 150 mols of air per mol of hydrocarbon mixture, separating phthalic anhydride from at least a portion of over-oxidation products of said meta and para xylenes by selective condensation from the gaseous reaction products, and separating said condensed phthalic anhydride from residual over-oxidation products by distillation.

3. A process of producing phthalic anhydride which comprises vaporizing a mixture of aliphatic substituted benzenes having aliphatic radicals of from 1 to 3 carbon atoms, said mixture containing a major proportion of ortho dialkyl benzenes and a minor but substantial proportion of alkyl benzenes selected from the group consisting of meta and para dialkyl benzenes, converting ortho alkyl benzene vapors in said mixture to phthalic anhydride by oxidation of the ortho alkyl groups with a vanadium oxide catalyst at a temperature of from about 800° F. to about 1175° F., concurrently rupturing the ring of said meta and para alkyl benzenes in said vapors by selective over-oxidation with a vanadium oxide catalyst at a temperature of from about 800° F. to about 1175° F., said concurrent oxidation reactions being effected with a molar excess of air in the ratio of from about 50 to about 150 mols of air per mol of hydrocarbon, separating phthalic anhydride from at least a portion of over-oxidation products of said meta and para alkyl benzenes by selective condensation from the gaseous reaction products and separating said condensed phthalic anhydride from residual over-oxidation products by distillation.

4. A process of manufacturing phthalic anhydride from a xylene fraction containing from 70 to 95% by volume of ortho-xylene and from about 5 to 30% by volume meta- and para-xylenes, said process comprising the steps of converting ortho-xylene of said fraction to phthalic anhydride by vapor phase oxidation in a phthalic anhydride forming zone with a vanadium oxide catalyst at phthalic anhydride forming temperatures, converting meta- and para-xylenes of said fraction to combustion products readily separable from the phthalic anhydride by concurrently selectively over-oxidizing said meta- and para-xylene at least to the point of ring rupture by vapor phase oxidation with a vanadium oxide catalyst in said phthalic anhydride forming zone, passing said vapor phase combustion products to a cooling zone, separating said phthalic anhydride from gaseous over-oxidation products of said meta- and para-xylenes by crystallization of phthalic anhydride in said cooling zone, and removing residual ring-rupture impurities condensed with the phthalic anhydride in the cooling zone by

distillation of the crystallized phthalic anhydride.

5. A process as defined in claim 4 in which said xylene fraction contains from about 80 to about 90% by volume of ortho-xylene and from about 20 to about 10% by volume of meta- and para-xylene.

6. A process as defined in claim 1 wherein said mixture of aliphatic substituted benzenes is a xylene fraction.

7. A process as defined in claim 1 wherein said mixture of aliphatic substituted benzenes is a xylene fraction containing from 70 to 95% by volume ortho-xylene and from about 5 to 30% by volume meta- and para-xylenes.

8. A process of manufacturing phthalic anhydride from a mixture of alkyl benzenes containing from about 70 to about 95% by volume of ortho di-alkyl benzene having from 1 to 3 carbon atoms in each alkyl group and from about 30 to about 5% by volume of meta- and para-di-alkyl benzenes having from 1 to 3 carbon atoms in each alkyl group, said process comprising the steps of oxidizing the ortho di-alkyl benzene to phthalic anhydride and concurrently selectively over-oxidizing said meta- and para-di-alkyl benzenes at least to the point of ring rupture by passing said mixture in a vapor phase over a vanadium oxide catalyst at a catalyst temperature of from 800° F. to 1175° F., and separating said phthalic anhydride from said over-oxidized components.

9. A process as defined in claim 8 wherein said mixture of alkyl benzenes is a xylene fraction.

10. A process as defined in claim 8 wherein said vanadium oxide catalyst is non-porous.

11. A process of manufacturing phthalic anhydride from a xylene fraction containing from 70 to 95% by volume of ortho xylene and from about 5 to 30% by volume of meta- and para-xylenes which comprises the steps of converting ortho xylene of said fraction to phthalic anhydride by vapor phase air oxidation in a phthalic anhydride forming zone with a vanadium oxide catalyst at a catalyst temperature of from about 800° F. to about 1175° F. and converting meta- and para-xylenes of said fraction to combustion products readily separable from the phthalic anhydride by concurrently selectively over-oxidizing said meta- and para-xylene at least to the point of ring rupture by vapor phase air oxidation with a vanadium oxide catalyst at a catalyst temperature of from about 800° F. to 1175° F., passing said vapor phase combustion products to a cooling zone, separating said phthalic anhydride from gaseous over-oxidation products of said meta- and para-xylenes by crystallization of phthalic anhydride in said cooling zone, and removing residual ring rupture impurities condensed with the phthalic anhydride in the cooling zone by distillation of the crystallized phthalic anhydride.

12. A process as defined in claim 11 wherein said vanadium oxide catalyst is non-porous.

13. A process as defined in claim 4 wherein the vanadium oxide catalyst has a silicon carbide catalyst support.

14. A process of manufacturing pthalic anhydride by oxidation in vapor phase of a mixture of xylene containing from 70% to 95% by volume of ortho xylene and from 30% to about 5% of meta and para xylenes, said process comprising the steps of oxidizing the ortho xylene to pthalic anhydride and simultaneously selectively over-oxidizing meta and para xylenes at least to the point of ring rupture by passing said mixture in vapor phase over a vanadium oxide catalyst having a silicon carbide catalyst support, at a catalyst temperature of from about 990° F. to about 1175° F., said concurrent oxidation reactions being effected with a molar excess of air in the ratio of from about 50 to about 150 mols of air per mol of xylene mixture, and separating said phthalic anhydride from said oxidized gases.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,142,678	Porter	Jan. 3, 1939
2,114,798	Foster	Apr. 9, 1938

OTHER REFERENCES

Mark and Hahn: Catalytic Oxid. of Org. Compounds in the Vapor Phase, page 395, Chem. Catalog Co.