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2,574,512

PRODUCTION OF DICARBOXYLIC ACIDS
OR ANHYDRIDES THEREOF

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This invention relates to the production of benzene ortho dicarboxylic anhydrides from mixtures of aliphatic-substituted benzenes containing a predominant proportion of aliphatic-substituted benzenes having two aliphatic groups in ortho relationship to each other, and a lesser but substantial amount of meta or para aliphatic-substituted benzenes, by oxidizing ortho aliphatic-substituted benzenes to a benzene ortho dicarboxylic acid anhydride and simultaneously selectively over-oxidizing the meta and para aliphatic-substituted benzenes at least to the point of ring rupture. More particularly, the invention is directed to an improved method of oxidizing such mixtures by which the selectivity of the over-oxidation of the meta and para aliphatic-substituted benzenes is increased with the result that substantially higher yields of benzene ortho dicarboxylic acid anhydrides are obtained.

The oxidation of aliphatic-substituted benzene mixtures of the character above described is set forth in considerable detail by Levine in U. S. Patent No. 2,438,369. Pursuant to the Levine teaching, mixtures of aliphatic-substituted benzenes containing a predominant proportion of ortho-substituted benzenes, and lesser but substantial amounts of meta- and/or para-substitute aliphatic benzenes, are oxidized by contacting the hydrocarbon mixture in vapor phase and an oxygen-containing gas with a vanadium oxide catalyst at temperatures in the range about 800 to 1175° F. The mixture of vaporized hydrocarbons and oxygen-containing gas is characterized by the presence of a substantial stoichiometrical excess of oxygen over the amount required for the complete oxidation of the hydrocarbon mixture. Where, in conformance with the usual practice, air is employed as the oxygen-containing gas, mol ratios of air to hydrocarbon in the range 50-150:1 and higher are employed. This patent particularly describes the oxidation of xylene feed stocks containing 70 to 95% of ortho xylene and 5 to 30% of other hydrocarbons including substantial amounts of meta xylene and/or para xylene to phthalic anhydride. The phthalic anhydride product contains usually less than 2% by weight of aromatic impurities, the meta xylene and para xylene being oxidized largely to carbon dioxide and water vapor under the conditions of the reaction.

The oxidation of the xylene cut recovered from catalytically reformed naphtha is described by Levine and Claussen in U. S. Patent No. 2,474,002. According to this patent, a straight run fraction of a naphthenic crude oil is subjected to

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a hydroforming treatment and a fraction of the hydroformed product boiling in the range about 285 to 300° F. is separated. This fraction contains at least 70% by volume of phthalic anhydride convertible alkyl benzenes and from about 3 to 30% by volume of phthalic anhydride incon-
vertible alkyl benzenes. The fraction is oxidized to produce phthalic anhydride from the phthalic anhydride convertible hydrocarbons. The phthalic anhydride inconvertible hydrocarbons are selectively over-oxidized at least to the point of ring rupture.

Phthalic anhydride has been produced commercially by the methods described by Levine for several years. In the commercial operation a xylene fraction separated from catalytically reformed naphtha and ordinarily containing 85 to 90% of ortho xylene, and lesser amounts of meta xylene and para xylene, is charged to the process. Yields of phthalic anhydride are usually in the range about 78% to 91% by weight based on ortho xylene contained in the feed. While the oxidation is highly selective, the conditions under which destructive oxidation of meta xylene and para xylene contained in the feed is effected cause ring rupture and over-oxidation of a minor but significant proportion of the ortho xylene which it is desired to convert to phthalic anhydride.

It is an object of this invention to increase the selectivity of over-oxidation of meta and para aliphatic-substituted benzenes in a process in which a feed comprising a predominant proportion of ortho aliphatic-substituted benzenes, and minor but substantial proportions of meta and para aliphatic-substituted benzenes, is oxidized by contact with a vanadium catalyst to produce phthalic anhydride. The increased selectivity of the over-oxidation directly results in higher phthalic anhydride yields.

Other and further objects will be apparent from the following detailed description of the invention.

It has now been discovered that mixtures of aliphatic-substituted benzenes containing a predominant proportion of aliphatic-substituted benzenes having two aliphatic groups in ortho relationship to each other, and lesser but substantial amounts of meta or para aliphatic-substituted benzenes, can be oxidized in vapor phase by an oxygen-containing gas in the presence of a vanadium oxide catalyst to effect a sharply selective conversion of the ortho aliphatic-substituted benzenes to phthalic anhydride, and a sharply selective over-oxidation of meta and

para aliphatic-substituted benzenes to at least the point of ring rupture by contacting the oxygen-containing gas and the hydrocarbons in vapor phase with the vanadium oxide catalyst in the presence of a small amount of sulfur dioxide gas. It has also been found that the introduction of substantial amounts of low boiling sulfur compounds such as carbon disulfide, hydrogen sulfide, methyl mercaptan, ethyl mercaptan, propyl mercaptan, butyl mercaptan, amyl mercaptan, lower boiling sulfides and disulfides, low boiling heterocyclic organic sulfur compounds and sulfur trioxide into the mixture of hydrocarbons and oxygen-containing gas prior to the contact of the mixture with the catalyst results in increased yields of phthalic anhydride by reason of increased selectivity in over-oxidation of meta and para aliphatic-substituted benzenes. It may be assumed that these low boiling sulfur compounds are converted in appreciable degree to sulfur dioxide under the conditions of the oxidation and that their beneficial effect is due to the presence of the sulfur dioxide thus produced. In the case of sulfur trioxide some reduction to sulfur dioxide occurs under the conditions of the reaction in the presence of a vanadium oxide catalyst and an equilibrium condition develops in which sulfur trioxide, sulfur dioxide and oxygen co-exist in the reaction mixture. Temporary improvement of the yield of phthalic anhydride is obtained by preconditioning the catalyst by passing a mixture of air and sulfur dioxide, or one or more of the other sulfur compounds named above, over the catalyst at a temperature approximately that of the oxidation reaction for a period of about 15 minutes or longer prior to contacting the hydrocarbon and oxygen-containing gas with the catalyst. The beneficial effect of the pretreatment persists for the most part for only a few hours if introduction of the sulfur compound with the feed is not continued.

Pursuant to the invention, from about 0.01% to about 15% by weight of sulfur dioxide is introduced into the mixture of alkyl aromatic hydrocarbons and air en route to contact with the vanadium oxide catalyst. The amount of sulfur dioxide employed does not appear to be critical, but it should be in excess of about 0.01% by weight based upon the hydrocarbon charge and can only be employed to advantage when a substantial stoichiometric excess of oxygen is present in the mixture of hydrocarbons and oxygen-containing gas. The oxidation is otherwise conducted in the general manner described in the Levine patents, this being true of the feed stocks suitable for oxidation, the hydrocarbon-air ratio, the catalyst, the temperature range except that it is preferred to operate in a temperature range about 950° F. to 1100° F. catalyst temperature, and the methods of recovering phthalic anhydride from the reaction product mixture.

The following examples are illustrative of the practice and advantages of the invention. In each of the examples 1 to 10, inclusive, below, the hydrocarbon feed employed contained 95% by volume of ortho xylene and the remainder consisted of meta xylene, para xylene, ethylbenzene and a small quantity of paraffinic hydrocarbons.

Example 1.—In this example 100 cubic centimeters of catalyst consisting of vanadium pentoxide supported on silicon carbide was packed in a single stainless steel tube. The tube was jacketed with a mercury bath maintained under nitrogen pressure to control the rate of evaporation and, as the result, the temperature of the

bath. The catalyst bed in the tube was 20 inches deep. The reactant mixture consisted of air and the above-described feed in vapor form. The rate of air introduction into the reaction tube was 0.75 cubic feet per minute and the rate at which the hydrocarbon feed was introduced was 0.91 liquid cubic centimeters per minute. The mercury bath was maintained at a temperature of 900° F. and the air hydrocarbon mixture was passed through the catalyst bed for a period of 1 hour. The yield of phthalic anhydride obtained was 88.8% by weight based on the ortho xylene content of the feed.

Example 2.—This example was conducted under the same conditions and with the same catalyst as that described in Example 1. Sulfur dioxide was introduced into the mixture of air and hydrocarbons during a 1 hour run. The sulfur dioxide introduced was equivalent to 4.86% by weight of the xylene fed to the reactor during the run. The phthalic anhydride recovered during this run amounted to 98.2% by weight of the ortho xylene fed.

Example 3.—A run was conducted in which the catalyst, the feed, and the reaction conditions were identical with those employed in Example 1. Sulfur dioxide was introduced into the reactor together with the xylene feed and air in amount such that the sulfur dioxide introduced was equal to 1% by weight of the xylene feed. In a run of 1 hour's duration, the phthalic anhydride recovered amounted to 94.2% by weight of the ortho xylene fed.

Example 4.—The run described in Example 3 was continued for a second period of 1 hour without change in reaction conditions and without variation in the proportion of the materials introduced into the reactor. During the second hour of operation, the phthalic anhydride recovered was equal to 97.0% by weight of the ortho xylene contained in the feed introduced into the reactor.

Example 5.—The feed and operating conditions employed in this run were identical with those employed in Example 1, but fresh catalyst was preconditioned by passing 40 grams of sulfur dioxide and 12 cubic feet of air over the catalyst surrounded by the mercury bath at 900° F. during a period of 15 minutes. After the preconditioning of the catalyst in this manner, a mixture of air and the xylene feed in the amounts and at the rates described in Example 1 were passed over the preconditioned catalyst for a period of 1 hour. The phthalic anhydride recovered during this run was equal to 95.3% by weight of the ortho xylene contained in the feed introduced. In three subsequent 1 hour runs without any sulfur dioxide treatment, yields of phthalic anhydride were 97.0, 95.3, and 95.0% by weight of the ortho xylene contained in the feed introduced.

Example 6.—The experiment described in Example 5 was repeated with the difference that the same catalyst was again preconditioned by passing 7.3 grams of sulfur dioxide and 12 cubic feet of air over the catalyst bed with a mercury bath temperature of 900° F. during a period of 15 minutes. Xylenes and air were then passed over the catalyst at the rates and under the conditions described in Example 1. The phthalic anhydride recovered during 1 hour of operation in this manner with the reconditioned catalyst was 97.3% by weight of the ortho xylene introduced during the run.

Example 7.—The experiment described in Example 1 was repeated using a fresh batch of

catalyst consisting of vanadium pentoxide supported on silicon carbide. The phthalic anhydride recovered during this run was equal to 93.9% by weight of the ortho xylene charged. The data obtained in this run indicated that the stainless steel catalyst tube had been affected by SO₂ treatment during this and earlier runs and that the surface of the steel exerted a selective catalytic effect on the reaction.

Example 8.—The catalyst employed in Example 7 was conditioned by passing 11.2 grams of sulfur dioxide and 15 cubic feet of air through the catalyst bed during a period of 20 minutes at a mercury bath temperature of 900° F. A mixture of air and the xylene feed were then passed through the catalyst bed at the rates and under the conditions described in Example 1 for a period of 5 hours. During the first hour phthalic anhydride recovery was equivalent to 95.1% of the ortho xylene introduced. During the second hour, phthalic anhydride recovery was equivalent to 98.3% by weight of the ortho xylene introduced. During the third hour, phthalic anhydride recovery was equivalent to 100.2% by weight of the ortho xylene introduced. During the fourth hour, phthalic anhydride recovery was equivalent to 102.9% by weight of the ortho xylene introduced. During the fifth hour, phthalic anhydride recovery was equivalent to 102.5% by weight of the ortho xylene introduced.

Example 9.—Air and the xylene feed were passed over a catalyst which had been employed in an earlier run after preconditioning with sulfur dioxide. The rates and conditions were the same as those employed in Example 1. During a 1 hour run, the phthalic anhydride produced was equal to 94.2% by weight of the ortho xylene charged. This catalyst was continued on stream after pretreating by passing 22 grams of hydrogen sulfide and 27 cubic feet of air over the catalyst during a period of 35 minutes. Phthalic anhydride production in a 1 hour run with the catalyst preconditioned by treatment with hydrogen sulfide and air amounted to 94.8% by weight of the ortho xylene charged. During the second hour of operation with the hydrogen sulfide preconditioned catalyst, the phthalic anhydride recovery rose to 95.8% of the ortho xylene charged and during a third hour of operation the phthalic anhydride production rose to 96.3% by weight of the ortho xylene charged. The same catalyst was continued on stream for an additional 1 hour period, during which 1 gram of hydrogen sulfide was introduced into the reaction tube together with the hydrocarbon feed and air during the run. Phthalic anhydride production during the run with added hydrogen sulfide amounted to 98.3% by weight of the ortho xylenes charged.

Example 10.—A fresh batch of vanadium pentoxide on silicon carbide catalyst was charged to the reaction tube. The xylene feed and air were introduced at the rates and under the conditions described in Example 1 for a period of 1 hour, during which the phthalic anhydride production amounted to 95.2% by weight of the ortho xylene charged. This same catalyst was continued on stream for an additional period of 3 hours, during which thiophene was added to the hydrocarbon air mixture in amount equivalent to 5% by weight of the xylenes fed. During the first hour of operation, phthalic anhydride recovery was 96.0% of the ortho xylenes charged, during the second hour of operation it rose to 99.4% of the ortho xylene charged, and during the third hour it

amounted to 99.7% by weight of the ortho xylene charged.

The foregoing examples clearly illustrate the increased yields of phthalic anhydride which are obtained when low boiling sulfur compounds are introduced into a mixture of an oxygen-containing gas and vaporized aliphatic benzenes containing predominantly ortho-substituted aliphatic benzenes. In Examples 1 and 2, the yields of phthalic anhydride obtained with and without the employment of sulfur dioxide are contrasted. The employment of sulfur dioxide produces an incremental yield of phthalic anhydride of more than 9%. In Examples 3 and 4, the efficiency of lesser amounts of sulfur dioxide introducing incremental yields of phthalic anhydride is illustrated. Examples 5 and 6 illustrate the effect of preconditioning the catalyst with sulfur dioxide and air on phthalic anhydride yields. Examples 7 and 8 show contrasting yields where the catalyst is employed with and without preconditioning by treatment with sulfur dioxide and air. Examples 9 and 10 show the effectiveness of hydrogen sulfide and thiophene in promoting phthalic anhydride yields. These compounds are exemplary of the low boiling sulfur compounds other than sulfur dioxide which may be employed for the purpose of increasing phthalic anhydride yields.

The effect of sulfur dioxide and other low boiling sulfur compounds upon phthalic anhydride yields in a process in which a mixture of aliphatic-substituted benzene hydrocarbons, consisting predominantly of ortho aliphatic-substituted benzenes and containing minor but significant amounts of meta- and para-substituted aliphatic benzenes, is oxidized by an oxygen-containing gas in the presence of a vanadium oxide catalyst under conditions adapted to oxidize the ortho-substituted benzenes to phthalic anhydride, and to selectively over-oxidize the meta and para aliphatic-substituted benzenes to at least a point of ring rupture, was extensively explored in a series of bench scale experiments, similar in character to those of the above examples. The results of these experiments suggested that the effect of sulfur dioxide and other low boiling sulfur compounds upon phthalic anhydride yield was sufficiently firm and significant to warrant a commercial scale test. Accordingly, commercial scale tests were conducted in an operating commercial phthalic anhydride plant in which the feed was a mixture of xylenes. In the commercial unit the ortho xylene contained in the feed is oxidized to phthalic anhydride and meta and para xylenes are selectively over-oxidized to produce principally carbon dioxide and water vapor. The commercial plant employs a plurality of oxidation reactors. Each reactor contains a large number of tubes packed with vanadium oxide catalyst. The catalyst tubes are in contact with a flowing molten eutectic mixture of inorganic salts which acts as a heat transfer material to remove the exothermic heat of reaction. The catalyst is a vanadium oxide catalyst supported on a non-porous carrier such as alundum or silicon carbide. The catalysts described in U. S. Patents Nos. 2,438,369, 2,474,001, and 2,474,002 are suitable catalysts for commercial operation.

The feed to the commercial plant consists predominantly of ortho xylene and is subject to minor variations during lone on-stream periods.

During the periods of the test runs reported below, the feed composition was as follows:

	Percent by volume
Ortho xylene -----	88-90
Meta xylene and para xylene -----	2-3
Paraffins and ethylbenzene -----	8-9

Certain of the catalyst tubes in each reactor are provided with thermocouples spaced along the length of the catalyst bed in the tube. The salt temperature is adjusted insofar as possible to prevent the maximum hot spot temperature in the catalyst tubes from rising above 1050° F. Fluctuations in the temperature frequently cannot be controlled by salt circulation alone and it is necessary to cut back on the feed rate in order to cool the catalyst in a particular reactor.

The reactor selected for the first commercial scale test was one in which the catalyst had been in use for a period of eleven months. The first test was conducted employing a feed rate of 31 gallons per hour and an air rate of 5400 pounds per hour. The weight ratio of air to hydrocarbons in the reactant mixture was 24:1. The salt temperature was 905° F. Prior to initiating the introduction of sulfur dioxide into the reactant mixture, the phthalic anhydride yield from the test reactor was 78.2% by weight based on the ortho xylene contained in the feed. Sulfur dioxide was then introduced into the reactant mixture at the rate of 2 pounds per hour. The phthalic anhydride content of the reaction mixture rose during a period of approximately 2 days as the employment of sulfur dioxide was continued, reaching a value of 85.0% by weight based on the ortho xylene content of the feed. The employment of sulfur dioxide was continued at the same rate during a period of 2 weeks and during this period phthalic anhydride production remained approximately constant at 85.0% by weight based on the ortho xylene content of the feed. During the two weeks' run, no adverse effect on the catalyst was noted.

Following the successful run with the old catalyst, it was decided to employ sulfur dioxide in a reactor containing a fresh catalyst charge. The reactor was used for several days charging the xylene feed at the rate of 210 pounds per hour and air at the rate of 5400 pounds per hour. Before the introduction of sulfur dioxide into the reactant mixture was initiated, the yield of phthalic anhydride produced in the reactor was 79.1% by weight based on the ortho xylenes contained in the feed. Sulfur dioxide was introduced into the reactant mixture at the rate of 2 pounds per hour and the phthalic anhydride content of the reaction product mixture rose somewhat more rapidly than was the case with the old catalyst, reaching a level of 90% by weight based on the ortho xylenes contained in the feed at the end of about two days. The test run was continued for a period of four months, during which sulfur dioxide was introduced at the rate of 2 pounds per hour. During the four months' period, the phthalic anhydride content of the reaction product mixture averaged 90.0% by weight based on the ortho xylenes contained in the feed to the reactor. During the run no adverse effect on the catalyst life was noted.

After the second commercial test reported above had been initiated, another reactor in the plant was charged with a fresh batch of catalyst. After it had been on stream for a period of two weeks without the employment of sulfur dioxide, it showed a phthalic anhydride yield of 87.6% by

weight based on ortho xylenes contained in the feed. The introduction of sulfur dioxide to this reactor was then commenced. The sulfur dioxide was introduced at the rate of 2 pounds per hour and its introduction was continued for a period of 3 months. During this period the phthalic anhydride content of the reaction product mixture averaged 94% by weight based on ortho xylene contained in the feed. During this run no adverse effect on the catalyst life was noted. The results of these commercial scale test runs are summarized in the following table:

	Yield Wt. Per Cent Phthalic Anhydride Based on Ortho Xylene Before SO ₂	Yield Wt. Per Cent Phthalic Anhydride Based on Ortho Xylene with 2 Lbs./Hr. of SO ₂	Yield Increase Wt. Per Cent Ortho Xylene Feed	Per Cent Yield Increase
Reactor #8, Old Catalyst, 2 weeks' run.....	78.2	85	6.8	8.0
Reactor #8, Fresh Catalyst, 4 months run.....	79.1	90.0	10.9	11.2
Reactor #4, Fresh Catalyst, 3 months' run.....	87.6	94.0	6.4	6.8

No explanation is available for the discrepancy between the phthalic anhydride yields obtained without sulfur dioxide and reactors 4 and 8, each charged with fresh batches of catalyst. Variations of this magnitude are commonly observed in commercial operation and frequently one or more of a plurality of reactors may show a yield which is significantly higher or lower than the average for the plant for reasons which cannot be explained.

Commercial scale experiments were conducted to determine the effect of varying amounts of sulfur dioxide and the effect of cutting off the flow of sulfur dioxide to a particular reactor. In one reactor the amount of sulfur dioxide charged was varied from 0.5 pound per hour to 7.0 pounds per hour over a fairly extended period. This variation was made after the reactor had been on stream for a period of several months to a charge consisting of about 210 pounds of xylenes per hour, 5400 pounds of air per hour, and 2 pounds of sulfur dioxide per hour. The variation in the amount of sulfur dioxide within the above limits appeared to have no significant effect upon the yield of phthalic anhydride produced in the reactor. After reactor No. 8, reported in the above table, had been on stream for a period of 4 months, receiving 2 pounds per hour of sulfur dioxide, the introduction of sulfur dioxide was discontinued. The phthalic anhydride yield from this reactor fell rapidly during the first 8 hours without sulfur dioxide to a level of about 85% by weight based on ortho xylenes contained in the feed. After the first 10 hours, a much slower decline in yield occurred during a period of three weeks, at the end of which the phthalic anhydride content of the reaction product mixture had fallen to 83% by weight based on ortho xylenes contained in the feed. When the introduction of sulfur dioxide at the rate of 2 pounds per hour was resumed, the phthalic anhydride content of the reaction product rose rapidly and in about 8 hours again reached a value of 90% by weight based on ortho xylenes contained in the feed. It has been observed that the residual effect of

sulfur dioxide is much less on an old catalyst than on a fresh catalyst and that substantially all the improvement in yield attributable to the sulfur dioxide is lost in about 2 hours when the introduction of sulfur dioxide to the old catalyst is discontinued.

When sulfur dioxide or other low boiling sulfur compounds are employed in the manner above described to increase the yield of phthalic anhydride during the oxidation of mixtures of ortho aliphatic-substituted benzenes and other aliphatic-substituted benzenes, caution must be exercised to avoid passing sulfur dioxide over the catalyst in the absence of air. When this is done the catalyst is deactivated and the performance of the reactor which has been subjected to contact with sulfur dioxide in the absence of air becomes very erratic. Several days' operation without sulfur dioxide is usually necessary in order to bring the behavior of the catalyst back to normal.

I claim:

1. In a process for the production of benzene dicarboxylic acid anhydride comprising oxidizing a mixture of aliphatic-substituted benzenes containing a major proportion of aliphatic 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 by contacting said aliphatic benzenes and a stoichiometrically excessive amount of an oxygen-containing gas with a vanadium oxide catalyst at a temperature above about 800° F., the improved method which comprises mixing a substantial amount of a low boiling sulfur compound selected from the group consisting of sulfur dioxide, sulfur trioxide, carbon disulfide, hydrogen sulfide, lower mercaptans, low boiling alkyl sulfides and disulfides, and thiophenes with the vaporized aliphatic-substituted benzenes and oxygen-containing gas prior to their contact with the catalyst, the amount of the sulfur compound calculated as equivalent sulfur dioxide being from about 0.01% to about 15% by weight based on the aliphatic-substituted benzene feed.

2. A process for producing phthalic anhydride which comprises contacting a mixture of a hydrocarbon vapor containing a major proportion of ortho xylene and minor proportions of meta xylene and para xylene, an oxygen-containing gas, and a quantity of a sulfur compound selected from the group consisting of sulfur dioxide, sulfur trioxide, carbon disulfide, hydrogen sulfide, lower mercaptans, low boiling alkyl sulfides and disulfides and thiophenes with a vanadium oxide catalyst at a temperature in the range about 800° F. to 1175° F. to oxidize ortho xylene to phthalic anhydride and concurrently rupture the benzene ring of the meta and para xylenes by selective over-oxidation and separating phthalic anhydride from the reaction product mixture by selective condensation, the quantity of the sulfur compound calculated as equivalent sulfur dioxide being from about 0.01% to about 15% by weight based on the hydrocarbon vapor.

3. The method as defined in claim 2, wherein the sulfur compound is sulfur dioxide.

4. 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 air in the presence of 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 and in the presence of from about 0.01% to 15% by weight based on the hydrocarbon charge of sulfur dioxide, 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.

5. 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 air in the presence of 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 and in the presence of from about 0.01% to 15% by weight based on the hydrocarbon charge of sulfur dioxide, 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.

6. 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, 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 stoichiometric excess of a free-oxygen-containing gas in the presence of a vanadium oxide catalyst at temperatures above 800° F. and in the presence of from about 0.01% to 15% by weight based on the hydrocarbon charge of sulfur dioxide, 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 cool-

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ing zone by distillation of the crystallized phthalic anhydride.

7. 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 in the presence of from about 0.01% to 15% by weight based on the hydrocarbon charge of sulfur dioxide and 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.

8. A process of manufacturing phthalic 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 phthalic 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 sup-

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port, 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 moles of air per mol of xylene mixture and in the presence of from about 0.01% to 15% by weight based on the hydrocarbon charge of sulfur dioxide, and separating said phthalic anhydride from said oxidized gases.

9. In a process of producing phthalic anhydride, the steps which comprise fractionally distilling a catalytically reformed naphtha to separate an overhead fraction boiling in the range about 285 to 300° F., said fraction comprising alkyl benzenes and containing at least about 70% by volume of phthalic anhydride convertible alkyl benzenes, oxidizing said fraction to phthalic anhydride and over-oxidizing phthalic anhydride inconvertible hydrocarbons therein at least to the point of ring rupture by passing said fraction in vapor phase and a free-oxygen-containing gas over a vanadium oxide catalyst at a catalyst temperature of from 800° F. to 1175° F. in the presence of from about 0.01% to 15% by weight based on the hydrocarbon charge of sulfur dioxide and separating phthalic anhydride from the over-oxidized compounds of the reaction product mixture.

10. The method as defined in claim 2, wherein the sulfur compound is a mixture of lower mercaptans.

11. The method as defined in claim 2, wherein the sulfur compound is carbon disulfide.

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REFERENCES CITED

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

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Number	Country	Date
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