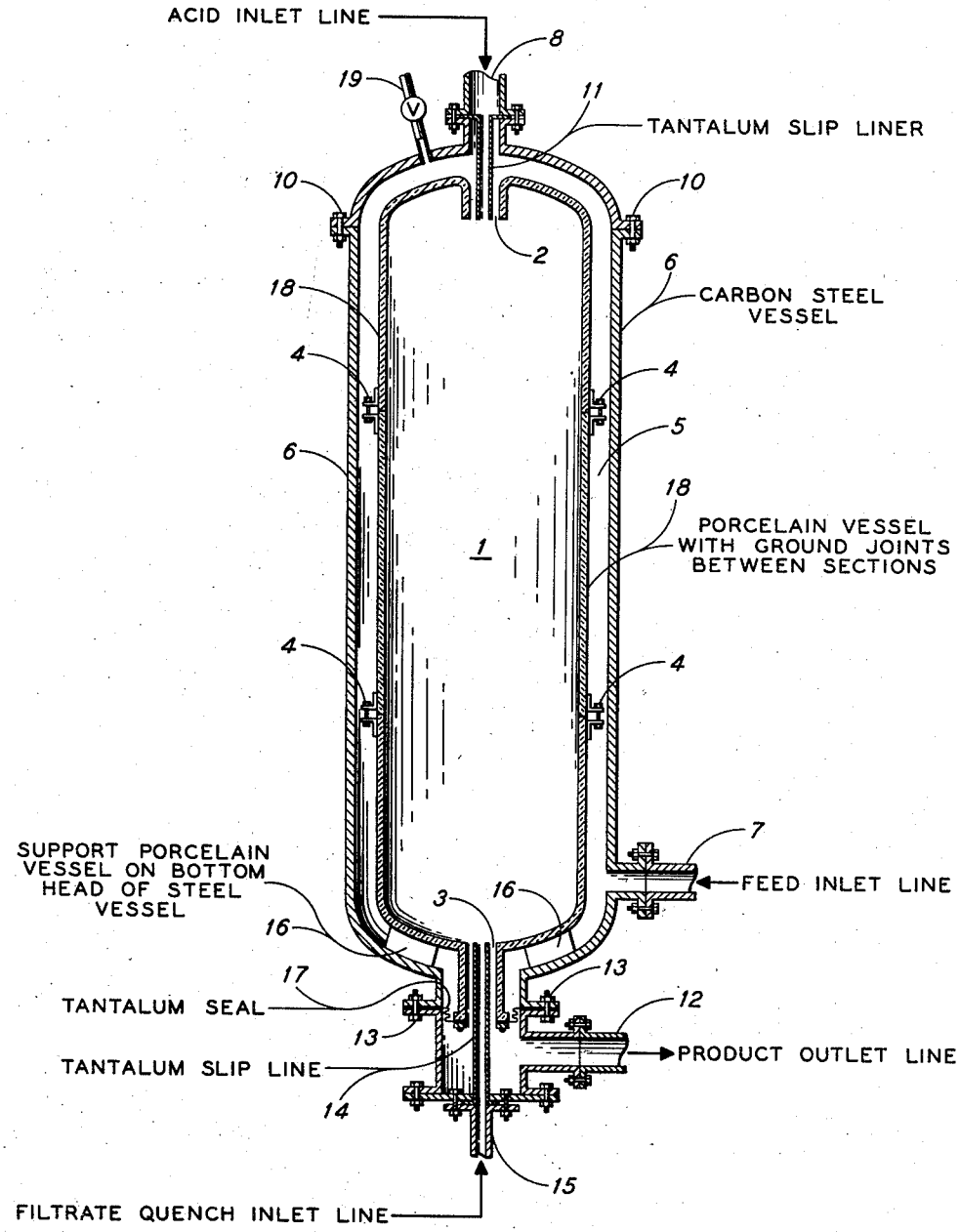
Oct. 23, 1956 L. E. BUSBY 2,768,200

PROCESS FOR CONDUCTING CHEMICAL REACTIONS
INVOLVING CORROSIVE MATERIALS
Filed May 7, 1953



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United States Patent Office 2,768,200 Patented Oct. 23, 1956

2,768,200

PROCESS FOR CONDUCTING CHEMICAL REACTIONS INVOLVING CORROSIVE MATERIALS

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Application May 7, 1953, Serial No. 353,599

3 Claims. (Cl. 260—515)

This invention relates to a process for conducing chemical reactions which involve the handling of highly corrosive reaction mixtures at elevated pressures.

There are a number of chemical reactions which involve the employment of reactants and operating conditions which give rise to extremely corrosive conditions. In many instances the corrosivity of the reaction mixture under reaction conditions is so great that none of the materials available for construction of pressure-resistant reaction vessels has a life expectancy sufficiently long to provide economic justification for their use in construction of a reaction vessel. Further, the pressures required in order to carry out the reactions at rates and to degrees of completion necessary in practical commercial operation are so great that the possible failure of the reaction vessel as a result of corrosion creates a safety hazard too great to be accepted. While there are a number of highly corrosion-resistant materials which have sufficiently low corrosion rates to enable them to function for long periods of time under highly corrosive conditions, these materials lack the structural strength necessary to enable them to withstand the reaction pressures.

It has now been found possible to carry out chemical reactions which involve contacting a fluid highly corrosive to ferrous metals with a fluid relatively non-corrosive to ferrous metals at high pressures and temperatures by maintaining a reaction zone bounded by a highly corrosion-resistant, pressure-unresistant material within and in free fluid communication with a hydraulic pressure zone bounded by a pressure-resistant material, continuously passing the non-corrosive fluid at an elevated pressure into the hydraulic pressure zone and through the hydraulic pressure zone into the reaction zone, continuously passing the corrosive fluid at an elevated pressure from a point outside the hydraulic pressure zone directly into the reaction zone and continuously removing the reaction product mixture directly from the reaction zone to a point outside the hydraulic pressure zone.

The invention may be better understood by reference to the appended drawing which is a diagrammatic illustration of an apparatus and process flow suitable for the practice of the invention.

Reaction zone 1 is enclosed or bounded by shell 18 formed from a material highly resistant to acid attack, such as porcelain. The reaction vessel is provided with an inlet 2 and an outlet 3. The reaction vessel may be a unitary structure or, if it is a large vessel, it is desirably fabricated in sections which are bolted together as indicated at joints 4, employing a nickel alloy having a coefficient of expansion approximately equal to that of the porcelain in fastening the sections together. The hydraulic pressure zone 5 is bounded on the inside by the wall of the reaction zone and on the outside by steel shell 6. It may be desired to line or clad the shell 6 with an alloy such as Type 304 or Type 316 steel to resist attack from the fluid flowing in the hydraulic pressure zone 5, or to line with an alloy such as Hastelloy B or Hastelloy C to reduce metal loss which would occur during an operational upset if acid should get into the hydraulic pressure zone. Type 304 and Type 316 steels are American Iron and Steel Institute designations for austenitic chromium-nickel steels. The hydraulic pressure zone has an inlet 7 and is in free fluid communication with the reaction zone through reaction zone inlet 2. Acid inlet line 8 is arranged as illustrated to pass the acid from a point outside the hydraulic pressure zone through the hydraulic pressure and into the reaction zone without permitting the acid to contact any part of the hydraulic pressure zone. A tantalum tube 11 is desirably employed to conduct the acid from the exterior of the hydraulic pressure zone into the reaction zone. Tantalum is highly resistant to corrosion and it is now feasible to construct small tubes and lines from it. The tantalum liner is desirably held in place by bolting it to a replaceable exterior acid line as shown. The porcelain reaction vessel 1 is supported on the base of the hydraulic pressure zone by blocks 16 which may be porcelain, steel, or alloy blocks. Provision can be made for stabilizing the reaction vessel within the hydraulic pressure vessel by inserting supporting blocks in the upper part of the annular space between the walls of the reaction vessel and the hydraulic pressure vessel. The upper portion of the hydraulic pressure vessel includes a removable top section which is fastened to the lower portion of the hydraulic pressure vessel by bolts 10. A tantalum seal 17 is provided as shown to prevent the corrosive reaction mixture leaving the reaction zone through outlet 3 from entering the hydraulic pressure zone. The reaction product mixture is withdrawn from the reaction zone through outlet 3 and from the outlet assembly illustrated through line 12. The outlet assembly and line 12 are desirably constructed of a highly corrosion-resistant alloy such as Hastelloy B or Hastelloy C, or lined with tantalum or glass. The outlet assembly is replaceable and is fastened to the exterior wall of the hydraulic pressure zone by bolts 13, the tantalum slip liner 17 being gripped between the wall of the hydraulic pressure zone and the wall of the outlet assembly. A quench line 14 is desirably provided to permit passage of a cold inert liquid into the reaction mixture just before its withdrawal in order to reduce the rate of corrosive attack upon the outlet assembly. Quench line 14 is desirably a tantalum tube held in place between the outlet assembly and alloy line 15 which is bolted to the outlet assembly and which carries the quench liquid to the point where it enters the tantalum tube.

Hydrolysis reactions requiring high temperature and pressure and high acid concentration may be carried out pursuant to the invention without difficulty. The amides of isophthalic acid and terephthalic acid may be hydrolyzed to produce the acids. These amides are difficult to hydrolyze and if the acid product is intended for use in alkyl resins, it is necessary that the hydrolysis be so complete that the acid product is substantially completely free of amide nitrogen. To achieve proper hydrolysis in a reasonable period of time, it is necessary to employ temperatures from about 300° F. to 550° F., preferably from about 400 to 500° F., and pressures ranging from about 100 p. s. i. a. to 1000 p. s. i. a. sufficient to maintain the water in liquid phase. Acid concentrations ranging from 2 normal to 15 normal, or higher, exist in the hydrolysis reaction zone during the reaction period. The amide feed to the hydrolysis reaction ordinarily contains ammonium phthalates in addition to the phthalic acid amides.

Pursuant to the invention, the amide feed and water are passed through inlet 7 into the hydraulic pressure zone 5 at a temperature of 400 to 500° F. The aqueous amide feed fills the annular space which constitutes hydraulic pressure zone 5 and flows through inlet 2 into the reaction zone. Sulfuric acid ordinarily at a concen-

tration of 50 to 100% is passed directly into the reaction zone through line 8 and tube 11. In the reaction zone the hydrolysis proceeds at a temperature ranging from 400 to 500° F. and ordinarily at a pressure in excess of 500 p. s. i. a. The hydraulic pressure of the amide feed exerted against the exterior surface of the reaction zone equalizes the reaction pressure exerted against the interior surface of the reaction zone, making it possible to fabricate the reaction zone from materials such as porcelain which have a high resistance to corrosion, but lack the structural strength to withstand the reaction pressure. The reaction vessel is ordinarily operated full of liquid and mixing may be obtained by providing a suitable mixing nozzle for acid injection.

The hot reaction product is withdrawn from the reaction vessel through outlet 3 and through line 12 of the outlet assembly. The reaction product is cooled to precipitate phthalic acids and filtered. The filtrate is cooled and returned through line 15 and tube 14 to quence the reaction product to a temperature below about 300° F. prior to its withdrawal.

A mixture of meta-xylene and para-xylene containing 85% meta-xylene and 15% para-xylene was oxidized by heating it with water, sulfur and ammonia to a temperature of about 630° F. under a pressure sufficient to maintain the water in liquid phase. The xylenes were oxidized to phthalic acids which existed in the reaction product as phthalic acid amides and ammonium phthalates. The reaction product was cooled, stripped with steam to remove hydrogen sulfide and ammonia, treated with activated charcoal, and filtered to remove the charcoal, color bodies and elemental sulfur. The treated reaction product had a calculated phthalic acid content of 8% by weight, the phthalic acids being present in the form of amides and ammonium salts. The nitrogen content of the mixture of phthalic acid derivatives was 7.5% by weight. Approximately 60% of the phthalic acids was in the form of ammonium salts and approximately 40% was in the form of amides. Hydrolysis of this reaction product is accomplished pursuant to the invention by preheating the reaction product to 480° F., passing it into the hydraulic pressure zone 5 shown in the drawing through line 7 and thence through inlet 2 into reaction zone 1. Sulfuric acid at a concentration of 93% by weight is introduced into the reaction zone through line 8 and tube 11 at a rate such that 2.3 moles of sulfuric acid to each mole of calculated phthalic acid contained in the salt-amide feed enter the reaction zone. The temperature of the mixture of sulfuric acid and feed in the reaction zone is approximately 500° F., heat being generated when the acid and feed are mixed, and the pressure in the reaction zone is approximately 700 p. s. i. g. The hydrolysis product is quenched and then withdrawn from the reaction zone through outlet 3 and line 12 at a rate such that the average residence time of the feed in the reaction zone is 5 minutes. The reaction product mixture is cooled to precipitate phthalic acids and filtered to recover phthalic acids as the filter cake. The nitrogen content of the hydrolysis product is below 0.03% by weight and phthalic acids having this low nitrogen content are entirely suitable for use in the manufacture of alkyd resins.

The hydrolysis may be conducted at somewhat lower temperatures and a satisfactorily low nitrogen content in the phthalic acid product is achieved if the residence time of the hydrolysis feed in the reaction zone is increased. At 450° F. a residence time of 12 minutes is required to reach a product nitrogen content of 0.03% by weight.

The reaction vessel can be fabricated from chemical porcelain and chemical stoneware. These terms are well understood by those skilled in the art and are well described in Engineering Materials Manual, Reinhold 1951, at page 226 et seq. The reaction vessel can also be fabricated from carbon or graphite, but if these materials are [illegible] vessel must be insulated from the steel hydraulic pressure vessel to prevent electrochemical corrosion of the latter. The reaction vessel can also be fabricated from thin sheets of metals such as gold, platinum, tantalum, and the like, which are highly corrosion-resistant, but which it is not feasible to make thick enough or strong enough to withstand the reaction pressures. The term "pressure unresistant material" employed in the appended claims connotes materials of low tensile strength which would be unable to serve as containers for fluids exerting great pressures against the interior surfaces.

The polymerization of normally gaseous olefins catalyzed by liquid phosphoric acid has been found extremely attractive on a laboratory scale, but the high corrosion rates experienced with phosphoric acid at the reaction conditions have prevented commercial application of this process. Propylene can be polymerized by contact with liquid phosphoric acid pursuant to the invention using phosphoric acid at a concentration of 90 to 115% by weight calculated as ortho-phosphoric acid, temperatures from 250 to 400° F., and pressures from 200 to 600 p. s. i. a. When propylene polymerization is undertaken the reaction vessel as shown in the drawing is inverted to permit withdrawal of the lighter hydrocarbon product from the top of the reaction zone or used in a horizontal position with internal baffles similar to H_2SO_4 alkylation vessels, but not steel. The space between acid inlet tube 11 and reactor inlet 2 is adjusted to achieve mixing by turbulent contact of the acid and the olefin feed.

I claim:

1. A process for conducting a chemical reaction involving contacting a fluid highly corrosive to ferrous metals with a fluid relatively non-corrosive to ferrous metals at high pressure, which comprises maintaining a reaction zone bounded by a ceramic imperforate wall in free fluid communication with a hydraulic pressure space bounded internally by the aforementioned wall and externally by a pressure-resistant wall of lower corrosion resistance, continuously passing the non-corrosive fluid at an elevated pressure into the hydraulic pressure space and through the hydraulic pressure space into the reaction zone, continuously passing the corrosive fluid at an elevated pressure from a point outside the hydraulic pressure zone directly into the reaction zone and continuously removing the reaction product mixture directly from the reaction zone to a point outside the hydraulic pressure zone.

2. A process for conducting hydrolysis reactions involving contacting a strong mineral acid with an aqueous dispersion of a relatively non-corrosive hydrolyzable compound at high pressures, which comprises maintaining a reaction zone bounded by a ceramic imperforate wall in free fluid communication with a hydraulic pressure space bounded internally by the aforementioned wall and externally by a pressure resistant wall of lower corrosion resistance, continuously passing said aqueous dispersion at a temperature above 250° F. and at a pressure sufficient to maintain the water in liquid phase into the hydraulic pressure space and through the hydraulic pressure space into the reaction zone, continuously passing the acid at an elevated pressure from a point outside the hydraulic pressure space directly into the reaction zone and continuously removing the hydrolysis product directly from the reaction zone to a point outside the hydraulic pressure space.

3. A process for hydrolyzing amides of isophthalic acid and terephthalic acid by contacting them with a strong mineral acid, which comprises maintaining a hydrolysis zone bounded by a ceramic imperforate wall in free fluid communication with a hydraulic pressure space bounded internally by the aforementioned wall and externally by a pressure-resistant wall of lower corrosion resistance, continuously passing an aqueous dispersion of the amide at a temperature in the range from 400 to 550° F. and at an elevated pressure sufficient to maintain the

water in liquid phase into the hydraulic pressure space and through the hydraulic pressure space into the reaction zone, continuously passing the acid at an elevated pressure from a point outside the hydraulic pressure space directly into the hydrolysis zone and continuously removing the hydrolysis product directly from the reaction zone to a point outside the hydraulic pressure space.

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