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PROCESS FOR PREPARING VINYL ACETATE

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7 Claims

ABSTRACT OF THE DISCLOSURE

Process for producing vinyl acetate which comprises subjecting a feed-stock consisting essentially of ethylene glycol diacetate to vapor phase pyrolysis within a pyrolysis zone having surfaces in direct contact with the reaction mixture during the pyrolysis consisting essentially of an austenitic stainless steel.

BACKGROUND OF THE INVENTION

Vinyl acetate is a large-scale article of commerce having wide utility in the production of polymeric compounds. While a variety of techniques have been proposed in the prior art for the preparation of this material, one recently proposed method appears of particular commercial interest. This method involves the vapor phase pyrolysis of a feedstock consisting essentially of ethylene glycol diacetate (i.e., 1,2-diacetoxyethane) to produce vinyl acetate and, as a by-product, acetic acid.

Recent discoveries (see co-pending application Ser. No. 83,221, filed Oct. 22, 1970) have enabled this vapor phase pyrolysis process to be carried out in a manner permitting the obtaining of high selectivity (selectivity being the molar ratio of vinyl acetate formed to ethylene glycol diacetate reacting and ideally would be 1.0). The obtaining of high selectivities (0.8–0.9 or more) involves the conduct of the pyrolysis reaction within a pyrolysis zone at feedstock mass velocities in excess of 200 lbs./hr./ft.² of pyrolysis zone cross-sectional area and preferably under controlled conditions of time and temperature within the pyrolysis zone. Pyrolysis temperatures between about 435° C. and about 560° C. and preferably between about 445° C. and about 550° C. are employed. It is also known that this pyrolysis is endothermic and thus requires some degree of heat input. Accordingly, materials capable of withstanding temperatures still higher than those used in the pyrolysis itself are necessary for construction of the pyrolysis zone. Such materials are well known and include a number of steels classified as high-strength, low-alloy steels and/or classified as heat-resisting steels (see Kirk-Othmer, "Encyclopedia of Chemical Technology," 2nd ed., vol. 18, pp. 787–796, Interscience [1969]). Such materials normally would be used since they possess the necessary temperature-strength characteristics and are widely available at low cost.

DESCRIPTION OF THE INVENTION

However, one highly desirable characteristic for the conduct of this process on commercial scale is the ability to sustain operation for long periods of time without shut-down. It has now been found that the use of such low-alloy and/or heat-resisting steels inhibits full attainment of this goal. It appears that such low-alloy materials act in some undefined manner to catalyze side reactions resulting in deposition of carbonaceous materials on the walls of

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the pyrolysis zone. This in turn necessitates frequent shut-down for cleaning, or duplication of equipment (connected in parallel) together with appropriate block valves and by-pass lines to enable operations to be sustained; this is clearly quite expensive and is therefore detrimental to the commercial attractiveness of the process as a whole.

It has further now been found that the rate of deposition of such carbonaceous materials is sharply reduced when those surfaces of the pyrolysis zone in direct contact with the reaction mixture during the pyrolysis are composed of austenitic stainless steels of high chromium and nickel contents, i.e., chromium content of 8 wt. percent or more and nickel contents of at least 6 wt. percent. Neither the martensitic or ferritic stainless steels of comparable composition are as suitable in this invention as the austenitic stainless steels.

Thus, it has been found that employment of surfaces composed of such materials are necessary for the attainment of sustained operation and the avoidance of equipment plugging. This discovery is quite surprising since it entails the use of high-nickel-content materials in contact with readily polymerizable materials (e.g., vinyl acetate) which has long been thought undesirable.

Generally speaking, the stainless steels found suitable for practice of the present invention are characterized by an austenitic grain structure and contain at least 8 wt. percent chromium and at least 6 wt. percent nickel as alloying agents. Desirably, stainless steels containing 16–26 wt. percent chromium and 6–22 wt. percent nickel are used. Especially advantageous are those containing 16–20 wt. percent chromium, 8–14 wt. percent nickel and particularly outstanding results are obtained when, in addition, the stainless steel contains 1–4 wt. percent of molybdenum. Thus, using type designations of the American Iron and Steel Institute for convenience, suitable materials include the 301, 302, 303, 304, 304L, 305, 308, 309, 310, 314, 316, 316L, 317, 321 and 347 stainless steels. Results obtained with types 304, 304L, 316, 316L and 317 stainless steels are especially advantageous and those obtained with types 316, 316L and 317 stainless steels are particularly outstanding.

Of course, steels of otherwise identical characteristics and utility in this invention are available from sources outside of the United States under different designations. Thus, for example, the material designated as 316 stainless steel within the United States (which is one particularly preferred material for use in the process of this invention) is known as type SUS-32 in Japan and as B.S. 1501–845 Grade B within the United Kingdom and has yet other designations in other countries.

Since the process of this invention involves what appear to be surface phenomena, it is, of course, clearly unnecessary for the material used in construction of the pyrolysis zone to be entirely made up of stainless steel. It is only necessary for the surfaces in contact with the feedstock and/or reaction products to be of this material. Thus, any material capable of withstanding the temperatures encountered can be employed in the construction so long as those surfaces in contact with the feedstock and/or reaction products meet the requirements of this invention. Accordingly, clad materials, bimetallic tubes and the like can be employed to minimize materials cost while achieving the advantages provided by this invention. Nor is it necessary for the surface in contact with the re-

action mixture within the pyrolysis zone to consist entirely of stainless steel. It is only necessary that the surface consist essentially of such steels since a small proportion of the surface therewithin can be of other materials without significantly affecting overall process operability, especially where such non-stainless steel surfaces are associated with a large cross-sectional area available for fluid flow. Such non-critical areas would include, for example, headers within the pyrolysis zone since these are normally both of large size and are within regions of significantly lower temperatures than other areas of the pyrolysis zone and would also include nozzles, clean-out ports, etc. Generally however, at least 60% of the surface in contact with the reaction mixture, desirably at least 65% and preferably at least 70% of the surface should be stainless steel whenever the reaction mixture is at a temperature of 450° C. or higher.

As used throughout this specification and in the claims, references to temperature are to bulk temperature which is intended as synonymous with the so-called "mixing-cup temperature;" see Jakob, "Heat Transfer," vol. I, p. 422 et seq., J. Wiley, New York (1959). Throughout this specification and in the claims, temperatures referred to are bulk temperatures unless otherwise stated.

The improvement of this invention relates to the vapor phase pyrolysis of a feedstock consisting essentially of ethylene glycol diacetate to vinyl acetate. In the pyrolysis the ethylene glycol diacetate is converted to a mixture containing, in an addition to unconverted ethylene glycol diacetate, vinyl acetate, acetic acid and, of course, some by-products. The feedstock alone or in admixture with its reaction products and by-products, diluents, etc. has been hereinabove and is hereinafter referred to as the "reaction mixture."

The source of the ethylene glycol diacetate does not appear to affect the rate of build-up of carbonaceous material. Material prepared, for example, by routine esterification of ethylene glycol with acetic acid or by the reaction of ethylene, oxygen and acetic acid in the presence of a halogen or halogen compound in conjunction with a variable valence cation of materials such as tellurium, manganese, copper, cobalt and chromium (see Belgian Pat. No. 738,104 which issued on Mar. 2, 1970) are equally suitable.

The ethylene glycol diacetate feedstock, especially when prepared in accordance with the process of the Belgian patent, often can contain, even after purification, some quantity, typically 20% (mole basis) or less of ethylene glycol monoacetate, ethylene glycol, diethylene glycol, and diethylene glycol diacetate and monoacetate, as well as smaller amounts of the formate analogues of the preceding acetates. Smaller amounts, preferably under 20 p.p.m. but possibly up to 1,000-2,00 p.p.m. (weight basis), of halogenated impurities such as halohydrin, ethylene dihalide, ethylene haloacetate, diethylene glycol monohalide and diethylene glycol haloacetate can also be present. All of the foregoing impurities are permissible components in the ethylene glycol diacetate feed to pyrolysis, and it is for this reason that the feedstock to the pyrolysis is described as one "consisting essentially of" ethylene glycol diacetate. It should be noted, however, that some of these impurities, during pyrolysis, can yield some vinyl acetate but their selectivities to vinyl acetate in such pyrolysis are very much lower than that observed with ethylene glycol diacetate itself.

Moreover, in continuous commercial operation, the pyrolysis would normally be carried out on a partial conversion basis, i.e., only from about 5% to about 60% of the ethylene glycol diacetate will be converted per pass through the pyrolysis zone and unconverted material together with by-products unavoidably formed during previous passes of the feedstock through the pyrolysis zone would be recycled. Such by-products can thereby build up in the feedstock to an appreciable extent and, even though purged in part, can accumulate to a point amounting to

as much as 20% (mole basis) of the total feed. Such by-products that can build up in this manner include additional ethylene glycol monoacetate, acetone, acetaldehyde, acetic anhydride, ketene, ethylidene diacetate and high-boiling materials of unknown structural formulae.

Finally, to assist in volatilization of ethylene glycol diacetate, it is often advantageous to introduce low-boiling materials during vaporization and prior to pyrolysis. Any material which is relatively inert under pyrolysis zone conditions can be used for this purpose. These materials include gases such as nitrogen, argon, helium, carbon monoxide and carbon dioxide, as well as light paraffins such as methane, ethane, propane and the butanes. Also suitable and preferred as a diluent is acetic acid since it does not introduce any extraneous material to the system. Acetic acid is substantially inert under pyrolysis zone conditions except that it may undergo partial dehydration to acetic anhydride; such dehydration is not in any way deleterious to the overall process. Whichever inert (including, in this context, acetic acid) is employed, it can be employed in amounts as little as 0.5-1.0 mole percent and up to amounts as great as 70-80 mole percent. It is normally desired to employ amounts of inert from about 1% to about 60% to facilitate ethylene glycol diacetate volatilization and it is preferred to employ inerts in an amount between about 3% and about 50%, all these percentages being on a mole basis.

The variety of material in the feedstock to the pyrolysis outlined in the preceding paragraphs together with reaction products and by-products are all permissible components of the reaction mixture. The feedstock, despite the presence of the other materials therein, is characterized as one consisting essentially of ethylene glycol diacetate since it is this material which undergoes highly selective pyrolysis to vinyl acetate and, except as hereinabove noted, these other materials display no effect on build-up of carbonaceous material and display no adverse effect upon the pyrolysis. In normal practice one would use feedstocks containing (exclusive of light diluents added to facilitate volatilization) 50-100% (mole basis), desirably 75-100% (mole basis) and preferably 80-100% (mole basis) of ethylene glycol diacetate.

To obtain high selectivities in the conversion of ethylene glycol diacetate to vinyl acetate by pyrolysis, the mass velocity (computed on the basis of contained ethylene glycol diacetate) within the pyrolysis zone should be in excess of 200 lbs./hr./ft.² of pyrolysis zone cross-sectional area. The higher the mass velocity, within broad limits, the better will be the selectivity up to a mass velocity of about 1,000 lbs./hr./ft.² of pyrolysis zone cross-sectional area. It is normally desired to operate with mass velocities in excess of 250 lbs./hr./ft.² of pyrolysis zone cross-sectional area, and it is preferred to operate with mass velocities in excess of 300 lbs./hr./ft.² of pyrolysis zone cross-sectional area.

The upper limit of mass velocity employable within the pyrolysis zone, on the other hand, is not associated with factors directly related to selectivity but rather is associated with economic considerations. These economic considerations normally dictate the use of mass velocities through the pyrolysis zone which are less than about 500,000 lbs./hr./ft.² of pyrolysis zone cross-sectional area, desirably less than 300,000 lbs./hr./ft.² of pyrolysis zone cross-sectional area and preferably less than 200,000 lbs./hr./ft.² of pyrolysis zone cross-sectional area.

Other conditions within the pyrolysis zone include pyrolysis temperatures between about 435° C. and about 560° C. and preferably between about 445° C. and about 550° C. Residence times within the pyrolysis zone between about 0.10 and about 200 seconds, preferably between about one second and 100 seconds are employed. Residence times within the pyrolysis zone, as used throughout this specification, are determined at the arithmetic average of inlet and outlet pyrolysis zone temperature and pressure and are determined on the basis

of feedstock without consideration of increase in the number of moles of gas flowing (and hence in gas velocity) as the feedstock is pyrolyzed.

It is generally desired to operate with pyrolysis zone pressures between about atmospheric and about 115 p.s.i.a., preferably between about 0.5 p.s.i.g. and about 80 p.s.i.g. Additionally, to maximize ease of equipment design, it is preferred to so configure the pyrolysis zone such that the pressure drop thereacross is between 0.5 p.s.i. and about 65 p.s.i., preferably between about 0.5 p.s.i. and about 25 p.s.i.

Also as hereinabove indicated it has been found that highest selectivities in the pyrolysis of ethylene glycol diacetate to vinyl acetate are obtained when the time-temperature characteristics of the pyrolysis zone are carefully controlled within specific limits. These limits are defined by the following equation:

$$\ln \theta = A + \frac{25,000}{T}$$

In the foregoing equation, $\ln$ is the symbol for the Napierian or natural logarithm, θ is the residence time of the feedstock within the pyrolysis zone in seconds and T represents the arithmetic average of inlet and outlet of pyrolysis zone temperatures expressed in degrees Kelvin and is at least 708 K. but not greater than 833° K. A is a number which varies from a minimum of -31.7002 to a maximum of -28.8175 . In an especially preferred mode of operation the value of A in the foregoing equation varies from a minimum of -30.9800 to a maximum of -29.0945 while θ is restricted to a value of 60 seconds or less and T is at least 728° K. but not above 823° K.

The configuration of the pyrolysis zone itself is not of substantial importance to this invention and any convenient type can be employed. Thus, for example, one or a plurality of pyrolysis zones connected in series or in parallel or both can be employed. The pyrolysis zone itself can be in the form of a furnace with the feedstock flowing through the tubes thereof or it can be in the form of a shell-and-tube heat exchanger with the feedstock flowing through either the shell or the tube side thereof. Whichever form adopted, however, the surface in contact with the reaction mixture should be an austenitic stainless steel of the requisite chromium and nickel contents. The heating medium employed in the pyrolysis zone is of no significance to this invention nor is the material of construction in contact therewith. Hot gas (e.g., combustion products) can be employed as can molten salt or other suitable high temperature media. Whatever form of pyrolysis zone is adopted, however, it is advantageous to minimize local overheating therein. The point at which such local overheating is most likely to occur is at the wall of the pyrolysis zone in contact with the reaction mixture, especially at points nearer to the outlet thereof. It is therefore desirable though not essential, to so configure the pyrolysis zone that the skin temperature is not more than 25° C. higher than the bulk temperature of the feedstock flowing through the pyrolysis zone and preferably not more than about 15° C. higher than this bulk temperature.

Once the pyrolysis is completed, the pyrolysis zone effluent is cooled and vinyl acetate is separated therefrom in conventional manner as, for example, by fractionation. As hereinabove indicated, unconverted feedstock can be recycled to the pyrolysis zone.

EXAMPLE

The following example is presented to illustrate this invention but is not intended as limiting the scope thereof. All runs of the example are carried out essentially as follows:

An ethylene glycol diacetate feedstock is charged as a liquid to an electrically heated one-inch diameter steel tube which acts as a vaporizer. To further facilitate vaporization, a small amount (0.2–2.5 wt. percent) of acetic acid is added to the feedstock in each run. To facilitate heat transfer, this tube is packed with glass beads.

The now-vaporized ethylene glycol diacetate is then passed to one of a series of identically configured pyrolysis zones. The pyrolysis zones are unpacked quarter-inch OD 20 BWG tubes, each of 20 feet in length, shaped into a spiral and totally immersed in a constant-temperature, molten salt bath. The series of runs described in the following table are carried out at mass velocities varying between approximately 2,000 and 8,300 lbs./hr./ft.² with no effect of mass velocity upon rate of build-up of carbonaceous material being noted. Each run described in the following table is continued for a minimum of 6 days or until complete plugging of the pyrolysis tube occurs if this takes place in less than 6 days. After termination of each run, the reactor is removed from the salt bath, allowed to cool, sectioned and axially split in order to determine the rate of build-up of carbonaceous material within the tube (denominated "Rate" in the following table).

Lettered runs are controls while numbered runs are illustrative of the invention.

Run No.	Reactor material	Temp., °C.	Rate (mm./hr.)
30 A	Type 4130 (1% Cr; 0.2% Mo) ¹	538	0.23
B	do. 1	500	0.08
C	—(1% Cr; 0.5% Mo) ²	538	0.19
D	—(5% Cr; 0.5% Mo) ²	538	0.11
E	Type 410	538	0.09
1	Type 304	500	(?)
2	do.	538	0.03
3	Type 316	500	(?)
4	do.	538	5×10 ⁻⁴
5	Type 317	538	3×10 ⁻⁴
6	Type 347	538	0.02
7	Type 316	565	2×10 ⁻³

¹ American Iron and Steel Institute designations; percentages are nominal, not by analysis, and are on a weight basis.

² See Simmons and Cross, "American Society for Testing Materials," Special Technical Publication No. 151, (1953). Percentages are nominal, not by analysis, and are on a weight basis.

³ No noticeable build-up.

The foregoing results clearly illustrate the characteristics of this invention. Other conditions being equal, no significant difference in conversion and selectivity is noted between the controls and the runs illustrative of this invention. Yet, rate of carbon build-up with low-alloy, temperature-resistant steels is essentially at least an order of magnitude higher than it is with the high-chromium, high-nickel austenitic stainless steels.

The foregoing description illustrates the methods of this invention. It will be understood that modifications and variations may be effected by those skilled in the art without departing from the spirit of this invention. Accordingly, it is intended that all matter contained in the foregoing description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process for producing vinyl acetate which comprises subjecting a feedstock consisting essentially of ethylene glycol diacetate to pyrolysis in the vapor phase at 435° C.–560° C. within a pyrolysis zone having surfaces in direct contact with the feedstock and its pyrolysis reaction products consisting essentially of austenitic stainless steels having a chromium content of at least 8 wt. percent and a nickel content of at least 6 wt. percent.

2. A process in accordance with claim 1 wherein the steel contains 16–26 wt. percent chromium and 6–22 wt. percent nickel.

3. A process in accordance with claim 1 wherein the steel contains 16–20 wt. percent chromium and 8–14 wt. percent nickel.

4. A process in accordance with claim 3 wherein the steel is a stainless steel designated by the American Iron and Steel Institute as type 304 stainless steel.

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5. A process in accordance with claim 3 wherein the steel contains 1-4 wt. percent molybdenum.

6. A process in accordance with claim 5 wherein the steel is a stainless steel designated by the American Iron and Steel Institute as type 316 stainless steel.

7. A process in accordance with claim 5 wherein the steel is a stainless steel designated by the American Iron and Steel Institute as type 317 stainless steel.

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5 VIVIAN GARNER, Primary Examiner

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