Oct. 18, 1949. W. H. GEHRKE 2,485,044

VINYL ACETATE PRODUCTION

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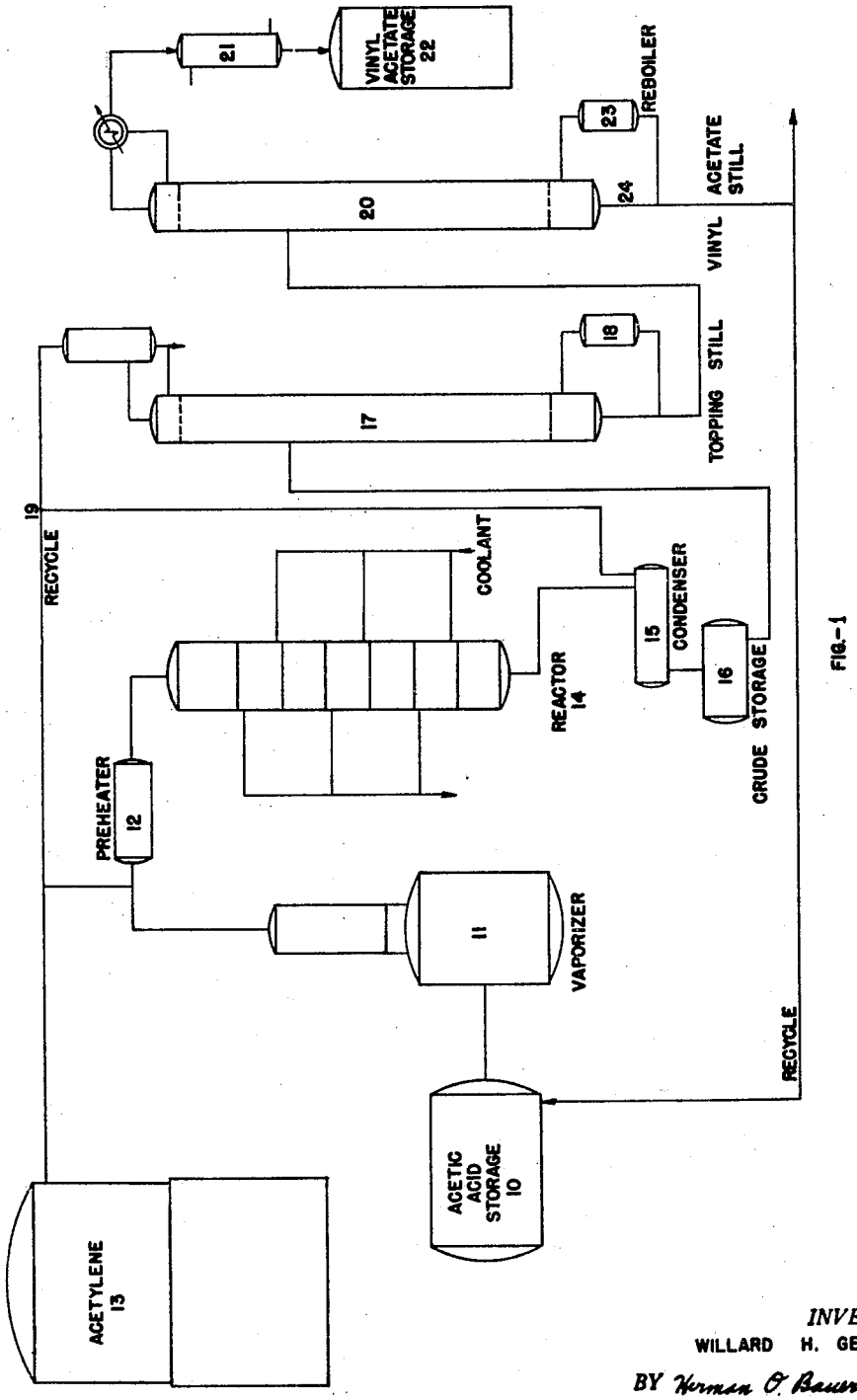


FIG.-1

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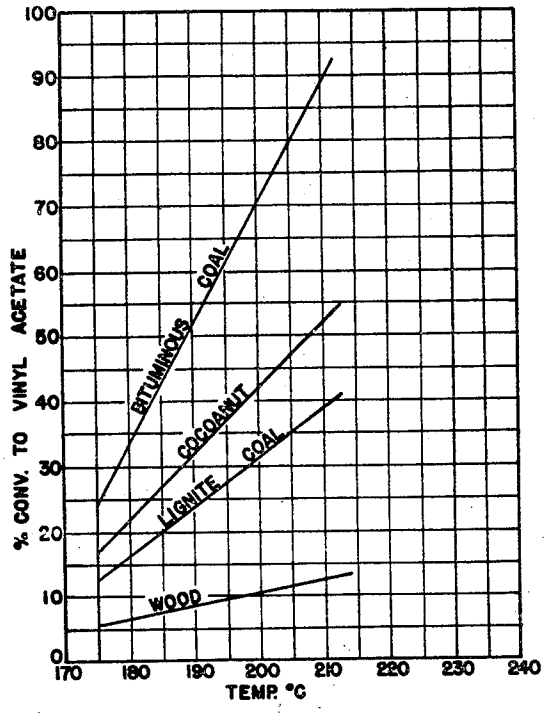


FIG. 2
RELATIVE ACTIVITY OF VARIOUS CARRIERS IMPREGNATED WITH ZINC ACETATE FOR VINYL ACETATE PRODUCTION.

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VINYL ACETATE PRODUCTION

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7 Claims. (Cl. 260—498)

1

My invention relates to the production of vinyl acetate by a catalytic process and to improvements in the catalyst adapted to furthering this reaction.

It is an object of the invention to facilitate the reaction of acetylene with acetic acid for the production of esters such as vinyl acetate. It is another object to provide a catalyst of high activity for this purpose and particularly a catalyst having long life in an industrial process.

It is another object to carry out an industrial method to apply the new catalyst which I have discovered.

It is known that vinyl esters may be produced by the reaction of acetylene and carboxylic acids by the use of catalysts such as mercury, zinc or cadmium salts which may be deposited upon a carrier. The art has recognized that activated charcoal from wood may be used in this relationship.

My invention resides in the discovery that a particular catalyst, when prepared under the procedure of the instant invention, provides results superior to those which could be obtained with prior art catalysts. I have discovered that a carrier of unusual efficacy may be made from coal as a base. At a result of extensive research in this field it has been discovered that an activated coal base may be produced without the use of chemicals, such as has heretofore been conventional. Such activating agents which have been used in prior art carbons include lime, caustic alkalis, zinc chloride, sulfuric acid and phosphoric acid. The designation of carbons generally is not applicable to the carrier of the present invention to achieve the improved results. I have found that wood derived chars are generally unsuitable, but that bituminous coal as a source furnishes a desirable carrier. Particularly good results are obtained when bituminous coal from the Pittsburgh bed, such as the Number Two Seam, is subjected to the treatment described below preparatory to use as a catalyst carrier for vinylation.

Activation of bituminous coal to produce the carrier of the present invention may be carried out with starting materials in either the lump or granular form. Cleaned coal is preferred since it reduces the amount of sulfur-containing impurities. The ash content of the coal, based upon the usual A. S. T. M. method may be in the range of 3% to 8%, but a preferred range is 4% to 6%.

I may initiate the activation process by devolatilizing, or in essence, pre-coking the coal, there-

2

by removing a major part of the volatile matter prior to activation. While the present invention is not limited to any theory it would appear the preliminary coking volatilizes the lower boiling hydrocarbon constituents of the coal so as to make them more readily removable by the subsequent steam activation.

The next part of the treatment consists of steam activation. Because of the relatively high temperatures which are employed, it is probable that the so-called water gas reaction is set into force, whereby some of the hydrocarbon constituents, particularly those which were previously volatilized in the pores of the coal are oxidized and removed. This has the effect of enlarging the pores of the carrier material. The mean average pore diameter of the coal may increase from the range of 50 to 100 Å. to the order of 100 to 100,000 Å. This is in contrast to the typical cocoanut base carbon in which the pores are usually considered as consisting of deep but relatively narrow valleys or fissures having an effective opening of about 100 Å. or less of effective aperture.

The above activation method makes it unnecessary to leach or wash the carbon, although such leaching may be employed to produce carriers of low ash content. The coal derived carbon retains in large part the original constituents which distinguish the present catalytic materials from the ordinary activated carbons. The mineral content of the coal is also substantially retained. The residual ash has been found not to be deleterious to the catalysis of the vinylation process. The nature of the ash is not critical in the vinylation reaction as long as copper is not too prominent (less than 0.1%). The chemical analysis of a typical ash sample from the activated bituminous coal was approximately as follows:

	Percent
SiO_2	53.0
Al_2O_3	27.9
Fe_2O_3	8.6
TiO_2	1.0
CaO	4.9
MgO	1.2
Na_2O	0.4
K_2O	0.95
Mn	0.08
Cu	under 0.01
P	0.10
SO_3	1.40
Ignition loss	0.30
Total	99.83

However, I regard it as essential that the coal source be a bituminous coal, and not anthracite nor lignite (brown) coals. Particularly good results have been achieved with bituminous coal from the Pittsburgh seam, which as is well known, is of considerable extent.

The coal base described above may be employed in combination with metal salts and metals to provide the final catalyst. The active material may be added to produce various types, such as impregnated catalysts for vinylation. Thus, I may utilize granular carbonaceous carriers which are impregnated with solutions of zinc acetate and then dried before use. I may also employ a finely powdered form of carbon for treatment by impregnation in solution. Deposition of the vaporized salt may likewise be accomplished by the vaporization of the catalytic material. It is not certain just what physical relationship exists between the active material and the carrier, but such active salt is quite firmly bound to the bituminous coal carrier, and is detectable at the surface of the carrier.

In carrying out the vinyl ester process, the above catalyst in granule form, either in the form of pellets, agglomerated pieces, or of extruded material, may be disposed in conventional catalytic converters, such as unitary columns. I may also employ tray type converters in which the catalyst is located on a series of trays in a tower through which the reactant gases are passed. It is also contemplated that the finely divided catalyst may be utilized as a moving catalyst bed, or in a fluid catalytic process be carried together with the reactant gases through a reactor section. In such cases, settling and separating sections may then be used to remove the catalyst from the gas stream. Slurry methods may also be employed in which the catalyst is utilized as a liquid suspension or slurry and in which such catalyst is agitated with the reactants to produce the desired vinyl acetate. Subsequent treatment may then be employed to separate the catalyst after which the products are worked up in the usual manner.

My invention will be best understood by reference to the accompanying drawings, where I have shown diagrammatically a flow sheet or apparatus layout in which my invention may be carried into practical effect.

Fig. 1 shows in diagrammatic manner the apparatus and a flow sheet of the vinyl acetate process of the invention using a continuous recycle system. In this figure, 10 represents the acetic acid storage from which acetic acid is pumped to vaporizer 11 and then to preheater 12. Here acetylene from a storage tank or generator tank 13, after being subjected to suitable purification to remove hydrogen sulfide and phosphine, is mixed with the acetic acid vapor to provide a gas stream charge for reactor 14. The reactor may be of a conventional type employing either a fixed bed of catalyst or if desired may utilize a moving bed or a fluid catalytic system. The liquid products drawn from the reactor are condensed in condenser 15 and then go to the crude storage tank 16.

Also leaving condenser 15 is a gas stream of any uncondensed acetylene which is recycled to the acetylene supply. The crude liquid accumulated in storage vessel 16 also contains dissolved acetylene which is removed overhead from the topping still 17. Such overhead gas, after removal of the major portion of the condensables, may also be recycled by means of the recycle line 19.

Finishing operations in Fig. 1 include the topping still 17 having heating means 18 and a vinyl acetate still 20 provided with a reboiler 23. The vinyl acetate still 20 gives an overhead product comprising principally vinyl acetate which is condensed in condenser 21 and held in vinyl acetate storage tank 22. The vinyl acetate still also provides a bottom stream 24 which, after proper purification, may be recycled with the acetic acid charge.

In order that the invention may be clearly understood, and readily carried into effect, some practical methods of carrying out the vinyl acetate process according to the instant teaching will now be described in somewhat greater detail by way of example.

EXAMPLE 1

A semi-commercial scale operation utilized an activated coal carrier comprising about 75% of the total weight of the catalyst, the remainder consisting of about 25% of zinc acetate impregnated upon the carrier. Operations were initiated in a reactor system of the type shown in Fig. 1 by first recycling acetic acid vapors through the entire unit until the reactor heating system had brought the catalyst to operating temperature. Acetylene was then slowly added to the gas stream until the desired space velocity of about 300 reciprocal hours was attained. The molar ratio of acetylene to acetic acid in the feed to the reactor for satisfactory operation was found to vary over the range of 2:1 to 5:1. The pressure was found to be desirably maintained at a positive pressure above atmospheric and as high as 5 atmospheres. Operations under the conditions set forth above gave very high yields ranging upwards from about 95% based upon the acetic acid charge, and up to substantially quantitative recoveries.

Tests made with impregnated catalysts utilizing various types of carriers gave data at various operating temperatures as summarized in Fig. 2. This drawing illustrates the variations in percentage conversion to vinyl acetate for several types of carriers tested over a portion of the temperature range, temperatures of 150°–300° C. being practicable in the vinylation process. It is apparent that the bituminous coal carrier made in accordance with the present invention results in a catalyst capable of providing vastly superior conversions to vinyl acetate.

The catalyst efficiency was found to depend principally upon the type of carrier which was employed; this variable was more important than the nature of the metal salt added, although the zinc and cadmium carboxylates having from 1 to 3 carbon atoms were all suitable as impregnating compounds. It has been found that the most desirable carrier for the vinyl acetate catalyst was a granular activated bituminous coal consisting essentially of granules made by devolatilizing a bituminous coal having from 3% to 8% of ash, or preferably 4% to 6% ash, and then treating such devolatilized coal with steam at an oxidizing temperature until the ash content reached the range of 15% to 35%. The preferred range of ash percentage of the carrier is in the region of 20% to 25% before the addition of the metal salt.

It was also found that the pore size of the finished catalyst lay in the average range of 100 to 100,000 Å. Due to the unusually high proportion of larger pores in the bituminous coal carrier it was possible to obtain a very large area of active impregnating compound per unit weight of

such active impregnant, thus increasing the effectiveness of the catalyst as a whole upon subsequent use in producing vinyl acetate.

The advantages derived from the use of steam activated bituminous coal carrier in accordance with the present invention can be specifically illustrated by reference to a series of catalytic vinylations carried out under comparable conditions. In each of these operations the catalyst employed comprised zinc acetate impregnated upon the respective carriers, all of which were prepared substantially as described below. The respective finished catalysts and the operations in which they were employed will be identified herein as A, B, C and D. Each catalyst contained about 30% of zinc acetate based upon the weight of the carrier and was employed in a granular form in which the effective particle size remained unchanged in the impregnating step.

TABLE I

Comparative tests with zinc acetate on various carriers

Test	A	B	C	D
Carrier	Steam activated bituminous coal.	Lignite	Cocoanut	Wood charcoal.
Ash in carrier	23.1%	18.2%	1.6%	1.4%.
Temperature	210° C.	210° C.	210° C.	210° C.
Space velocity	300 RH.	300 RH.	300 RH.	300 RH.
Acetylene mol ratio	4:1	4:1	4:1	4:1.
Per Cent Conversion $\left(\frac{\text{Vinyl acetate}}{\text{Acetylene feed}}\right)$	93	41	55	13.

In the respective operations, identical apparatus was used. An equal volume of the catalyst was placed in the reaction chamber maintained under a positive pressure slightly in excess of atmospheric and at a series of temperatures. Carefully controlled amounts of acetylene and of vaporized acetic acid were passed together in the presence of and in contact with the catalyst in the reaction chamber. After a run had reached equilibrium, the reactants and products were all carefully measured during the test period, after which the catalytic system was allowed to cool. Further runs made at other temperatures for each of these catalysts supplied the data expressed in Fig. 2 in the form of comparative results for the individual catalysts expressing the percentage conversion as related to the temperature of operation.

The conversions shown in Fig. 2 express the vinyl acetate obtained in the products of the reaction. The separated materials were individually analyzed. In each operation the composition of the feed, the feed rates, proportions of acetylene to acetic acid and space velocities, i. e., volume of gaseous reactants (S. T. P.) per volume of catalyst per hour, were comparable.

It may be seen from the results expressed in Fig. 2 and summarized in Table I that the catalyst employing steam activated bituminous coal as a carrier gives substantially greater conversions under comparable conditions than could be obtained with the prior art charcoal bases. Thus the carriers made from wood charcoal, lignite coal and cocoanut all gave considerable lower conversions. Under these comparable operating conditions catalyst A, the bituminous coal carrier, also showed that when the catalysts were removed from the reaction chamber the amount of polymer formed on the catalyst was very low. This is important in industrial operations since a limiting factor in catalyst longevity is the build up of polymer which results in an increase in the increase of pressure necessary to force the reactants through the catalyst bed. Certain of the prior art materials, such as the lignite coal carrier showed excessive polymer depositions which invariably resulted in the plugging of the catalyst chamber necessitating the shut down of the catalytic reaction system.

Consequently the advantageous results obtained by the present invention are surprising and unexpected in view of the fact that the use of carbons from other coal than bituminous not only does not produce the aforesaid advantageous results, but causes the formation of prohibitive amounts of undesirable reaction products.

EXAMPLE 2

Operations carried out substantially as in Example 1 made use of a catalyst prepared by crushing 4 inch lumps of bituminous coal, washing to reduce the sulfur content, and then sizing the crushed material to 4 x 10 mesh. Any similar range, such as 2 x 14 mesh is also satisfactory. The coal was then devolatilized by a slow oxidation process as distinguished from a coking process. Consequently, this may be termed a calcination and may also be augmented by the use of steam. The temperatures utilized in this step are those of conventional coal treatment to accomplish the result of removing the volatile constituents without going so high in temperature as to crack the evolved gases. The latter is undesirable, since it results in redeposition of carbon in a form which cannot be activated. I may also utilize graduated heating, such as by a preliminary heating at 400° C. to 500° C. for 1 to 2 hours, followed by higher temperatures of 600° C. to 750° C. for 2 to 3 hours to sweep the surface free of tarry materials.

The devolatilized coal which may have added a binder such as pitch is then activated by a mixture of steam and flue gas at approximately 1800° F. Control of the severity and time of activation are probably determinative of the pore size distribution and total surface area of the finished catalyst carrier. In this step a water gas reaction takes place on the surface of the carbonaceous material which, as shown by physical testing, pass through a change in which the deep, narrow pores are broadened by means of the carbon removal reactions to provide the relatively wide pores which are essential in the instant process. However, this theory is not regarded as limiting the present invention which is generic to steam activation.

Conventional methods are available to measure the pore size distribution and surface area of the activated and impregnated catalysts. The measurement of surface area may be carried out in accordance with the method of Brunauer, Emmett, and Teller, Journal of American Chemical Society, 60, 309, (1938). The measurement of the distribution of pore sizes may be deter-

mined by a pressure method such as is shown in Industrial and Engineering Chemistry, Analytical Edition, 17, 782 and 787 (1945). This method employs a fluid which is forced into the pores of the catalyst by applied pressure which may be measured with extreme precision. Correlation of the pressure and change in the apparent volume upon the system enables a determination to be made of the various size pores present on the surface of the catalyst. A further method is available as shown by Ries, Van Nordstrand, Johnson and Bauermeister, Journal of American Chemical Society 67, 1242 (1945) to measure the type of pores present upon a microporous surface.

EXAMPLE 3

Another catalyst was prepared by treating Pittsburgh bituminous coal by grinding to about 50 microns and then briquetting under pressure. Extrusion may also be used as a forming means to achieve larger catalyst particles for future processing. It has been found that the ultimate particle size of the first grinding is a controlling factor in the pore size of the finished catalyst. This is due to the fact that finer grinding makes available a larger surface for the water gas reaction which occurs in the activation step. This reaction primarily employs steam and carbon to form carbon monoxide and hydrogen, by which method carbon is essentially removed from the surface of the material. The additional use of flue gas also controls the extent of reaction and makes possible the production of harder and stronger catalysts.

Treatment of the briquetted or extruded material from bituminous coal may make use of a preliminary calcination to be followed by the steam activation. Temperatures in the activation step may be of the order of 800° C. and at times varying from 1 to 24 hours to obtain the desired porosity. The results obtained in vinylation using such a carrier are of the same order of magnitude as is shown in the above Example 1 for the granule type.

It has been found as revealed by the test methods listed in Example 2 that the pore structure of the activated coal, instead of being narrow and deep openings (approximately 100 A. diameter) of the cocoanut charcoal type are relatively broad and having diameter at the surface as large as 100,000 A. It would appear also that the broad diameter pores may have such diameter extending throughout the major proportion of the individual pores although such individual pores may extend further into the material in the form of a very small opening of perhaps 1 to 5 A., i. e., of the ink bottle type, but with the large end open.

Comparison of such pore shapes shows that the effective diameter of the final pores depends upon the structure of the original material, as well as the method of activation. In the preparation of a catalyst from coal, the particle size of the ground coal fixes to a considerable extent the nature of the pore size in the finished briquette. Such pore is then undoubtedly increased in size in the succeeding steam activation. It is known that in the case of carbons made from wood, certain nut materials like cocoanut, peach kernels, etc., the pores have narrow, tubular structures. In general, the lighter woods give larger pore sizes. Peat, since it is derived from wood and other vegetable fibers, retains the original wood structure and coal also shows related properties, although it has been to a considerable degree transformed as the result of pressure.

The present invention sets forth a new process of producing vinyl acetate by means of a novel catalyst. The catalyst is based upon a carrier made from steam-activated bituminous coal. This catalyst differs from activated carbon of the prior art, including wood, coal, nut and vegetable sources in its critical ash content, and the consequent surface structure. While the exact surface topography of the catalyst carrier of the invention is not known, the range of effective pore diameters shows the presence of unusually large pores resulting from the steam activation. Consequently the catalyst carrier may be defined in terms of the product resulting from the particular treatment. The vinyl acetate catalyst carrier may be characterized as having been produced from bituminous coal having from 3% to 8% ash by first devolatilizing the coal. The next step is steam activation at an oxidizing temperature to bring the ash content to 15% to 30% in the finished carrier. The deposition of zinc acetate or the formate or propionate of this metal or of cadmium, to the extent of 20% to 35% upon the carrier then provides the finished catalyst. The actual vinylation may be carried on at temperatures from 150° to 300° C., the preferred range being 200° to 250° C.

Since many changes may be made in the above process and catalyst without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative, and not in a limiting sense, and that the invention is to be construed broadly, and restricted solely by the appended claims.

What I claim is:

1. The method of vinylating acetic acid with acetylene which comprises contacting a gaseous mixture of acetic acid and acetylene at a regulated temperature between about 200° and 250° C. with a catalyst consisting essentially of particles of a carrier made by devolatilizing bituminous coal having from 4% to 6% of ash, and then activating said devolatilized coal by means of steam until the ash content of said carrier is in the range of 20% to 25% ash, said particles having zinc acetate present upon their surface.

2. The method of vinylating acetic acid with acetylene which comprises contacting a gaseous mixture of acetic acid and acetylene at a regulated temperature between about 200° and 250° C. with a catalyst consisting essentially of particles of a carrier made by devolatilizing bituminous coal having from 4% to 6% of ash, and then activating said devolatilized coal by means of steam until the ash content of said carrier is in the range of 15% to 35% ash, said particles having zinc acetate present upon their surface.

3. The method of vinylating acetic acid with acetylene which comprises contacting a gaseous mixture of acetic acid and acetylene at a regulated temperature between about 200° and 250° C. with a catalyst consisting essentially of particles of a carrier made by devolatilizing bituminous coal having from 3% to 8% of ash, and then activating said devolatilized coal by means of steam until the ash content of said carrier in the range of 15% to 35% ash, said particles having zinc acetate present upon their surface.

4. The method of vinylating acetic acid with acetylene which comprises contacting a gaseous mixture of acetic acid and acetylene at a regulated temperature between about 150° and 300°

C. with a catalyst consisting essentially of particles of a carrier made by devolatilizing bituminous coal having from 3% to 8% of ash, and then activating said devolatilized coal by means of steam until the ash content of said carrier is in the range of 15% to 35% ash, said particles having zinc acetate present upon their surface.

5. The method of vinylating acetic acid with acetylene which comprises contacting a gaseous mixture of acetic acid and acetylene at a regulated temperature between about 150° and 300° C. with a catalyst consisting essentially of particles of a carrier made by devolatilizing bituminous coal having from 4% to 6% of ash, and then activating said devolatilized coal by means of steam until the ash content of said carrier is in the range of 15% to 35% ash, said particles having zinc acetate present upon their surface.

6. The method of vinylating acetic acid with acetylene which comprises contacting a gaseous mixture of acetic acid and acetylene at a regulated temperature between about 150° and 300° C. with a catalyst consisting essentially of particles of a carrier made by devolatilizing bituminous coal having from 3% to 8% of ash, and then activating said devolatilized coal by means of steam until the ash content of said carrier is in the range of 20% to 25% ash, said particles having zinc acetate present upon their surface.

7. The method of vinylating acetic acid with acetylene which comprises contacting a gaseous mixture of acetic acid and acetylene at a regulated temperature between about 150° and 300° C. with a catalyst consisting essentially of particles of a carrier made by devolatilizing bituminous coal having from 4% to 6% of ash, and then activating said devolatilized coal by means of steam until the ash content of said carrier is in the range of 20% to 25% ash, said particles having zinc acetate present upon their surface.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,238,774	Ittner	Sept. 4, 1917
2,098,842	Walter	Nov. 9, 1937
2,100,352	Pier	Nov. 30, 1937
2,191,156	Pier	Feb. 20, 1940
2,239,763	Toussaint	Apr. 29, 1941
2,382,586	Solomon	Aug 14, 1945