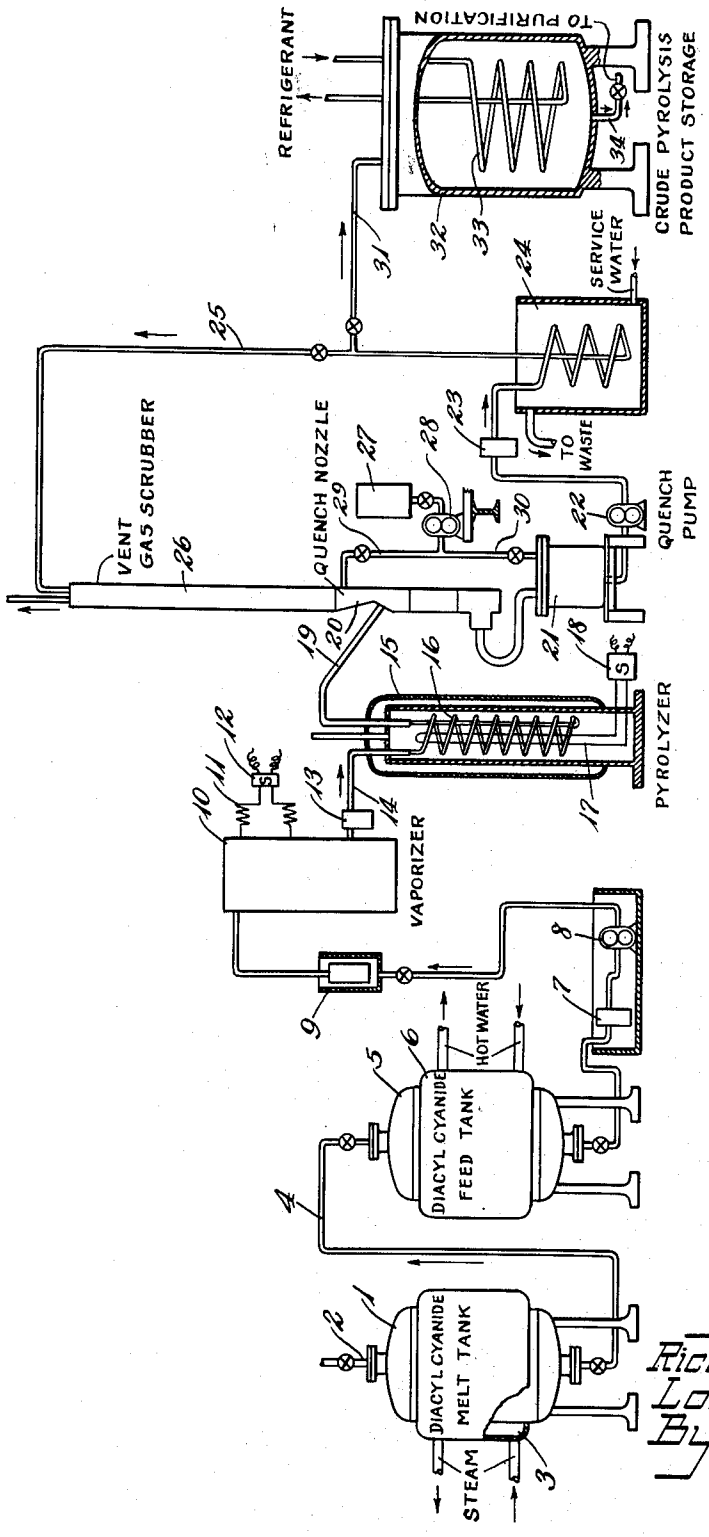
Dec. 22, 1953 L. F. REUTER ET AL 2,663,725

METHOD FOR THE PYROLYSIS OF DIACYL CYANIDES

Filed May 7, 1952



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Patented Dec. 22, 1953

2,663,725

UNITED STATES PATENT OFFICE

2,663,725

METHOD FOR THE PYROLYSIS OF DIACYL CYANIDES

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Application May 7, 1952, Serial No. 286,496

6 Claims. (Cl. 260—465.8)

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This invention relates to a method for pyrolyzing diacyl cyanides to give monomeric vinylidene cyanide (also known as 1,1-dicyano ethylene or methylene malononitrile) or one of its homologs is obtained, and pertains more particularly to a process whereby diacyl cyanides are pyrolytically decarboxylated in an efficient manner in high yield at atmospheric pressure without attendant losses of the desired monomeric product.

It is disclosed in U. S. Patent 2,476,270 that the diacyl cyanide, 1-acetoxy-1,1-dicyano ethane, can be pyrolyzed at temperatures of 400° C. to 750° C. to give monomeric vinylidene cyanide, an extremely valuable polymerizable material which is especially useful in the preparation of polymers and interpolymers suitable as synthetic fibers, synthetic resins and plastics.

However, unless the process as described in the patent is carried out at reduced pressures, preferably from 2 to 50 mm. of mercury, the yield of the desired monomeric vinylidene cyanide is not as high as is desirable and carbonization of the pyrolysis tube occurs to a considerable extent. This dependency on reduced pressure for optimum results is quite undesirable for a number of reasons. For example, the production and maintenance of such a vacuum involves the installation of expensive equipment and the necessity for close operational control both of which add materially to the initial cost and up-keep of the pyrolysis plant. Also, reduced pressure makes necessary on a large scale the use of a large pyrolysis tube and/or a high temperature and limits severely the amount of pressure drop through the pyrolysis tube. These conditions in turn lead to a pronounced temperature drop across the gas film at the pyrolysis tube interface with attendant overcracking along the tube walls and reduced stability of the pyrolysis product. Additionally, reduced pressure pyrolysis requires the use of very low temperatures for pyrolysis product condensation, this factor again adding to the cost of a pyrolysis plant. Also, the reduced pressure process is not well suited for use on a continuous scale. As a result of these disadvantages, the process specifically described in U. S. Patent 2,476,270 is not as well suited for practical commercial usage as is desired.

Accordingly, it is an object of the present invention to provide a process whereby 1-acetoxy-1,1-dicyano ethane (diacetyl cyanide), as well

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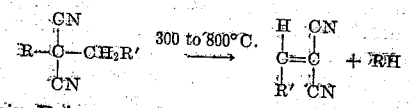
as other diacyl cyanides, may be readily and economically pyrolyzed at atmospheric pressure to give high yields of monomeric vinylidene cyanide or a homolog thereof.

It is another object of the invention to provide a continuous process whereby diacyl cyanides can be pyrolyzed at substantially atmospheric pressure and in such a manner that a stable pyrolysis product comprising the desired monomer can be continuously recovered from the process in high yields.

It is still another object of the invention to provide a continuous process whereby diacyl cyanides can be pyrolytically deacyloxyated, and the resulting pyrolysis vapors condensed without the occurrence of substantial polymerization of the monomers present in the pyrolysis product. Other objects of the invention will be apparent from the description which follows.

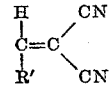
It has now been discovered that the above and other objects may be readily attained by a process involving the steps of first vaporizing the diacyl cyanide, pyrolyzing the vapors, instantaneously quenching the hot pyrolysis product vapors with large volume, as compared to the volume of the vapors, of a liquid stream of cold pyrolysis product or a diluent liquid or a mixture of both, thereby simultaneously removing the condensed pyrolysis product from the quench zone. By carrying out the pyrolysis process in this manner it is possible to operate at atmospheric pressure or at pressures slightly above atmospheric and yet obtain very high conversions of diacyl cyanide to monomeric vinylidene cyanide or homolog, with only negligible polymerization of the desired monomer, or carbonization of the pyrolysis tube. Moreover, the process can be operated continuously and economically to give consistently high yields of the desired monomeric vinylidene cyanide or homolog.

The pyrolysis of diacyl cyanides according to the process of the present invention proceeds substantially as follows:



wherein R is an acyloxy radical, preferably containing from 2 to 6 carbon atoms, and R′ is hydrogen or a lower alkyl radical preferably containing from 1 to 4 carbon atoms. When R′ is hydrogen there is produced vinylidene cyanide

and carboxylic acid whereas when R' is lower alkyl there is obtained, in place of vinylidene cyanide, a homolog thereof of the formula



The temperature at which the pyrolysis process is carried out may be varied widely. For example, temperatures as low as 300° C. or lower to 800° C. or even higher are operative. However, temperatures in the range of 500° C. to 600° C. are especially preferred since temperatures above about 600° C. sometimes lead to "overcracking" of the diacyl cyanide accompanied by substantial polymerization of the monomer. At temperatures below about 500° C. the pyrolysis proceeds quite slowly and requires a large pyrolysis tube in order that the process be operated efficiently.

It is desirable but not absolutely essential to carry out the pyrolysis in the presence of an inert diluent material which may be either a gas or a liquid at room temperature. The use of such a diluent, especially one which is a liquid at room temperature, is advantageous in that it eliminates the need for installation of a diacyl cyanide drier and lowers the melting point of the feed, so that less heat treatment for the molten diacyl cyanide in the feed system is required, and the dew point of the pyrolysis product vapors is lowered. Also, the use of a diluent lowers the partial pressure of vinylidene cyanide in the condensed pyrolysis product vapors. The diluent material which is utilized may be any material which is inert toward both the diacyl cyanide and the monomeric vinylidene cyanide or homolog, i. e., it must neither react with nor affect in any substantial manner said compounds at any stage of the pyrolysis process. Included among the substances which are inert toward diacyl cyanides and monomeric vinylidene cyanide and its homologs are the liquid aromatic hydrocarbons or halogen substituted aromatic hydrocarbons such as benzene, o, m, or p-toluene, o, m, or p-xylene, monochlorobenzene, dichlorobenzene, trichlorobenzene and the like. Inert diluent gases which may be utilized include methane, ethane, propane, nitrogen, hydrogen and helium as well as mixtures of such gases and the like. It is to be understood, of course, that the inert diluents disclosed above do not represent all of the inert substances which can be utilized. It is also to be understood that the use of an inert diluent, while desirable for the reasons set forth hereinabove, is not a critical expedient in the present process.

Proper and rapid condensation of the pyrolysis product vapors is highly important to the successful operation of the atmospheric pressure pyrolysis process. The condensation is best carried out by directing the pyrolysis product vapors from the pyrolyzer into a quench zone which desirably is a quench nozzle of restricted volume where the hot vapors are met with a relatively large liquid flow of preformed pyrolysis product or an inert liquid diluent, or a mixture of both, maintained at a temperature no higher than room temperature hereinafter referred to as being "cold" because of its low temperature in relation to that of the hot pyrolysis vapors. The cold flow of liquid instantaneously condenses the pyrolysis product vapors and removes the condensate from the quench zone immediately, so that the condensate is not in contact with hot vapors for more than an instant. Prolonged contact with hot vapors which causes polymerization of the monomer, reduction in yield of the desired product, as well as plugging of the pyrolysis system, is thus eliminated. In order that polymerization will be held at a minimum, it is important that the pyrolysis vapors be maintained above the dew point until the exact moment at which they are contacted by the cold flow of quench liquid. This is readily accomplished by heating the line through which the vapors pass from the pyrolyzer to the quench nozzle.

As disclosed hereinabove, the use of large quantities of quench liquid is important in the present process. Accordingly, it is desirable that the ratio of quench liquid to pyrolysis product vapors be at least 50 to 1 on a weight basis, and preferably nearer 200 to 1, although higher or lower ratios may also be utilized. This ratio may be controlled accurately either by adding liquid diluent to the diacyl cyanide fed into the pyrolyzer or by adding the diluent to the quench liquid continuously.

It is also desirable that an inhibitor of polymerization be incorporated in the liquid pyrolysis product either simultaneously with the condensation process or as soon as possible after condensation of the pyrolysis vapors in order that the polymerization of the monomeric vinylidene cyanide will not be initiated by other of the materials present in the pyrolysis product mixture. Many of the commonly used polymerization inhibitors such as hydroquinone, phenyl beta-naphthylamine and the copper salts are not useful for this purpose since they actually catalyze the polymerization of monomeric vinylidene cyanide. However, certain other materials are useful for inhibiting the polymerization of monomeric vinylidene cyanide. Such materials include sulfuric acid, preferably of a concentration of 100% or higher, the halosulfonic acids such as chlorosulfonic acid, the sulfonyl chlorides such as toluene sulfonyl chloride or benzene sulfonyl chloride, sulfur dioxide and the like. Only catalytic quantities of inihibitor are utilized; for example, amounts of from 0.01% to 2% of stabilizer, based on the weight of the crude pyrolysis product, give excellent results. Larger amounts are not desirably utilized since reduced pyrolysis product stability is likely to result.

The pyrolysis of diacyl cyanides in accordance with the present invention will be described in greater detail below. Reference is also made to the accompanying drawing which is a diagrammatic illustration of a preferred method for carrying out the pyrolysis process.

Referring to the drawing, there is shown a melt tank 1 into which diacyl cyanide and diluent, if one is utilized in the diacyl cyanide feed, are supplied through feed inlet 2. The diacyl cyanide and diluent, if any, are heated to about 100° C. by steam in jacket 3 and the resulting hot solution is blown by pressure at feed inlet 2 through line 4 into feed tank 5, which is heated by hot water in jacket 6. The hot diacyl cyanide (or diacyl cyanide solution if a solvent is utilized) then discharges through basket strainer 7 where any tarry residue is removed and is then fed by metering pump 8 through rotameter 9 and into vaporizer 10. In the vaporizer 10, the diacyl cyanide feed is vaporized and maintained at a temperature of about 260° C. by heat supplied by electrical heating coil 11 which is supplied with electrical energy at source 12. The heated vapors then pass through tar trap 13 where any tarry

materials are removed so as to prevent plugging of line 14 through which the vapors enter the pyrolyzer 15. Line 14 is preferably heated to prevent condensation of the vapors and to maintain the temperature of the vapors at about 250° C. as they enter the pyrolyzer. In pyrolyzer 15 helical coiled tubing 16, preferably constructed of stainless steel or other corrosion resistant material is surrounded by a lead bath heated to the pyrolysis temperature by electrical heater 17, supplied with electrical energy source 18. As the vapors from vaporizer 10 pass through the heated helical coiled tube 16 they are thermally decomposed into monomeric vinylidene cyanide or homolog, a carboxylic acid and by-products. These pyrolysis product vapors, which also contain some unreacted diacyl cyanide and diluent, if one is utilized, pass through line 19 which is desirably heated to prevent condensation of the pyrolysis product vapor, into quench nozzle 20. In the quench nozzle 20, the pyrolysis product vapors are condensed instantaneously by a large flow of crude pyrolysis product pumped from tank 21 by pump 22 through basket strainer 23 (to remove tarry residue), quench cooler 24 where heat taken up in the quenching operation is removed, line 25 and vent gas scrubber 26. The quench nozzle 20 is so designed that the vapors are kept at a temperature above their dew point until they enter the quenching zone. Non-condensable gases (nitrogen, carbon dioxide and the like) pass upward through the vent gas scrubber 26 where the downward flow of cold quench liquid removes substantially all of the monomeric vinylidene cyanide or homolog from the gases before they are vented to the atmosphere. The downward flow of large quantities of quench liquid through vent gas scrubber 26 and through quench nozzle 20 removes the condensed pyrolysis product from the quenching zone immediately after condensation takes place so that a temperature rise of only a few degrees takes place between the quench liquid entering and leaving the condensation zone. This procedure prevents prolonged contact of the liquid condensate in quench nozzle 20 with the pyrolysis product vapors entering the quench nozzle through line 19 and prevents polymerization of the monomeric vinylidene cyanide or homolog in the liquid pyrolysis product.

As disclosed hereinabove, it is desirable that an inhibitor be added to the crude liquid pyrolysis product in order to prevent polymerization of the monomeric vinylidene cyanide after it is removed from the quench zone. The inhibitor is added to the crude pyrolysis product either in quench nozzle 20 or tank 21, or both, being drawn from storage tank 27 and fed by metering pump 28 through lines 29 and/or 30 into the crude liquid pyrolysis product. The crude pyrolysis product is removed from the quench system continuously and fed through lines 31 into the crude pyrolysis product storage tank 32 which is cooled by a refrigerant which is continuously passed through coil 33.

The crude liquid pyrolysis product in tank 32 may be used as such or may be drawn off through purification line 34 and purified by distillation or by one of several other methods. For example, monomeric vinylidene cyanide can be recovered from the crude pyrolysis product in substantially pure form by treating the pyrolysis product with a conjugated diolefin such as butadiene or cyclopentadiene which reacts with the monomeric vinylidene cyanide to form a solid substituted cyclohexene which can be separated from the carboxylic acid and other impurities and pyrolyzed at temperatures in excess of about 400° C. to give monomeric vinylidene cyanide and the conjugated diolefin.

Alternatively, the vinylidene cyanide can be recovered by pouring the liquid product into water to bring about its polymerization, after which the solid polymer can be easily separated from the liquid materials by filtration or decantation. The polymerized vinylidene cyanide can be depolymerized by pyrolysis, preferably at temperatures of 170° C. to 250° C., to give monomeric vinylidene cyanide, a process described more fully in U. S. Patent 2,535,827.

The following examples illustrate in detail the preparation of pyrolysis product comprising monomeric vinylidene cyanide according to the process of the present invention. The examples are not intended to limit the invention, however, for there are, of course, numerous possible variations and modifications in the procedures described. In the examples all parts are by weight.

Example I

Referring again to the accompanying drawing, 1-acetoxy-1,1-dicyano ethane is melted in tank 1 and passed, together with monochlorobenzene into feed tank 5. From the feed tank the solution is pumped into vaporizer 10 at such a rate that 3.33 parts of 1-acetoxy-1,1-dicyano ethane are fed into the vaporizer each hour, together with about 0.5 part of monochlorobenzene per part of the diacyl cyanide. Vapors from 10 pass into pyrolyzer 15 which contains a stainless steel helical coil, 40 feet in length, with a ⅜ inch outside diameter and a wall thickness of 0.049 inch. In the pyrolyzer the 1-acetoxy-1,1-dicyano ethane vapors are pyrolytically deacetoxylated at a temperature of 530° C. The crude pyrolysis product vapors then pass through line 19 into quench nozzle 20 where the vapors are met with a large downward flow of a mixture of monochlorobenzene and condensed crude pyrolysis product which is cooled by service water in quench liquid cooler 24 and pumped through line 25 and vent gas scrubber 26. The downward flow of quench liquid quickly flushes the condensed vapors from the condensing zone and thus prevents prolonged contact of condensed pyrolysis product with heated vapors from the pyrolyzer and consequently polymerization of the monomeric vinylidene cyanide in the condensate is substantially eliminated.

Sulfuric acid, to further aid in inhibiting the polymerization of monomeric vinylidene cyanide, is continuously metered from acid storage 27 into the quench nozzle and/or the quench liquid storage tank. The flow of acid is adjusted so that the crude pyrolysis product in storage tank 21 contains about 0.01% by weight of the acid.

The liquid pyrolysis product, which contains 28.4% of monomeric vinylidene cyanide, is continuously withdrawn through line 31 into refrigerated tank 32, from which the product can be purified or utilized in the crude form in polymerizations. A conversion of 97.1% is obtained, the conversion being calculated according to the following formula:

$$\text{Conversion} = \frac{\text{Diacyl cyanide fed to pyrolyzer} - \text{Diacyl cyanide in product}}{\text{Diacyl cyanide fed to pyrolyzer}}$$

The yield of monomeric vinylidene cyanide, based on the quantity of diacyl cyanide fed to the pyrolyzer, is 80.7%.

Examples II to IV

1-acetoxy-1,1-dicyano ethane is pyrolyzed according to the general method of Example I except that the pyrolysis conditions are varied in order to demonstrate the effect of varying temperatures, feed rates and quantity of diluent. The operational data are recorded in the table below.

Example	II	III	IV
Weight percent 1-acetoxy-1,1-dicyano ethane in feed.	66.7	100 (no diluent).	66.7.
Parts 1-acetoxy-1,1-dicyano ethane fed per hour.	6.67	10.0	6.67.
Pyrolysis tube size.	40′ × ⅜″ O. D., 0.049″ wall th.	27′ × ⅜″ O. D., 0.049″ wall th.	60′ × ⅜″ O. D., 0.049″ wall th.
Weight ratio of quench medium to vapors.	100	50	200.
Temperature, ° C.	560	520	535.
Inhibitor	0.01% sulfuric acid.	0.01% chlorosulfonic acid.	0.01% sulfuric acid.
Percent conversion.	99.1		95.8.
Percent yield	79.9	84.0	60.3.

Monomeric vinylidene cyanide or a homolog thereof is also obtained in very good yields when other diacyl cyanides of the structure set forth hereinabove, for example, 1-propionoxy-1,1-dicyano propane, 1-propionoxy-1,1-dicyano ethane, or 1-acetoxy-1,1-dicyano butane, are substituted for 1-acetoxy-1,1-dicyano ethane in the examples. Also, when other temperatures in the range of 300° C. to 800° C. are utilized or when the process is carried out utilizing other of the diluents disclosed hereinabove, the process operates efficiently to give high yield of the desired products.

Although specific examples of the invention have been herein described, it is not intended to limit the invention solely thereto, but to include all of the variations and modifications falling within the spirit and scope of the appended claims.

We claim:

1. In the method for the preparation of monomeric 1,1-dicyano ethylene and its lower alkyl 2-substituted homologs by the vapor phase pyrolytic deacyloxyation of a diacyl cyanide at a temperature of 300 to 800° C., the step of rapidly condensing the hot pyrolysis vapors by bringing a stream of hot pyrolysis vapors into concurrent flow with a moving stream of a cold inert quench liquid, the weight ratio of quench liquid to pyrolysis product being at least 50 to 1 and the said quench liquid containing an inert liquid aromatic compound and being at a temperature not higher than room temperature.

2. In the method of preparing monomeric 1,1-dicyano ethylene by the vapor phase pyrolytic deacetylation of 1-acetoxy-1,1-dicyano ethane at atmospheric pressure and at a temperature of 500 to 600° C., the improvement which comprises rapidly condensing the pyrolysis product vapors by bringing a stream thereof at a temperature above the dew point of said vapors into concurrent flow with a moving stream of a cold inert quench liquid selected from the class consisting of liquid aromatic hydrocarbons and liquid halogenated aromatic hydrocarbons, the weight ratio of said quench liquid to pyrolysis product being at least 50 to 1 and the said quench liquid being at a temperature not higher than room temperature, and rapidly removing the condensed pyrolysis product and quench liquid from contact with hot incoming pyrolysis vapors.

3. The method of claim 2 in which the quench liquid comprises a mixture of the cooled condensate resulting from the pyrolysis at 500 to 600° C. of 1-acetoxy-1,1-dicyano ethane and condensing the effluent vapors, and at least one other liquid selected from the class consisting of liquid aromatic hydrocarbons and liquid halogenated aromatic hydrocarbons.

4. In the method of preparing 1,1-dicyano ethylene by the vapor phase pyrolytic deacetylation of 1-acetoxy-1,1-dicyano ethane at a temperature of 300 to 800° C., the improvement which comprises vaporizing a solution of said 1-acetoxy-1,1-dicyano ethane in an inert solvent selected from the class consisting of liquid aromatic hydrocarbons and liquid halogenated aromatic hydrocarbons, pyrolyzing the resultant vapors at atmospheric pressure and at a temperature of 300 to 800° C. whereby said 1,1-dicyano ethylene is formed, rapidly condensing the pyrolysis product vapors by bringing a stream thereof, at a temperature above the dew point of said vapors, in concurrent flow with a moving stream of a cold inert quench liquid containing an inert aromatic liquid, the weight ratio of quench liquid to pyrolysis product being at least 50 to 1 and the temperature of said quench liquid being not in excess of room temperature, and rapidly flowing the combined stream of pyrolysis condensate and quench liquid away from contact with hot incoming pyrolysis vapors.

5. In the method of preparing 1,1-dicyano ethylene by the vapor phase pyrolytic deacyloxyation of 1-acetoxy-1,1-dyciano ethane at atmospheric pressure and at a temperature of 300 to 800° C., the improvement which comprises rapidly condensing the pyrolysis product vapors by bringing a stream thereof into concurrent flow with a moving stream of a cold inert quench liquid containing an inert aromatic compound, the weight ratio of quench liquid to pyrolysis product being at least 50 to 1 and the said quench liquid being at a temperature not higher than room temperature, adding to the condensate as it forms an inhibitor selected from the class consisting of sulfuric acid, and chlorosulfonic acid, and rapidly flowing the combined stream of pyrolysis condensate, quench liquid and inhibitor from further contact with hot incoming pyrolysis vapors.

6. The method of claim 5 in which the quench liquid is a mixture of monochlorobenzene and the cooled pyrolysis condensate obtained from the pyrolysis at 500 to 600° C. of 1-acetoxy-1,1-dicyano ethane and condensing the effluent vapors, and the inhibitor is sulfuric acid.

LOUIS F. REUTER.
RICHARD D. SMITH.

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