# United States Patent [19]

Fitzpatrick et al.

[11] **3,908,046** 

[45] **Sept. 23, 1975** 

[54]	P-XYLENE VAPOR PHASE POLYMERIZATION COATING OF ELECTROSTATOGRAPHIC PARTICLES			
[75]	Inventors:	John W. Fitzpatrick, Fairport; Rudolph Forgensi, Webster; Robert G. Johnston, Rochester; H. Ronald Thomas, Penfield, all of N.Y.		
[73]	Assignee:	Xerox Corporation, Stamford, Conn.		
[22]	Filed:	Feb. 25, 1974		
[21]	Appl. No.:	445,376		
[52]	U.S. Cl			
[56]	LINIT	References Cited		
3,300,		57 Gorham et al 117/4 X		
	-			

3,526,533	9/1970	Jacknow et al	117/100 M
3,600,216	8/1971	Stewart	117/100 X
3,672,928	6/1972	Madrid et al	117/100 X
3,833,366	9/1974	Madrid et al	117/100 X

Primary Examiner-Michael R. Lusignan

[57] ABSTRACT

A particulate substrate is coated with a p-xylylene polymer by subliming a cyclic p-xylylene, pyrolyzing the resulting vapor to form a vaporous diradical, and contacting the vaporous diradical with an agitated bed of the substrate particles. The diradical vapor and particulate substrate are brought into intimate association and contact sufficient that the polymerization occurs even at temperatures above the ceiling condensation temperature of the particular diradical.

9 Claims, 3 Drawing Figures

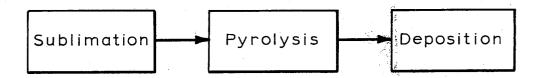
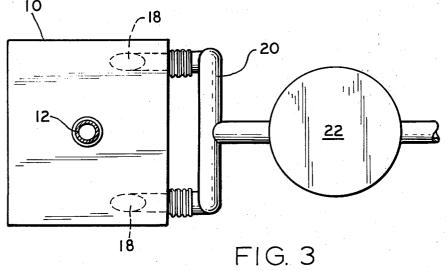


FIG. 1 Sublimation Pyrolysis Deposition -12 Cold Vacuum Trap Pump 22 24 20 F1G. 2 81 10



## P-XYLENE VAPOR PHASE POLYMERIZATION COATING OF ELECTROSTATOGRAPHIC **PARTICLES**

#### BACKGROUND OF THE INVENTION

The present invention relates generally to the coating of particulate materials. More specifically, the invention is directed toward a process for coating electrostatographic particles with p-Xylylene polymer via vapor phase polymerization.

The present invention is further related to a process for producing improved electrostatographic developing materials.

While ordinarily capable of producing good quality images, conventional developing materials suffer seri- 15 ous deficiencies in certain areas. The developing materials must flow freely to facilitate accurate metering and even distribution during the development and developer recycling phases of the electrostatographic process. Some developer materials, though possessing 20 desirable properties such as proper triboelectric characteristics, are unsuitable because they tend to cake, bridge and agglomerate during handling and storage. Adherence of carrier particles to reusable electrostatographic imaging surfaces causes the information of un- 25 desirable scratches on the surfaces during the image transfer and surface cleaning steps. The tendency of carrier particles to adhere to imaging surfaces is aggravated when the carrier surfaces are rough and irregular. The coatings of most carrier particles deteriorate rap- 30 idly when employed in continuous processes which require the recycling of carrier particles by systems such as bucket conveyors partially submerged in the develcoating separates from the carrier core. The separation may be in the form of chips, flakes or entire layers and is primarily caused by fragile, poorly adhering coating material which fails upon impact and abrasive contact with machine parts and other carrier particles. Carriers 40 condensation temperature of the diradicals. having coatings which tend to chip and otherwise separate from the carrier core or substrate must be frequently replaced thereby increasing expense and loss of productive time. Thus, generally, coated carrier particles having coatings which tend to chip or separate from the carrier core cannot be reclaimed and reused after many machine cycles. Print deletion and poor print quality occur when carriers having damaged coatings are not replaced. Fines and grit formed from carrier disintegration tend to drift and form undesirable and damaging deposits on critical machine parts. Many carrier coatings having high compressive and tensile strength either do not adhere well to the carrier core or do not possess the desired triboelectric characteristics. In addition, carriers having discontinuous coatings generally promote adhesion failure between the carrier substrate and the carrier coating materials giving rise to the aforementioned problems and result in variations in triboelectric characteristics, premature discharge of the photoconductive imaging surface causing degradation of the electrostatic latent image, scratching of the imaging surface, not to mention manufacturing difficulties in reproducing carriers having discontinuous coatings. Further the triboelectric and flow characteristics of many carriers are adversely affected when relative humidity is high. For example, the triboelectric values of some carrier coatings fluctuate with changes in rela-

tive humidity and are not desirable for employment in electrostatographic systems, particularly in automatic machines which require carriers having stable and predictable triboelectric values.

Another factor affecting the stability of carrier triboelectric properties is the susceptibility of carrier coatings to "toner impaction." When carrier particles are employed in automatic machines and recycled through many cycles, the many collisions which occur between the carrier particles and other surfaces in the machine cause the toner particles carried on the surface of the carrier particles to be welded or otherwise forced onto the carrier surfaces. The gradual accumulation of impacted toner material on the surface of the carrier causes a change in the triboelectric value of the carrier and directly contributes to the degradation of copy quality by eventual destruction of the toner carrying capacity of the carrier.

Thus, it will be appreciated that there is a continuing need for better developer materials and improved coatings for carrier particles, in particular.

It has heretofore been suggested that substrates, including particular materials, may be coated or encapsulated with p-xylylene polymers. For example, U.S. Pat. No. 3,300,332 discloses a process wherein a cyclic dip-xylylene is vaporized and pyrolyzed to form reactive diradicals. These diradicals are then condensed on a particulate substrate to form a polymeric coating.

In the prior art process, however, it is necessary to cool the vaporous diradicals to below their "ceiling condensation temperature" in order to obtain condensation and polymerization. This ceiling condensation temperature for the various p-xylylene diradicals is said Deterioration occurs when portions of or the entire 35 to range from about 25° to 140°C. Since the vaporous diradicals are at an extreme, elevated temperature as they exit from the pyrolysis zone of the process, the prior art teaches that the vapor must be cooled—or that the substrate be maintained-below the ceiling

> Due to the excellent physical characteristics and favorable chemical properties exhibited by p-xylylene polymers, these materials may be advantageously utilized as coatings for electrostatographic particles and, specifically, for the carrier beads of electrostatographic developing materials.

> However, the extremely small size of the electrostatographic particles makes implimentation of the prior art processes difficult. For example, when attempting to use the process disclosed in U.S. Pat. No. 3,300,332 to coat electrostatographic particles having an average diameter of about 100 microns, agglomeration of the substrate material occurs which adversely affects the efficiency of the process and the quality of the product.

# SUMMARY OF THE INVENTION

The present invention is directed toward an improved process for the coating of particulate materials. Generally, the vapor phase polymerization process of the present invention makes possible the coating of very small particulate matter, as for example electrostatographic particles, with p-xylylene polymers. Significantly, according to the present invention it is not necessary to cool the vaporous diradicals nor the particulate substrate to below the ceiling condensation temperature in order to effect polymerization. Thus, the vaporous diradicals may enter directly into the poly30

·

merization or deposition zone from the pyrolysis zone without the need of any cooling systems.

In accordance with the process of the present invention, the particulate material which is to be coated is maintained in continuous agitation and motion in order to provide a maximum surface area in contact with the vaporous diradicals. It has been found that the use of a high frequency vibrating chamber is particularly advantageous when coating particles having an average diameter of less than 250 microns.

Furthermore, it has now been discovered that forcing the vaporous diradicals to travel a circuitous path directly through the agitated bed of particulate material provides sufficient contact to effect polymerization, even at temperatures above the ceiling condensation 15 temperature of the particular p-xylylene diradical.

When vapor phase polymerization of p-xylylene is employed, according to the present invention, to coat electrostatographic carrier beads, it has been found that the coatings are uniform and that they adhere tenaciously to the carrier substrates. Moreover, the coatings are resistant to cracking, chipping, flaking and disintegration. The coatings are also non-tacky and of sufficient hardness at normal operating temperatures so as to minimize impaction.

Finally, carrier beads coated with p-xylylene polymers in accordance with the techniques of the present invention have been found to have a greatly increased service life.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The novel features which are believed to be characteristic of the invention are set forth in the appended claims. The invention itself, however, together with further objects and attendant advantages thereof, will best be understood by reference to the following description taken in connection with the accompanying drawings, in which:

FIG. 1 is a schematic representation of the vapor phase polymerization process.

FIG. 2 is a side elevational view of an apparatus which may be utilized to effectuate the deposition step of the process in accordance with the present invention.

FIG. 3 is a plain view of the apparatus illustrated in <sup>45</sup>

# DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, it has now been discovered that p-xylylene polymeric coatings can be produced on particulate substrates, and particularly on electrostatographic particulate substrates, without first cooling the vaporous p-xylylene diradical to below its ceiling condensation temperature.

This discovery is in striking contrast to the prior art which teaches that the polymerization mechanism requires the initial condensation of the diradical before polymerization. While the theory underlying this discovery is not completely understood, it is believed that as the temperature of the substrate to be coated increases past the ceiling condensation temperature, the adherence of the diradical to the surface of the substrate is minimized. That is, as the temperature within the deposition zone increases, the diradical's "sticking coefficient", its ability to adhere to the substrate, decreases. Thus, for a given number of collisions fewer diradicals will stick to the substrate. It is believed,

therefore, that by greatly increasing the number of collisions, sufficient adherence of diradical to the substrate is effected to accommodate the polymerization reaction.

It has also been found that by drawing the vacuum ordinarily employed in the vapor phase polymerization process directly through the agitated bed of particles the desired contact is provided.

It should be noted that the process of the present invention is particularly advantageous when employed in
a batch system. It has been considered, heretofore, difficult to utilize a batch system in the deposition portion
of the process, since in such a system it is difficult to
maintain substrate temperatures below the ceiling condensation temperature. The present invention, of
course, eliminates this problem.

In carrying out the process of the present invention, p-xylylene cyclic dimer and derivatives thereof, or both, may be employed as the starting material.

The reactive vaporous diradicals hereinabove mentioned can be produced by the thermal homolytic cleavage of at least one cyclic dimer represented generally by the structure:

wherein R and R' are nuclear substituents which may be the same or different, x and y are integers from 1 to 4, inclusive, thus forming two separate reactive vaporous diradicals having the structure:

and

Thus, where x and y are the same, and R and R' are the same, two moles of the same diradical are formed, and when condensed yield a substituted or unsubstituted homopolymer having the structure:

When R and R' and/or x and y are different, polymerization of such diradicals will yield copolymers having the general structure:

It is also possible to combine several different dimers with various nuclear substituents to form a large number of different and often complicated polymers. Of course, the formation of such polymers is well known to those skilled in the art. Furthermore, analogous systems having fused aromatic rings in the dimer structure and polymers resulting therefrom should not be considered the scope of this invention and are known to those skilled in the art.

Inasmuch as the coupling of these reactive diradicals involves the methylene linkages, many unsubstituted or nuclear substituted p-xylylene polymers can be prepared. Thus, the substituent group can be any organic or inorganic group which can normally be substituted on aromatic nuclei. Illustration of such substituent groups are alkyl, aryl, alkenyl, amino, cyano, carboxyl, alkoxy, hydroxy alkyl, carbaloxy, hydroxyl, nitro, halogen, and other similar groups which may normally be substituted on aromatic nuclei. Otherwise, the position on the aromatic ring is filled by a hydrogen atom.

Particularly preferred of the substituted groups are those simple hydrocarbon groups such as the lower alkyls like methyl, ethyl, propyl, butyl, hexyl; lower aryl hydrocarbons such as phenyl alkylated phenyl, naphthyl; and the halogen groups, particularly chlorine, bromine, iodine, and fluorine because electrostatographic carrier coating materials having maximum adhesion to carrier substrates and stable triboelectric properties are obtained.

The substituted di-p-xylylenes from which these reactive diradicals are prepared, can be prepared from the cyclic dimer, di-p-xylylene, by appropriate treatment such as halogenation, acetylation, nitration, alkylation, and like methods of introduction of substituent groups 60 onto aromatic nuclei.

Referring now to FIG. 1, it will be seen that the vapor phase polymerization process as employed in the present invention consists, generally, of three steps: sublimation, pyrolysis, and deposition.

In the process of the present invention a di-p-xylylene cyclic dimer is first vaporized from the solid state at low temperatures of between about 100° and 250°C. This primary sublimation step, rather than direct pyrolysis, is used to prevent local overheating and degradation of the dimer and also to insure a more efficient pyrolysis. The sublimation step, however, is not absolutely critical to the process.

In the pyrolytic step of the process, the reactive diradicals are prepared by pyrolyzing the dimer vapor at a temperature less than about 800°C, and preferably at a temperature between about 600°C and 780°C. While pyrolysis begins at temperatures as low as about 450°C, operation in the range of from about 450° to 550° serves only to increase the time of reaction and may also result in entraining unpyrolyzed dimer in the polymer film. At temperatures above about 800°C cleavage of the dimer substituent group may occur resulting in polyfunctional radical species causing cross-linking or highly branched polymers.

The pyrolysis temperature is essentially independent of the operating pressure. It is, however, preferred that reduced or sub-atmospheric pressures be employed. For most operation, pressures within the range of 0.0001 to 10 mm Hg. absolute are most practical. However, if desired, greater pressures can be employed. Likewise, if desirable, inert vaporous diluents such as nitrogen, argon, carbon dioxide, steam, and the like can be employed to vary the optimum temperatures of operation or to change the total effective pressure in the system.

In the deposition step of the process the reactive diradicals formed in the manner described above are made to contact or impinge upon the surface of the particulate material to be coated. As the diradicals adhere or collect upon the surface of the particles they spontaneously polymerize to form a uniform coating of p-xylylene polymeric material.

When a process run is first started, the particular substrate and the deposition chamber are, generally, above room temperature. This is due to the fact that the pyrolysis zone is preheated and evacuated through the deposition chamber prior to the start of sublimation. Moreover, the temperature of the particulate substrate rises further during the run itself. This increase in temperature is caused by several factors. First, the diradical vapor entering the deposition chamber is at an elevated temperature; second, the polymerization reaction is of an exothermic character; and third, agitation of the particulate material develops heat through friction. Therefore, the temperature of the particulate substrate is above the ceiling condensation temperature of p-Xylylene (25°-30°C) throughout the polymerization 55

In spite of this increased temperature, adherence of the diradicals on the surface of the particles and their polymerization thereon can still be effected.

Thus, as is illustrated in FIG. 2, the vaporous diradical, designated by the arrows, enters the deposition chamber 10 via the flexible tubing 12. The chamber 10 comprises an elongated, roundbottom trough or tub which subjects the material contained therein to high-frequency vibration by means of the electromagnetic mechanism 14. It is, of course, necessary that the particulate material be maintained in continuous motion

to insure uniformity of coating thereon. The agitation of the particulate substrate also serves to increase the surface area exposed to the diradical vapor. This, in turn, results in an increased number of collisions between the diradicals and the substrate thereby further 5 enhancing the rate of polymerization.

A suitable device, which performs satisfactorily as a vibrating deposition chamber, is manufactured under the trade name Vibrodyne by Vibrodyne, Inc.

within the deposition chamber 10 above the vacuum exhaust ports 18. This arrangement insures that the diradical vapor must travel by a circuitous path through the agitated bed of particulate substrate. This, of course, is important so as to provide sufficient contact 15 between the diradical vapor and the surfaces of the substrate to allow for polymerization of the film coating even at temperatures above the ceiling condensation temperature.

As is shown in FIGS. 2 and 3 a plurality of vacuum 20 ports 18 may be utilized to assure a uniform vapor flow throughout the particulate material. Any diradical vapor which does not polymerize within chamber 10 passes via conduit 20 through a cold trap 22 which protects the vacuum pump 24 from contamination.

While various apparatus may be employed to maintain the particulate material in a state of continuous motion, the deposition chamber 10 disclosed above and illustrated most clearly in FIG. 2 has proven particularly effective. For example, when electrostatographic 30 carrier beads having a size of about 100 microns are used as the particulate substrate, coating efficiency is improved using the vibrating tub described above in comparison to the rotating drum systems described in the prior art.

Moreover, the desposition chamber 10 disclosed herein includes the further advantage of being expeditiously assembled to the other apparatus used in the process. For example, the limited motion association with the vibration of the chamber 10 is easily accommodated by using flexible conduit to connect the chamber with the pyrolysis oven and the vacuum pump. Accordingly, the need for vacuum seals is obviated.

Any suitable electrostatographic carrier coating thickness may be produced via the process of the present invention. However, a carrier coating having a thickness at least sufficient to form a thin continuous film on a substrate is preferred because the carrier coating will then possess sufficient thickness to resist abrasion and prevent pinholes which adversely affect 50 the triboelectric properties of the coated carrier particles. Generally, for cascade and magnetic brush development, the p-xylylene polymer carrier coating may comprise from about 50 angstroms to about 5 microns 55 in thickness. Preferably, the p-xylylene polymer electrostatographic carrier coating should comprise from about 500 angstroms to about 1 micron in thickness because maximum durability, toner impaction resistance, and copy quality are achieved.

Any suitable well-known coated or uncoated carrier material may be employed as the particulate substrate for the polymerization process of this invention. Typical carrier core materials include sodium chloride, ammonium chloride, aluminum potassium chloride, Ro- 65 chelle salt, sodium nitrate, potassium chlorate, granular zircon, granular silicon, methyl methacrylate, glass, silicon dioxide, flintshot, iron, steel, ferrite, nickel, carbo-

rundum and mixtures thereof. Many of the foregoing and other typical carrier materials are described by L. E. Walkup in U.S. Pat. No. 2,618,551; L. E. Walkup et al in U.S. Pat. No. 2,638,416; E. N. Wise in U.S. Pat. No. 2,618,552; and C. R. Mayo in U.S. Pat. Nos. 2,805,847 and 3,245,823. An ultimate coated carrier particle having an average diameter between about 1 micron to about 1,000 microns may be produced. However, a coated carrier particle having an average diame-The particulate substrate 16 is maintained at a level 10 ter between about 50 microns and about 600 microns is preferred in cascade systems because the carrier particle then possesses sufficient density and inertia to avoid adherence to the electrostatic images during the cascade development process. Adherence of carrier particles to an electrostatographic drum is undesirable because of the formation of deep scratches on the drum surface during the image transfer and drum cleaning steps, particularly where cleaning is accomplished by a web cleaner such as the web disclosed by W. P. Graff, Jr., et al, in U.S. Pat. No. 3,186,838.

> The following examples further define and describe the polymerization process of the present invention.

# EXAMPLE I

Electrostatographic steel carrier beads having an average size of about 450 microns are coated via the following procedure. A supply of p-Xylylene dimer is placed in a sublimer which is heated to a temperature of about 225° to 240°C. The sublimed vapors enter at a rate of about 10.4 gms/min. into the pyrolysis furnace which has been preheated at about 680°C and is maintained at a vacuum of about 300 microns of Hg. In the pyrolysis zone the dimer is converted to reactive diradical vapor which passes into the deposition chamber. The deposition chamber contains the carrier beads which are maintained in a state of continuous motion and at a level which covers the vacuum exhaust ports. Thus, the diradical vapors are forced to follow a circuitous path through the agitated bed of electrostatographic particles which reaches a temperature of about 270°C. The run continues for about 105 minutes during which time about 76 percent of the original dimer has been converted to a uniform, polymeric film coating on the carrier beads. The temperature within the nonagitated bed of coated carrier beads after the run has been terminated is about 60°C.

#### **EXAMPLE II**

Electrostatographic steel carrier beads having an average size of about 450 microns are coated via the following procedure. A supply of p-Xylylene dimer is placed in a sublimer which is heated to a temperature of about 225°C to 240°C. The sublimed vapors enter at a rate of about 10.4 gms/min, into the pyrolysis furnace which has been preheated to about 770°C and is maintained at a vacuum of about 300 microns of Hg. In the pyrolysis zone the dimer is converted to reactive diradical vapors which pass into the deposition chamber. The deposition chamber contains the carrier beads which are maintained in a state of continuous motion and at a level which covers the vacuum exhaust ports. Thus, the diradical vapors are forced to follow a circuitous path through the agitated bed of electrostatographic particles which reaches a temperature of about 290°C. The run is continued for about 105 minutes during which time about 80 percent of the original dimer has been converted to a uniform, polymeric film coating on

the carrier beads. The temperature within the non-agitated bed of coated carrier beads after the run has been terminated is about 55°C.

#### **EXAMPLE III**

Ferrite carrier beads having an average size of about 100 microns are coated via a process similar to that disclosed in Examples I and II. However, the dimer is sublimed at a temperature of about 160°C, and flows at a rate of about 0.6 gms/min. into the pyrolysis oven 10 which is preheated to about 680°C. The run proceeds for about 90 minutes during which time about 82.5 percent of the original dimer is converted to a uniform polymeric coating on the ferrite carrier beads. The temperature within the bed of coated carrier beads at the 15 termination of the run is about 52°C.

The following examples were run as were examples I-III with the different process parameters as listed.

particulate substrate	<ul> <li>450 micron steel</li> </ul>	
	beads	
sublimation temperature	— 170°C	
pyrolysis temperature	— 680°C	
flow rate of vapor	<ul> <li>1.71 gms/min.</li> </ul>	
run time	— 35 minutes	
percent dimer converted to	<b>—</b> 80%	
coating		
temperature of bed at end of	— 45°C	
run		
EXAME	PLE V	
particulate substrate	- 450 micron steel	
	beads	
sublimation temperature	— 80° to 170°C	
pyrolysis temperature	— 680°C	
flow rate of vapor	<ul> <li>0.46 gms/min.</li> </ul>	
run time	— 130 min.	
percent dimer converted to	- 81.1%	
coating	_+	
temperature of bed at end of	— 43℃	
run EXAMP	LE VI	
	450	
particulate substrate	— 450 micron steel	
,	beads	
sublimation temperature	— 127° to 240°C	
pyrolysis temperature	680°C	
flow rate of vapor	<ul> <li>1.33 gms/min.</li> </ul>	
run time	— 45 min.	
percent dimer converted to	<b>— 79.2%</b>	
coating	— 47°C	
temperature of bed at end of	= 4/C	
run EXAMP	LE VII	
particulate substrate	- 100 micron ferrite	
particulate substrate	beads	
sublimation temperature	− 200°C	
pyrolysis temperature	_ 550°C	
	0.84 gms/mm.	
flow rate of vapor	<ul><li>— 0.84 gms/min.</li><li>— 63 min.</li></ul>	
flow rate of vapor run time	0.84 gms/min. 63 min. 74%	
flow rate of vapor run time percent dimer converted to	<ul><li>— 63 min.</li></ul>	
flow rate of vapor run time percent dimer converted to coating	<ul><li>— 63 min.</li></ul>	
flow rate of vapor run time percent dimer converted to	— 63 min. — 74%	
Now rate of vapor run time percent dimer converted to coating temperature of bed at end of	— 63 min. — 74% — 52°C	
Now rate of vapor run time percent dimer converted to coating temperature of bed at end of run  EXAMP	— 63 min. — 74% — 52°C	
Now rate of vapor run time percent dimer converted to coating temperature of bed at end of run	- 63 min 74% - 52°C  LE VIII - 100 micron ferrite beads	
Now rate of vapor run time percent dimer converted to coating temperature of bed at end of run  EXAMP	— 63 min. — 74% — 52℃ LE VIII — 100 micron ferrite	
Now rate of vapor run time percent dimer converted to coating temperature of bed at end of run  EXAMP  particulate substrate sublimation temperature	- 63 min 74% - 52°C  LE VIII - 100 micron ferrite beads	
Now rate of vapor run time percent dimer converted to coating temperature of bed at end of run  EXAMPI  particulate substrate sublimation temperature pyrolysis temperature	- 63 min 74% - 52°C  LE VIII - 100 micron ferrite beads - 200°C	
Now rate of vapor run time percent dimer converted to coating temperature of bed at end of run  EXAMP  particulate substrate sublimation temperature pyrolysis temperature flow rate of vapor	- 63 min 74% - 52°C  LE VIII - 100 micron ferrite beads - 200°C - 550°C - 0.99 gms/min 54 minutes	
Now rate of vapor run time percent dimer converted to coating temperature of bed at end of run  EXAMP  particulate substrate sublimation temperature pyrolysis temperature flow rate of vapor run time	- 63 min 74% - 52°C  LE VIII  - 100 micron ferrite beads - 200°C - 550°C - 0.99 gms/min.	
Now rate of vapor run time percent dimer converted to coating temperature of bed at end of run  EXAMP:  particulate substrate sublimation temperature pyrolysis temperature flow rate of vapor run time percent dimer converted to	- 63 min 74% - 52°C  LE VIII - 100 micron ferrite beads - 200°C - 550°C - 0.99 gms/min 54 minutes	
Now rate of vapor run time percent dimer converted to coating temperature of bed at end of run  EXAMP  particulate substrate sublimation temperature pyrolysis temperature flow rate of vapor run time percent dimer converted to coating	- 63 min 74% - 52°C  LE VIII - 100 micron ferrite beads - 200°C - 550°C - 0.99 gms/min 54 minutes	
Now rate of vapor run time percent dimer converted to coating temperature of bed at end of run  EXAMP:  particulate substrate sublimation temperature pyrolysis temperature flow rate of vapor run time percent dimer converted to coating temperature of bed at end of run	- 63 min 74% - 52°C  LE VIII  - 100 micron ferrite beads - 200°C - 550°C - 0.99 gms/min 54 minutes - 70.9% - 51°C	
Now rate of vapor run time percent dimer converted to coating temperature of bed at end of run  EXAMP  particulate substrate sublimation temperature pyrolysis temperature flow rate of vapor run time percent dimer converted to coating temperature of bed at end of	- 63 min 74% - 52°C  LE VIII  - 100 micron ferrite beads - 200°C - 550°C - 0.99 gms/min 54 minutes - 70.9% - 51°C	
Now rate of vapor run time percent dimer converted to coating temperature of bed at end of run  EXAMP  particulate substrate sublimation temperature pyrolysis temperature flow rate of vapor run time percent dimer converted to coating temperature of bed at end of run  EXAMP	- 63 min 74% - 52°C  LE VIII  - 100 micron ferrite beads - 200°C - 550°C - 0.99 gms/min 54 minutes - 70.9% - 51°C	
Now rate of vapor run time percent dimer converted to coating temperature of bed at end of run  EXAMP:  particulate substrate sublimation temperature pyrolysis temperature flow rate of vapor run time percent dimer converted to coating temperature of bed at end of run	- 63 min 74% - 74% - 52°C  LE VIII  - 100 micron ferrite beads - 200°C - 550°C - 0.99 gms/min 54 minutes - 70.9% - 51°C  PLE IX	

#### EXAMPLE IX - Continued

pyrolysis temperature	— 680°C	
flow rate of vapor	- 0.51 gms/min.	
run time	- 165 minutes	
percent dimer converted to coating	<b>—</b> 77.3%	
temperature of bed at end of	— 55°C	
EXAN	1PLE X	
particulate substrate	- 250 micron steel	
•	beads	
sublimation temperature	— 150 to 210°C —	
pyrolysis temperature	— 640°C	
flow rate of vapor	<ul> <li>— 0.142 gms/min.</li> </ul>	
run time	- 240 minutes	
percent dimer converted to coating	70.9%	
temperature of bed at end of	— 45°C	

Of course, it is to be understood that various modifications of the preferred embodiments of the vapor phase polymerization process disclosed herein may be made without departing from the spirit and scope of the 25 present invention or without loss of its attendant advantages.

What is claimed is:

40

45

50

- 1. A process for coating electrostatographic carrier particles having an average diameter of between about 1 micron and about 1,000 microns with a p-xylylene polymeric material comprising the steps of:
  - a. subliming a cyclic di-p-xylylene dimer to form a dimer vapor,
  - b. pyrolyzing said dimer vapor in a vacuum of between about 0.0001 and 10.0 millimeters of mercury to form vaporous p-xylylene diradicals,
  - c. agitating a bed of said carrier particles within a high frequency vibrating chamber, and
  - d. contacting said vaporous p-xylylene diradicals with said agitated bed of carrier particles at a temperature above about 30°C by drawing said vacuum through said agitated bed of carrier particles thereby forcing said vaporous diradicals to travel a circuitous path directly through said agitated bed of carrier particles whereby sufficient contact is effected between said carrier particles and said vaporous diradicals to allow polymerization of said diradicals on said carrier particles at temperatures above the ceiling condensation temperature of said vaporous p-xylylene diradicals.
- 2. A process for coating electrostatographic carrier particles in accordance with claim 1 wherein said bed of carrier particles is maintained within said vibrating chamber at a level above the vacuum exhaust parts of said chamber to insure that said vaporous diradicals travel said circuitous path through said bed of said carrier particles.
  - 3. A process for coating electrostatographic carrier particles in accordance with claim 1 wherein said carrier particles are at a temperature above about 40°C and said cyclic di-p-xylylene is unsubstituted di-p-xylylene.
  - 4. A process for coating electrostatographic carrier particles in accordance with claim 1 wherein said carrier particles are metallic carrier beads having an average diameter between about 50 and 600 microns.

- 5. A process for coating electrostatographic carrier particles in accordance with claim 4 wherein said metallic carrier beads comprise steel.
- 6. A process for coating electrostatographic carrier particles in accordance with claim 1 wherein said carrier particles are ferrite carrier beads having an average diameter of less than about 100 microns.
- 7. A process for coating electrostatographic carrier particles in accordance with claim 1 wherein said pyrolysis is conducted at temperatures of between about 10 680°C and 780°C.
- 8. A process for coating electrostatographic carrier particles having an average diameter of between about 1 micron and about 1,000 microns with a homopolymer of p-xylylene comprising the steps of:
  - a. heating unsubstituted, cyclic di-p-xylylene in a vacuum of between about 0.0001 and 10.0 millimeters of mercury to a temperature of between about 100°C and 240°C thereby forming vaporous cyclic di-p-xylylene dimer;
  - b. pyrolyzing said vaporous dimer to form vaporous p-xylylene diradicals;
  - c. agitating a bed of said carrier particles within a high frequency vibrating chamber; and
  - d. contacting said vaporous p-xylylene diradicals with 25 said agitated bed of carrier particles at a temperature above about 30°C by drawing said vacuum through said agitated bed of carrier particles thereby forcing said vaporous diradicals to travel a circuitous path directly through said agitated bed 30 of carrier particles whereby sufficient contact is ef-

- fected between said carrier particles and said vaporous diradicals to allow polymerization of said diradicals on said carrier particles at temperatures above the ceiling condensation temperature of said vaporous p-xylylene diradicals.
- 9. In a process for coating electrostatographic carrier particles having an average diameter of between about 1 micron and about 1,000 microns with a p-xylylene polymeric material comprising the steps of:
  - a. subliming a cyclic di-p-xylylene dimer to form a dimer vapor, and
  - b. pyrolyzing said dimer vapor in a vacuum of between about 0.0001 and 10.0 millimeters of mercury to form vaporous p-xylylene diradicals, the improvement comprising;
  - c. agitating a bed of said carrier particles within a high frequency vibrating chamber, and
  - d. contacting said vaporous p-xylylene diradicals with said agitated bed of carrier particles at a temperature above about 30°C by drawing said vacuum through said agitated bed of carrier particles thereby forcing said vaporous diradicals to travel a circuitous path directly through said agitated bed of carrier particles whereby sufficient contact is effected between said carrier particles and said vaporous diradicals to allow polymerization of said diradicals on said carrier particles at temperatures above the ceiling condensation temperature of said vaporous p-xylylene diradicals.

### 45

# 50

# 55

### 60