COATING METHOD AND APPARATUS FOR DEPOSITION OF POLYMER-FORMING VAPOR UNDER VACUUM

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ABSTRACT OF THE DISCLOSURE

A method and apparatus is provided for coating substrate surfaces with a polymer-forming vapor. The substrate is coated in a vapor deposition zone having terminal differential pressure gaseous seals. The deposition zone and substrate handling means are confined within a housing adapted to provide a pressure envelope to aid in confining polymer forming vapors to the deposition zone.

This invention relates to a method and apparatus for coating substrate surfaces with a polymer-forming vapor. More particularly, this invention relates to a coating method and apparatus for continuously or semi-continuously coating metallic or non-metallic substrates of various cross-sectional profiles with a continuous polymeric film formed by vapor deposition.

Recently, it has been found that extremely thin, yet continuous, polymeric films can be vapor deposited on a wide variety of substrate surfaces. Foremost, among such vapor-deposited polymers are the polymers of the p-xylene family. Poly-p-xylene is insoluble in every common organic solvent at room temperature and are tough, moisture resistant and exhibit low permeability to most gases and vapors. These polymers have been found to remain tough and flexible at extremely low temperatures, thus permitting their use in electrical circuitry such as that employed in high speed switching circuits and super-conductor units. Experiments conducted at temperatures of liquid helium (−270° C.) have established that these polymers are quite resistant to breakage on flexing and that the substrate surface such as a metal foil backing member is more susceptible to fracture than is the polymer.

Poly-p-xylene is obtained by the condensation of a polymer-forming vapor comprised of vaporous diradicals having the general structure

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Y \quad \text{wherein } Y \text{ can represent any inert monovalent group as hereinbefore more fully described. These p-xylene diradicals are quite stable in the vapor phase, i.e., at temperatures above about 250° C. Upon cooling, the diradicals condense and immediately polymerize into a thin void free film of a solid poly-p-xylene which can be characterized by the general structure }
\]

\[
Y \quad Y
\]

also more fully described hereinbefore. Void-free coatings of p-xylene polymers have been prepared in this manner in thicknesses of about 100 A. units or greater.

Heretofore, vapor deposition of p-xylene polymers has been limited to batch coating of relatively small substrates such as sheetlike, flexible or rigid materials of paper, plastic, glass, metal, fabrics or other similar materials. Preparation of unsupported p-xylene films has similarly been limited to vapor coating onto a substrate and subsequent batch-wise removal by stripping. These batch-wise methods have severely limited the scope of application and commercial usefulness of the p-xylene polymer family.

The primary difficulty which has severely hindered the development of a continuous p-xylene polymeric coating operation arises from the inability which has heretofore existed in providing satisfactory means for confining the diradicals vapors during the coating operation. These vapors, under the pressures employed, behave as a highly randomly diffusive gas which penetrates minute openings and, upon contact with cool surfaces, polymerizes thereon as a tough, horny deposit which interferes with the substrate handling means such as the supporting surfaces, rollers, bearings, and other mechanical parts and soon renders these inoperative by restraining movement of said parts. These extraneous deposits on the handling means can also damage fragile, low tensile substrates such as thin aluminum foils, paper and other thinly coated products by scratching, abrading or tearing such products.

Application of known methods for confining vaporous substances have proven unsatisfactory. Mainly, these methods pertain to vaporized metals or gases which do not have the diffusive flow properties of the vapors containing p-xylene diradicals or the characteristics of the polymeric p-xylene deposits at the pressures conventionally employed in these methods. Low pressure metal vaporization or gas formation techniques result in a purely physical phase change resulting in molecularstraight-line flow which is relatively simple to contain. Most prior methods depend on passage of the substrate through gradient pressure stages. Multiple pressure graded stages such as differentially pumped vacuum chambers are connected by seals through which the substrate or coated material pass. These seals are restricted passages typically consisting of contacting resilient material or close clearance orifices. These seals are designed to minimize external air or gas leakage. Where, however, thin, yet continuous, depositions are required, these restricted designs are severely limiting because of the possibility of damage to the delicate substrates by abrading, scratching or tearing.

Accordingly, it is an object of the present invention to provide a method and apparatus for continuously or semi-continuously coating substrate surfaces of various cross-sectional profiles with a polymer-forming vapor.

It is another object of the present invention to provide a method and apparatus for continuously or semi-continuously coating substrate surfaces with extremely thin, yet continuous, coatings without damage to such delicate substrates as was caused by prior existing methods which depend on passage of such substrates through close clearance orifices.

It is still another object of the present invention to provide means for confining highly diffusive vapors and for preventing their condensation and polymerization on substrate handling means.

It is a still further object of the present invention to provide a method and apparatus for continuously or semi-continuously forming unsupported p-xylene polymeric films.

These and other objects are accomplished by the present invention one aspect of which provides an apparatus for coating substrate surfaces with a polymer-forming vapor which comprises a vapor deposition chamber, means for creating and maintaining a vacuum in said chamber, a generator adapted to provide and distribute within said
chamber a highly diffusive stream of a polymer-forming vapor, substrate handling means freely communicating with said deposition chamber and adapted to provide at least one pass of the substrate surface through a pressure envelope 36 surrounding said deposition chamber and substrate handling means adapted to provide a pressure envelope about said chamber sufficient to confine the vaporous stream thereto.

Another aspect of the present invention provides a method for coating substrate surfaces with a polymer-forming vapor which comprises feeding a substrate surface from a first zone of reduced pressure into a close clearance vapor deposition zone, contacting the substrate surface upon at least one pass of said substrate surface through the deposition zone with the polymer-forming vapor and condensing said vapor thereon to form a continuous polymeric film, said first zone encompassing said deposition zone and freely communicating therewith, said first zone adapted to be maintained at a higher pressure relative to said deposition zone to confine the polymer-forming vapors thereto, and thereafter returning the coated substrate to said first zone.

FIGURE 1 is a schematic representation, partially in section, of an embodiment of the coating apparatus of the present invention particularly suitable for single pass coating of a substrate;

FIGURE 2 is a schematic representation, partially in section, of another embodiment of the coating apparatus of the present invention which provides for continuous formation of an unsupported vapor-deposited film;

FIGURE 4 is a schematic illustration of another embodiment of the coating apparatus which employs two skewed rolls enabling a large number of passes, e.g., up to about 16 or more, per unit without a commensurate increase in the number of rolls needed for substrate handling;

FIGURE 5 is a schematic plan view of the skewed rolls shown in FIGURE 4;

FIGURE 6 is a schematic representation, partially in section, illustrating the use of a barometric leg seal which permits passage of the substrate through wide pressure differentials without allowing atmospheric in-leakage. Movement permits continuous feeding and removal of substrates to and from the deposition chamber from and to the atmosphere.

Referring now to FIGURE 1, there is shown an embodiment of the coating apparatus of the present invention adapted to provide a single pass of the substrate through the deposition chamber. Deposition chamber 10 has an inlet 12 and outlet 14 therein to allow free passage therebetween of a substrate 16 to be coated. A vacuum is created and maintained within said deposition chamber 10 by means of vacuum ports 18 and 20 externally connected to vacuum pumps (not shown). These vacuum ports are of sufficiently large volume and so spaced with respect to the deposition chamber 10 so as to provide effective removal of excess vapor and proper maintenance of vacuum conditions. The walls of the deposition chamber 10 in the immediate vicinity of the vacuum ports 18 and 20 are preferably enlarged to reduce the velocity of the vapors in those areas permitting more effective vapor removal. A generator 22 is adapted to provide and distribute through distribution nozzle 24 a stream of polymer-forming vapor to said chamber 10. Substrate handling means such as substrate supply roll 26 and windup roll 28 for the coated product along with appropriate guide rolls such as rolls 30 and 32 are adapted to provide a single pass of the substrate 16 through the deposition chamber 10. A housing 24 surrounds both the deposition chamber 10 and the substrate handling means such as rolls 26, 28, 30 and 32 and is adapted to provide a pressure envelope about said chamber 10 which cooperates with the inlet 12 and outlet 14 of said chamber 10 to confine the stream of polymer-forming vapor within the deposition chamber 10. This can be accomplished by maintaining a higher pressure in said chamber, relative to the pressure within the deposition chamber or by maintaining a lower pressure in said envelope relative to said chamber pressure. In the latter instance, however, it is considered critical that the capacity of the vacuum pumps be sufficient to provide complete removal of excess vapors.

In actual operation, the pressure within the deposition chamber 10 is reduced to from about 1.0 micron to about 25 mm. Hg as more fully described hereinafter by means of vacuum ports 18 and 20. A suitable precursor of the polymer-forming vapor is pyrolyzed in generator 22. The vaporous stream thus formed is passed through distribution nozzle 24 into the deposition chamber 10 and there deposits on the substrate 16 passing through said chamber 10. The deposition chamber 10 is preferably encompassed by a relative higher pressure envelope 36 contained within housing 34. Housing 34 is a substantially airtight chamber of suitable size and shape to accommodate both the deposition chamber 10 and substrate handling means such as substrate supply roll 26, transport handling facilities such as rollers 30 and 32 for tensioning, supporting, cooling and guiding, as well as coated substrate wind-up roll 28. Also, there can be included in said housing 34 means (not shown) for pressure measurement, chamber access, driving means for substrate supply and windup, and the like.

Deposition chamber 10 provides maximum deposition rate and efficiency by employing close clearances between the substrate 16 and walls of the deposition chamber 10 thereby providing maximum system pressure which provides maximum collision of the vaporous impurities with the substrate surfaces. Although readily apparent, the dimensions of the deposition chamber are commensurate with practical regard to the behavior of the coated substrate, e.g., warpage or edge curling tendencies of some substrates, or webs such as aluminum foil, and also the degree of polymeric build-up on the substrate walls although this can be minimized by heating said chamber walls. It has been found that a minimum clearance of about 1/4-inch is sufficient in most instances to provide free passage of the substrate through the deposition chamber without damaging the substrate or coated product. Preferably however, the clearance between the substrate and the inner walls of the deposition chamber are from about 1/2-inch to about 2 inches. Greater clearances can be employed; however, there is a substantial reduction in deposition efficiency as the clearance is increased much above 2 inches. The length of the deposition chamber 10 can vary depending upon the required residence time needed to obtain the thickness of coating desired and also practical handling limitations imposed by the substrate. For example, with thin metallic foil substrates such as aluminum foil, distances over which the foil is unsupported are kept to a minimum in order to attain proper flatness of the substrate. In such instances the length of the deposition chamber 10 which is substantially the length of the unsupported span is less than about 4 feet although a longer or shorter deposition chamber can be employed with appropriate modifications readily apparent to those skilled in the mechanical arts. The linear speed of the substrate through the deposition chamber can be varied to obtain the desired coating thickness; however, it is preferably from about 1 inch per minute to about 500 feet per minute.

The deposition chamber 10 is provided with vacuum ports 18 and 20 along guide rolls which are of sufficiently large volume and are so situated with respect to the deposition chamber proper and the inlet 12 and outlet 14 thereto as to provide for effective vapor removal. External cold traps (not shown) are preferably attached in the vacuum lines. Use of such cold traps in the vacuum lines has been found to aid in the removal of an appreciable amount of unreacted polymer forming vapor.
able amount of the condensable excess vapors, thereby increasing pumping efficiency and minimizing cleaning requirements of the vacuum lines.

Where space or other considerations do not permit vacuum ports which are of adequate size to provide substantially complete removal of the excess diradical vapors, it is preferred to have the envelope 36 between the deposition chamber 10 and the housing 34 at a relatively higher pressure although still sub-atmospheric, than that which exists within the deposition chamber 10 in order to assure no migration or leakage of diradical vapors into envelope 36 thereby preventing deposition on the substrate handling means situated in said envelope 36. Inert gases such as nitrogen, argon and the like can be injected through nozzle 38 in the housing 34 which provides communication of an external inert gas supply (not shown) with the envelope 36. This means of increasing the envelope pressure is also available when it is desired to increase the total system pressure for increased deposition rate.

Polymer-forming vapors formed in generator 22 enter the deposition chamber 10 through distribution nozzle 24 either transverse to the longitudinal axis of the substrate 16 as shown in FIGURE 1 or normal to the substrate surface as shown in FIGURE 4. The distribution nozzle 24 is preferably situated in the middle of the deposition chamber 10 thereby providing equidistribution of the vapors along the substrate length as well as facilitating confinement of the excess vapors.

The vapors containing the p-xylene diradicals can be formed by either of several techniques. The method found most convenient and preferred is by the pyrolysis at temperatures between 450° C. and 700° C. of at least one cyclic dimer represented generally by the structure

wherein Y is any monovalent inert substituent group, preferably hydrogen, although on the aromatic nucleus, it can be any inert substituent group when starting with this dimer. On pyrolysis, the dimer cleaves into two separate reactive vaporous diradicals each having the structure

Thus, where all the Y groups are hydrogen, or where the nuclear substituent on each diradical is the same, two moles of the same p-xylene diradical are formed, and when condensed yield a substituted or unsubstituted p-xylene homopolymer. When the aromatic nuclear substituent Y groups on each diradical are different, two different diradicals are formed, condensation of which will yield copolymers as hereinafter set forth.

Alpha substituted p-xylene diradicals are also prepared by the pyrolysis of an aryl bis-sulfone of the structure:

where R is a lower hydrocarbon group, and Y is any non-polar substituent. These sulfones pyrolyze on heating to temperatures of about 600°–1000° C. into sulfur dioxide and the reactive diradical

as is disclosed in copending application Ser. No. 232,247 entitled, "Decomposition of Bis-Sulfones," filed Oct. 22, 1962, which is included herewith by reference. This technique is particularly desirable for introducing alpha halo substituent groups in the polymer, outstanding of which is the highly thermally stable poly(α,ω,ω'-tetrafluoro-p-xylene).

Reactive diradicals are also prepared by the pyrolysis of a diaryl sulfone of the structure

wherein Y is a non-polar substituent. These sulfones pyrolyze on heating to temperatures of about 400°–800° C. into sulfur dioxide and 2 moles of monoradical of the formula

which disproportionates into a p-xylene and a diradical of the structure

as is disclosed in copending application Ser. No. 232,247 entitled, "Diarylsulfones and Process for the Pyrolysis Thereof to the Corresponding Diarylethanes and Polymers," filed Oct. 22, 1962, which is hereewith included by reference.

Any other technique of making the vaporous diradicals can of course be used. Since some of these techniques produce other gaseous by-products (such as SO3) and since certain of the metallic substrates employed may be subjected to attack by such by-products, care should obviously be used in selecting the metallic substrate when employing such reactive diradicals. Since the pyrolysis of the cyclic dimer di-p-xylene involves no other by-products and the dimer cleaves quantitatively into two moles of the reactive diradical, this method is most preferred. Inasmuch as the coupling and polymerization of these reactive diradicals upon the condensation of the diradicals does not involve the aromatic ring, any unsubstituted or desired substituted p-xylene polymer can be prepared since the substituent groups function essentially as an inert group. Thus, the substituent group can be any organic or inorganic group which can normally be substituted on an aromatic nuclei or on the aliphatic α-carbon atoms of such a diradical.

Notable among the monovalent inert groups that have been placed on the aromatic nuclei of aliphatic α-carbon atoms of such poly(p-xylene)s other than hydrogen are the halogens including chlorine, bromine, iodine and fluorine, alkyl groups such as methyl, ethyl, propyl, butyl and hexyl, cyano, phenyl, amino, nitro, carboxyl, benzyl and other similar groups. While some of the above groups are potentially reactive in certain conditions or with certain reactive materials, they are unreactive under the conditions of the present invention and hence are truly inert in the instant case.
The substituted di-p-xylylenes and the aryl sulfones from which these reactive diradicals are prepared, can be prepared by well known techniques. For example, the cyclic dimer, di-p-xylylene, is susceptible to halogenation, alkylation and/or oxidation and reduction techniques and like methods of introduction of such substituent groups into aromatic nuclei. Inasmuch as the cyclic dimer is a very stable product up to temperatures of about 400 °C, elevated temperature reactions can also be employed for the preparation of various substituted materials. When used herein, the term "di-p-xylylene" refers to any substituted or unsubstituted cyclic di-p-xylylene as hereinabove discussed, and the term "p-xylylene diradical" refers to any substituted or unsubstituted p-xylylene structure having a free radical on each of the alpha carbon atoms as hereinabove discussed.

In the polymerization process, the vaporous diradicals condense and polymerize nearly instantaneously at the condensation temperature of the diradicals. The coupling of these diradicals involves such low activation energy and the chain propagation shows little or no preference to the particular diradical, so that steric and electronic effects are not important as they are in vinyl polymerization. The substituted and/or unsubstituted p-xylylene homopolymers can be made by cooling the vaporous diradical down to any temperature below the condensation temperature of the diradical. It has been observed that for each diradical species, there is a definite ceiling condensation temperature above which the diradical essentially will not condense and polymerize. All observed ceilings of substituted p-xylylene diradicals have been below about 200 °C. but vary to some degree upon the operating pressure involved. For example, at 0.5 mm. Hg pressure, typical condensation and polymerization temperatures observed for the following diradicals are:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature Range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Xylylene</td>
<td>25 to 30</td>
</tr>
<tr>
<td>Chloro-p-xylylene</td>
<td>70 to 80</td>
</tr>
<tr>
<td>n-Butyl-p-xylylene</td>
<td>130 to 140</td>
</tr>
<tr>
<td>Iodo-p-xylylene</td>
<td>180 to 200</td>
</tr>
<tr>
<td>Dichloro-p-xylylene</td>
<td>200 to 250</td>
</tr>
<tr>
<td>α,α',α′,α′-Tetrafluoro-p-xylylene</td>
<td>35 to 40</td>
</tr>
</tbody>
</table>

Thus, by this process, homopolymer films are made by maintaining the substrate surface at a temperature below the ceiling condensation temperature of the particular di-radical species involved, or desired in the homopolymer. This is most appropriately termed "homopolymerizing conditions." Where several different diradicals existing in the pyrolyzed mixture have different vapor pressure and condensation characteristics, as for example, p-xylylene and chloro-p-xylylene and dichloro-p-xylylene or any other mixture with other substituted diradicals, homopolymerization will result when the condensation and polymerization temperature is selected to be at or below that temperature where only one of the diradicals condense and polymerize. Thus, for purposes within this application, the terms "under homopolymerization conditions" are intended to include those conditions where only homopolymers are formed. Therefore it is possible to deposit homopolymer film from a mixture containing one or more of the substituted diradicals when any other diradicals present have different condensation or vapor pressure characteristics, and wherein only one diradical species is condensed and polymerized on the substrate surface. Of course, other diradical species not condensed on the substrate surface can be drawn through the vacuum ports of the apparatus as hereinabove described, in vaporous form to be condensed and polymerized in a subsequent cold trap.

Inasmuch as unsubstituted p-xylylene diradicals, for example, are condensed at temperatures about 25° to 30° C, which is much lower than dichloro-p-xylylene diradicals, i.e., about 200° to 250° C, it is possible to have present such diradicals in the vapor pyrolyzed mixture along with the dichloro-substituted diradicals. In such a case, homopolymerization conditions are secured by maintaining the substrate temperature at a temperature below the ceiling condensation temperature of the substituted p-xylylene but above that of the p-xylylene, thus permitting the p-xylylene vapors to pass through the vapor ports of the apparatus without condensing and polymerizing but collecting the poly-p-xylylene in a subsequent cold trap.

It is also possible to obtain such units through the pyrolysis process hereinabove described. Copolymers of p-xylylene and substituted p-xylylene diradicals, as well as copolymers of different substituted p-xylylene diradicals wherein the substituted groups are all the same but each diradical containing a differing number of substituent groups can all be obtained through said pyrolysis process.

Copolymerization occurs simultaneously with condensation upon cooling of the vaporous mixture of reactive diradicals to a temperature below 200 °C under copolymerization conditions.

Copolymerization can be made maintaining the substrate surface at a temperature below the ceiling condensation temperature of the lowest boiling diradical desired in the copolymer, such as at room temperature or below. This is considered "copolymorizing conditions," since at least two of the diradicals will condense and copolymerize in a random copolymer at such temperature.

In the pyrolytic process of a di-p-xylylene the reactive diradicals are prepared by pyrolyzing the substituted and/or unsubstituted di-para-xylene at a temperature between about 450 °C and about 700 °C, and preferably at a temperature between about 550 °C to about 600 °C. At such temperatures, essentially quantitative yields of the reactive diradicals are secured. Pyrolysis of the starting di-p-xylylene begins at about 450°C to 550°C but such temperatures serve only to increase time of reaction and lessen the yield of polymer secured. At temperatures above about 700°C, cleavage of the substituent group can occur, resulting in a tri- or polyfunctional species causing cross-linking and highly branched polymers.

Pyrolysis temperature is essentially independent of the operating pressure. For most operations, pressures within the range of 1.0 micron to 25 mm. Hg are most practical for pyrolysis. Likewise if desirable, inert vaporous diluents such as nitrogen, argon, carbon dioxide, helium and like can be employed to vary the optimum temperature of operation or to change the total effective pressure in the system.

Various modifications of the apparatus shown in FIGURE 1 can be conveniently made to increase productivity. For example, multiple successive coating treatments can be obtained by passing the substrate through a series of deposition chambers of the type shown in FIGURE 1 all contained within a common housing. Suitable guide and cooling rolls situated in the common outer envelope can provide communication between successive deposition chambers.

A preferred embodiment shown in FIGURE 2 provides series multiple passage of the substrate through the deposition chamber with interstage passes being supported and cooled in the outer envelope. The apparatus shown in FIGURE 2 is similar to that shown in FIGURE 1 except that the substrate handling means have been modified to provide a series multipass system. Rollers 29, 30 and 31 provide multiple passage of the substrate 16 through the deposition chamber 10 and are adapted to be internally cooled. The vacuum ports of the apparatus are provided in the substrate surface and increasing the deposition rate of the p-xylylene diradicals thereon. Rollers 32, 33 and 35 are appropriate tensioning idlers and guide rolls. This embodiment provides a highly compact and economic coating apparatus.

FIGURE 3 shows another embodiment of the present invention which permits unsupported poly-p-xylylene films
to be continuously formed by being vapor cast onto a cooled, continuously moving carrier surface such as a belt or drum, continuously stripped therefrom and thereafter passed to wind-up in the outer envelope. By this method, it is possible to obtain continuous lengths of poly-p-xylene ribbon of extremely thin cross section. As shown in FIGURE 3, an endless ribbon of the film is formed by a rotating drum 19 continuously rotates within the deposition chamber 10. The ribbon is then passed through a cooling chamber 20 where it is continuously formed by being vapor cast onto a cooled, continuously moving carrier surface such as a belt or drum. The ribbon is then passed through an outlet 21 in the deposition chamber 10 to wind-up on roll 22. The apparatus can also be easily modified to permit coating of substrate surfaces and simultaneous temperature control of the substrate by contact with the drum surface. The substrate is then fed into a coater 10, and the coating process is continued until the desired thickness is achieved.

FIGURE 4 illustrates a modification of the apparatus of FIGURE 3 in which the ribbon is formed and passed through a coater 23. The ribbon is then passed to a roll 46 whose axis is skewed in relation to the axis of roll 40. The coated substrate thereafter passes through the second deposition chamber 13 equipped with vacuum ports 43 and 44 and passes between the split distribution nozzle 25 whereby the substrate surfaces are coated by condensing di-racid vapor which impinges perpendicularly on both surfaces thereof. The coated substrate is then passed to a roll 46 whose axis is skewed in relation to the axis of roll 40. The coated substrate thereafter passes through the second deposition chamber 13 equipped with vacuum ports 43 and 45 where it is additionally coated upon passage through split distribution nozzle 27 and is then returned to roll 40. Due to the cross-axis or skewed axis main process rolls, the substrate is made to follow a spiral path as it passes over the rolls and can therefore easily be made to undergo multiple passes of the type described above; the number of said passes depending solely on the size of the rollers and the amount of coating desired on a particular substrate as dictated by end-use considerations. The use of split distribution nozzles 25 and 27 enables the di-racid vapors emanating from generator 22 to impinge perpendicularly on the substrate surfaces on successive passes through the split distribution nozzles 25 and 27 thereby improving uniformity of coating across the width of the substrate substantially eliminating any problems of non-uniform coating which can arise in transverse coating.

FIGURE 5 is a plan view of the skewed axis rolls of FIGURE 4 illustrating the relationship of the roll axes. It is considered preferable that the axis of the bottom roll 40 be perpendicular to the back wall of the housing whereas the axis of the top roll 46 be skewed relative to the axis of the bottom roll 40; however, it is critical that the skewed roll, whether it be the top or bottom roll have its axis offset so that the sum of the offset distances shown as X and Y is as equal to and preferably greater than the width of the substrate to be coated. It is considered desirable that the central axis of both rolls cross at the longitudinal midpoint of each axis when viewed vertically as shown.

It is often desirable, especially in continuous coating operations, to feed the substrate and/or wind-up the coated product under normal atmospheric conditions. Due to the need for vacuum conditions in the process, however, a wide pressure differential must be overcome to allow feed or wind-up under normal conditions. It has been found that this transfer can be conveniently accomplished by passing the substrate from the atmosphere through a barometric leg seal into the deposition chamber wherein the poly-p-xylene film-forming composition is continuously deposited on the substrate which then returns to the atmosphere through another barometric leg seal and passed to wind-up. FIGURE 6 is a partial schematic illustration, partly in section, of such an atmosphere-vacuum-atmosphere transfer system. For simplicity, only that portion of the apparatus relating to the removal of the coated substrate from the deposition chamber to the atmosphere is shown. The reverse situation of feeding a substrate supply into the deposition chamber is readily apparent to those skilled in the art. The housing shown in FIGURE 3 is modified to housing 35 of FIGURE 6 by removing wind-up roll 28 from within the envelope 36 and replacing it with guide roller 39 and attaching barometric leg 48. Barometric leg 48 is a substantially air tight J-shaped housing containing a liquid metal sealant 50 and guide roller 52 for the coated product. The roller 52 and external roller 54 support the coated product passing from the sub-atmospheric envelope 36 in transit through the leg 48 to the atmosphere and wind-up on roll 28. Drain 56 controlled by valve 58 is provided in order to drain the liquid sealant 50 for convenience in threading the substrate through the roll system for start-up.

Liquid metals such as mercury or low melting alloys such as Woods metal are considered preferable for use as the liquid sealant due to the nominal size leg required as opposed to a 54 foot leg for water or oil. Moreover, the use of such liquid metals or low melting alloys substantially preclude the problem of contamination or carry-over due to wetting. Due to the possibility of alloying with mercury of some unprotected substrates, it may not always be desirable to employ a mercury barometric leg for introducing such substrates into the vacuum deposition chambers. Substrates coated with a film of poly-p-xylene, however, are completely resistant to attack or permeation by mercury or other liquid metals and are therefore readily amenable to wind-up through a mercury barometric leg seal.

The following examples are for illustrative purposes only and are not to be construed as imposing any limitations on the present invention.

**EXAMPLE I**

Employing the apparatus shown in FIGURE 1, dead soft aluminum foil 1 inch in width and 0.00025-inch gauge thickness was passed through the deposition chamber maintaining a clearance of 1/40-inch with the deposition chamber walls and was coated on both sides with a 0.0001 inch thick layer of poly-p-xylene film. An external cold trap was employed as well as a 13 cubic feet/minute mechanical rotary vacuum pump system having an estimated effective capacity for noncondensables at 6–8 cubic feet/minute, which developed an absolute pressure of about 0.8 and 0.4 mm. Hg. in the outer envelope and deposition chamber, respectively, when nitrogen at 100 cc./minute. STP was bled into the outer envelope. The nitrogen bleed raised the total system pressure thereby promoting high deposition rates. The inert gas flow also added in developing a pressure gradient from the envelope into the end openings of the deposition chamber which then swept away the excess di-racid vapors. During operation, pressure at the deposition chamber outlet rose to about 0.45–0.60 mm. Hg. The poly-p-xylene di-racidals were generated by subliming cyclic di-p-xylene at an average dimer sublimation rate of about 0.5 grams/minute in a quartz sublimation chamber connected to a quartz pyrolysis tube.
The cyclic dimer was sublimed at a temperature of about 125°-250° C. and a pressure of 0.1-1 mm. Hg absolute. The vapors were passed to the pyrolysis zone maintained at temperatures between about 650°-700° C. thereby forming the reactive p-xylene diradicals which were fed through a distribution nozzle into the deposition chamber and there condensed on the cool substrate surfaces passing therethrough. The substrate was cooled by passage over cooling rolls in the outer envelope. The rolls were cooled by recirculating temperature controlled methanol at — 20° C. rolls. The polymer, poly-p-xylene, was deposited as a transparent, flexible, tough coating on each face and the edges of the aluminum foil as it passed through the deposition chamber. Polymeric deposits on the deposition chamber walls was not considered objectionable. There was no evidence of diradical vapors entering the outer envelope.

Several runs were made in the above manner varying only the linear speed of the unsupported aluminum foil web through the deposition chamber. It was found that the average coating thickness varied with the linear speed as follows:

<table>
<thead>
<tr>
<th>Coating thickness (microns)</th>
<th>Linear speed (feet/min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>1.4</td>
</tr>
<tr>
<td>1.1</td>
<td>0.8</td>
</tr>
<tr>
<td>2.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**EXAMPLE II**

Employing the apparatus shown in FIGURE 2, a triple series passage of 1-inch-wide aluminum foil web through the deposition chamber was obtained. Clearances between the foil web and the walls of the deposition chamber were between 0.05-0.07 inch. An external cold trap was employed as well as a 24 c.f.m. mechanical vacuum pump system having an estimated effective capacity of non-condensables at 10-12 c.f.m. which developed an absolute pressure of about 0.34 and 0.27 mm. Hg in the outer envelope and deposition chamber, respectively, when nitrogen was bled into the outer envelope at 80 cc./min. STP. Pressure at the deposition chamber outlet rose during operation to about 0.30-0.40 mm. Hg. The p-xylene diradicals were produced as described in Example I with an average dimer sublimation rate of about 0.23 grams/minute. The surface of the aluminum foil webs were cooled between passes through the deposition chamber by passage over cooling rolls in the outer envelope. The rolls were cooled by recirculating temperature controlled methanol at — 20° C. within said rolls. The linear speed of the aluminum foil web through the deposition chamber was about 0.9 ft./min. with a resulting uniform coating of poly-p-xylene thereon having a thickness of about 1.6 microns per side. Deposits on the deposition chamber walls were not considered objectionable. There was no evidence of diradical vapors entering the outer envelope.

Although the present invention has been described mainly in reference to coating of substrate surfaces with films of poly-p-xylene, it is readily apparent that various modifications of the apparatus or coating process can be made to accomplish other objectives. For example, preformation of the substrate or intermix passage treatments of the partial or completely coated substrate can be made, such as vacuum metallizing, sputtering, ionic bombardment for cleaning or processing, or codeposition with metallic and/or other organic vapors from the vapor phase or as alternate deposits therewith. In these embodiments, modified deposition chambers of the present invention or those of known design for accomplishing such treatments can be employed within a common housing. Thus, the substrate can undergo a series of varying treatments upon passage through a series of deposition or treatment chambers with suitable guide and cooling rolls interposed between the chambers in the common outer envelope, employing the higher pressure envelope of the present invention, larger clearance seals at the inlet and outlets to these chambers can be used thereby eliminating any possible contamination by the fragile substrates to fragility points. As described hereinabove, vapors having highly diffusive tendencies, such as those vapors containing p-xylene diradicals, are confined to the deposition chamber thereby eliminating any fear of harmful deposits on the substrate handling means in the outer envelope deposits the use of larger inlets and outlets to the deposition chamber.

Further modifications of the apparatus of the present invention can be made to provide means of regulating the areas to be coated. Coating only one side of a substrate is often desirable in order to obtain high coating productivity, economy, and/or maximum product quality by selective use of the best surface of the substrate. In coating aluminum foil for use as capacitors, for example, it is desirable to coat only the best side, i.e., the smooth or bright side, for peak electrical functionality. One-surface coating of substrates can easily be accomplished in the present invention by running two substrates back to back, i.e., in close contact with each other and with their respective bright surfaces exposed, through the deposition chamber at the same linear speed or preferably at differential speeds, and subsequently separating the substrates by wind-up on separate rolls. This could also be accomplished by employing an expendable dummy web moving through the deposition chamber in close contact with the substrate—the substrate having its bright surface exposed.

Still a further modification can be employed to provide not only single surface coating but also a substantial increase in coating capacity by continuously cooling the substrate during passage through the deposition zone. This is conveniently accomplished by providing a stationary sintered or porous stage which extends through the deposition chamber and is coextensive with the path the substrate will follow through the deposition chamber. The porous stage is adapted to admit a slight bleed of a cool inert gas through the pores thereof into the deposition chamber. This inert gas bleed both cools and cushions the substrate, simultaneously sweeping the di-radical vapors away from the underside of said substrate and thus permitting only one surface of the substrate to be coated.

Due to the extremely thick coatings provided by the present invention, the substrates so coated are useful in miniaturized or microminiaturized electric circuitry, for example, a metallic foil or wire substrate can be completely coated with a thin film of a poly(p-xylene) and subsequently with a conductive metal vapor deposited film. The thus formed laminate can then be used as a planar capacitor or it can be wounded in the conventional manner and used as a rolled capacitor.

Since certain changes can be made in the above method and apparatus without departing from the scope of the invention herein described, it is intended that no matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

Although the present invention has been described with particular reference to the vapor deposition of continuous films of p-xylene, it is also considered as within the scope and spirit of the present invention that the method and apparatus herein described is equally applicable to other polymer-forming compositions which can be vapor deposited or, being polymers initially, can be transferred in the vapor state and subsequently condensed as a continuous film.

What is claimed is:

1. Apparatus for coating substrate surfaces with a film-forming composition which comprises a deposition chamber, having an open inlet and outlet, a generator adapted to provide and distribute within said chamber a highly diffusive vaporous stream of a film-forming
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Apparatus for coating substrate surfaces with a film-forming composition which comprises a deposition chamber, a generator adapted to provide and distribute within said chamber a highly diffusive vaporous stream of a film-forming composition, substrate handling means freely communicating with said deposition chamber and adapted to provide multiple passes of the substrate surfaces through said chamber, a housing surrounding said deposition chamber and substrate handling means, said housing adapted to provide a capacity commensurate with the capacity of said deposition chamber and means for drawing a vacuum between said chamber and substrate handling means from the inlet and outlet thereof to provide effective removal of the excess film-forming composition, thereby creating a gaseous seal.

3. Apparatus for coating substrate surfaces with a film-forming composition which comprises a deposition chamber, having an inlet and outlet therein allowing unrestricted passage of said substrate through the deposition chamber while maintaining a close clearance between the substrate and the inner walls of the deposition chamber to provide maximum deposition rate, a generator adapted to provide and equally distribute within said chamber a highly diffusive stream of a film-forming composition, substrate handling means adapted to cool the substrate and provide at least one pass of the cooled substrate surfaces through the deposition chamber, and a housing surrounding said deposition chamber and substrate handling means, said housing adapted to provide a pressure about said deposition chamber and means for drawing a vacuum of from about 1 micron to about 25 mm. Hg in said chamber comprising vacuum ports having a capacity commensurate with and positioned within said chamber and proximately spaced from the inlet and outlet thereof to provide effective removal of the excess film-forming composition, thereby creating a gaseous seal to confine the film-forming vapors to the deposition chamber.

4. Apparatus for coating substrate surfaces with a film-forming composition as defined in claim 3 wherein a clearance of from about 1/2 to about 2 inches is maintained between the substrate and the inner walls of the deposition chamber.

5. Apparatus for coating substrate surfaces with a film-forming composition as defined in claim 3 wherein the housing having a nozzle therein adapted to inject an inert gas stream into the envelope between said housing and the deposition chamber to increase the pressure in said envelope assuring no migration of vapors into said envelope and increasing the deposition rate of the film-forming composition by increasing the total system pressure.

6. Apparatus for coating substrate surfaces with a film-forming composition as defined in claim 3 wherein the housing having a nozzle therein adapted to inject an inert gas stream into the envelope between said housing and the deposition chamber to increase the pressure in said envelope assuring no migration of vapors into said envelope and increasing the deposition rate of the film-forming composition by increasing the total system pressure.

7. Apparatus for coating substrate surfaces with a film-forming composition which comprises a deposition chamber divided into two laterally adjacent zones by at least one intervening wall, each zone having an inlet and outlet therein allowing unrestricted passage of said substrate there-through, a generator adapted to provide and distribute to each zone a highly diffusive stream of a film-forming composition which impinges on both surfaces of the substrate passing through each of said zones, substrate handling means including two driven, cooled, main process rolls situated outside the deposition chamber at the opposed extremities thereof, one of said rolls having its axis skewed in relation to the axis of the other of said rolls causing the substrate to follow a spiral path through each of said zones and enabling said substrate to undergo multiple passes through each of said zones, a housing surrounding said deposition chamber and substrate handling means adapted to provide a pressure envelope about said chamber which freely communicates with the inlet and outlet of each of said zones, means for creating a drawing vacuum in each of said zones comprising vacuum ports having a capacity commensurate with and positioned within each of said zones and proximately spaced from the inlet and outlet of each of said zones to provide effective removal of the excess film-forming composition to create a gaseous seal to confine the film-forming vapors to the deposition chamber.

8. Apparatus for coating substrate surfaces with a film-forming composition as defined in claim 7 wherein the axis of one of the two driven, cooled main process rolls is skewed in relation to the axis of the other of said rolls so that, when viewed vertically, the longitudinal axes of both rolls cross at the mid-point of each axis and the sum of the distances by which the leading edge of one roll extends beyond the corresponding edge of the other roll plus the distance by which the laterally opposed edge of said one roll lags the corresponding edge of said other roll is at least equal to the width of the substrate to be coated.

9. Apparatus for coating substrate surfaces with a film-forming composition as defined in claim 8 wherein the housing surrounding said deposition chamber and substrate handling means has an outlet therein adjacent the outlet to the deposition chamber to which is affixed a J-shaped extension of said housing partially filled with a liquid metal and through which the coated substrate is passed from the envelope to wind-up in the external atmosphere.

10. Apparatus for forming a continuous film from a vapor deposited film-forming composition which comprises an endless, cooled, revolving surface, a deposition chamber having at least one aperture therein and disposed about said cooled surface, a generator adapted to provide within said chamber and to deposit on said cooled surface a highly diffusive vaporous stream of a film-forming composition, stripping means adapted to continuously strip the film formed on said cooled surface and freely pass said stripping film to wind-up means along an aperture in said deposition chamber, a housing surrounding said deposition chamber and stripping means adapted to provide a pressure envelope about said chamber to form a vacuum positioned within said chamber and proximately spaced from the aperture thereof, said vacuum drawing means being of sufficient capacity to create a gaseous seal thereby confining the vaporous film-forming composition to the deposition chamber.

11. Apparatus for forming a continuous film from a vapor-deposited film-forming composition which comprises an internally, cooled, rotatable drum, a deposition chamber having an inlet and outlet therein disposed about said drum, substrate handling means freely communicating with said deposition chamber and adapted to provide passage of a substrate surface therethrough, a generator adapted to provide within said chamber and deposit on said substrate surface a highly diffusive vaporous steam of a film-forming composi-
tion, a housing surrounding said deposition chamber and substrate handling means adapted to provide a pressure envelope about said chamber, means for drawing a vacuum process within said chamber and proximately spaced from the inlet and outlet thereof said vacuum drawing means being of sufficient capacity to create a gaseous seal thereby confining the vaporous film-forming composition to the deposition chamber.

12. Apparatus as defined in claim 11 wherein the substrate handling means additionally includes means for stripping the vapor-deposited film from the substrate surface to provide continuous unsupported film.

13. Apparatus for forming a continuous film from a vapor-deposited film-forming composition as defined in claim 11 wherein the housing surrounding said deposition chamber and stripping means has an outlet therein adjacent to the outlet of the deposition chamber to which is affixed a J-shaped extension of said housing partially filled with a liquid metal and through which the stripped film is passed from the envelope to wind-up in the external atmosphere.

14. Method for coating substrate surfaces with a polymer-forming vapor which comprises feeding a substrate surface from a first zone of reduced pressure into a close clearance vapor deposition zone, contacting the substrate upon at least one pass of said substrate surface through the deposition zone with the polymer-forming vapor and condensing said vapor thereon to form a continuous polymeric film of the condensed vapors, said first zone encompassing said deposition zone and freely communicating therewith, maintaining said first zone at a sufficient pressure relative to said deposition zone to create a differential pressure gaseous seal to confine the polymer-forming vapor thereto, and thereafter returning the coated substrate to said first zone.

15. Method for coating substrate surfaces with a polymer-forming vapor which comprises continuously feeding a substrate surface from a first zone of reduced pressure wherein said substrate surface is cooled to a temperature below the condensation temperature of the polymer-forming vapor, into a close clearance vapor deposition zone maintained at a pressure of from about 1 micron to about 25 millimeters Hg, contacting the cooled substrate surface for at least one pass of said substrate surface through the deposition zone with the polymer-forming vapor and condensing said vapor thereon to form a continuous polymeric film of the condensed vapors, said first zone encompassing said deposition zone and freely communicating therewith, maintaining said first zone at a sufficient subatmospheric pressure relative to said deposition zone to create a differential pressure gaseous seal to confine the polymer-forming vapor thereto, and thereafter returning the coated substrate to said first zone.

16. Method for coating substrate surfaces with a polymer-forming vapor as defined in claim 15 wherein the linear speed of the substrate surface passing through the deposition zone is from about 1 inch per minute to about 500 feet per minute.

17. Method for coating substrate surfaces with a polymer-forming vapor as defined in claim 15 wherein a close clearance of from about 1/4-inch to about 2 inches is maintained between the substrate and the inner walls of the deposition zone.

18. Method for coating substrate surfaces with a polymer-forming vapor as defined in claim 15 wherein an inert gas stream is injected into the first zone increasing the system pressure and by freely communicating with the deposition zone, confining the polymer-forming vapor to said deposition zone.

19. Method for coating substrate surfaces with a polymer-forming vapor as defined in claim 15 wherein a coolant gas stream enters the first zone increasing the system pressure and by freely communicating with the deposition zone, confining the polymer-forming vapor to said deposition zone.

20. Method for coating substrate surfaces with a polymer-forming vapor as defined in claim 15 wherein the coated substrate upon re-entering the first zone is passed through a J-shaped barometric seal partially filled with a liquid metal to wind-up in the atmosphere.

21. Method for coating substrate surfaces with a film-forming composition as defined in claim 15 wherein the polymer-forming vapor is comprised of p-xylene di-tert-butyl.

22. Method for coating substrate surfaces with a polymer-forming vapor which comprises continuously cooling a substrate surface to a temperature below the condensation temperature of the film-forming composition by passing said substrate over a first cooling means in a subatmospheric zone, passing said coated substrate from said sub-atmospheric zone into a first close clearance vapor deposition zone, feeding a stream of polymer-forming vapor to said first deposition zone wherein it impinges and condenses on said substrate passing therethrough, imparting a spiral configuration to the path of the coated substrate by passing said coated substrate over a second cooling means in said subatmospheric zone, the axis of said second cooling means being skewed relative to the axis of said first cooling means, reversing the direction of the path of said coated substrate by passing over said second skewed cooling means, passing said cooled coated substrate from said sub-atmospheric zone into a second close clearance vapor deposition zone, feeding a stream of polymer-forming vapor to said second deposition zone wherein it impinges and condenses on said substrate passing therethrough, said subatmospheric zone encompassing both of said first and second deposition zones and freely communicating therewith, said first and second deposition zones maintained at a pressure of from about 1 micron to about 25 mm. Hg, said subatmospheric zone maintained at a sufficient pressure relative to said deposition zones to create a differential pressure gaseous seal to confine the polymer-forming vapor thereto, returning the thus coated substrate to said first cooling means to complete at least one cycle and thereafter returning the coated substrate to said subatmospheric zone.

23. Method for coating substrate surfaces with a polymer-forming vapor as defined in claim 22 wherein the linear speed of the substrate surface passing through the deposition zones is from about 1 inch per minute to about 500 feet per minute.

24. Method for coating substrate surfaces with a polymer-forming vapor as defined in claim 22 wherein the coated substrate upon re-entering the sub-atmospheric zone is passed through a J-shaped barometric seal partially filled with a liquid metal to wind-up in the atmosphere.

25. Method for coating substrate surfaces with a polymer-forming vapor as defined in claim 22 wherein the polymer-forming vapor is comprised of p-xylene di-tert-butyl.

26. Method for forming a continuous film from a polymer-forming vapor which comprises revolving an endless internally cooled surface within a vapor deposition zone maintained at a pressure of from about 1 micron to about 25 mm. Hg, feeding a stream of a polymer-forming vapor to said deposition zone which impinges and condenses on the cooled surface revolving therein, continuously stripping the film thus formed from the revolving surface, and thereafter passing said stripped film to wind-up in a sub-atmospheric zone encompassing said deposition zone and freely communicating therewith, said subatmospheric zone maintained at a sufficient pressure relative to said deposition zone to create a differential pressure gaseous seal to confine the vaporous stream thereto.

27. Method for forming a continuous film from a polymer-forming vapor as defined in claim 26 wherein the stripped film is passed from the sub-atmospheric zone through a J-shaped barometric seal partially filled with a liquid metal to wind-up in the atmosphere.
28. Method for forming a continuous film from a polymer-forming vapor as defined in claim 26 wherein the polymer-forming vapor is comprised of p-xylylene di-radicals.

References Cited
UNITED STATES PATENTS
2,879,739 3/1959 Bugbee et al. -------- 118—49
2,971,862 2/1961 Baer et al. ---------- 117—61
3,043,715 7/1962 Clough ----------- 117—107
3,181,209 5/1965 Smith ----------- 118—49
3,301,707 1/1967 Loeb et al. -------- 117—227

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