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CORONA DISCHARGE COATING PROCESSES

John A. Coffman, Ballston Spa, and William R. Browne, Scotia, N.Y., assignors to General Electric Company, a corporation of New York

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ABSTRACT OF THE DISCLOSURE

This invention relates to the discovery that organic materials in the vapor form may be deposited upon substrates such as bare metal surfaces or paper-like materials in a corona reaction zone as adherent organic coatings resembling polymer films formed by conventional chemical techniques. These organic materials include vapors not generally polymerizable by conventional chemical techniques such as methane, benzene and toluene, for example. Such substrates as the interior surface of metal cans or the outer surface of metal rod-like bodies or wires, kraft paper and asbestos-paper are specifically disclosed.

The invention relates to a process of forming organic coatings within a corona discharge.

A corona discharge is produced by capacitatively exciting a gaseous media lying between two spaced electrodes, at least one of which is insulated from the gaseous media by a dielectric barrier. Being capacitive in nature, corona discharge is limited in origin to alternating currents. Further, corona discharge is a high voltage, low current phenomenon with voltages being typically measured in kilovolts and currents measured in milliamperes. A corona discharge may be maintained over wide ranges of pressure and frequency, although approximate atmospheric pressures and frequencies substantially above power transmission values are typically employed. When dielectric barriers are employed adjacent each of two spaced electrodes in achieving a corona discharge, the discharge phenomenon is frequently termed an electrodeless discharge, whereas when a single dielectric barrier is employed to insulate a single electrode, the resulting phenomenon is frequently termed a semicorona discharge. Both the terms "electrodeless discharge" and "semicorona discharge" are intended as species designations for corona discharge.

A completely unrelated and electrically distinct discharge phenomenon is a glow discharge, which is sometimes confused with corona discharge by those having only casual acquaintance with electrical discharge phenomena, since both corona discharge and glow discharge yield a soft or diffused visual display. Glow discharge is produced by ionization of low pressure gaseous media using bare electrodes in contact therewith. Pressures are typically maintained well below 5 mm. Hg in order to benefit from reduced voltage requirements in accordance with Paschen's law. Operation at or near atmospheric pressure as in the case of corona discharge is precluded by arcing. Inasmuch as glow discharge is not a capacitive phenomenon, it may be produced by either direct or alternating current. Although widely variable, lower voltages and frequencies are typically employed with glow discharge than are typical with corona discharge.

A third, completely distinct form of gaseous electrical discharge is electrical arcing, which is a high current, low voltage phenomenon. Arcing occurs when two conductive surfaces of dissimilar electrical potential sufficiently ionized the gaseous media in association therewith to form a conductive ionic path therebetween. Arcing is

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visually dissimilar from a corona discharge in that the former is areally limited and exhibits distinct boundaries whereas the latter exhibits a soft or diffused appearance.

The scope and volume of coated product manufacture in recent years has forced considerable improvement and development in assembly line coating techniques. Modern coating processes to be economically competitive must be capable of providing thin, uniform, pin-hole-free, tenaciously adherent coatings using any one of a variety of inexpensive, readily obtainable modern organic coating materials, including polymers and polymerizable monomers. Such coating processes should desirably be practicable without elaborate and expensive atmospheric control equipment and without substantial wastage of coating material. Further, such coating processes must be applicable to widely dissimilar product configurations including continuous and unitary articles as well as articles having protuberances and asperities.

It is an object of the invention to provide a process of coating in a corona discharge.

It is another object of the invention to deposit organic polymeric coatings within a corona discharge using organic monomeric vapors, including organic vapors not generally polymerizable by ordinary chemical means.

It is a further object to provide a coating process which preferentially coats substrate asperities and protuberances.

Finally, it is an object to provide a coating process applicable to a wide range of pressures, including atmospheric pressure.

It has long been known that corona discharge is capable of activating certain specific chemical reactions. We have discovered that organic materials in vapor form may be deposited in a corona discharge to yield organic coatings physically resembling polymers formed by conventional chemical techniques. Further, we have discovered that organic vapors not generally polymerizable by chemical techniques may be deposited as coatings in the presence of a corona discharge. Additionally, organic coatings laid down in a corona discharge are more thickly deposited on substrate asperities than on relatively smooth substrate areas. The process is practicable over a wide range of pressure conditions.

The invention may be practiced under any set of conditions in which a corona discharge is maintainable. However, certain corona discharge producing conditions offer distinct procedural advantages and are preferred.

Unlike glow discharge, a corona discharge may be maintained over a wide range of pressure conditions without arcing. Atmospheric and near-atmospheric pressures offer particular advantages in avoiding the use of expensive pressure control equipment. Pressures of 0.2 to 10 atmospheres generally define the preferred limits of operation.

A corona discharge can be generated using only an alternating current. Generally, high frequencies are preferred since the phenomenon is capacitive in nature. Frequencies ranging from 20 c.p.s. to 500,000 c.p.s. are contemplated. A preferred frequency range is from 3,000 c.p.s. to 10,000 c.p.s.

The current voltage and power utilized in generating a corona discharge for a specific coating process will vary over wide limits depending on the thickness of the dielectric barrier or barriers employed, the electrode spacing, and the nature of the gaseous media lying within the discharge area. As a general rule, more complex materials will absorb more energy than less complex materials. The inert gas argon, for example, will absorb much less energy than air. In an electrodeless application utilizing two quartz barriers of 2 mm. thickness separated by a 4 mm. spacing, the voltage should suitably be maintained at 12 to 15 kilovolts. In a semicorona application,

a single quartz barrier having 4 mm. thickness is required to operate at equivalent voltages. For a given organic material, the energy used is proportioned to the coating thickness deposited.

The exact chemical mechanism by which a corona discharge attacks an organic material is not known. In acting on monomeric organic materials, polymerizable by conventional chemical techniques, it would appear that the products obtained by corona discharge resemble the polymeric materials which could be obtained by conventional chemical processes. The materials which can be deposited by corona discharge activation, however, are not limited to those polymerized by known chemical processes. Corona discharge may, for example, deposit polymer resembling coatings when a vapor of methane, benzene, toluene, or any other generally unpolymizable organic material is passed therethrough. Generally, better yields are obtained with materials known to be polymerizable by conventional chemical techniques.

The nature of the substrate on which the coating is deposited may vary within wide limits. When dealing with electrically conductive substrates, the substrate being coated may be employed as a bare electrode separated from an insulated electrode. The substrate is preferably employed as a ground electrode. A semicorona discharge is generated between the insulated electrode and the substrate acting as the ground electrode. Coating material lying between the substrate and the insulated electrode is deposited on the substrate. The thickness and uniformity of the coating deposited can be controlled by regulating the gap between the insulated electrode and the substrate. The coating thickness is proportionately greater in any area where the gap is reduced, since the potential gradient is higher.

In coating electrically nonconductive materials, the substrate to be coated is, of course, unsuitable for use as an electrode itself and two electrodes must be employed. One or both of the electrodes may be insulated to provide a dielectric barrier between the spaced electrodes. An organic vapor and the substrate are both positioned within the corona between the electrodes.

Whether conductive or nonconductive, the substrate may either be coated while moving through the corona or while remaining stationary therein. The organic vapor may be either circulated through the corona or allowed to remain stagnant within the discharge.

The maintenance of a corona discharge is dependent on the potential gradient between electrodes. With higher voltages the electrodes may be more widely spaced. The minimal spacing between electrodes is determined either by the dielectric breakdown of the insulation barrier, resulting in arcing, or by the electrodes becoming too closely spaced to conveniently position the substrate and coating material therebetween. Using 2 to 4 mm. thickness of quartz in the form of either one or two dielectric barriers, it has been determined that electrode spacings of 1 to 5 mm. are convenient.

Numerous variations in the configurations of the electrodes and their relative positionings are possible. In coating conducting indefinite length articles elongated along a single axis, such as wire, it is generally preferred to employ the wire as a bare electrode, preferably a ground electrode and to concentrically position an annular insulated electrode about the wire. On the other hand, in dealing with cylindrical conductive articles, as for example cans, it is preferred to employ the can as a bare ground electrode and to position an insulated electrode concentrically within the can. In dealing with nonconductive articles of various forms, it is desired to place the articles between two electrodes, at least one of which is insulated. Numerous possible configurations will be apparent to one skilled in the art.

The coatings laid down in a corona discharge may be fully cured therein or may be subjected to subsequent treatments to complete the cure. Generally, polymeric

coatings exhibit three separate stages of cure. In the first stage the coating is adhesive. Coatings cured only to the adhesive stage may be useful in combination with laminating processes. In a second stage of curing, coatings are not tacky but are still extractable by solvents indicating less than a complete cure. Nontacky, incompletely cured coatings are conveniently handled and yet may be subsequently rendered adhesive by heat or solvent treatment. Completely cured polymeric coatings are nonadhesive and insoluble in most solvents. Coating cure treatments employing temperatures up to 250° C. are specifically contemplated by this invention.

The following examples are intended to illustrate and not to limit our invention.

Example 1

An open ended, previously weighed tin can of the type conventionally employed to package foods and beverages having an inside diameter of 64 mm. and a length of 4¾ inches is suitably grounded. A glass insulated electrode having an outside diameter of 59 mm. and a length of 8 inches is centered within the tin can. A vapor conduit is connected between the base of the tin can and a pressure tank of butadiene. A sealing element including an exhaust conduit is placed on the top of the tin can to prevent diffusion of air between the can and the insulated electrode. The valve on the pressure tank is opened and the flow rate of gaseous butadiene controlled to 13 cc./min. The flow rate is determined at approximately atmospheric pressure and a room temperature of 25° C. The system is purged for four minutes to remove any air from between the insulated electrode and the tin can. An alternating current of 13 kv. peak is applied to the electrode and can generating a soft, diffused corona. A frequency of 10,000 c.p.s. is employed. The coating process is continued 3 minutes at 320 watts.

The tin can is removed from the corona coating apparatus and subjected to a temperature of 200° C. for a period of 4 minutes. The coated can is again weighed and determined to have received 0.031 gram of coating material. It is noted that the can coating is somewhat thicker along the longitudinal seam.

Example 2

The process of Example 1 is repeated using the tin can as the high potential electrode and the insulated electrode as a ground. The coated can is noted to have a thicker coating along the longitudinal seam.

Example 3

An open ended tin can and insulated electrode of the type described in Example 1 are similarly arranged. The space between the insulated electrode and the tin can is connected by fluid conduits to a source of butadiene and a source of argon. Argon is used to purge the system and subsequently butadiene is supplied at a flow rate of 700 cc./min. and argon at a flow rate of 1150 cc./min. A voltage of 13.9 kv. peak at 10,000 c.p.s. is supplied to the insulated electrode while the tin can is grounded. The corona discharge is maintained for 10 minutes with a power input of 114.5 watts.

Upon removal from the coating apparatus, the tin can is subjected to an after-treatment as described in Example 1.

The coated can is noted to have a thicker coating along the longitudinal seam.

Example 4

An open ended, previously weighed tin can and insulated electrode of the type described in Example 1 are similarly arranged. The system is purged with argon and coating material is subsequently supplied to the system by bubbling argon through liquid toluene. A voltage of 20.2 kv. peak at 10,000 c.p.s. is supplied to generate a

corona discharge. The corona is maintained 3 minutes with a power input of 272.5 watts.

Upon removal from the coating apparatus, the tin can is subjected to an after-treatment as described in Example 1. The coated can is again weighed and determined to have received 0.0052 gram of coating material.

The coated can is noted to have a thicker coating along the longitudinal seam.

Example 5

A tin can having a length of $4\frac{3}{4}$ inches, an inside diameter of 64 mm., an open top and a closed bottom is suitably connected to electrical ground. Two glass fluid inlet tubes are positioned within the tin can and extending near the bottom. An insulated electrode having a bottom outside diameter of 55 mm. and a top outside diameter adjacent the can top of 59 mm. is mounted within the can with the bottom end of the insulated electrode spaced 3.5 mm. from the end of the can. Duct sealing material is hand molded between the insulated electrode, the can top, and the inlet tubes. The duct sealing material is left spaced from the exterior walls of the inlet tubes an amount sufficient to allow vapor to exhaust.

The inlet tubes are connected by suitable fluid conduits to a source of butadiene and argon. The space between the insulated electrode and the can is purged for fifteen minutes using argon. The flow of butadiene and argon are controlled to provide respective flow rates of 150 cc./min. and 1150 cc./min. A 10.9 kv. peak voltage at 10,000 c.p.s. is applied to the insulated electrode to generate a corona discharge. The discharge is maintained for 15 minutes with a power input of 164 watts.

The coated can is noted to be more thickly coated along the seam.

Example 6

An electrodeless coating process is performed utilizing an outer electrode comprising a glass cylinder having a wall thickness of 1.5 mm. and an inside diameter within the discharge area of 42 mm. A length of the glass cylinder is exteriorly coated with a transparent, conductive coating of tin oxide to define the discharge area. The glass tube above the electrical discharge area is provided with an exhaust conduit connected to a vacuum pump, and below the discharge area the glass tube forms a glass mixing and heating pot having two inlet conduits.

Mounted concentrically within the first glass tube is a second glass tube, forming an inner electrode, having a similar wall thickness and an outside diameter of 35 mm. The inside surface of the glass tube is similarly lined with the tin oxide. The interior of the inner electrode is filled with copper shavings in which a metal encased thermometer is mounted.

A 1 inch wide, 40 inches long, and 10 mils thick strip of asbestos paper is spirally wound about the outer surface of the inner electrode. The inlet conduits of the heating and mixing pot are connected to sources of meta-cresol and argon. The system is purged with argon while the mixing pot is maintained at 250° C. When the metal encased thermometer in the inner electrode reads 150° C., the system is reduced to a pressure of 300 mm. Hg. A flow rate of 0.5 cc./min. meta-cresol, measured as a liquid, and 30 cc./min. argon, measured at 25° C. and atmospheric pressure, is established through the system.

A corona discharge is established using a voltage of 7 kv. peak at 10,000 c.p.s. The corona is maintained 20 minutes with a power input of 34 watts. A visible deposit is formed at the end of 10 minutes and at the end of 20 minutes the deposit is dry to the touch.

Example 7

The coated asbestos paper strip obtained from Example 6 is heated to 125° C. in air. The strip is subsequently placed in toluene. None of the coating is extractable by toluene.

Example 8

The process of Example 6 is performed using a 0.5 cc./min. flow of indene and a 30 cc./min. flow argon. A corona discharge is established using a voltage of 6.2 kv. peak at 10,000 c.p.s. The corona is maintained for 20 minutes with a power input of 41 watts. The coated asbestos paper strip is noted to be dry to the touch.

Example 9

The coated strip of Example 8 is divided into two portions. One portion of the strip is soaked in toluene for 5 minutes while another portion is soaked in methyl ethyl ketone for 5 minutes. In each case the coating discolored the solvent indicating that the coating is not completely cross-linked and may be further cured.

Example 10

The process of Example 8 is repeated using a $\frac{3}{4}$ inch wide strip of polytetrafluoroethylene. A corona discharge is maintained using a voltage of 9.0 kv. peak at 10,000 c.p.s. The corona is continued 15 minutes with a power input of 45 watts. The resultant product displays a tacky, adherent coating.

Example 11

A coating apparatus as described in Example 6 is modified by the addition of a water cooling jacket adjacent the outer electrode. The apparatus is connected to a source of acrylonitrile vapor and a source of argon. A strip of kraft paper 10 mils thick, 1 inch wide, and approximately 40 inches long is spirally mounted adjacent the exterior surface of the inner electrode.

The system is purged and operated using the same sequence of steps described in Example 6. A flow rate of 0.4 cc./min. liquid acrylonitrile is maintained together with 25 cc./min. argon measured at atmospheric pressure and 25° C. The space between the inner and outer electrodes is maintained at 600 mm. Hg during coating. A corona discharge is maintained between the electrodes using a voltage of 7 to 10 kv. peak over a period of 8 minutes. A power input of 50 watts is maintained.

At the termination of coating, the kraft paper is noted to have a light brown coating which extends throughout the thickness of the paper and is visible on each face. The coating is noted to be nonadhesive to touch. The coated paper is noted to be insoluble in toluene and soluble in methyl ethyl ketone.

Example 12

An annular electrode is formed from an eight inch long quartz tube having an outside diameter of 6 mm. and an interior diameter of 3 mm. by placing a silver outer conductive coating on the tube. A 20 gauge wire is centered within the quartz electrode and suitably grounded. The glass tube is provided with means conducting vapor to the lower end thereof and is suitably provided with a gas exhaust at the upper end. A butadiene vapor is conducted upwardly through the tube at a flow rate of 8 cc./min. measured at 25° C. and atmospheric pressure. The silver, outer electrode is connected to a source of alternating current at a voltage of 20 kv. peak so that a corona discharge is formed. The corona discharge is continued 2 minutes with a power input of 50 watts. The resulting product is a coated wire having a hard, insoluble coating.

Example 13

A wire is coated as in Example 12, except that the wire is connected to a source of alternating current and the silver electrode is grounded. A similar product is obtained.

While numerous obvious modifications of this invention have not been described, the invention is intended to include all such as may be embraced within the following claims.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A process of coating within a desired zone comprising:

introducing an organic vapor within the zone,
maintaining a pressure of 0.2 to 10 atmospheres within the zone,

positioning two spaced conductive surfaces within the zone separated by at least one dielectric barrier in juxtaposition to and in contact with an associated conductive surface and presenting a dielectric surface to said zone,

generating a corona discharge between the conductive surfaces utilizing an alternating current with a frequency range of 20 to 500,000 cycles per second, and

controlling the duration of corona discharge, whereby a coating of desired thickness is formed on a surface within the zone which is not said dielectric barrier surface.

2. A process according to claim 1 in which at least one of the spaced conductive surfaces is the surface coated.

3. A process of coating between two electrodes, at least one of which is dielectrically insulated, comprising:

introducing a substrate between the electrodes,
introducing an organic vapor between the electrodes,
maintaining a pressure of 0.2 to 10 atmospheres between the electrodes,

generating a corona discharge between the electrodes utilizing an alternating current within a frequency range of 20 to 500,000 cycles per second, and

controlling the duration of corona discharge, whereby a coating of desired thickness is formed on the substrate.

4. A process according to claim 3 wherein the coated substrate is subsequently subjected to a coating curing treatment.

5. A process according to claim 3 wherein the pressure between the electrodes is maintained at approximately atmospheric pressure.

6. A process according to claim 3 wherein the organic vapor is diluted with an inert gas.

7. A process of coating an electrically conductive substrate utilizing a dielectrically insulated electrode comprising:

introducing an organic vapor between the insulated electrode and the substrate, and

generating a corona discharge between the insulated electrode and the substrate, whereby a coating is formed on the substrate.

8. A process of coating an electrically conductive substrate utilizing a dielectrically insulated electrode comprising:

introducing an organic vapor between the insulated electrode and the substrate,

maintaining a pressure of 0.2 to 10 atmospheres between the insulated electrode and the substrate,

generating a corona discharge between the electrode and the substrate utilizing an alternating current within a frequency range of 20 to 500,000 cycles per second, and

controlling the duration of the corona discharge, whereby a coating of desired thickness is formed on the substrate.

9. A process according to claim 8 wherein the substrate is grounded.

10. A process according to claim 8 wherein the substrate is subsequently subjected to a coating curing treatment.

11. A process according to claim 8 wherein the pressure between the substrate and the insulated electrode is maintained at approximately atmospheric pressure.

12. A process according to claim 8 wherein the organic vapor is diluted with an inert gas.

13. A process of coating a cylindrical, electrically conductive substrate utilizing a dielectric insulated electrode comprising:

centering the insulated electrode within the cylindrical substrate and separated therefrom by an annulus, introducing an organic vapor between the insulated electrode and the substrate through the annulus, maintaining an annulus pressure of 0.2 to 10 atmospheres,

generating a corona discharge within the annulus utilizing an alternating current within a frequency range of 20 to 500,000 cycles per second, and

controlling the duration of corona discharge, whereby a coating of desired thickness is formed on the substrate.

14. A process according to claim 13 wherein the substrate is grounded.

15. A process according to claim 13 wherein the pressure between the substrate and the insulated electrode is maintained at approximately atmospheric pressure.

16. A process of coating an open-ended tin can having a longitudinal seam comprising:

grounding the can,
centering an insulated electrode within the can and spaced therefrom by an annulus,
introducing an organic vapor through the annulus, and

generating a corona discharge between the can and the insulated electrode, whereby a coating is deposited on the interior surface of the can having a greater thickness overlying the longitudinal seam.

17. A process according to claim 16 wherein one end of the can is closed.

18. A process of selectively coating a substrate having a protuberance on the surface thereof to be coated comprising:

mounting an insulated electrode spaced from the substrate surface,

introducing an organic vapor between the substrate surface and the insulated electrode,

generating a corona discharge over the entire surface to be coated of the substrate, and

controlling the duration of the corona discharge, whereby a coating of desired thickness is obtained on the substrate surface and a coating of a desired greater thickness is obtained on the protuberance.

19. A process of coating an indefinite length, electrically conductive article comprising:

positioning an annular, insulated electrode around the article and spaced therefrom by an annulus,

introducing an organic vapor through the annulus, and

generating a corona discharge between the insulated electrode and the article, whereby a coating is uniformly applied to the article.

20. A process of coating a paper substrate comprising:

mounting two electrodes at least one of which is dielectrically insulated in spaced relation,

positioning a paper substrate between the electrodes, introducing a monomeric organic vapor between the electrodes,

maintaining a pressure of 0.2 to 10 atmospheres between the electrodes,

generating a corona discharge between the electrodes utilizing an alternating current within a frequency range of 20 to 500,000 cycles per second, and

controlling the duration of corona discharge, whereby a coating of desired thickness is formed on the paper.

21. A process of providing a polymeric coating on paper at atmospheric pressure comprising:

mounting two electrodes at least one of which is dielectrically insulated in spaced relation,

positioning a paper substrate between the electrodes,
introducing a monomeric organic vapor between the
electrodes, and

generating a corona discharge between the electrodes,
whereby at least a portion of the paper substrate is
coated with an organic polymer. 5

22. A process of coating according to claim 19 wherein
the polymer coating is subject to a curing treatment.

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ALFRED L. LEAVITT, *Primary Examiner*.

10 J. H. NEWSOME, *Assistant Examiner*.

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