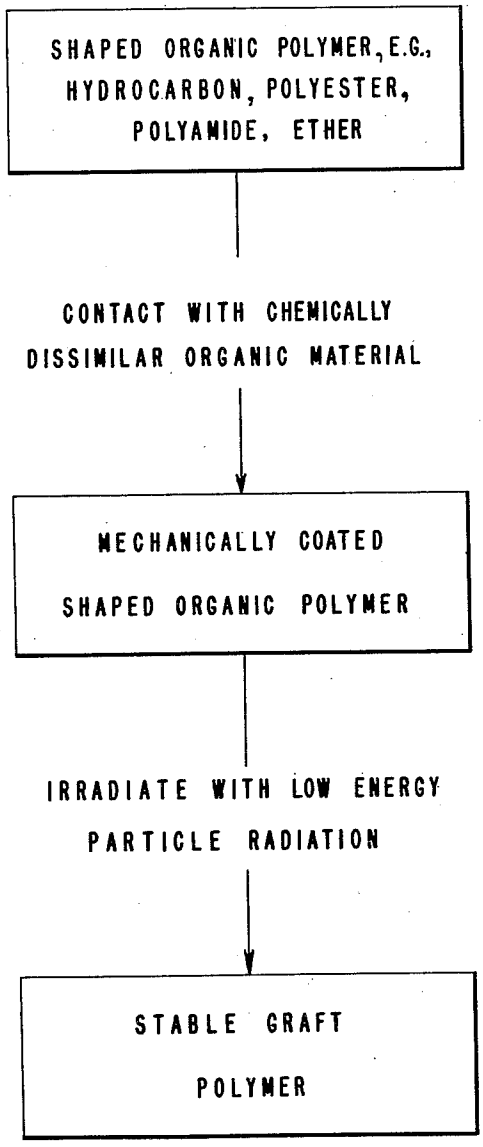
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PROCESS OF ADHERING AN ORGANIC COATING TO A SUBSTRATE

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PROCESS OF ADHERING AN ORGANIC COATING TO A SUBSTRATE

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This invention is concerned with a new method of affixing a coating of organic material to an organic polymer substrate.

The application is a continuation-in-part of my copending application Serial No. 589,372, filed June 5, 1956, and now abandoned.

It has been observed that coatings of organic materials can be affixed to organic polymer substrates by the action of high energy ionizing radiation. However, the exposure of synthetic polymers to high energy radiation involves many side effects, including crosslinking and degradation, which alter the physical properties of the irradiated polymer.

It is an object of the invention to provide a process which utilizes relatively low energy radiation to cause organic coatings to be affixed to organic polymer substrates without affecting the bulk physical properties of the substrate. Other objects of the invention will become apparent from the specification and claims.

There has now been discovered a process for affixing to an organic polymer substrate a coating of a dissimilar organic material by coating the organic polymer substrate with a thin coating of the dissimilar organic material and subjecting the coated substrate to ionizing charged particle radiation having an energy of from 15 to 50,000 electron volts for a minimum exposure of 0.01 watt-second per square centimeter to bond the coating to the substrate. This invention is illustrated broadly by the appended drawing, a self-explanatory flowsheet of the process.

This new process can be used with all types of ionizing charged particle radiation which have energies in the above voltage range when they impinge on the coating. It is particularly advantageous to subject a precoated substrate to radiation in the form of electrons, which therefore represents the preferred species of the invention. A critical condition in the practice of this invention is that the energy of the beam must be more than sufficient for penetration through the coating to the adjacent surface of the polymer substrate so that the radiation can produce a chemical bond between the polymer surface and the coating. With electrons within the above energy limits, the energy absorbed by any particular coating can be estimated by the following equation, where D represents the weight of the coating in g./cm.^{2} and A represents the radiation energy absorbed by the coating in millions of electron volts (mev.):

$$A=1.92D^{0.725}$$

Within the range indicated above, it is desirable to employ an excess of radiation energy of at least 0.000005 mev. over the amount absorbed by the coating. Thus, the value for $1.92D^{0.725}$ mev. may represent from about 1% to about 99% of the total radiation energy employed. Since the intensity of radiation is difficult to control within strictly defined limits, it is best for practical operation that the value for $192D^{0.725}$ mev. represent from about 5% to about 95% of the total radiation energy employed and preferably from 20% to 80%, i.e., the total energy is about 1.05 to 20 times, and preferably 1.25 to 5.0 times, the energy absorbed by the coating. It has been found that when the radiation is in the form of electron bombardment, the most effective bonding of the coating to the substrate is achieved when the value for $1.92D^{0.725}$ mev. represents about one third of the total radiation energy employed.

It will be readily appreciated that the upper limit of 0.05 mev. radiation energy places a practical limit on the weight of the organic coating which may be employed. With electron irradiation, as the value for $1.92D^{0.725}$ approaches 0.05 mev., the permissible coating weight approaches a value of about 0.00652 g./cm.^{2}. With all types of ionizing charged particle radiation it is advantageous to use coating weights of only up to 0.0065 g./cm.^{2} because within this range the surface effects produced are substantially independent of the thickness of the coating at the time of irradiation.

It will likewise be readily appreciated that the coating may be extremely thin and, therefore, require a very low energy of radiation to cause it to be affixed to the polymeric substrate. For example, a monomolecular layer of an organic compound of molecular weight 100 would represent a coating weight of about 5.5×10^{-8} g./cm.^{2}. To penetrate such a coating would require electron energy of about 0.000011 mev. Radiation energy of about 0.000015 mev. thus represents a practical lower limit of energy which is useful in the present invention, and a lower limit of 0.000033 mev. is preferred.

The temperature at which the irradiation step is carried out may be varied widely. For example, irradiations may be conducted in the range from low temperatures such as −80° C. up to the decomposition temperature of the organic coating or substrate, for example as high as 300° C. However, there is little advantage in employing extremes of temperature, and for reasons of convenience and economy, room temperature is preferred.

The process of this invention may be carried out in air, in the presence of inert atmospheres such as nitrogen or helium, or, if the reacting system is sufficiently nonvolatile, in a vacuum. Operating in a vacuum, or at least under reduced pressure, is frequently desirable, since this lowers the number of collisions of the radiation particles with other gases that might be present, and thereby increases the efficiency of the irradiation.

Under some circumstances, particularly when the process of this invention is carried out in air, it is preferred that the suface being irradiated be electrically grounded. This is preferably accomplished by selecting a substrate or coating material which is at least somewhat electrically conductive and grounding said substrate or coating. Grounding of either the substrate or the coating increases the efficiency of the irradiation.

By organic polymer substrate we mean any natural or synthetic normally solid organic polymeric material, particularly those with molecular weights in excess of 500. The polymer may be oriented or unoriented. Thus, there may be employed hydrocarbon polymers such as polyethylene, polypropylene, polystyrene, polybutadiene, rubber, polyisobutylene, butadiene/styrene copolymers and the like; halogenated hydrocarbon polymers, such as polyvinyl chloride, polyvinylidene chloride, polychloroprene, polytetrafluoroethylene, polyvinyl fluoride, vinylidene fluoride/hexafluoropropylene copolymers, chlorinated and chlorosulfonated polyethylene and the like; ester-containing polymers, such as polyvinyl acetate, polymethyl methacrylate, polyethylene terephthalate and the like; hydroxyl-containing polymers, such as polyvinyl alcohol, cellulose, regenerated cellulose and the like; ether-containing polymers, such as polyethylene oxide, polymeric formaldehyde, solid polytetrahydrofuran, dioxolane polymers and the like; condensation polymers, such as nylons, polyimides, phenol-formaldehyde polymers, urea-formaldehyde polymers, triazine-formaldehyde polymers and the like, polypeptides, silicones, and olefin polysul-

fones; and natural polymers, such as wool, cotton, silk, rubber and the like.

The chemical nature of the organic material used to form coatings in accordance with this invention is limited only by the requirement that it be chemically distinguishable from the substrate. Thus, the invention comprises adhering a layer of organic material which is chemically dissimilar to the polymeric substrate. It will be apparent that the organic coating material must be either a liquid or a solid at the time of irradiation. Liquids may be applied to the substrate by any of the usual methods of coating, such as by dipping, spraying, brushing, printing and the like. Solids may be applied to the substrate by sublimation or by coating from melt, from solution or from dispersion. Thus, the liquid or solid which comprises the coating may be a hydrocarbon, halogenated hydrocarbon, alcohol, amine, aldehyde, ketone, ether, acid, ester, amide, phenol, sulfonic acid, nitro compound, fat, protein, synthetic polymer and other organic compounds which contain at least one C—X bond, where X is hydrogen or halogen. It is preferable that the organic compound be a material which is normally incompatible with the substrate and has no solvent action thereon.

Among the non-polymeric organic compounds a preferred group of coating materials for use in this invention are the chain transfer agents, e.g., compounds containing active hydrogen or halogen such as chloroform, carbon tetrachloride, triphenylmethane, thiols, secondary alcohols, maleic anhydride, and the like, since these compounds exhibit enhanced reactivity in the affixing reaction.

Preferred non-polymeric organic compounds are those which are normally non-polymerizable since the amount of coating affixed by the process of this invention is most readily controlled with them.

Another preferred group of organic compounds are the polymers, and particularly the polymeric ethers, since these give large changes in surface properties.

The low energy ionizing charged particle radiation employed in the present invention may be in such forms as alpha particles or electrons and is limited only by the energy it possesses at the time it reaches the coating to be affixed. The low-energy charged particle radiation may be generated by known methods that do not form a part of this invention. Thus, particles of suitable energy may be obtained by means of appropriate voltage gradients, using such devices as a cathode ray tube, a resonant cavity accelerator, a Van de Graaff generator or the like. The accelerated particles may be utilized in a vacuum by introducing the reacting system into the vacuum chamber of the accelerator. Alternatively, the accelerated electrons or alpha-particles may be lot out in known manner through a window and utilized in air or a gas, with due precautions being taken that the particles have the desired energy when they impinge on the reacting system. A preferred radiation in the process of this invention is that obtained from low energy electrons which are readily generated by means of a suitable voltage gradient, such as that supplied by an induction coil of the Tesla type. This form of radiation is preferred because of its ready availability, low cost and sharply defined penetration.

The invention will be better understood by reference to the examples, which illustrate specific embodiments of the process.

Example I

A film of polyethylene terephthalate 0.001 inch thick is immersed in a 10% aqueous solution of a polyethylene oxide of 20,000 molecular weight (commercially available as "Carbowax" 20M) containing a trace of a wetting agent of the octyl phenyl polyglycol ether type (commercially available as "Triton" X–100). The film is allowed to drain and air dry. The coating of polyethylene oxide on the film weighs 0.3847 mg./cm.^{2}. The coated film is taped to a rubber base and introduced into an irradiation chamber which is evacuated to a pressure of about 1 mm. mercury. The film is then exposed to the electron beam generated by the full output of a Tesla-type high-frequency induction coil (BD No. 10 Leak Tester sold by A. H. Thomas Company). The discharge tip of the coil is located four inches above the film, and the energy of the electron beam is about 0.010 mev. The sample is exposed for two hours. It is then extracted for 20 hours with ethanol in a Soxhlet extractor. The extracted film exhibits a 1.5% weight gain over the original weight before coating. It carries a visible coating of the polyether on the irradiated face of the film. The coating cannot be removed by hard scrubbing with cheesecloth. The coated face of the film has a surface electrical resistivity of $10^{10.9}$ ohm-cm., whereas an untreated control similarly tested has a surface resistivity of $10^{12.9}$ ohm-cm.

Example II

A film of polyethylene 0.002 inch thick is coated with polyethylene oxide as in Example I. The coating weighs 0.2467 mg./cm.^{2}. The coated film is irradiated and extracted as described in Example I. The treated film exhibits a weight gain of 2.8% over the original weight before coating and carries a visible coating of the polyether on the irradiated face of the film. The coating cannot be removed by scrubbing with cheesecloth. The water wettability of the film is determnied by measuring the angle of inclination at which the retreating edge of a 0.05 ml. droplet of water travels at a rate of 0.1 mm./second. In this "sliding-tilt angle" test the coated surface of the film gives a value of 40°, while the uncoated lower surface maintains the initial untreated value of 34°. The upper surface exhibits a wetting angle against water of 26–36°, whereas the lower surface has a wetting angle of 53–62°. The treated film has a zero strength temperature of 110° C., whereas a film similarly treated with 2 mev. electron irradiation has a zero strength temperature of 160–170° C. Thus, the low energy treatment serves to avoid the deep-seated cross-linking which is encountered in high energy radiation.

Example III

A film of polyethylene terephthalate 0.001 inch thick is immersed in a solution of 2 parts of polyvinyl chloride in 97.5 parts of tetrahydrofuran and 2.5 parts of dimethylformamide. The film is allowed to drain and is then dried for two hours at 60° C. The coating of polyvinyl chloride weighs 0.305 mg./cm.^{2}. The film, which is coated on both sides, is then irradiated for one hour on each side in the irradiation chamber described in Example I. The polyvinyl chloride coating turns brown during the first two or three minutes of radiation. The irradiated film is extracted for 40 hours with dioxane in a Soxhlet extractor, followed by a similar extraction for 20 hours with tetrahydrofuran. After the extraction, the film maintains a visible brown coating of adhered polyvinyl chloride and exhibits a weight gain of 7.2% over the original uncoated weight, whereas a control film which has been coated with polyvinyl chloride, but not irradiated, has no visible coating after extraction and shows a weight gain of only 1.6%. The adhered coating of polyvinyl chloride cannot be removed by rubbing or scraping.

Example IV

A film of polyethylene 0.002 inch thick is coated with polyvinyl chloride as in Example III. The coating of polyvinyl chloride weighs 0.2844 mg./cm.^{2}. The coated film is irradiated and extracted as described in Example III. The extracted film retains a visible coating of adhered polyvinyl chloride and shows a loss of only 16.9% in weight during extraction, where a control film which has been coated with polyvinyl chloride, but not irradiated, has no visible coating and shows a 28.3% weight loss after extraction.

It will be noted that in the foregoing examples the

energy of the radiation employed is sufficient to penetrate through the coating and into the substrate. From the factor $1.92D^{0.725}$ mev. where D is the weight of the coating in g./cm.^{2}, it will be seen that the energy consumed in penetrating the coatings in the several examples is approximately as follows:

Example:	Mev. (approx.)
I	0.0064
II	0.0045
III	0.0054
IV	0.0053

Example V

A film of polyethylene 0.002 inch thick is wet out with a solution of 0.5 g. of palmitic acid-1-C^{14} (0.1 millicurie/gram) in 49.5 g. of ether. The ether solvent is allowed to evaporate and the coated film is then placed in a demountable cathode ray tube so arranged as to direct a stream of electrons against the surface of the coated film. The system is evacuated to about 0.03 micron pressure, and the coated film is then exposed to a beam of 50 volt electrons at 25–50 microamps to a total exposure of 0.2 watt-sec./cm.^{2}. The film is then extracted with ether in a Soxhlet apparatus for six days. Retained radioactivity of the film, as indicated by an end window Geiger counter (Tracerlab Superscaler) is then constant at a level of 12 counts/min./2.5 cm.^{2} above background. On the basis of a separate calibration by combustion analysis, this degree of activity is equivalent to 0.04% of palmitic acid based on the initial weight of the film, or 1.8 micrograms/cm.^{2} of palmitic acid attached to the irradiated film surface.

Example VI

Polyethylene film is coated and irradiated as described in Example V, except that 25,000 electron volts (25 kev.) electrons are utilized at 25 microamps and a total exposure of 0.03 watt-sec./cm.^{2}. After extracting with ether to constant activity as in Example V, the film exhibits a retained radioactivity of 9–16 counts/min./2.5 cm.^{2} above background, which is equivalent to 1.4–2.4 micrograms/cm.^{2} of attached palmitic acid.

Example VII

Polyethylene film is coated and irradiated as described in Example V, except that 25 kev. electrons are utilized at 25 microamps and a total exposure of 12.35 watt-sec./cm.^{2}. After extracting with ether to constant activity as in Example V, the film exhibits a retained radioactivity of 37–42 counts/min./2.5 cm.^{2} above background, which is equivalent to about 6 micrograms/cm.^{2} of attached palmitic acid. In a control run as above but using 2 mev. electrons for the same total exposure, the retained radioactivity was only 11 counts above background. This shows the greater efficiency of the lower energy radiation in the present process.

Example VIII

A film of 0.0015 inch thick cellophane which has been coated on each side with a vinylidene chloride copolymer film of about 0.2 mil thickness is irradiated in a demountable cathode ray tube with 25 kev. electrons at 25 microamps to a total exposure of 0.2 watt-sec./cm.^{2}. The irradiated film is still tough and pliable, whereas a similar exposure with 2 mev. electrons results in severe stiffening and embrittlement. The film is extracted with dioxane in a Soxhlet apparatus for 20 hours. After this extraction, the side of the film which had been exposed to the electron beam still retains a coating of vinylidene chloride copolymer and is not wet by liquid water, whereas the side of the film which was not exposed to the electron beam no longer has a coating of vinylidene chloride copolymer, and is readily wet by liquid water.

An important advantage of the present invention is that coatings of non-polymerizable as well as polymerizable materials are affixed by the utilization of low-cost radiation energy with an attendant minimum radiation hazard. Another important advantage is that by limiting the energy of radiation employed, excessive crosslinking, degradation and other changes in the physical properties of the organic polymer substrate are avoided.

The process of this invention is particularly useful for permanently affixing sizes to fibrous organic polymeric materials; finishing agents, antistatic coatings, and coloring materials to fabrics; and "slip" agents, waterproofing layers, etc., to films such as cellophane.

In the low-energy range of radiation employed in the process of this invention, charged particle radiation is an effective bonding means whereas electromagnetic radiation and neutral particle radiation show little activity. This is in contrast with situations involving higher energy radiation where the several types of radiation are substantially interchangeable for many purposes. The specificity of charged particle radiation in the energy range from 15–15,000 electron volts is confirmed as follows:

The procedure of Example II is repeated with the exception that the polyethylene glycol-coated polyethylene film is shielded from the direct action of the Tesla coil beam of 10 kev. electrons by an 0.5 mil film of polyethylene terephthalate which is of a thickness just sufficient to intercept 10 kev. electrons and convert their energy to 10 k.v.p. X-rays. Under these conditions no measurable weight gain is observed and no visible coating of polyether remains after extracting with ethanol.

Since many different embodiments of the invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited by the specific illustrations except to the extent defined in the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a process for coating an organic polymer with a nongaseous dissimilar organic material, the improvement of subjecting the polymer, coated to the extent of not greater than about 0.0065 g./cm.^{2} of surface thereof with said dissimilar organic material, to ionizing charged particle radiation having an energy of from 15 to 50,000 electron volts for a minimum exposure of 0.01 watt-second per square centimeter but for a maximum exposure insufficient to degrade said organic polymer to bond the coating of dissimilar organic material to the organic polymer.

2. A process as defined in claim **1** wherein the organic polymer is coated with up to 0.0065 gram per square centimeter of a dissimilar organic material and the coated polymer is subjected to electron radiation having a total energy of 1.05 to 20 times the energy absorbed by the coating.

3. A process as defined in claim **1** wherein the polymer is coated with a dissimilar non-polymeric organic compound.

4. A process as defined in claim **1** wherein the polymer is coated with a dissimilar organic polymer.

5. A process as defined in claim **1** wherein the polymer is coated with a dissimilar polymeric ether.

6. A process as defined in claim **1** wherein the energy of the ionizing charged particle radiation is from 50 to 25,000 electron volts.

7. A process as defined in claim **1** wherein the organic polymer is polyethylene terephthalate.

8. The process of claim **7** wherein the dissimilar organic material is polyethylene oxide.

9. The process of claim **7** wherein the dissimilar organic material is polyvinyl chloride.

10. A process as defined in claim **1** wherein the organic polymer is polyethylene.

11. The process of claim **10** wherein the dissimilar organic material is polyvinyl chloride.

12. The process of claim **10** wherein the dissimilar organic material is palmitic acid.

13. The process which comprises coating an organic polymer to the extent of not more than about 0.0065 g./cm.^{2} of surface thereof with a nongaseous dissimilar organic material and irradiating the thus-coated organic polymer with ionizing charged particle radiation of the group consisting of electrons and alpha particles having an energy of about 15–50,000 electron volts for a minimum exposure of 0.01 watt-second/cm.^{2} but for a maximum exposure insufficient to degrade said organic polymer and thereby bonding the dissimilar organic material to the organic polymer.

14. The process which comprises coating polyethylene terephthalate to the extent of not more than about 0.0065 g./cm.^{2} of surface thereof with a nongaseous polyethylene oxide and irradiating the thus-coated polyethylene terephthalate with electrons of an energy of 15–50,000 electron volts for a minimum exposure of 0.01 watt-second/cm.^{2} but for a maximum exposure insufficient to degrade the same, and thereby bonding the polyethylene oxide to the polyethylene terephthalate.

15. The process which comprises coating polyethylene to the extent of not more than about 0.0065 g./cm.^{2} of surface thereof with a nongaseous polyethylene oxide and irradiating the thus-coated polyethylene with electrons of an energy of 15–15,000 electron volts for a minimum exposure of 0.01 watt-second/cm.^{2} but for a maximum exposure insufficient to degrade the same, and thereby bonding the polyethylene oxide to the polyethylene.

16. The process which comprises coating polyethylene terephthalate to the extent of not more than about 0.0065 g./cm.^{2} of surface thereof with a nongaseous polyvinyl chloride and irradiating the thus-coated polyethylene terephthalate with electrons of an energy of 15–50,000 electron volts for a minimum exposure of 0.01 watt-second/cm.^{2} but for a maximum exposure insufficient to degrade the same, and thereby bonding the polyvinyl chloride to the polyethylene terephthalate.

17. The process which comprises coating polyethylene to the extent of not more than about 0.0065 g./cm.^{2} of surface thereof with a nongaseous polyvinyl chloride and irradiating the thus-coated polyethylene with electrons of an energy of 15–50,000 electron volts for a minimum exposure of 0.01 watt-second/cm.^{2} but for a maximum exposure insufficient to degrade the same, and thereby bonding the polyvinyl chloride to the polyethylene.

18. The process which comprises coating polyethylene to the extent of not more than about 0.0065 g./cm.^{2} of surface thereof with palmitic acid and irradiating the thus-coated polyethylene with electrons of an energy of 15–50,000 electron volts for a minimum exposure of 0.01 watt-second/cm.^{2} but for a maximum exposure insufficient to degrade the same, and thereby bonding the palmitic acid to the polyethylene.

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