

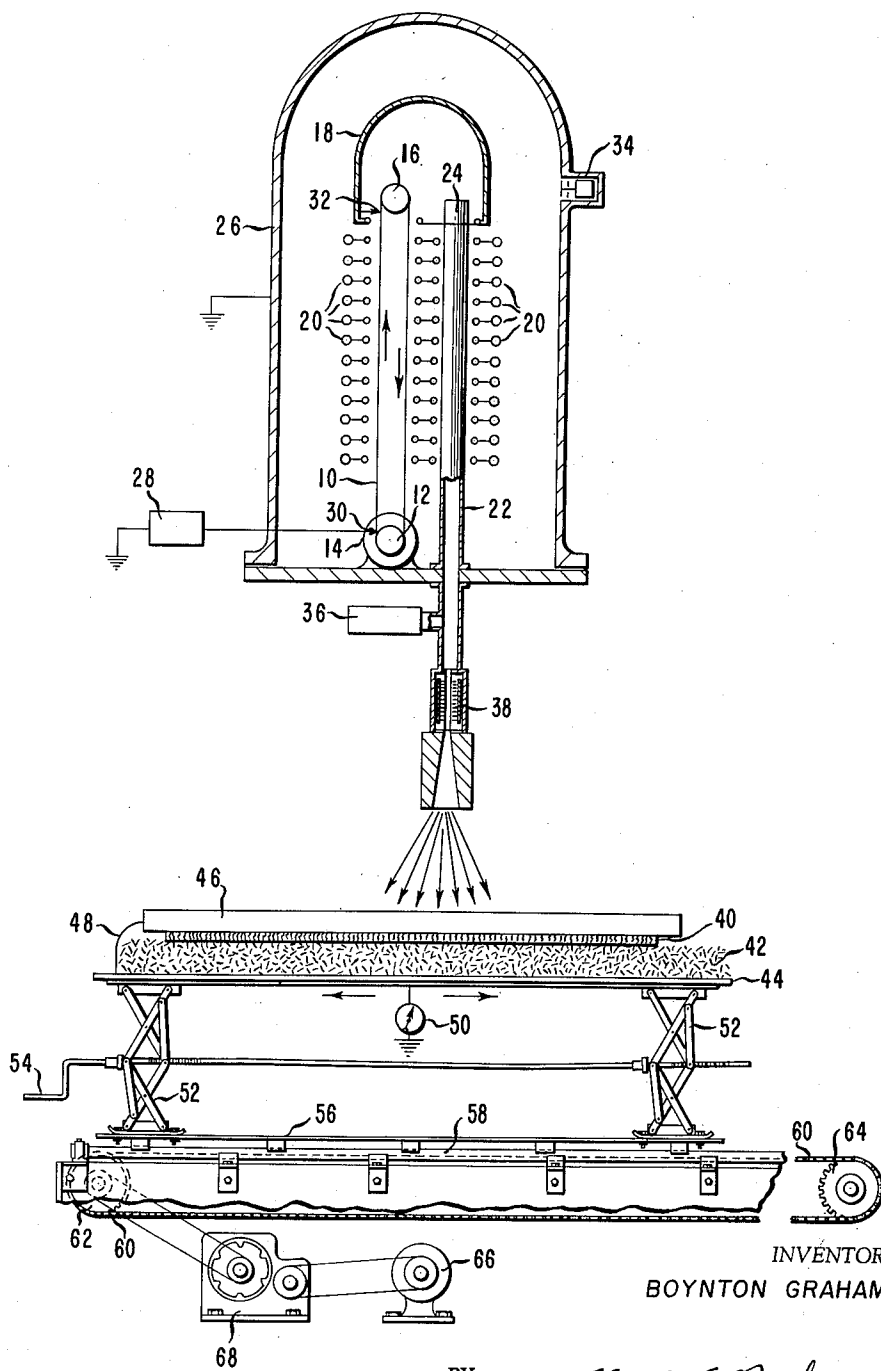
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IRRADIATION PROCESS

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IRRADIATION PROCESS

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This invention is concerned with a process and apparatus for inducing chemical reactions by high energy electron radiation, and is more particularly concerned with an improvement for inducing such reactions in a thin layer of material which is normally penetrated by the radiation without making effective use of it, as when reaction is desired at the surface of a synthetic polymer.

The depth of penetration of electron radiation is a function of the density of the material irradiated and of the electron energy, which will be expressed by the empirical formula

$$PD=0.542E-0.133+0.133e-3.3E(1+E^2)$$

where P is the penetration in centimeters, D is the density of the material in gm./cc. and E is the energy of the electrons in millions of electron volts (m. e. v.). In the third term e is the base of natural logarithms (2.718 . . .); this term becomes negligible for values of E above 0.8 m. e. v.

The effect of high energy electron radiation in inducing chemical reactions will be called the ionization effect. During penetration the nature of the radiation is apparently modified in some manner to develop this ionization effect. An unmodified beam of electrons has been found to have little ionization effect at the exposed surface of irradiated material, and substantial ionization effect is only obtained after appreciable penetration, with the maximum occurring at a depth of about one-third of the total depth of penetration for the material. The modification is independent of the nature of the material irradiated and the characteristics of the electron radiation, i. e., as shown by the above equation, relating the penetration P with the density of material D and electron energy E, changes in the values of D or E will change the value of P but the maximum ionization effect will nevertheless occur at a depth of penetration of about P/3. On the contrary, development of the ionization effect occurs in a manner which suggests that electron energy has been changed into other energy having an extremely short range of effectiveness.

It is an object of the present invention to provide a process for irradiating inanimate materials with high energy electrons to produce maximum ionization effects for chemical reactions at the exposed surface of the material or at much shorter depths of penetration than would normally be the case. Another object is to provide an improved apparatus for conducting such irradiations. Other objects will become apparent from the specification and claims.

In accordance with this invention it has been found that greatly improved ionization effects are obtained at relatively short distances of penetration with electron energies of at least 0.1 m. e. v. by passing the electrons through an electrically conductive shield before impinging the electrons on the material to be irradiated when using a grounded shield which is in close proximity to the material treated and has a thickness in the direction of electron travel of 0.1P to 0.5P, where P is the penetra-

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tion distance calculated by the above formula for the electron energy and density of shield used.

The drawing shows an embodiment of the apparatus of this invention suitable for use in practicing the above process. A conventional electrostatic accelerator is shown diagrammatically in the upper part of the figure. A charge conveyor belt 10 of high dielectric strength passes around pulley 12 of driving motor 14 and idler pulley 16 which is located in the field-free space of hollow, rounded metallic terminal 18. The high-voltage terminal is supported from ground by an insulating column 20 constructed of spaced metallic equipotential members and glass disk insulators. This column surrounds the charge conveyor belt and an electron acceleration tube 22, both being arranged parallel to the axis of the column. An electron source 24 is provided at the end of the acceleration tube within the high-voltage terminal. All of the elements so far described are contained within grounded pressure tank 26, which is filled with nitrogen-carbon dioxide mixture under pressure.

A transformer rectifier 28 is the source of accelerating charge, and this is sprayed on the charge conveyor belt by spray points 30 located at the motor pulley end of the belt travel. The charge is carried up the column into the high voltage terminal, where charge remover points 32 transfer the charge to the terminal. A negative potential is thereby built up on the terminal and maintained at any equilibrium value, e. g., 2 million volts, by regulating the transformer 28, a voltmeter 34 being provided for control purposes. Electrons from source 24 at the terminal end of the tube 22 are repelled by this negative potential and are progressively accelerated down the tube, along which a uniform voltage distribution is secured by flow of charge from terminal to ground through resistors between the metal members of the column. The tube is evacuated by high vacuum pump 36. The tube extends out of the pressure tank to direct the electron radiation onto the material being treated, and scanning coils 38 are provided to improve the efficiency and uniformity of treatment.

The material to be treated is shown as a film or sheet 40. It is supported on a mat of glass fibers 42 on a metal traversing table 44. An electrically conductive shield 46 is placed on top of the material so that the radiation passes through the shield immediately before reaching the material. The shield may be a sheet of solid metal or other conductive material, or a tank containing an electrically conductive liquid or solution. The thickness is predetermined to provide the desired improvement in treatment as described subsequently. The shield is grounded to the table by lead 48, and the table is grounded through ammeter 50 to indicate the electron flux.

The table is supported on jacks 52 so that the height can be adjusted. Adjustment is accomplished by turning crank 54. The jacks are in turn supported on carriage 56 mounted on track 58 to traverse the material beneath the radiation. The carriage is moved by chain 60 passing over sprocket wheels 62, 64, wheel 62 being driven by motor 66 through speed reducer 68. Suitable remote controls are provided for operating the motor to provide the desired rate of traverse and number of passes.

Beams of electrons with energies of at least 0.1 m. e. v. for use in this invention may be obtained by accelerating electrons with such devices as a resonant cavity accelerator, a Van de Graaff generator, a betatron, or the like, or from a natural or artificial source of beta radiation. It is to be understood that this invention is limited to the use of electron irradiation plus whatever X-rays the electron beam may generate in the shield, substrate and support. All electron energies noted in this discussion refer

to the strength of the electron beam just before it enters the grounded conductive shield.

The grounded electrically conductive shield is a layer of material substantially uniform in thickness which is maintained at earth potential by being electrically grounded. Such a shield may be a sheet of a solid metal, such as aluminum, copper, iron, nickel, lead or the like, or it may be a layer of an electrically conductive liquid, such as mercury, an aqueous salt solution or the like. The reason for the superior results obtained with a grounded shield in the present invention over the same shield in an insulated ungrounded condition is not understood, but a surprising improvement is obtained as shown in the examples below. When an accelerator is used in producing the electron beam, the grounding may be carried out through an ammeter to give an indication of the electron flux.

The thickness of the shield can be selected to provide maximum ionization effect at the surface of the material treated or at a given depth of penetration in the substrate. The proper thickness is readily determined by the formula

$$PD = 0.542E - 0.133 + 0.133e^{-3.3E(1+E^2)}$$

where P is the penetration in centimeters, D is the density of the material in gm./cc. and E is the electron energy in m. e. v. Thus, for 2 m. e. v. electrons

$$PD = 1.084 - 0.133 = 0.951$$

gm./cm.² and the maximum ionization effect is obtained at one-third this value or 0.317 gm./cm.². If the density and thickness of the shield are selected to give this value, then the maximum ionization effect will occur at the surface of material in contact with the shield. If the density and thickness of the shield are such that the product is 0.217, then the maximum ionization effect will occur at a depth of 0.100 gm./cm.² in a substrate in contact with the shield. The value of 0.317 gm./cm.² indicates the point at which optimum ionization effects occur, but this represents the peak, or center, of a somewhat broader range of useful ionization effects. For surface treatment of material, or treatment of thin substrates, substantial improvements in the effect of electron irradiation are obtained with grounded shields having thicknesses ranging from 0.1 to 0.5 the penetrating range of the electrons. For 2 m. e. v. electrons, this represents a preferred range of thickness-density value for the shielding from 0.0951 to 0.4755 gm./cm.². When the grounded shield is aluminum of specific gravity 2.699 and 2 m. e. v. electrons are used, shielding ranging from 0.0352 cm. to 0.1762 cm. in thickness is thus preferred.

It is necessary that the grounded shield be in close proximity to the surface of the substrate being irradiated. The most preferred arrangement is for direct contact between the grounded shield and the substrate. In some instances, as in the irradiation of a knitted or woven fabric, it is not possible for the shield to contact all of the surface of the substrate. In such instances it is preferred that the shield and substrate should touch as much as possible, for instance, by being pressed together. The effect of the grounded shield is somewhat reduced when a gap of as much as 0.5 cm. of air, inert gas or vacuum intervenes between the shield and the substrate, and gaps of more than 2 cm. result in such attenuation of the effect of the shield as to be of little value.

This invention is applicable to the treatment of all manner of inanimate substrates. It is, for example, useful in surface treatment of massive solid objects where the entire electron radiation emerging from the grounded shield is absorbed in the object, with maximum ionization effect taking place at or near the surface of the object. The invention is particularly useful in the treatment of thin, solid and/or liquid substrates in which a substantial portion of the radiation emerging from the shield passes on through the substrate. In such instances it is highly desirable to have the peak ionizing effect of the radiation occur within the confines of the substrate.

The use of this invention is not confined to the treatment of liquids and solids since gaseous substrates are readily passed adjacent to the grounded shield either in a separate container, such as a glass tube or the like, or in contact with the shield, as in an apparatus in which the grounded shield is the upper member of the container for the gas. Thus, intermolecular reactions between the species in a mixture of gases are readily induced by passing the gaseous mixture into the path of the electron beam as it emerges from the grounded shield.

In a preferred embodiment of this invention a coated or uncoated film of polyethylene, or a coated polyethylene terephthalate film, is arranged not more than 1 mm. below an electrically grounded sheet of metal having a thickness-density value of 0.32 g./cm.², is irradiated from above with 2 m. e. v. electrons for an exposure of 10 to 1000 watt-sec./cm.². The ionization produced in the case of polyethylene film results in crosslinking of the polymer. This is shown by a marked rise in the temperature at which self-supporting film retains tensile strength and form stability. In the case of either type of film, coatings of organic or inorganic materials are grafted onto the surface of the polymer by the ionizing effect of the radiation.

As is shown particularly in Example I, the practice of this invention gives results which are not attainable simply by prolonging the exposure of a substrate to an unshielded electron beam.

In the following examples, which illustrate specific embodiments of the process, parts are by weight except where otherwise indicated:

Example I

A film of polyethylene terephthalate 0.001" thick with a surface electrical resistivity of greater than $10^{13.7}$ ohm-cm. is immersed in a 10% aqueous solution of a polyethylene oxide of 20,000 molecular weight ("Carbowax" 20 M) containing 0.1% of a wetting agent, octylphenyl polyglycol ether ("Triton" X-100). The film is allowed to drain and air dry and is then wrapped in 0.8 mil aluminum foil. The foil-wrapped film is placed on a 1" thick mat of glass fibers on an electrically grounded traversing table. Over the film is placed a 31 mil aluminum plate and on top of this a 10 mil aluminum plate whose edges are immersed in pans of water which are in electrical contact with the traversing table. The total thickness of grounded aluminum shielding is 41.8 mil or 0.28 g./cm.². The assembly is passed 40 times under the electron beam of a Van de Graaff accelerator operating at 2 m. e. v. and 250 microamps. The scan width is 20 cm., the window-to-sample distance 10 cm. and the pass rate is 2 cm./sec. Under these conditions, the assemblage is exposed to a total radiation of 500 watt-sec./cm.² during the 40 passes. The irradiated film is then extracted in a Soxhlet apparatus for 30 hours with ethanol and dried to constant weight in a vacuum. After this treatment, the film retains a visible coating of the polyether which amounts to 15.4% of the original weight of the film. The film is further extracted for 3 days with water in a Soxhlet extractor. The coating of polyether is still visible and amounts to 1.1% of the original weight of the film. The extracted film has an electrical surface resistivity of $10^{11.5}$ ohm-cm. This lower value of surface resistivity results in improved static dissipation.

In contrast, a film which has been similarly coated and irradiated except that the 0.28 g./cm.² aluminum shield is not electrically grounded during the irradiation, retains a coating which amounts to only 9.5% of its initial weight after the ethanol extraction and only 0.5% after the water extraction and then has a surface electrical resistivity of $10^{11.9}$ ohm-cm. In further contrast, a film which is similarly irradiated in the absence of any shielding shows no retained polyether, no measurable weight gain, and a surface electrical resistivity greater than $10^{13.7}$ ohm-cm. after simple extraction with hot

running water. A similar irradiation wherein the exposure is increased to 5,000 watt-sec./cm.² (400 passes) without use of any shielding results in a product which, after extraction with water in a Soxhlet apparatus, has a surface electrical resistivity of $10^{13.2}$ ohm-cm. and no measurable weight gain. This film is extremely brittle.

Example II

A 2 mil film of polyethylene is immersed in aqueous polyethylene oxide of 20,000 molecular weight ("Carbowax" 20 M), dried and irradiated under an 0.28 g./cm.² grounded aluminum shield to an exposure of 500 watt-sec./cm.² under the conditions described in Example I. After extraction with alcohol, the film exhibits a weight gain of 0.5%, has a visible coating of polyether, and an improved receptivity for the acetate dye, "Acetamine" Rubine B. In contrast, a film which is similarly coated and irradiated without use of any shield, does not exhibit any measurable weight gain after simple extraction with hot running water.

Example III

A stack of similar 2 mil films of polyethylene is irradiated on a support of matted glass fibers and under two 31 mil aluminum plates plus a 0.7 mil aluminum film which is electrically grounded to the table. The irradiation conditions are those described in Example I except that an exposure of 12.5 watt-sec./cm.² is utilized (1 pass). The 62.7 mils of aluminum shielding is equivalent to 0.43 g./cm.² The topmost film of the stack exhibits a "zero strength temperature" of 118° C. and the third film from the top has a zero strength temperature of 132° C.

When a stack of films is similarly irradiated except that the 0.43 g./cm.² of aluminum shielding is not electrically grounded, the zero strength temperature of the topmost film is 100–105° C., and of the third film is 113° C. Essentially similar results are obtained when ungrounded shields of copper (0.32 g./cm.²) and lead (0.29 g./cm.²) are used.

In contrast, similar irradiation of an unshielded stack of polyethylene film gives a zero strength temperature of 100° C. for the topmost film, and a zero strength temperature of 130° is obtained only at the level of the 105th film.

In carrying out the zero strength temperature test, a 0.5 x 4.0 cm. sample of film, taken in the "machine direction," is weighted with a small clamp to give a stress of 10 lb./sq. in. and heated in an oven at a rate of 2–3° C./min. until the film breaks. Under these conditions, an unirradiated polyethylene film exhibits a zero strength temperature of 100–105° C.

Example IV

A 1 mil film of polyethylene terephthalate is immersed in a 1% hydrosol of calcium fluoride prepared essentially according to the method of Bachmann and Pinnow, Kolloid-Z. 62, 131 (1933). While still wet with the calcium fluoride sol, the film is wrapped in 0.7 mil aluminum foil and irradiated directly upon the electrically grounded traversing table under an electrically grounded shield comprising 54.4 mils of aluminum (0.37 g./cm.²). The irradiation exposure is 500 watt-sec./cm.² delivered under the conditions described in Example I. After irradiation, the film is allowed to air dry. It exhibits a weight gain of 1.6% and has a surface electrical resistivity of $10^{10.9}$ ohm-cm., whereas a similarly coated film, which is simply allowed to air dry without irradiation, exhibits a weight gain of 0.1% and a surface electrical resistivity greater than $10^{13.7}$ ohm-cm.

Example V

A film of 2 mil polyethylene is immersed in the calcium fluoride hydrosol and irradiated as in Example IV. After rinsing with hot running tap water, the irradiated film

exhibits a weight gain of 1.3% whereas a film which has been similarly immersed in the sol and rinsed without irradiation shows no weight gain.

Example VI

Four 1 mil polyethylene terephthalate films are immersed in a 10% aqueous solution of polyethylene oxide of 20,000 molecular weight ("Carbowax" 20 M), air dried, enclosed separately in 0.7 mil aluminum foil, and irradiated respectively under the electrically grounded shields noted below at an exposure of 500 watt-sec./cm.² under the conditions described in Example I. After irradiation, the films are extracted with water in a Soxhlet apparatus and dried under vacuum to constant weight. The film which has been irradiated under an 0.22 g./cm.² aluminum shield exhibits a weight gain of 3.9% and a surface electrical resistivity of greater than $10^{13.7}$ ohm-cm. The film which has been irradiated under an 0.29 g./cm.² aluminum shield exhibits a weight gain of 4.2% and a surface electrical resistivity of $10^{12.8}$ ohm-cm. The film which has been irradiated under 0.36 g./cm.² aluminum shield exhibits a weight gain of 5.1% and a surface electrical resistivity of $10^{12.3}$ ohm-cm. The film which has been irradiated under an 0.43 g./cm.² aluminum shield exhibits a 3.2% weight gain and a surface electrical resistivity of greater than $10^{13.7}$ ohm-cm. In contrast, films similarly coated with polyethylene oxide and irradiated under ungrounded aluminum shields exhibit weight gains of 3.1% at 0.22 g./cm.² of shielding, 1.3% at 0.29 g./cm.² of shielding, 2.1% at 0.36 g./cm.² of shielding and 1.7% at 0.43 g./cm.² of shielding.

Example VII

A 1 mil film of polyethylene terephthalate is immersed in a 10% aqueous solution of stannic chloride containing 0.1% of octylphenyl polyglycol ether ("Triton" X-100), wrapped while still wet in 2 mil polyethylene film, which serves as a parting or stripping agent, and irradiated under 0.35 g./cm.² of electrically grounded aluminum shielding at an exposure of 500 watt-sec./cm.² as in Example I. The irradiated film is then extracted for 20 hours with hot running tap water and dried to constant weight in a vacuum. The weight gain is 3.8% and the surface electrical resistivity is $10^{13.2}$ ohm-cm., whereas a control film which has been similarly treated with stannic chloride but not irradiated exhibits a weight gain of 3.0% and a surface electrical resistivity greater than $10^{13.7}$ ohm-cm.

Example VIII

A 1 mil film of polyethylene terephthalate is immersed in a 10% aqueous solution of polymethacrylic acid, wrapped while still wet in aluminum foil and irradiated at an exposure of 500 watt-sec./cm.² as in Example I under 0.43 g./cm.² of electrically grounded aluminum shielding. The film is then extracted for 3 days with cold running water. It exhibits a weight gain of 2.9%, whereas a film similarly treated with polymethacrylic acid but allowed to air dry and then extracted with water without irradiation exhibits a weight gain of only 1.0%.

Example IX

A 2 mil film of polyethylene is immersed in a 10% aqueous solution of polymethacrylic acid, wrapped while still wet in aluminum foil and irradiated as in Example I under 0.43 g./cm.² of electrically grounded aluminum shielding at an exposure of 500 watt-sec./cm.². After extracting with cold running water, the film exhibits a weight gain of 2.2%, whereas a film which had been similarly immersed in 10% aqueous polymethacrylic acid and then air dried and extracted without irradiation, exhibits a weight gain of only 0.6%.

Example X

A 1 mil film of polyethylene terephthalate is immersed in a 10% aqueous solution of polyacrylic acid, wrapped while still wet in 0.7 mil aluminum foil and irradiated as

in Example I under 0.43 g./cm.² of electrically grounded aluminum shielding. The film is then extracted for 24 hours with water in a Soxhlet apparatus and dried to constant weight. It exhibits a weight gain of 19% and a surface electrical resistivity of $10^{12.9}$ ohm-cm., whereas a film which has been similarly immersed in 10% aqueous polyacrylic acid and then air dried and extracted without irradiation exhibits a weight gain of only 0.2% and a surface electrical resistivity greater than $10^{13.7}$ ohm-cm.

Example XI

A 2 mil film of polyethylene is immersed in a 10% aqueous solution of polyacrylic acid containing 0.1% of the dioctyl ester of sodium sulfosuccinate ("Aerosol" OT), wrapped while still wet in 0.7 mil aluminum foil and irradiated as in Example I under 0.44 g./cm.² of electrically grounded aluminum shielding. After extracting with water in a Soxhlet extractor and drying to constant weight, the film exhibits a weight gain of 19.7% and a surface electrical resistivity of $10^{12.7}$ ohm-cm., whereas a film which has been immersed in the aqueous polyacrylic acid solution and then air dried and extracted without irradiation exhibits a weight gain of only 0.5% and a surface electrical resistivity greater than $10^{13.7}$ ohm-cm.

Example XII

A 1 mil film of polyethylene terephthalate is immersed in a 10% aqueous solution of polyacrylic acid, air dried, wrapped in 0.7 mil aluminum foil and irradiated as in Example I under 0.43 g./cm.² of electricity grounded aluminum shielding. After extracting for 3 days in cold running water and drying to constant weight, the film exhibits a weight gain of 5.5%.

Example XIII

A 2 mil film of polyethylene is immersed in a 10% aqueous solution of polyacrylic acid containing 0.1% of the dioctyl ester of sodium sulfosuccinate ("Aerosol" OT) wetting agent, allowed to air dry, wrapped in 0.7 mil aluminum foil, and irradiated as in Example I under 0.43 g./cm.² of electrically grounded aluminum shielding. After extracting for 3 days with cold running water and drying to constant weight, the film exhibits a weight gain of 15.9%.

Example XIV

A 1 mil film of polyethylene terephthalate is immersed in a 3.3% alumina hydrosol prepared essentially according to the process of U. S. Patent No. 2,590,833. The film is allowed to air dry, wrapped in 2 mil polyethylene film and irradiated as in Example I under 0.35 g./cm.² of electrically grounded aluminum shield. After extracting for 20 hours with water in a Soxhlet apparatus and drying to constant weight, the film exhibits brilliant interference colors and analysis shows a retention of 1.03% aluminum, whereas a film similarly coated with alumina, dried and extracted without irradiation retains only 0.63% aluminum.

Example XV

A 2 mil film of polyethylene is immersed in a 3.3% alumina hydrosol containing 0.1% of octylphenyl polyglycol ether ("Triton" X-100), allowed to air dry, wrapped in 2 mil polyethylene film and irradiated as in Example I under 0.35 g./cm.² of electrically grounded aluminum shield. After extraction with water and drying, analysis of the film shows a retention of 0.98% aluminum, whereas a film which has been similarly immersed in the alumina hydrosol but dried and extracted without irradiation retains only 0.63% aluminum.

It will be readily understood that the amount of electron radiation which will be effective in producing ionization in a substrate will vary widely with the nature of the substrate being irradiated and the extent of ionization desired to obtain a particular effect.

Usually a minimum exposure of at least 1 watt-

sec./cm.² (calculated from the beam strength just before it enters the grounded shield) is necessary since lower degrees of exposure do not give useful amounts of ionization in the substrate. The amount of ionization usually increases with increasing degrees of exposure. Upper exposure limits depend on the degree of ionization desired and on the radiation resistance of the substrate. Exposures as high as 1000 to 10,000 watt-sec./cm.² may be utilized in the case of radiation-resistant substrates, such as polystyrene, whereas exposures of 100 to 1000 watt-sec./cm.² may suffice for more sensitive substrates, such as polyvinyl chloride and the polyamides. Excessive exposures resulting in major degradation of the substrate are to be avoided.

Beam energies may also vary between wide limits. A minimum of 0.1 m. e. v. is required to produce a useful amount of ionization. For convenience of operation, higher beam energies are frequently desirable. Thus, electron beams of 10 m. e. v. and higher are useful in obtaining a maximum of ionization in a minimum of time, and there is no practical upper limit to the beam energies which may be employed in this invention.

In the foregoing examples there has been shown the use of this invention in improving the physical properties of organic solids (Example III), in grafting organic liquids to organic solids (Examples I, II, IV, and VIII-XIII), and in grafting inorganic solids to organic solids (Examples IV, V, VII, XIV and XV).

The products of the grafting reactions shown in the examples are solid composites, but this invention is not limited to use in preparing solid products. Intermolecular reactions between materials in any state are readily accomplished. For example, intermolecular reactions between components in a solution may be brought about as well as reaction between a solvent and solute. Dispersions of gases in liquids, and of gases and solids in liquids, as well as mixtures of gases, are readily treated according to this invention by passing the dispersions, or mixtures, preferably while being vigorously agitated, under a grounded conductive shield in the path of electron bombardment.

Since ionization by electron bombardment is much more readily produced in organic materials than in inorganic materials, the substrates preferred for treatment according to this invention are organic materials, i. e., compounds containing at least one C—X bond, where X is hydrogen, halogen or another carbon atom.

This preference for organic substrates includes both those instances involving a single molecular species as in the crosslinking of an organic polymer by reaction between molecules as well as in grafting reactions in which substantial reaction between two or more species of organic compounds is produced.

Time and temperature of treatment in this invention are not critical except to the extent that temperatures must not exceed the stability limits of the substrate being treated. The heating effects of electron bombardment are well known. When high intensity electron radiation is used, suitable means for dissipating heat are preferably employed. In the examples this is accomplished by the interval between passes of the assembly being irradiated under the electron beam. This allows for dissipation of heat into the surrounding air. Mechanical cooling, as with ice, cooling coils and the like may also be employed. The material of the electrically conductive grounded shield is limited only by the requirement that it be sufficiently conductive to come to earth potential when electrically connected to an adequate ground and that such conductivity also be adequate for maintaining the shield at earth potential by the action of the ground during the irradiation process.

Many relatively poor conductors are operable for use as shields in this invention, but it is preferred that the material of the shield have an electric resistivity not greater than 1×10^{-3} ohm-cm. at room temperature.

It is further preferred that the substrate be chemically different from the material of the grounded shield, and that the substrate be either electrically insulated from the shield or be a poorer conductor than the shield. Thus, substrates which are to be irradiated in direct contact with the shield should preferably have electrical resistivities greater than 1×10^{-3} ohm-cm. at room temperature. When substrates with electrical resistivities less than 1×10^{-3} ohm-cm. at room temperature are irradiated according to this invention, it is preferred that they be electrically insulated from the grounded shield.

The process of this invention is particularly suited for the continuous irradiation of substrates by passing the substrate in the form of a film, fiber, fabric, fluid or the like continuously under a grounded shield from which a modified electron beam is emerging.

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.

What is claimed is:

1. In a process utilizing the energy of a high-speed electron beam from an electron accelerator for inducing a chemical reaction in a substrate, the step improving the utilization of said energy which comprises interposing a grounded, electrically-conductive shield in the path of the electron beam between the electron accelerator and the substrate and not more than about 2 cm. from the latter.
2. The invention of claim 1 in which the grounded shield is not more than about 0.5 cm. from the substrate.
3. The invention of claim 1 in which the grounded shield is in contact with the substrate.
4. The invention of claim 1 in which the shield is metallic.

5. The invention of claim 4 in which the shield is made of aluminum.

6. The invention of claim 5 in which the aluminum is about 0.035–0.176 cm. thick.

7. In the modification of a polyethylene terephthalate substrate with a modification agent under the influence of a beam of high-speed electrons from an electron accelerator, the step of interposing a grounded, electrically-conductive shield in said beam between the electron accelerator and the substrate and not more than about 2 cm. from the latter.

8. The invention of claim 7 in which the shield is an aluminum plate.

9. In the modification of a polyethylene substrate with a modification agent under the influence of a beam of high-speed electrons from an electron accelerator, the step of interposing a grounded, electrically-conductive shield in said beam between the electron accelerator and the substrate and not more than about 2 cm. from the latter.

10. The invention of claim 9 in which the shield is an aluminum plate.

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