

(19)



(11)

EP 3 645 769 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
30.04.2025 Bulletin 2025/18

(21) Application number: **18755304.5**

(22) Date of filing: **27.06.2018**

(51) International Patent Classification (IPC):
C23C 24/02 ^(2006.01) **B05D 1/28** ^(2006.01)

(52) Cooperative Patent Classification (CPC):
C23C 24/02

(86) International application number:
PCT/IB2018/054772

(87) International publication number:
WO 2019/003153 (03.01.2019 Gazette 2019/01)

(54) METHOD OF MAKING AN ARTICLE

VERFAHREN ZUR HERSTELLUNG EINES ARTIKELS

METHODE DE FABRICATION D'UN ARTICLE

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **29.06.2017 US 201762526720 P**

(43) Date of publication of application:
06.05.2020 Bulletin 2020/19

(73) Proprietor: **3M Innovative Properties Company**
Saint Paul, Minnesota 55133-3427 (US)

(72) Inventors:
• **CREIGHTON, Megan A.**
Saint Paul, Minnesota 55133-3427 (US)
• **PRIOLO, Morgan A.**
Saint Paul, Minnesota 55133-3427 (US)

- **GETSCHEL, Joel A.**
Saint Paul, Minnesota 55133-3427 (US)
- **KOBE, Taylor J.**
Saint Paul, Minnesota 55133-3427 (US)
- **YORDEM, Onur Sinan**
Saint Paul, Minnesota 55133-3427 (US)
- **COONCE, Benjamin R.**
Saint Paul, Minnesota 55133-3427 (US)
- **VANDRE, Eric A.**
Saint Paul, Minnesota 55133-3427 (US)

(74) Representative: **Mathys & Squire**
Theatinerstraße 7
80333 München (DE)

(56) References cited:
US-A- 4 741 918 **US-A- 5 925 402**
US-A1- 2014 329 082 **US-A1- 2015 344 712**
US-B1- 6 511 701

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

TECHNICAL FIELD

- 5 **[0001]** The present disclosure broadly relates to methods for improving the durability of particle coatings on thermally-softenable films, and articles preparable thereby.

BACKGROUND

- 10 **[0002]** Coatings of certain particles (e.g., graphite) on substrates can be formed by rubbing a powder containing the particles against a substrate such as, for example, a thermoplastic film. Such powder coatings will be referred to herein as "powder-rubbed coatings". Examples of powder-rubbed coatings and methods of forming them include those disclosed in U. S. Pat. No. 6,511,701 B1 (Divigalpitiya et al.). However, such films are typically prone to damage by methods such as abrasion and/or rinsing with solvent.
- 15 **[0003]** US Patent 6511701B1 discloses a method of coating a polymer substrate with a dry composition comprising particles. The particles have a Mohs hardness between 1 and 2.5 and preferably a largest dimension of less than 100 microns. The particles are buffed on the substrate with an applicator which moves in a manner parallel to the surface of the substrate.
- 20 **[0004]** US patent US4741918 discloses a substrate coated with a coating material by rubbing substantially dry discrete particles of the coating material across the surface of the substrate with a sufficient rate of energy input to cause them to adhere. The particles are carried on the surface of a soft, resilient buffing wheel rotating sufficient rapidly to give peripheral speeds of from 2 to 200 m/s. Exemplified coating materials include metals, metal oxides and plastics. US patent application US2014329082 discloses an article including a substrate having a first major surface and optionally a second major surface. A layering arrangement is disposed on either or both of the first major surface and the second major surface. The
- 25 layering arrangement includes a carbon layer and a conducting polymer layer.
- [0005]** US patent US5925402 discloses coating powder is applied to a substrate as a means of providing a patterned coating on a substrate, either decorative or functional. Then the coating powder is fused or fused and cured in selected portions by computer-guided laser.
- 30 **[0006]** US patent application US2015344712 discloses methods and compositions for creating durable surface marks and/or decorations on substrates including metal, glass, ceramic, porcelain, natural and engineered stone, as well as plastics, polymer composites and other organic materials with color, high resolution and high contrast using inkjet technology and laser, NIR diode or UV LED energy. Smoothness and durability are obtained by using nanoparticles of silica, pigments and other materials in such marking processes.

35 SUMMARY

- [0007]** In a first aspect, the present disclosure provides a method of making an article comprising exposing a particle coating disposed on a thermally-softenable film to a modulated source of electromagnetic radiation wherein the thermally-softenable film comprises a thermoplastic polymer, wherein the modulated source of electromagnetic radiation comprises
- 40 a flashlamp, wherein the particle coating consists essentially of graphite, wherein the particle coating comprises loosely bound distinct particles that are not covalently bonded to each other, and are not retained in a binder material other than the thermally-softenable film.
- [0008]** By this technique, durability of the powder coating is improved, while alternative heating methods were prone to damaging (e.g., warping) the thermally-softenable film.
- 45 **[0009]** An article prepared according to the above method comprises a thermally-softenable film having a particle coating disposed thereon, wherein the particle coating comprises distinct particles that are not covalently bonded to each other, and are not retained in a binder material other than the thermally-softenable film, and wherein at least one portion of the particle coating corresponding to a predetermined pattern has a greater transmittance to visible light than at least one portion of the particle coating that is not disposed within the predetermined pattern.
- 50 **[0010]** An article prepared according to the above method comprises a thermally-softenable film having a particle coating disposed thereon, wherein the particle coating comprises distinct particles that are not chemically bonded to each other and are not retained in a binder material other than the thermally-softenable film, and wherein the change in transmittance is at most 60 percent after abrading the particle coating according to ASTM D6279-15 "Standard Test Method for Rub Abrasion Mar Resistance of High Gloss Coatings" with the 25 mm friction element being outfitted with a two
- 55 inch square Crockmeter cloth soaked in isopropanol for three seconds.
- [0011]** As used herein:
The term "visible light" refers to electromagnetic radiation having a wavelength of 400 to 700 nanometers (nm).
- [0012]** The term "powder" refers to a free-flowing collection of minute particles.

[0013] The term "pulsed electromagnetic radiation" refers to electromagnetic radiation that is modulated to become a series of discrete spikes with increased intensity. The spikes may be relative to a background level of electromagnetic radiation that is negligible or zero, or the background level may be at a higher level that is substantially ineffective to increase adhesion of particles in the particle coating to the film.

[0014] The term "thermally-softenable" means softenable upon heating.

[0015] The term "particle coating" refers to a coating of minute particles which may or may not be free-flowing.

[0016] Features and advantages of the present disclosure will be further understood upon consideration of the detailed description as well as the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017]

Fig. 1 is an enlarged schematic side view of an exemplary article 100 according to the present disclosure.

Fig. 2 is a digital photograph of a mask used in Example 9 (EX-9).

Fig. 3 is a digital photograph of the flashlamp treated graphite-coated film in EX-9.

Fig. 4 is a digital photograph of the flashlamp treated graphite-coated film in EX-9 after abrading with a solvent soaked wiper.

[0018] It should be understood that numerous other modifications and embodiments can be devised by those skilled in the art, which fall within the scope and spirit of the principles of the disclosure.

DETAILED DESCRIPTION

[0019] Advantageously, the present disclosure provides an easy method to enhance the durability of particle coatings (e.g., to solvent abrading) on thermally-softenable films using instantaneous heating by exposure to a modulated source of electromagnetic radiation comprising a flashlamp.

[0020] Referring now to Fig. 1, exemplary article 100 comprises a thermally-softenable (e.g., thermoplastic) film 110 having a particle coating 120 disposed thereon. The particle coating comprises distinct particles that are not covalently bonded to each other and are not retained in a binder material other than the thermally-softenable film.

[0021] Particle coatings on thermally-softenable films can be prepared by various known methods including, for example, exposure to an aerosolized powder cloud, contact with a powder bed, coating with a solvent-based powder dispersion coating followed by evaporation of solvent, and/or triboadhesion (rubbing dry particles against a substrate to form a powder-rubbed coating) of the powder using a rubbing process. Examples of triboadhesion methods can be found in U. S. Pat. Nos. 6,511,701 B1 (Divigalpitiya et al.), 6,025,014 (Stango), and 4,741,918 (Nagybaczon et al.). The remaining methods will be familiar to those of ordinary skill in the art.

[0022] Useful powders comprise minute loosely bound particles capable of absorbing at least one wavelength of the pulsed electromagnetic radiation, preferably corresponding to a majority of the energy of the pulsed electromagnetic radiation. Suitable powders are preferably at least substantially unaffected by electromagnetic radiation, but are moderate to strong absorbers of it. This is desirable to maximize the light (electromagnetic radiation) to heat conversion yield without altering the chemical nature of the powder particles.

[0023] Powders include powders comprising graphite, clays, hexagonal boron nitride, pigments, inorganic oxides (e.g., alumina, calcia, silica, ceria, zinc oxide, or titania), metal(s), organic polymeric particles (e.g., polytetrafluoroethylene, polyvinylidene difluoride), carbides (e.g., silicon carbide), flame retardants (e.g., aluminum trihydrate, aluminum hydroxide, magnesium hydroxide, sodium hexametaphosphate, organic phosphonates and phosphates and ester thereof), carbonates (e.g., calcium carbonate, magnesium carbonate, sodium carbonate), dry biological powders (e.g., spores, bacteria), and combinations thereof. Preferably, the powder particles have an average particle size of 0.1 to 100 micrometers, more preferably 1 to 50 micrometers, and more preferably 1 to 25 micrometers, although this is not a requirement. The particle coating according to the invention consists essentially of graphite.

[0024] - The particle coating, after application, consists essentially of (i.e., be at least 98 percent by weight, preferably at least 99 percent by weight, or even consist of) graphite particles.

[0025] Prior to exposure to the electromagnetic radiation the particle coating comprises loosely bound distinct particles that are not covalently bonded to each other, and are not retained in a binder material other than the thermally-softenable film itself.

[0026] The thermally-softenable film comprises one or more thermally-softenable (e.g., lightly crosslinked and/or thermoplastic) polymers. Exemplary thermally-softenable polymers that may be suitable for inclusion in a thermally-softenable film include polycarbonates, polyesters, polyamides, polyimides, polyurethanes, polyetherketone (PEK), polyetheretherketone (PEEK), polyphenylene sulfide, polyacrylics (e.g., polymethyl methacrylate), polyolefins (e.g.,

polyethylene, polypropylene, biaxially-oriented polypropylene), and combinations of such resins.

[0027] In general, a pulsed electromagnetic radiation may come from any source(s) capable of generating sufficient fluence and pulse duration to effect sufficient heating of the thermally-softenable film to cause the particle coating to bind more tightly to it. At least three types of sources may be effective for this purpose: flashlamps, lasers, and shuttered lamps.

The selection of appropriate sources will typically be influenced by desired process conditions such as, for example, line speed, line width, spectral output, and cost.

[0028] According to the invention, the pulsed electromagnetic radiation is generated using a flashlamp. Of these, xenon and krypton flashlamps are the most common. Both provide a broad continuous output over the wavelength range 200 to 1000 nanometers, however the krypton flashlamps have higher relative output intensity in the 750-900 nm wavelength range as compared to xenon flashlamps which have more relative output in the 300 to 750 nm wavelength range. In general, xenon flashlamps are preferred for most applications, and especially those involving graphite powder. Many suitable xenon and krypton flashlamps are commercially available from vendors such as Excelitas Technologies Corp. of Waltham, Massachusetts and Heraeus of Hanau, Germany.

[0029] A pulsed electromagnetic radiation can be generated using a pulsed laser. Suitable lasers may include, for example, excimer lasers (e.g., XeF (351 nm), XeCl (308 nm), and KrF (248 nm)), solid state lasers (e.g., ruby 694 nm)), and nitrogen lasers (337.1 nm).

[0030] A pulsed electromagnetic radiation is generated using a continuous light source and a shutter (preferably a rotating aperture/shutter to reduce overheating of the shutter). Suitable light sources may include high-pressure mercury lamps, xenon lamps, and metal-halide lamps.

[0031] For maximum efficiency, the electromagnetic radiation spectrum is preferably most intense at wavelength(s) that are strongly absorbed by the powder particles, although this is not a requirement. Likewise, in the case of reflective powders, the electromagnetic radiation spectrum is preferably most intense in spectral regions in which the powder is least reflective, although this is not a requirement.

[0032] Preferably, the source of pulsed electromagnetic radiation is capable of generating a high fluence (energy density) with high intensity (high power per unit area), although this is not a requirement. These conditions assure that the sufficient heat is absorbed to effect increased adhesion of the powder particles to the film. However, the combination of intensity and fluence should not be so great/high as to cause ablation, excessive degradation, or volatilization of the thermally-softenable film. Selection of appropriate conditions is within the capability of one of ordinary skill in the art.

[0033] To minimize heating of interior portions of the thermally-softenable film that cannot interact with the powder particles, the pulse duration is preferably short; e.g., less than 10 milliseconds, less than 1 millisecond, less than 100 microseconds, less than 10 microseconds, or even less than 1 microsecond, although this is not a requirement.

[0034] To achieve high line speed in continuous manufacturing processes, not only should the pulsed electromagnetic radiation preferably be powerful, but the exposure area is preferably large and the pulse repetition rate is preferably fast (e.g., 100 to 500 Hz).

[0035] Advantageously, the modulated electromagnetic radiation may be directed through a mask having transmissive and non-transmissive regions according to a predetermined pattern (e.g., see Fig 2.). Accordingly, exposed regions of the particle coating may become more transparent to visible light than unexposed region of the particle coating (see Fig. 3). After, an optional development step (e.g., mild abrasion with a solvent-soaked wiper), a particle coating remains in the exposed region according to the predetermined pattern while it is substantially or completely removed in the unexposed (i.e., blocked) region (see FIG. 4).

SELECT EMBODIMENTS OF THE PRESENT DISCLOSURE

[0036] In a first embodiment, the present disclosure provides a method comprising exposing a particle coating disposed on a thermally-softenable film to a modulated source of electromagnetic radiation, wherein the thermally-softenable film comprises a thermoplastic polymer, wherein the modulated source of electromagnetic radiation comprises a flashlamp, wherein the particle coating consists essentially of graphite, wherein the particle coating comprises loosely bound distinct particles that are not covalently bonded to each other, and are not retained in a binder material other than the thermally-softenable film.

[0037] In a second embodiment, the present disclosure provides a method according to the first wherein the particle coating comprises a powder-rubbed coating.

[0038] In a third embodiment, the present disclosure provides a method according to any one of the first to second embodiments, wherein the particle coating is exposed to the pulsed electromagnetic radiation according to a predetermined pattern.

[0039] Objects and advantages of this disclosure are further illustrated by the following non-limiting examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this disclosure.

EXAMPLES

[0040] Unless otherwise noted, all parts, percentages, ratios, etc. in the Examples and the rest of the specification are by weight. All reagents used in the examples were obtained, or are available, from general chemical suppliers such as, for example, Sigma-Aldrich Company, Saint Louis, Missouri, or may be synthesized by conventional methods.

MATERIALS USED IN THE EXAMPLES

[0041]

DESIGNATION	DESCRIPTION
Melinex PET	polyethylene terephthalate (PET) film, 125 micrometers thick, glass transition temperature (T_g) of 76°C, obtained from DuPont Tejin Films, Chester Virginia, as MELINEX ST505 polyester film
Bare PET	PET film, 2-mil, (51 micrometers) thickness
MICRO 850	Graphite powder, 3-5 micrometers particle size, 13 m ² /g surface area, 0.088 ohm·cm resistivity, obtained from Ashbury Graphite Mills, Inc., Kittanning, Pennsylvania as MICRO850 graphite
Isopropanol (IPA)	solvent, obtained from Aldrich Chemical Company, Milwaukee, Wisconsin

GENERAL METHOD FOR COATING GRAPHITE ON SUBSTRATES

[0042] To make Examples and Comparative Examples described below, graphite coatings were applied onto PET films by placing a small amount of MICRO850 on the PET films. The graphite was then rubbed against the film using a WEN 10PMC 10-inch (25.8-cm) random orbital waxer/polisher (WEN Products, Elgin, Illinois) equipped with a wool polishing bonnet. The relative amount of graphite coating deposited on the PET film was determined by measuring the surface resistivity using a four-point probe and/or light transmittance.

[0043] For Examples EX-1 to EX-12 and Comparative Examples CEX-A to CEX-C, visible light transmittance was measured using a HAZE-GARD PLUS haze meter from BYK Additives and Instruments, Wesel, Germany.

[0044] For Examples EX-6 to EX-8, surface resistivity was measured using an RC2175 R-CHEK Surface Resistivity Meter from EDTM, Inc, Toledo, Ohio.

[0045] For Comparative Examples CEX-D to CEX-L, light transmittance was measured using a Flame-T-XR1-ES spectrophotometer from Ocean Optics, Dunedin, Florida. These transmittance measurements were recorded over the range of wavelengths from 325 to 1000 nm and averaged.

[0046] If thicker coatings were desired, more graphite was applied and the coating step was repeated.

GENERAL METHODS FOR DETERMINING DURABILITY

[0047] The samples prepared according to the Examples and Comparative Examples, described below, were tested for durability (resilience of coatings).

[0048] Durability of graphite-coated film specimens was evaluated using a Model 5750 Linear Abrader from Taber Industries, North Tonawanda, New York. For CEX-A, CEX-B, EX-1 to EX-9, and CEX-D to CEX-L, a 25mm flat head on the linear abrader was covered with an L40 WYPALL all-purpose wiper from Kimberly-Clark and saturated with isopropanol. The films were then subjected to 60 cycles/minute of abrasion using the 5750 Linear Abrader for a total of one minute, with a total mass loading of 350 g on the head. CEX-C and EX10 to EX12 were evaluated for durability according to ASTM D6279-15 "Standard Test Method for Rub Abrasion Mar Resistance of High Gloss Coatings", ASTM International, West Conshocken, Pennsylvania, with the 25 mm friction element being outfitted with a two inch (5.1 cm) square Crockmeter cloth soaked in isopropanol for three seconds. Crockmeter cloth is available from Testfabrics, Inc. West Pittson, Pennsylvania. Crockmeter cloth conforms to the specifications of ASTM D3690-02(2009) "Standard Performance Specification for Vinyl-Coated and Urethane-Coated Upholstery Fabrics-Indoor". Transmittance of graphite-coated film specimens was measured before and after durability testing. All transmittance measurements represent an average of at least 3 measurements.

[0049] All reported percent changes in transmittance were calculations from the following equation:

$$\Delta T(\%) = \frac{T_C - T_{\text{abraded}}}{T_C - T_{\text{film}}} \times 100$$

[0050] Where T_{film} is the transmittance of the underlying polymer film, T_C is the transmittance of that same film after the coating and treatments had been applied, and T_{abraded} is the transmittance of the coating after being subjected to the desired number of abrading cycles. Transmittance values of the films are typically around $92 \pm 5\%$, depending on the quality of the substrate used. Smaller changes in transmittance (ΔT , %) are indicative of higher retention of the total fraction of carbon on the original film.

EXAMPLES EX-1 to EX-12 and COMPARATIVE EXAMPLES CEX-A to CEX-C

[0051] CEX-A to CEX-C and EX-1 to EX-12 were prepared by subjecting graphite coated PET substrate films prepared as described above to an Intense Pulsed Light (IPL) irradiation. In all cases of IPL, the source used was a SINTERON S-2100 Xe flashlamp equipped with Type C bulb from Xenon Corporation, Wilmington, Massachusetts.

[0052] For CEX-A and EX-1, the substrate was Bare PET. EX-1 was placed under the flashlamp with the graphite-coated surface facing up and treated ten times at a pulse rate of 1 Hz and an energy density of 0.4 J/cm^2 .

[0053] CEX-B was prepared in the same manner as CEX-A, except that the substrate was Melinex PET.

[0054] EX-2 was prepared in the same manner as EX-1, except that the substrate was Melinex PET and treated 5 times at a pulse rate of 1 Hz and an energy density of 0.3 J/cm^2 .

[0055] EX-3 and EX-4 were prepared in the same manner as EX-2, except that the film was treated 1 time at a pulse rate of 1 Hz and an energy density of 0.5 J/cm^2 (EX-3) and 1.0 J/cm^2 (EX-4).

[0056] EX-5 was prepared similarly to EX-4, except the film was flipped over such that the graphite coated surface was facing away from the flashlamp bulb.

[0057] Table 1, below, reports the IPL effects on Bare PET and Melinex PET.

TABLE 1

EXAMPLE	IPL PULSES	ENERGY DENSITY PER PULSE, J/cm^2	ΔT , %
CEX-A	0	0	100.0
EX-1	10	0.4	13.3
CEX-B	0	0	98.3
EX-2	5	0.3	29.9
EX-3	1	0.5	20.9
EX-4	1	1.0	10.5
EX-5	1	1.0	5.4

[0058] EX-6 to EX-8 were prepared by coating three separate sheets of Bare PET with differing amounts of graphite to achieve differing surface resistivity values for each Example. EX-6 to EX-8 were placed under the flashlamp with the graphite-coated surface facing up and treated ten times at a pulse rate of 1 Hz and an energy density of 0.4 J/cm^2 . Table 2, below, reports the change in transmittance ΔT in %.

TABLE 2

EXAMPLE	INITIAL SURFACE RESISTIVITY, Ω/square	ΔT , %
EX-6	250	14.5
EX-7	564	22.3
EX-8	975	23.4

[0059] For EX-9, the substrate coated with graphite was Bare PET. Prior to exposure to IPL, a chromium/glass patterned photomask (shown in Fig. 2) was situated between the flashlamp and the graphite. The area directly adjacent to the mask is denoted as the unmasked area, whereas the area beneath the mask was shielded from IPL and is denoted as the masked area. Additionally, the photomask included linear shape openings in the chrome layer having width of approximately about 250 micrometers or having width of approximately about 500 micrometers. This demonstrates the ability of these coatings

to be patterned, with the openings portion of the mask representing a desired pattern for improved particle retention. Table 3 report the effects of IPL on particle retention of masked and unmasked (patterned) graphite coated PET.

[0060] Fig. 3 shows the resulting pattern, with the portion beneath the openings and masked portion. Fig. 4 shows the resulting pattern after being subjected to abrasion as described above, with the portion beneath the openings remaining coated with carbon and the masked portion being devoid of carbon due to abrasion.

TABLE 3

EX-9	ΔT , %
Masked	99.3
Unmasked	15.0

[0061] For CEX-C to EX-10, the substrate was Bare PET. EX-10 was placed under the flashlamp with the graphite-coated surface facing up and treated ten times at a pulse rate of 1 Hz and an energy density of 0.4 J/cm².

[0062] EX-11 was prepared in the same manner as EX-10, except that the film was coated with a different amount of graphite to achieve a higher surface resistivity value than EX-10.

[0063] EX-12 was prepared in the same manner EX-10, except that the substrate was Melinex PET and treated 5 times at a pulse rate of 1 Hz and an energy density of 0.3 J/cm².

[0064] Table 4, below, reports the change in transmittance ΔT in %.

TABLE 4

EXAMPLE	IPL PULSES	ENERGY DENSITY PER PULSE, J/cm ²	ΔT , %
CEX-C	0	0	79.4
EX-10	10	0.4	5.9
EX-11	10	0.4	11.1
EX-12	5	0.3	8.2

COMPARATIVE EXAMPLES CEX-D to CEX-L

[0065] For CEX-D to CEX-L, several sheets of Bare PET were coated with graphite as described above and subjected to several different methods to induce particle retention.

[0066] For CEX-D to CEX-F, graphite coated Bare PET films were subjected to blowing heat from a temperature controlled heat gun (Steinel Electronic Heat Gun, Model HL 2010 E, Type 3482 from Steinel America Inc., Bloomington, Minnesota). With the heat gun setting on level II, the end of the nozzle was situated 2 inches (about 5 cm) above and normal to the film surface, which was secured to the bench top with tape at each end, and applied heat to the film for a given amount of time.

[0067] For CEX-G to CEX-J, graphite coated Bare PET films were subject to e-beam irradiation, carried out using an electron beam system (MODEL CB-300 ELECTRON BEAM SYSTEM from Energy Sciences, Inc., Wilmington, Massachusetts). The coated PET specimens were taped on to a moving PET web and conveyed through the e-beam processor at a voltage of 110 keV. The web speed and e-beam current applied to the cathode were varied to ensure delivery of the targeted dose.

[0068] For CEX-K to CEX-L, graphite coated Bare PET films were subject to biaxial strain using a laboratory stretching machine (Brückner Maschinenbau, Model Karo IV Biaxial Stretcher from Brückner Maschinenbau GmbH & Co. KG, Siegsdorf, Germany). The machine's oven was set to 150°C, and the sample was placed in the oven for 5 minutes before being stretched biaxially at a constant rate of 1% per second.

[0069] Tables 5-7 summarize the effect of heat gun (Table 5), e-beam (Table 6), and biaxial stretch (Table 7) exposures had on particle retention (ΔT , %, average normalized change in transmission). For heat gun, an output greater than 232°C and/or for longer than 10 minutes was also applied, but was found to result in both excessive thermal degradation of the polymer or unrealistic processing conditions for manufacturing. For biaxial stretching, stretching larger than 5% was also applied, but was found to result in excessive tension of the polymer leading to film fracture.

TABLE 5

EXAMPLE	TEMPERATURE, °C	DURATION, minutes	ΔT , %
CEX-D	232	1	90.4
CEX-E	232	5	89.1
CEX-F	232	10	81.3

TABLE 6

EXAMPLE	DOSAGE, MRad	ΔT , %
CEX-G	2.5	90.0
CEX-H	5	88.9
CEX-I	10	91.3
CEX-J	20	90.4

TABLE 7

EXAMPLE	TEMPERATURE, °C	% STRETCH	ΔT , %
CEX-K	150	0	92
CEX-L	150	5	93.8

Claims

1. A method of making an article, the method comprising exposing a particle coating disposed on a thermally-softenable film to a modulated source of electromagnetic radiation, wherein the thermally-softenable film comprises a thermally softenable polymer, wherein the modulated source of electromagnetic radiation comprises a flashlamp, wherein the particle coating consists essentially of graphite, wherein the particle coating comprises loosely bound distinct particles that are not covalently bonded to each other, and are not retained in a binder material other than the thermally-softenable film.
2. The method of claim 1, wherein the particle coating comprises a powder-rubbed coating.
3. The method of claim 1 or 2, wherein the particle coating is exposed to the pulsed electromagnetic radiation according to a predetermined pattern.

Patentansprüche

1. Ein Verfahren zur Herstellung eines Gegenstandes, das das Aussetzen einer Teilchenbeschichtung, die auf einer thermisch-erweichbaren Folie abgeschieden ist, einer modulierten Quelle elektromagnetischer Strahlung umfasst, wobei die thermisch-erweichbare Folie ein thermisch-erweichbares Polymer umfasst, wobei die modulierte Quelle elektromagnetischer Strahlung eine Blitzlampe umfasst, wobei die Teilchenbeschichtung im Wesentlichen aus Graphit besteht, wobei die Teilchenbeschichtung lose gebundene einzelne Teilchen umfasst, die nicht kovalent aneinander gebunden sind und nicht in einem anderen Bindemittel als der thermisch-erweichbaren Folie gehalten werden.
2. Verfahren nach Anspruch 1, wobei die Teilchenbeschichtung eine geriebene Pulverbeschichtung umfasst.
3. Verfahren nach Anspruch 1 oder 2, wobei die Teilchenbeschichtung der gepulsten elektromagnetischen Strahlung nach einem vorgegebenen Muster ausgesetzt wird.

Revendications

1. Procédé de fabrication d'un article, le procédé comprenant l'exposition d'un revêtement de particules disposé sur un film apte à être ramolli thermiquement à une source modulée de rayonnement électromagnétique, dans lequel le film apte à être ramolli thermiquement comprend un polymère apte à être ramolli thermiquement, dans lequel la source modulée de rayonnement électromagnétique comprend une lampe flash, dans lequel le revêtement de particules consiste essentiellement en graphite, dans lequel le revêtement de particules comprend des particules distinctes faiblement liées qui ne sont pas liées de manière covalente les unes aux autres, et ne sont pas retenues dans un matériau de liaison autre que le film apte à être ramolli thermiquement.
2. Procédé selon la revendication 1, dans lequel le revêtement de particules comprend un revêtement frotté avec de la poudre.
3. Procédé selon la revendication 1 ou 2, dans lequel le revêtement de particules est exposé au rayonnement électromagnétique pulsé selon un schéma prédéterminé.

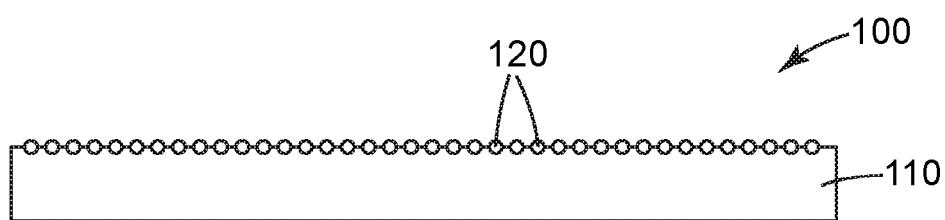


Fig. 1

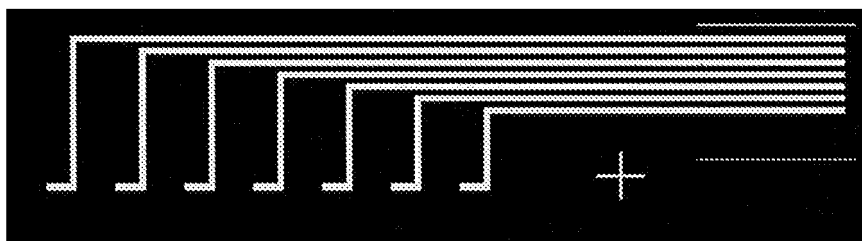


Fig. 2

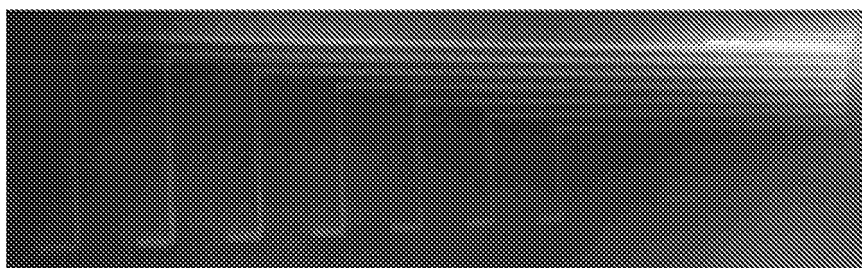


Fig. 3

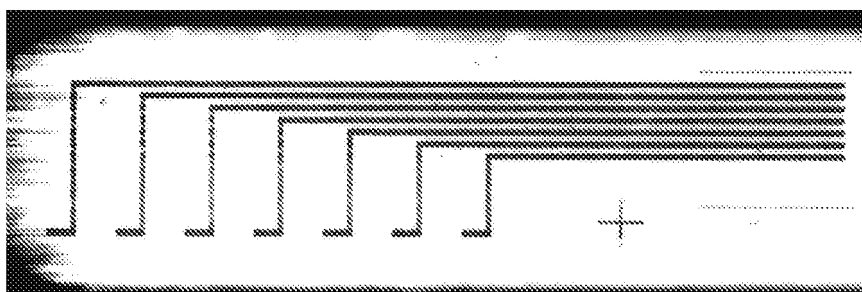


Fig. 4

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 6511701 B1, Divigalpitiya [0002] [0003] [0021]
- US 4741918 A [0004]
- US 2014329082 A [0004]
- US 5925402 A [0005]
- US 2015344712 A [0006]
- US 6025014 B1, Stango [0021]
- US 4741918 B1, Nagybaczon [0021]