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(54) **Title:** A PRINTABLE MAGNETIC RECEPTIVE COMPOSITE SHEET AND METHOD OF MAKING

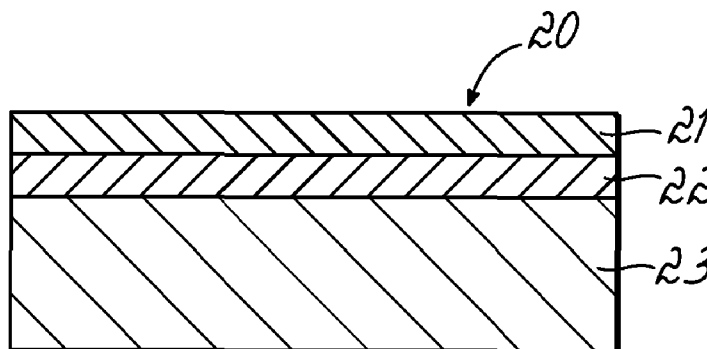


FIG. 2

(57) **Abstract:** Composite sheets are made by calendering thin layers of magnetic compositions and bonding to a top printable layer wherein the calendered layer has thickness up to 10 mils.



A PRINTABLE MAGNETIC RECEPTIVE COMPOSITE SHEET AND METHOD OF MAKING

FIELD OF THE INVENTION

[0001] Printable magnetic receptive composite sheets are disclosed. These composite sheets are made by calendering thin layers of magnetic compositions and bonding to a top printable layer wherein the calendered layer has thickness up to 10 mils.

BACKGROUND OF THE INVENTION

[0002] Magnetic printable assemblies that will self-adhere to a magnetically attractable surface are well known. Flexible materials in the form of sheets or rolls have been commercially available and are typically prepared by mixing a powdered ferrite material with a suitable polymeric or plastic binder into a uniform mixture and then extruding or calendering them into sheets or films. The magnetic material may then be permanently magnetized and the resulting pieces may then be placed on a magnetically attracted surface where they are often used in conveying information. Examples of prior art patents in this field include U.S. 7128798; 7338573; 5843329; 5609788 and the patents cited in these patents as representative of the prior art. Efforts have been made to produce relatively thin printable magnetic receptive films or sheets. However, no known methods are believed to allow for acceptable products having relatively thin layers of the binder/magnetic material mixture less than 10 mils.

SUMMARY OF THE INVENTION

[0003] This invention is directed to a printable magnetic receptive composite sheet having multiple layers. The sheet or film comprises a calendered magnetic layer of a thermoplastic binder and a magnetic material and a top printable layer bonded to the calendered layer, wherein the calendered magnetic layer has a thickness up to 10 mils. Printable magnetic receptive sheets are provided that are flexible, readily printable and employed for securement to a magnetically attracted surface. The thin printable magnetic sheets or films have outer surfaces that may be printed with a decorative pattern and/or promotional information. Therefore, they serve a very useful function in easily conveying information and/or promotional material on a variety of surfaces.

[0004] The printable magnetic receptive composites of this invention are several times more effective in magnetic capacity than presently available magnetic assemblies. This property is attributable to the method of making and assembly of the components in the printable magnetic receptive composite.

The amount of magnetic material in the composite magnetic layer is on the order of about 50% by wt. with the balance being about 50% by wt. of thermoplastic binder. More generally, a range of about 50% to 60% by wt. of magnetic material and 60% to 40% by wt. of thermoplastic binder is suitable.

The printable composite is of indefinite length and widths of up to about 60 inches are obtainable with the relatively think flexible construction of magnetic composite total layers up to 20 mils.

[0005] An additional unique feature of the inventive printable magnetic receptive composite is the inclusion of a prodegradant additive in the magnetic thermoplastic

binder and magnetic material layer composition to enhance the compatibility of the components, and yet facilitate the biodegradability of the composite. Thus, the magnetic receptive composite of the invention is especially adapted to be compostable in municipal solid waste composting facilities such that it may be degraded by physical, chemical, thermal and/or biological degradation. Therefore, after its usage as a composite to convey decorative patterns and/or other information by attachment of the magnets to a variety of surfaces, the composite may be disposed of by degradation in a municipal solid waste composting facility.

[0006] The printable magnetic receptive composite of this invention, its method of manufacture and compostability would be further understood with reference to the following detailed description.

DETAILED DESCRIPTION OF THE INVENTION

[0007] The printable magnetic receptive composite comprises a calendered magnetic layer of a thermoplastic binder and a magnetic material, typically a ferrous alloy powder. A printable top layer is bonded to the calendered layer, wherein the calendered magnetic layer has a thickness up to 10 mils. The thickness of the calendered magnetic layer is relatively thin and is on the order of about 6 to 10 mils. Thin, flexible composites are provided without pinholes or voids. The printable layer usually has a thickness of up to about 5 mils, resulting in an overall dimensional thickness of about 10 to 20 mils for the composite. Other features of this invention would be better understood with reference to the following drawings and description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] **FIG. 1** is a schematic of an in-line calendering and lamination apparatus for making the printable magnetic receptive composite of this invention.

[0009] **FIG. 2** is a magnified diagrammatic sketch and cross section of the printable magnetic receptive composite after lamination.

Thermoplastic Binder

The thermoplastic binder for the magnetic material employed in making a printable magnetic receptive composite may be selected from the classes of olefin polymer, vinyl halide polymer and vinyl acetate polymer as defined as follows.

A. Olefin Polymer

[0010] The olefin polymer employed is most commonly a homopolymer, copolymer, or terpolymer of monomers such as ethylene, propylene or a diene. The principles of this invention are applicable to polymers of unsaturated hydrocarbons containing one or more pairs of carbon atoms linked by a double bond. While this invention has been illustrated with specific olefin polymers in the operating examples which follow, it is to be understood that this invention is not limited to the specific examples. The olefin monomers that may be polymerized alone or in admixture with other ethylenically unsaturated monomers include, e.g., ethylene; propylene; 1-butene; isobutene; 1-pentene; vinyl benzenes and naphthalenes such as styrene or vinyl naphthalene; and dienes such as butadiene, isoprene, cyclopentadiene, and ethylidene norbornene (ENB). Copolymers of such monomers include acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile (SAN). Suitable elastomeric polymers may also

be biodegradable. Suitable elastomeric polymers include terpolymers of ethylene, propylene, and a diene, such as ENB (EPDM). Other elastomers include poly(ethylene-butene), poly(ethylene-hexene), poly(ethylene-octene), poly(ethylene-propylene), poly(styrene-butadiene-styrene), poly(styrene-isoprene-styrene), poly(styrene-ethylene-butylene-styrene), poly(ethylene-propylene-diene), and ethylene-propylene. A new class of rubber-like polymers may also be employed and they are generally referred to as polyolefins produced from single-site or metallocene catalysts whereby ethylene, propylene, styrene and other olefins may be polymerized with butene, hexene, octene, etc., to provide elastomers suitable for use in accordance with the principles of this invention, such as poly(ethylene-butene), poly(ethylene-hexene), poly(ethylene-octene), poly(ethylene-propylene) and/or polyolefin terpolymers thereof.

B. Vinyl Halide Polymer

[0011] The vinyl halide resin employed is most commonly a homopolymer of vinyl chloride, i.e., polyvinyl chloride. It is to be understood, however, that this invention is not limited to a particular vinyl halide resin such as polyvinyl chloride (PVC) or its copolymers. Other halogen-containing polymers or resins which are employed and which illustrate the principles of this invention include chlorinated polyethylene, chlorosulfonated polyethylene, chlorinated polyvinyl chloride, and other vinyl halide polymer or resin types. Vinyl halide polymer or resin, as understood herein, and as appreciated in the art, is a common term and is adopted to define those resins or polymers usually derived by polymerization or copolymerization of vinyl monomers including vinyl chloride with or without other comonomers such as ethylene, propylene, vinyl acetate, vinyl ethers, vinylidene chloride, methacrylate, acrylates, styrene, etc. A simple case is the conversion of vinyl chloride $\text{H}_2\text{C}=\text{CHCl}$ to polyvinyl chloride $(\text{CH}_2\text{CHCl})_n$

wherein the halogen is bonded to the carbon atoms of the carbon chain of the polymer. Other examples of such vinyl halide resins would include vinylidene chloride polymers, vinyl chloride-vinyl ester copolymers, vinyl chloride-vinyl ether copolymers, vinyl chloride-vinylidene copolymers, vinyl chloride-propylene copolymers, chlorinate polyethylene, and the like. Of course, the vinyl halide commonly used in the industry is the chloride, although others such as bromide and fluoride may be used. Examples of the latter polymers include polyvinyl bromide, polyvinyl fluoride, and copolymers thereof.

C. Vinyl Acetate Polymer

[0012] The vinyl acetate polymer employed is most commonly a homopolymer of vinyl acetate, i.e., polyvinyl acetate. Copolymers of vinyl acetate are also suitably employed. It is to be understood, however, that this invention is not limited to polyvinyl acetate or its copolymers. Other vinyl acetate based polymers which are employed and which illustrate the principles of this invention include partially hydrolyzed polyvinyl acetate, e.g. polyvinyl alcohol, ethylene-vinyl acetate, vinyl chloride-vinyl acetate copolymer or other copolymer types. Vinyl acetate based polymer, as understood herein, and as appreciated in the art, is a common term and is adopted to define those polymers usually derived by polymerization or copolymerization of vinyl acetate monomer with or without other comonomers such as ethylene, propylene, vinyl chloride, vinyl ethers, vinylidene chloride, methacrylate, acrylates, styrene, etc. A simple case is the conversion of vinyl acetate to polyvinyl acetate wherein the ether oxygen of the ester group is bonded to the carbon atoms of the carbon chain of the polymer.

Magnetic Material

[0013] The term "magnetic material" refers to any material which exhibits permanent magnetic behavior or is readily permanently magnetized. Typically, a magnetic powder is particularly suitable for use including the ferrites and other examples that are well known in the art. Specifically, the following Table describes a suitable ferrous alloy powder that is employed.

Table

Compound	Compound Name	Conc (wt%)	Element	Conc (wt%)
Fe₂O₃	Iron(III) oxide	82	Fe	57
MnO	Manganese(II) Oxide	13	Mn	10
ZnO	Zinc Oxide	4.2	Zn	3.3
SiO₂	Silicon dioxide	0.34	Si	0.16
Na₂O	Sodium Oxide	0.32	Na	0.24
SrO	Strontium oxide	0.13	Sr	0.11
Al₂O₃	Aluminum oxide	0.11	Al	0.057
ZrO₂	Zirconium dioxide	0.1	Zr	0.078
CaO	Calcium Oxide	0.1	Ca	0.072
P₂O₅	Phosphorus pentoxide	0.06	P	0.026
TiO₂	Titanium dioxide	0.059	Ti	0.035
MgO	Magnesium Oxide	0.05	Mg	0.03
SO₃	Sulfur Trioxide	0.042	S	0.017
Cr₂O₃	Chromium(III) oxide	0.032	Cr	0.022
V₂O₅	Vandium(V) oxide	0.029	V	0.016
Cl	Chloride	0.019	Cl	0.019
Nb₂O₅	Niobium pentoxide	0.015	Nb	0.01
		100.606		

Auxiliary Agent or Compatibilizer

[0014] An auxiliary agent or compatibilizer, used to facilitate the blending of the magnetic material in the thermoplastic binder, includes, for example, an ethylene vinyl acetate (EVA) and a polyolefin elastomer of the type defined above. A compatibilizing prodegradant additive such as an organotitanate or zirconate may be employed as coupling agents in binder compositions to essentially increase the stability of the polymeric compositions. These additives may be used to couple the thermoplastic binder with the magnetic powder in the composition. In addition, these organotitanates or zirconates have been found, according to U.S. Patent 7,956,101 to act as anaerobic prodegradants thereby achieving a further objective of the composite of this invention by rendering the useful printable magnetic receptive composites anaerobically degradable in landfills. The entire disclosure of U.S. Patent 7,956,101 is incorporated herein by reference to describe these additives and polymer binder compositions for use in the magnetic receptive composites of this invention.

EXAMPLE

[0015] With reference to the drawings **FIGS. 1 & 2**, a chlorinated polyethylene polymer is blended with an auxiliary agent such as EVA and polyolefin elastomer along with the ferrous alloy powder as defined above. The ferrous powder is manufactured by BGRIMM Materials & Technology Co., Ltd. in China. The percentages in the mixture of the composition include about 30% polyethylene, about 50% ferrous alloy powder and about 20% auxiliary agents, such as, the combination of EVA and polyolefin elastomer.

[0016] With reference to **FIG. 1**, the composition is calendered by passing the polymer binder/magnetic material blend as a continuous sheet **10** through a number of

pairs of heated rollers **11** shown diagrammatically in **FIG. 1**. Roller temperatures typically range from about 165°C to 180°C during calendering. The resulting flexible calendered sheet **12** is then laminated to a printable substrate **13** in-line as shown in **FIG. 1** to form the magnetic composite sheet **20** of **FIG. 2**. The lamination can occur in different ways. One way is to bond the printable substrate **13** at suitable temperature and then cooling the substrate. Another method is to use an adhesive such as a water-based polyurethane adhesive or EVA adhesive to bond the printable substrate **13** to the cooled sheet **12**. Either of these methods is acceptable and, in this example, a polyethylene terephthalate (PET) **22** having a universal coating **21** for solvent, eco-solvent, latex, UV or epoxy ink printing is employed with magnetic receptive layer **23**. The printable coating contains either a silicone dioxide or a titanium oxide pigment, dispersed in a polymeric binder of water-based polyurethane, water-based EVA, or polyacrylic emulsion, thereby rendering the printable surface of the PET white. The thickness of the universal coating may vary, but is on the order of 1 mil. The thickness of the printable layers is on the order of 1 to 6 mil(s), but may vary. The thickness of the calendered magnetic layer is up to 10 mils, normally 6 to 10 mils. Accordingly, a flexible printable magnetic receptive film with the multiple layers having an overall or total thickness up to about 20 mils, preferably 12 mils, is obtained.

[0017] While the printable layer is a polyethylene terephthalate in the above example, it is understood that the substrate for the printable layer is variable to include any polymeric material, cotton, textile, or paper products, and the like, that may suitably carry a universal coating for solvent, eco-solvent, latex, UV or epoxy type printing. In view of this description, other embodiments of this invention will become apparent to those skilled in the art.

What is claimed is:

1. A printable magnetic receptive composite sheet comprising:
a calendered magnetic layer containing a thermoplastic binder and a magnetic material and;
a printable top layer bonded to said calendered layer, wherein said calendered magnetic layer has a thickness up to 10 mils.
2. The sheet of claim 1 wherein said calendered magnetic layer has a thickness from about 6 to 10 mils.
3. The sheet of claim 1 wherein said printable top layer is a substrate selected from the group of a polymeric material, cotton, textile or a paper product.
4. The sheet of claim 3 having an indefinite length and a width of up to about 60 inches with a total thickness of up to about 20 mils.
5. The sheet of claim 3 wherein the polymeric material is a thermoplastic polymer.
6. The sheet of claim 5 wherein said polymer is a polyester.
7. The sheet of claim 6 wherein the polyester is polyethylene terephthalate.
8. The sheet of claim 3 wherein said printable top layer has a surface with printable coating deposited thereon.

9. The sheet of claim 8 wherein said printable coating has a silicon dioxide or a titanium oxide pigment dispersed in a polymeric binder selected from the group of a water-based polyurethane, water-based ethylene vinyl acetate polymer and polyacrylic emulsion.

10. The sheet of claim 1 wherein the said thermoplastic binder is a polymer with a monomeric group of an olefin, vinyl halide and vinyl acetate, and copolymers thereof.

11. The sheet of claim 1 wherein the thermoplastic binder is a chlorinated polyethylene, ethylene vinyl acetate, or polyolefin elastomer, and mixtures thereof.

12. The sheet of claim 1 wherein the calendered magnetic layer is bonded to the printable top layer with the aid of an adhesive.

13. The sheet of claim 1 wherein said calendered magnetic sheet contains an anaerobic prodegradant.

14. The sheet of claim 13 wherein said anaerobic prodegradant is a monomeric adduct of an organotitanate or organozirconate.

15. A method of making a printable composite magnetic receptive sheet having multiple layers comprising:

calendering a thermoplastic composition containing a thermoplastic binder and a magnetic material into a continuous magnetic layer having a thickness up to 10 mils and;
laminating a printable top layer onto said magnetic layer.

16. The method of claim 15 conducted at an elevated temperature for laminating the magnetic layer to said printable top layer.

17. The method of claim 15 wherein the lamination is conducted with the aid of an adhesive selected from the group of water-based polyurethane and water-based EVA.

18. The method of claim 15 wherein the said thermoplastic binder is a polymer having the monomeric group of an olefin, vinyl halide and vinyl acetate, and copolymers thereof.

19. The method of claim 15 wherein said printable top layer is a substrate selected from the group of a polymeric material, cotton, textile or a paper product.

20. The method of claim 15 wherein said printable top layer has a surface with a printable coating deposited thereon.

21. The method of claim 15 said printable coating has a silicon dioxide or a titanium oxide pigment dispersed in a polymeric binder selected from the group of a water-based polyurethane, water-based ethylene vinyl acetate polymer and polyacrylic emulsion.

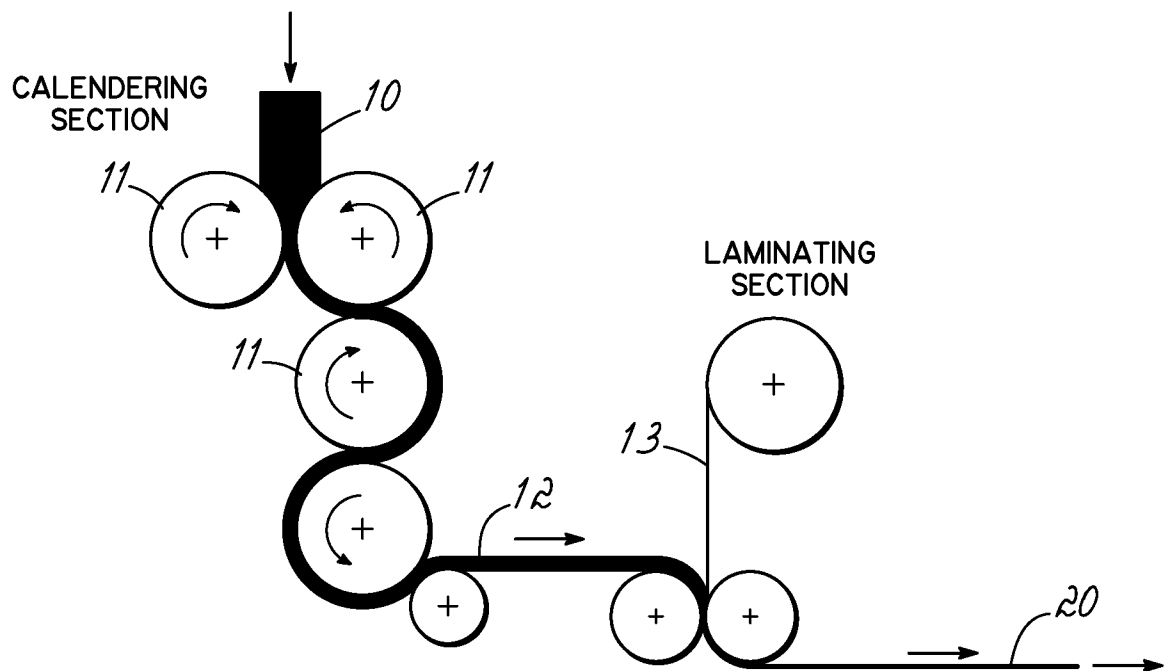


FIG. 1

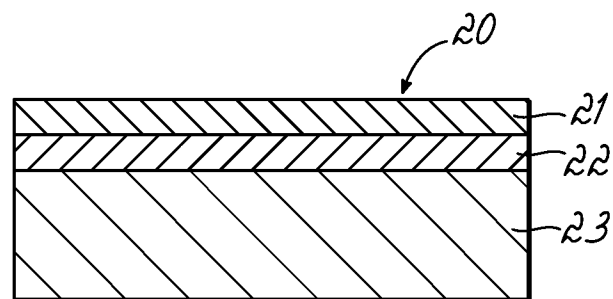


FIG. 2