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(71) Applicant: **AMPACET CORPORATION** [US/US]; 660
White Plains Road, Tarrytown, NY 10591 (US).

(72) Inventors; and

(71) Applicants : **DAVIS, Don** [US/US]; 4705 Duke Drive,
Suite 450, Mason, OH 45040 (US). **NEVINS, Danny**
[US/US]; 4705 Duke Drive, Suite 450, Mason, OH 45040
(US). **MICKEY, Tom** [US/US]; 4705 Duke Drive, Suite
450, Mason, OH 45040 (US). **MCMANUS, Mark**
[US/US]; 4705 Duke Drive, Suite 450, Mason, OH 45040
(US). **BROWNFIELD, Doug** [US/US]; 4705 Duke Drive,
Suite 450, Mason, OH 45040 (US). **CARROLL, Linda**
[US/US]; 4705 Duke Drive, Suite 450, Mason, OH 45040
(US).

(74) Agents: **LANIER, J., Gibson III** et al.; Smith Gambrell &
Russell LLP, 1230 Peachtree Street, N.E., Suite 3100
Promenade, Atlanta, GA 30309 (US).

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(54) Title: MULTILAYERED POLYMERIC FILM

(57) Abstract: Disclosed are compositions and methods for creating a textured or patterned surface on elastomeric extruded film.

MULTILAYERED POLYMERIC FILM

I. BACKGROUND

1. Traditionally, elastomeric extruded film has been limited to a smooth outer layer
5 surface. Attempts have been made to create a disrupted pattern in the outer surface but have not
been consistently successful. Today, extruded elastomeric film has to go through a secondary
converting process to emboss the outer layer surface of the film to create texture or a disrupted
pattern.

2. The elastomeric film industry is looking for process methods to eliminate the
10 need for secondary processing to create a textured or patterned surface on elastomeric extruded
film. Industry demand is for a technology to allow for a film surface to create texture or pattern
effect on a consistent lot to lot basis during the initial extrusion process.

II. SUMMARY

3. Disclosed are methods and compositions related to a multilayered polymeric film
15 with a visual effect produced by the particular ordered combination of the polymeric layers
(such as, for example, REPTYLEFX by Ampacet Corp.).

4. In one aspect disclosed herein are multilayered polymeric films comprising first
polymeric layer comprising a foaming agent and a second layer comprising a polymeric resin
20 and a special effect agent; wherein the special effect reflects through the first layer to create a
multi-dimensional, textured color effect; and wherein the foaming agent of the first layer is on
the side of the first layer opposite to the second layer.

III. BRIEF DESCRIPTION OF THE DRAWINGS

5. The accompanying drawings, which are incorporated in and constitute a part of
25 this specification, illustrate several embodiments and together with the description illustrate the
disclosed compositions and methods.

IV. DETAILED DESCRIPTION

6. Before the present compounds, compositions, articles, devices, and/or methods
30 are disclosed and described, it is to be understood that they are not limited to specific synthetic
methods or specific recombinant biotechnology methods unless otherwise specified, or to
particular reagents unless otherwise specified, as such may, of course, vary. It is also to be

understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting.

A. Definitions

7. As used in the specification and the appended claims, the singular forms “a,”
5 “an” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a pharmaceutical carrier” includes mixtures of two or more such carriers, and the like.

8. Ranges can be expressed herein as from “about” one particular value, and/or to
10 “about” another particular value. When such a range is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another embodiment. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that
15 each value is also herein disclosed as “about” that particular value in addition to the value itself. For example, if the value “10” is disclosed, then “about 10” is also disclosed. It is also understood that when a value is disclosed that “less than or equal to” the value, “greater than or equal to the value” and possible ranges between values are also disclosed, as appropriately understood by the skilled artisan. For example, if the value “10” is disclosed the “less than or
20 equal to 10” as well as “greater than or equal to 10” is also disclosed. It is also understood that throughout the application, data is provided in a number of different formats, and that this data, represents endpoints and starting points, and ranges for any combination of the data points. For example, if a particular data point “10” and a particular data point 15 are disclosed, it is understood that greater than, greater than or equal to, less than, less than or equal to, and equal to
25 10 and 15 are considered disclosed as well as between 10 and 15. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

9. In this specification and in the claims which follow, reference will be made to a number of terms which shall be defined to have the following meanings:

30 10. “Optional” or “optionally” means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

11. Throughout this application, various publications are referenced. The disclosures of these publications in their entireties are hereby incorporated by reference into this application

in order to more fully describe the state of the art to which this pertains. The references disclosed are also individually and specifically incorporated by reference herein for the material contained in them that is discussed in the sentence in which the reference is relied upon.

B. Compositions

5 12. Disclosed are the components to be used to prepare the disclosed compositions as well as the compositions themselves to be used within the methods disclosed herein. These and other materials are disclosed herein, and it is understood that when combinations, subsets, interactions, groups, etc. of these materials are disclosed that while specific reference of each various individual and collective combinations and permutation of these compounds may not be
10 explicitly disclosed, each is specifically contemplated and described herein. For example, if a particular multilayered polymeric film is disclosed and discussed and a number of modifications that can be made to the film are discussed, specifically contemplated is each and every combination and permutation of the components of the multilayered polymeric film and the modifications that are possible unless specifically indicated to the contrary. Thus, if a class of
15 components A, B, and C are disclosed as well as a class of components D, E, and F and an example of a combination of the components, A-D is disclosed, then even if each is not individually recited each is individually and collectively contemplated meaning combinations, A-E, A-F, B-D, B-E, B-F, C-D, C-E, and C-F are considered disclosed. Likewise, any subset or combination of these is also disclosed. Thus, for example, the sub-group of A-E, B-F, and C-E
20 would be considered disclosed. This concept applies to all aspects of this application including, but not limited to, steps in methods of making and using the disclosed compositions. Thus, if there are a variety of additional steps that can be performed it is understood that each of these additional steps can be performed with any specific embodiment or combination of embodiments of the disclosed methods.

25 13. The present disclosure relates to the creation of visual and textured effects through the use of multilayered polymeric films, special effects, and foaming agents. In one aspect, disclosed herein are multilayered polymeric film comprising first polymeric layer comprising a foaming agent and a second layer comprising a polymeric resin and a special effect agent; wherein the special effect reflects through the first layer to create a multi-dimensional,
30 textured color effect; and wherein the foaming agent of the first layer is on the side of the first layer opposite to the second layer (such as, for example, with REPTYLEFX by Ampacet Corp.)

14. It is understood and herein contemplated that the polymeric layers comprise, amongst other things a polymeric resin. Resins suitable for the present invention are polyolefins which may include low density polyethylene (LDPE), linear low density polyethylene (LLDPE),

high density polyethylene (HDPE), medium density polyethylene (MDPE), ultra high molecular weight polyethylene(UHMWPE), cross-linked polyethylene (XLPE), polypropylene (PP) polymers, and metallocene catalyzed polyolefin (i.e. plastomer) resins. The resins of the present invention may either be homopolymers or copolymers. Examples of the latter are olefin-
5 copolymers such as polyethylene butylacrylate, polyethylene methacrylate and polyethylene vinyl acetate.

15. Because the disclosed film comprises multiple polymeric layers, it is understood, that that the polymeric composition of each layer can contribute to the visual and textural effects given to the film as well as the other physical attributes of the film given the intended use of the
10 film. Accordingly, the composition of each layer of the multilayered polymeric film can be different or the same as any one or more additional layers. In one aspect, each layer of the multilayered polymeric film can comprise the same or different polyolefin resins. For example, in one aspect, disclosed herein are multilayered polymeric films wherein all polymeric layers
15 low density polyethylene (LDPE), linear low density polyethylene (LLDPE), or high density polyethylene (HDPE). In another example, the disclosed multilayered polymeric films can comprise one or more polymeric layers comprising low density polyethylene (LDPE), linear low density polyethylene (LLDPE), or high density polyethylene (HDPE) and at least one polymeric
layer wherein the polymer comprises a different polymer structure.

16. While in its simplest form the multilayered polymeric film comprises two layers.
20 However, it is fully contemplated herein that the multilayered polymeric film can comprise 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 29, 20, 25, 30, 35, 40, 45, or 50 or more additional polymer layers. Thus, in one aspect, disclosed herein are multilayered polymeric films comprising 2, 3, 4, 5, 6, 7, 8, 9, or 10 or more layers. For example, disclosed herein are multilayered polymeric films further comprising a third polymeric layer adjacent to the second
25 layer and on the opposite side from the first layer. Any subsequent layer being added to the proceeding layer and not to the face of the first layer comprising the foaming agent.

17. It is understood and herein contemplated that the individual polymeric layers can comprise the same or different portion of the multilayered polymeric film and that the ratio of individual layers can be modified to achieve different visual effects. For example each layer of
30 a two layered film can comprise 50% of the film. Alternatively, one polymeric layer of a two layered polymeric film can comprise 1, 2,3 ,4, 5,6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97,

98, or 99 percent of the multilayered film while the remaining layer comprises the remaining percentage of the multilayered film. Similarly, in a three layered film each layer can comprise the same portion (i.e., a 1/3 portion) of the film structure or be differently proportioned such that at most two of the layers comprise the same amount of the film while the remaining layer
5 comprise a different portion. For example, it is disclosed herein that the first (i.e., the outer) layer and the third layer (inner layer) can each comprise 20% of the multilayered film (a total of 40%) while the second (middle or core layer) comprises the remaining 60% of the film. That is, any combination of layer ratios can exist in the multilayered film, including, but not limited to, an outer:middle:inner percentage of 5:90:5; 10:80:10; 15:70:15; 20:60:20; 25:50:25; 30:40:30;
10 35:30:35; 40:20:40; 45:10:45; 5:5:90; 10:10:80; 15:15:70; 20:20:60; 25:25:50; 30:30:40; 35:35:30; 40:40:20; 45:45:10; 90:5:5; 80:10:10; 70:15:15; 60:20:20; 50:25:25; 40:30:30; 30:35:35; 20:40:40; 10:45:45; 5:10:85; 10:15:75; 15:20:65; 20:25:55; 25:30:45; 10:5:85; 15:10:75; 20:15:65; 25:20:55; 30:25:45; 85:10:5; 75:15:10; 65:20:15; 55:25:20; 45:30:25; 85:5:10; 75:10:15; 65:15:20; 55:20:25; 45:25:30; 5:85:10; 10:75:15; 15:65:20; 20:55:25;
15 25:45:30; 10: 85:5; 15:75:10; 20:65:15; 25:55:20; or 30:45:25 or any other combination.

18. A variety of foaming agents may be utilized for incorporation into the first polymeric layer. The first (i.e., outer) layer comprises the foaming agent to achieve the visual and/or textural effects. For example, Azo compounds, N'-nitroso compounds and sulfonyl hydrazide compounds can be used as foaming agents. Furthermore, mixtures of these groups of
20 compounds may also be used herein. Typical usage levels of the foaming agent range from 1% to 2% in the outer layer of the film structure, but the percentage of foaming agent used can be modified depending on the degree of texture of visual effect desired. Examples of azo compounds that can be used in the disclosed multilayered polymeric films include, but are not limited to azodicarbonamide, azobisisobutyronitrile, and diazoaminobenzene. Among the nitroso
25 compounds, examples of compounds that can be used in the disclosed multilayered polymeric films include, but are not limited to N,N'-dimethyl, N,N'-dinitrosoterephthalamide, and N,N'-dinitrosopentamethylenetetramine. Examples of foaming agents falling under the genus of sulfonyl hydrazides include, but are not limited to benzenesulfonyl hydrazide, toluene-(4)-sulfonyl hydrazide, benzene-1,3-disulfonylhydrazide, diphenylsulfon-3,3'-disulfonyl hydrazide,
30 and 4,4'-oxybis(benzenesulfonyl hydrazide). Mixtures of any of the above foaming agents may also be used.

19. Inorganic carbonates may also be suitable as constituents of foaming agents. Examples include sodium bicarbonate, sodium aluminum hydroxyl carbonate, magnesium carbonate and mixtures thereof. Polycarboxylic acids are also useful. These include citric acid,

fumaric acid, tartaric acid, sodium hydrogen citrate and disodium citrate as well as mixtures of carbonates and acids.

20. In some embodiments, an activator may be included to assist the activity of the foaming agent. Suitable for this purpose are zinc oxide, dibasic lead phthalate, ethylene glycol and urea and derivatives thereof (e.g. hydroxyethyl urea). These activators may be formulated in amounts from about 0.1 to about 15%, preferably from about 0.5 to about 7%, optimally from about 1 to about 3% by weight of the foaming agent.

21. To achieve the visual effect, the disclosed multilayered films comprise a special effect agent. It is understood and herein contemplated that the visual effect occurs via the visual perception of special effect in any one or more polymer layers interacting with the texture and residue left by the foaming agent in the first layer. For example, the special effect agent in the second layer reflects through the cellular structure in the outer layer creating a unique dimensional film effect.

22. As used herein, "special effect agent" refers to any agent that can create a visual effect, including but not limited to colored pigments, pearlescent pigments, light interference pigments, or other special effect pigments. Special effect agents can be incorporated into any layer of the multilayered polymeric film. For example, disclosed herein are 3-layered multilayered polymeric films wherein the second and third layers comprise a special effect agent. Also disclosed are 3-layered multilayered polymeric films wherein all three layers comprise a special effect.

V. CLAIMS

What is claimed is:

1. A multilayered polymeric film comprising first polymeric layer comprising a foaming
5 agent and a second layer comprising a polymeric resin and a special effect agent;
wherein the special effect agent reflects through the first layer to create a multi-
dimensional, textured color effect; and wherein the foaming agent of the first layer is on
the side of the first layer opposite to the second layer.
2. The polymeric film of claim 1, wherein the special effect agent is a colored pigment,
10 pearlescent pigment, light interference pigment or other special effect metallic pigment.
3. The polymeric film of claim 2, wherein the special effect agent in the second layer
reflects through the cellular structure in the outer layer creating a unique dimensional
film effect.
4. The polymeric film of claim 1, wherein the outermost layer of the polymeric film
15 comprises polyolefin polymers.
5. The polymeric film of claim 4, wherein the polyolefin polymer of the outermost layer of
the polymeric film comprises low density polyethylene (LDPE), linear low density
polyethylene (LLDPE), high density polyethylene (HDPE) medium density polyethylene
(MDPE), ultra high molecular weight polyethylene(UHMWPE), cross-linked
20 polyethylene (XLPE), or polypropylene (PP) polymers.
6. The polymeric film of claim 1, further comprising a third polymeric layer adjacent to the
second layer and on the opposite side from the first layer.
7. The polymeric film of claim 6, wherein the proportion of the layers in the 3 layer film
structure is 20% outer; 60% core/middle; 20% inner.
- 25 8. The polymeric film of claim 6, wherein the third layer comprises a second special effect
agent; and wherein the special effect agent is a colored pigment, pearlescent pigment, or
light interference pigment different from the first special effect.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US16/30553

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B32B 5/18, 5/22, 27/08, 27/18, 27/20, 27/32; C08J 9/06 (2016.01)

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): B32B 5/18, 5/22, 27/08, 27/18, 27/20, 27/32; C08J 9/06 (2016.01)

CPC: B32B 5/18, 5/22, 27/08, 27/18, 27/20, 27/205, 27/32; C08J 9/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); IP.com; Google/Google Scholar; EBSCO; polymer, film, multilayer, multiple layer, sheet, membrane, layer, foaming, blowing, agent, pigment, colorant, brightener, blocker, reflect, cell, cavity, pore, multidimensional, dimensional, texture, visual effect, color effect, resin, polyolefin, outer, outermost, inner, innermost, middle

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2009/0305030 A1 (SRIRAMAN, R et al.) 10 December 2009; abstract; paragraphs [0024], [0031], [0037], [0045], [0058]; claim 14	1-8
Y	WO 1988/06520 (RAYCHEM CORPORATION) 07 September 1988; abstract; page 3; page 5, lines 1-3; claim 11; figure 2	1-8
Y	US 7,820,282 B2 (HAAS, CK et al.) 26 October 2010; column 2, lines 6-10, 20-22; claims 1, 7	4-5
Y	US 2005/0282000 A1 (HOWIE JR, DW) 22 December 2005; abstract; paragraphs [0027], [0049]; example 1	7-8
A	US 8,859,091 B2 (TADROS, SE) 14 October 2014; entire document	1-8
A	US 8,163,810 B2 (HOWIE JR, D et al.) 24 April 2012; entire document	1-8
A	US 4,303,716 A (ESHBACH, JR et al.) 01 December 1981; entire document	1-8

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

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Authorized officer

Shane Thomas

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