#### (12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

# (19) World Intellectual Property Organization

International Bureau

(43) International Publication Date





(10) International Publication Number WO 2013/027219 A1

28 February 2013 (28.02.2013)

(51) International Patent Classification:

**B29C 43/00** (2006.01) **B29C 33/40** (2006.01)

E04C 2/20 (2006.01)

**B29C** 70/06 (2006.01)

**E04C 2/22** (2006.01)

(21) International Application Number:

PCT/IL2012/050322

(22) International Filing Date:

23 August 2012 (23.08.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/526,956 24 August 2011 (24.08.2011)

IL

- (71) Applicant (for all designated States except US): GREEN NEIGHBORHOOD LIMITED PARTNERSHIP [IL/IL]; 7 Derech Menachem Begin, 52681 Ramat Gan (IL).
- (72) Inventor; and
- (75) Inventor/Applicant (for US only): ZACK, Ramy [IL/IL]; 4 Even Chen Street, 75401 Rishon Le-Zion (IL).
- (74) Agent: REINHOLD COHN AND PARTNERS; P.O.B.13239, 61131 Tel Aviv (IL).

- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

#### **Declarations under Rule 4.17:**

— of inventorship (Rule 4.17(iv))

[Continued on next page]

#### (54) Title: AN ARTICLE OF MANUFACTURE AND METHOD FOR ITS PREPARATION

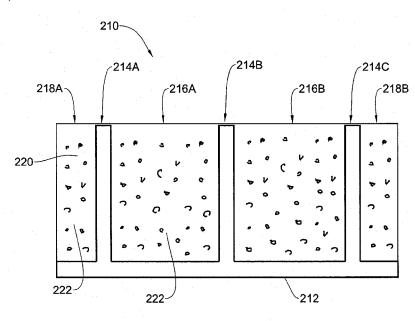


Figure 2

(57) Abstract: The present disclosure provides an article of manufacture and a method for its production, the article of manufacture comprising at least one support element (210) comprising fiber reinforced polyester (FRP), the at least one support element constructed in a form of a base (212) and at least two projections (214A, 214B and 214C) extending from the base (212), the base (212) and at least two projections (214A, 214B, and 214C) forming together at least one compartment (216A, 216B) which is filled with a composite material (220) comprising rubber particles (222).



# 

# Published:

— with international search report (Art. 21(3))

- 1 -

# AN ARTICLE OF MANUFACTURE AND METHOD FOR ITS PREPARATION

#### FIELD OF THE INVENTION

This invention relates in general to green technology, and in particular to the use of used rubber, e.g. vulcanized rubber from used or recycled tires, for manufacturing various articles.

### **BACKGROUND OF THE INVENTION**

The use of waste materials and recycling has grown in recent years mainly due to the growing interest in green technology. One example for waste material that is constantly recycled is tires. The tire is a commonly used source for crosslinked or vulcanized rubber.

Various publications exists that describe methods for manufacturing products from recycled rubber. These include, inter alia, US Patent No. 6,766,963 describing a method for the manufacture of a railroad crosstie from recycled rubber; US Patent application publication No. 2010/230861 describing systems and methods for manufacturing crumb rubber products, such as a floor mat, for decorative or industrial applications; US Patent application publication No. 2010/00704 describing methods for making shapeable composite materials or shaped articles from recycled materials for example ground tire rubber; US patent No. 6,972,144 describing a composite structural material comprising a core material which includes polyurethane foam and optionally filled with granulated rubber and/or expandable polymer beads and finally, Japanese patent application publication No. JP2003213614 describing a block comprising a double structure of an elastic body layer comprising rubber chips, fragments of thermosetting resin molding and a urethane resin as a binder and a rigid body layer comprising solidified thermosetting resin molding with a thermosetting resin as a binder.

#### SUMMARY OF THE INVENTION

In accordance with a first aspect, the present disclosure provides an article of manufacture comprising at least one support element comprising fiber-reinforced polyester (FRP), the at least one support element constructed in a form of a base and at least two projections extending from the base, the base and at least two projections forming together at least one compartment which is filled with a composite material comprising rubber particles.

In accordance with a second aspect, the present disclosure provides a method of manufacture an article, the method comprising:

- (a) providing at least one support element, the support element comprising fiber-reinforced polyester (FRP) constructed in a form comprising a base and at least two projections extending from the base, the base and the at least two projections forming together at least one compartment;
- (b) placing the at least one support element on a steel casting mold (SCM) while heating the SCM;
- (c) introducing into the steel casting mold carrying the at least one support element a pulp composite material comprising rubber particles;
- (d) compressing the pulp composite material against the at least one support element;
- (e) allowing the SCM to cool down; and
- (f) releasing compressing, whereby the article of manufacture comprising the at least one support element and the composite material is formed.

In yet a third aspect, the present disclosure provides an article of manufacture whenever obtained by the method disclosed herein.

In yet a further aspect, the present disclosure also concerns the various uses of the article of manufacture.

# BRIEF DESCRIPTION OF THE DRAWINGS

In order to understand the invention and to see how it may be carried out in practice, embodiments will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

**Figures 1A-1B** are perspective side views of support elements in accordance with some embodiments of the invention, where Figure 1A illustrates a support element comprising a base and three projections, while Figure 1B illustrates two, spaced apart support elements, each having a "U" shape profile.

Figure 2 is cross sectional view of a support element according to Figure 1A filled with composite material.

**Figure 3** is a side view of an illustrated support element as shown in Figure 1A placed within a steel casting mold (SCM) having end plugs circumventing the support element.

**Figure 4** is a cross sectional view of a SCM holding a support element as shown in Figure 1A, and filled with composite material, and a compression piston applied thereto.

## DETAILED DESCRIPTION OF SOME NON-LIMITING EMBODIMENTS

The present disclosure relates to articles of manufacture comprising recycled materials, and more specifically to recycled tire rubber. The articles of manufacture are unique in that they are relatively light, have a high cantilever strength and stiffness and are thus suitable to carry heavy loads.

Thus, in accordance with one aspect of the present disclosure, there is provided an article of manufacture comprising a support element comprising fiber reinforced polyester (FRP), the support element constructed in a form of a base and at least two projections extending from the base, the base and at least two projections forming together at least one compartment which is filled with a composite material comprising rubber particles.

The term "article of manufacture" should be understood to have the meaning as known in the art, namely, a product of a manufacturing process. In accordance with the invention, the article of manufacture is characterized by unique properties such as low bulk density, high strength allowing it to withstand heavy loads. Such properties are measurable by acceptable physical techniques such as bending strength test.

In one embodiment, the article of manufacture is characterized by a *bending* strength of between about 50MPa to 120MPa, preferably 50-110MPa. A bending

- 4 -

strength at this range is indicative that the article of manufacture can resist deformation under load of 50MPa to 120MPa, preferably 50MPa to 110MPa. For example, the bending strength of the product Plywood (timber made from thin sheets of wood veneer) is up to 85MPa.

In a further embodiment, the article of manufacture is characterized by an *elastic modulus* of at least 3,000MPa, and in some embodiments between 3,000MPa and 7,000MPa, in some specific embodiments between 6,000MPa and 6,500MPa and one particular embodiment the elastic modulus is about 6,230MPa. The elastic modulus, also known by the term modulus of elasticity, defines the tendency of an article to be deformed elastically (i.e., non-permanently) when a force is applied to it.

In yet a further embodiment, the article of manufacture is characterized by *bulk density* of between 1,300kg/m<sup>3</sup> to 1,400kg/m<sup>3</sup>.

The article of manufacture comprises two main constituents, the support element comprising, and preferably consisting, of fiber reinforced polyester (FRP) and the composite material comprising rubber particles. As noted below, the composite material may include other additives.

The support element is used, as such, to support the composite material once the latter hardens. The support element thus comprises voids for holding the composite material. The voids are formed from projections extending from a bottom portion of the support element. In this connection, reference is made to **Figures 1A-1B** which are schematic illustrations of two exemplary support element that may be used in the article of manufacture and method subject of the present disclosure and appended claims.

In Figure 1A, there is illustrated a support element 10 comprising a base 12, extending from first end 12A to second end 12B and three spaced apart projections 14A, 14B and 14C extending upwardly from the upper surface of base 12. Each two neighboring projections 14A and 14B or 14B and 14C form therebetween a two-sided compartment 16A and 16B, while the two external projections 14A and 14C form two, open-end compartments 18A and 18B.

The support element 10 in Figure 1A comprises three essentially identical and equally spaced apart projections 14A, 14B and 14C, which are also essentially parallel and perpendicular to base 12.

Each pair of projections such as 14A and 14B or 14B and 14C define a compartment height (h) from base 12 and compartment width (w) defined between facing surfaces of paired projections. Generally the height (h) may be in the range between 15mm to 50mm and the width (w) may be in the range between 7mm and 35mm. In one preferred embodiment, the height (h) is in the range between 25mm to 50mm and the width (w) is in the range between 15mm and 35mm. In the illustrated embodiment of Figure 1A, the height (h) is 30mm the width (w) is 19 nm and the width of the open end compartment is w/2, i.e. 8.5mm.

Further, base 12 of the support element 10 has a defined thickness range, which is generally between 2 to 5 mm. Yet further, each projection has a thickness (which may be the same or different in the two or more projections of a particular element) and is generally between 2 to 5 mm.

For simplicity, like reference numerals to those used in **Figure. 1A**, shifted by 100, 200, 300 are used to identify components having a similar function in any of the following figures. For example, component **12** in **Figure 1A** is a base having the same function as base **112** in **Figure 1B**.

Referring now to **Figure 1B**, there are illustrated two, spaced apart, support elements **110A** and **110B** are illustrated, each having a U shape configuration, thus forming a set of four projections **114A**, **114B**, **114C** and **114D**. The two U shaped support elements form two compartments, **116A**, and **116B**. When using two or more support elements, as illustrated in Figure 1B, the distance "d" between the support elements is within the range of "w", namely at least between 7mm to 35mm.

In the illustrated embodiment of **Figure 1B**, the height (h) of each projection in the U-shaped support element is 30mm and the width (w) of each compartment is 30mm. The distance between the two U-shaped support elements is within the range defined for "w", being in this particular embodiment about 10mm.

While **Figures 1A** and **1B** provide exemplary embodiments, it is to be understood that additional configurations are equally applicable, for instance, such configuration that includes a base with a plurality projections with different heights, different compartment widths, or a set of two or more support elements having, therebetween, different heights, different widths, etc.

The compartments as well as the spaces formed therebetween and open end compartments are filled with a composite material comprising rubber particles. In this connection, reference is made to Figure 2 showing a support element 210 having a base 212 and projections 214A, 214B and 214C, similar to the support element in Figure 1A, where all compartments 216A, 216B, and open-end compartments 218A and 218B are filled with composite material 220 comprising the rubber particles 222.

In accordance with the invention, the support element comprises FRP profile and while is widely available in the market, it may also be prepared by experimental methods known in the field. For example, the FRP profile may be prepared by using unidirectional glass fibers, which are subjected to a pultrusion process by pulling the glass fibers together and dipping them into a resin bath comprising a resin composition comprising a mixture of polyester resin, a catalysts and a hardener. The resin impregnated fibers are then introduced into a steel-made pultrusion mold at a desired pre-determined shape where curing takes place and a support element is obtained.

With respect to the composite material, is to be understood that the "rubber particles" are breakdown products of rubber material. In some particular embodiments, the rubber particles comprise vulcanized recycled tire rubber. The particles may be obtained by shredding, chopping, crushing, mincing, etc. rubber containing items suitable for recycling. As appreciated, recycling processes of rubber typically carry out a first stage of shredding followed by removal of steel, reinforcing fibers and cotton. Accordingly, the rubber particles according to the invention are essentially free of steel and cotton.

The recycled rubber within the article of manufacture in accordance with the invention is vulcanized rubber. The term "vulcanized rubber" is to be understood as referring to any cross-linked rubber polymers. Rubber polymers are typically cross-linked hydrocarbon elastomers, such as polyisoprene (either natural rubber e.g. gum rubber or synthetic rubber) or cross-linked styrene-butadiene rubber (SBR). The cross-linking typically includes reaction of the rubber polymer with sulfur, peroxides or any other cross linking agent known to those versed in the art, during which individual polymer chains are covalently interlinked to each other to yield a three dimensional matrix. The vulcanization of the rubber polymers gradually transforms the elastomers

- 7 -

into thermosets. The degree of vulcanization may vary from one rubber to the other, depending on the application of the vulcanized rubber.

It is to be understood that any vulcanized rubber at any degree of vulcanization may be used in the context of the present disclosure.

It should also be noted that the vulcanized rubber may comprise a portion of non-vulcanized or devulcanized rubber, e.g. when the source of vulcanized rubber is rubber residues and discarded vulcanized rubber from rubber manufacturing plants. Typically, non-vulcanized or de-vulcanized rubber would not exceed more than 10% or even 5% or even as low as 1% of the total weight of the vulcanized rubber mass.

The vulcanized rubber may also comprise rubber additives such as fillers and fibers including residues or contaminants to which the rubber was exposed to during vulcanization reaction, during its use, or processing (e.g. retreading, recycling treatment or size reduction into crumb rubber).

Thus, it is to be understood that when referring to vulcanized rubber, the latter may be less than 100% pure and may comprise small amounts of other residues in an amount of between 0.1 and 20 % w/w of the total weight of the vulcanized rubber, at times between 0.5 and 10 % w/w residues, or between 1 and 5 % w/w residues. These residues include tire cords, steel, silica, anti-tackifying agents, oil, sand, iron, ash, and calcium carbonate.

In some particular embodiments, the *vulcanized rubber* is from disposed vulcanized rubber products, such as, without being limited thereto, used tires, bumpers, shoe soles, latex and rubber gloves, conveyor belts and may also arrive from industrial rubber residues and discarded vulcanized rubber from rubber manufacturing plants.

In a particular embodiment, the rubber particles are recycled tires. Recycled tires may be in the form of crumb rubber, tire debris, tire slits, tire chips, ground tire rubber, crumb tire rubber, tire shreds, tire powder, tire cords etc.

In one embodiment, the recycled tires are crumb rubber.

Crumb rubber is to be understood as referring to rubber particles (e.g. scrap tires) that are irregularly shaped with an average size from 4.75 mm to less than 0.075 mm.

According to some particular embodiments, the rubber particles have a size of between 0.5 mm and 10mm, preferably between 0.5mm and 5mm. In some particular example, the rubber particles have a round shape and the size corresponds to the particle's diameter.

Needless to note that the size and shape may be controlled by the process of shredding, the equipment and condition used etc. For example, the production of rubber particles may be achieved by granulators, hammer mills, or fine grinding machines, where granulators typically produce particles that are regularly shaped and cubical with a comparatively low-surface area.

The rubber particles may also be obtained from commercial suppliers. Thus, in the context of the present invention also commercially available rubber particles are included and applicable. Exemplary recycled tire suppliers include, without being limited thereto ETRA (www.ETRA-EU.org), EXIMLINK (Austria); KAHL (Germany).

In some embodiments, the vulcanized rubber originates from virgin material, either natural or synthetic.

According to some embodiments, the ratio between the FRP and the composite material in the manufactured article is of between 15:85 and 35:65. In some specific embodiments, the ratio between the FRP and the composite material in the manufactured article was 29:71.

The composite material also comprises a chemical binder and a hardener.

A *chemical binder* as used herein includes any non-natural adhesive or glue. In some embodiments, the chemical binder according to the invention is a *thermoplastic binder*. Thermoplastic binder also known as hot adhesive or hot melt adhesive, may be applied in a molten form that solidifies on cooling to form strong bonds between a wide ranges of materials.

In accordance with some embodiments, the chemical binder is a thermoplastic elastomer, such as, without being limited thereto, a thermoplastic polyester elastomer.

Thermoplastic elastomer may be selected from a group consisting of a thermoplastic styrenic block copolymer, a thermoplastic polyolefin blend, a thermoplastic blend of polypropylene with crosslinked rubber (thermoplastic

vulcanizates), thermoplastic polyurethane, thermoplastic polyester and a thermoplastic polyamide.

Non-limiting examples of thermoplastic elastomers that can be used as binders include the following commercially available (and Trade Marked) products: Arnitel, Engage, Hytrel, Kraton, Pebax, Pellethane, Riteflex, Styroflex, Alcryn, Dryflex, Evoprene, Forprene, Geolast, Mediprene, Santoprene and Sarlink.

According to a specific embodiment, the chemical binder is Hytrel<sup>TM</sup>.

An additional possible chemical binder is the thermoplastic binder ethylenevinyl acetate.

The composite material may also comprise a hardener, namely, a substance that is added to the rubber particles and binder in order to facilitate in the hardening of the composite. Without being limited thereto, a hardener may be selected from a group consisting of silica powder, quartz silica sand and silica granules. According to some preferred embodiments, the hardener is silica granules.

According to some embodiments, the composite material comprises between 70%-95% (w/w) rubber particles, the remainder 30%-5%, respectively, comprising non-rubber components. In some preferred embodiments, the composite material comprises, between 85%-95% (w/w) rubber particles, the rest, 15%-5% comprising the non-rubber components.

The non-rubber component, being no more than 30% of the composite material, typically comprises 75% binder, 10% hardener, 5% water and 10% other additives as detailed below.

For example, a composite material composition may comprise 70% rubber particles and the rest 30% may be divided to include about 22.5% binder, about 3% hardener, about 3% additives and about 1.5%water. Further, as an example, a composite material composition comprising 95% rubber particles, may be divided to include about 3.75% binder, about 0.5% hardener, about 0.5% additives and about 0.25% water.

Notwithstanding the above, the additives, such as sawdust (typically wetted, albeit not dripping), hydrated magnesium silicate, and flame retardant (e.g. aluminum

hydroxide (ATH), magnesium hydroxide (MDH), and boron compounds such as borates).

The manufacturing of the article subject of the present invention involves a method comprising the following operations:

- (a) providing a support element comprising fiber reinforced polyester (FRP) constructed in a form comprising a base and at least two projections extending from the base, the base and the at least two projections forming together at least one compartment;
- (b) placing the support element on a steel casting mold (SCM) while heating the SCM;
- (c) introducing into the at least one compartment a pulp composite material comprising rubber particles;
- (d) compressing the composite material against the support element
- (e) allowing the SCM to cool down; and
- (e) releasing compressing, whereby the article of manufacture comprising the support element and the composite material is formed.

Accordingly, the support element having the characteristics as detailed above, is placed in a SCM, such as a steel container in the form of a tray comprising suitable end plugs, for example in the form of a wall, that circumferentially enclose the support element. As a result, the various compartments are fully side-walled. In this connection, reference is made to **Figure 3** schematic illustration a support element **310** placed within a SCM **340**, the SCM **340** having a base **342** end plugs/side walls **344** circumventing the support element and thus enclosing compartments **316A**, **316B**, and open-end compartments **318A** and **318B**.

The SCM is heated to temperature between 55°C and 80°C, preferably between 55°C to 65°C, more preferably to about 60°C. The temperature of the SCM may be determined by dedicated temperature sensors, as known in the art.

In addition to heating the SCM, also the composite material is prepared by mixing the various components, as detailed above. The mixed composite material is also heated, the heating may take place while mixing or thereafter. At any rate, heating

is to a temperature of between 50°C and 80°C, preferably between 55°C and 65°C. It is appreciated that the mixed composite material is in the form of a pulp (playable form).

Once the SCM and the composite material are set to the desired temperature, the pulp composite material is introduced into the compartments of the support element.

In some embodiments, the pulp composite material is added in an amount sufficient to essentially cover at least a portion of projections (i.e. not reaching the maximal height of the projection, and thus not fully filling the compartments). In some other embodiments, the pulp composite material is added in an amount allowing coverage of all projections.

Once the composite material is introduced into the support element, the composite material is compressed. Compression may be performed by any commonly used compression piston, adapted to press the composite material in the compartments, against the support element's base. The structure of the piston may be configured to adapt to the shape of the support element, i.e. to the number, dimensions and arrangement of the projections and compartments. As an example only, reference is made to **Figure 4**, schematically illustrating a support element **410**, placed within a SCM **440** holding a composite material **420** and a compression piston **450** having depressions or indentations **452A**, **452B** and **452C** configured to accommodate the projections. Upon operation, the piston applies pressure to the composite material in the direction of arrows **456**. The pressure applied by the compression piston is typically in the range of between 1.2MPa and 2.0MPa.

Concomitant with or shortly after applying the pressure by the compression piston, the heating of the SCM is terminated and compression continues until the SCM's temperature lowers down, actively (e.g. by a heat control device, such as cooler) or passively, the temperature is lowered to a temperature between 5°C to 45°C, preferably to 40°C or any temperature below, e.g. room temperature. During compression, the composite material cures, and once the SCM reaches the desired temperature, the piston may be removed whereby the article of manufacture is obtained.

As may be appreciated by those versed in the art, the article of manufacture may be produced in a variety of shapes and forms. In accordance with one embodiment, the article of manufacture is formed in a form of a laminate. The laminate may be used for a

variety of applications, including, without limited thereto, to flooring, tiles, roofing, ceiling, walls, covering, cladding, boards, fencing, plates, railroad ties (also known as railway sleeper), noise insulating materials, structure frames, machines and vehicle shield parts, vehicle and road bumpers and bullet-proof shielding, all being tailored to customer requirements.

The flooring, tiles, roofing, ceiling, walls, covering, cladding, boards may be used for example for containers, buildings, and housing namely, in the building industry, housing industry or container manufacturing.

In some specific embodiments, the article of manufacture is used for flooring a container. In some embodiments, the container is a shipping container. The shipping container may be used for sea shipping or surface shipping.

Non limiting examples of shipping container are twenty-foot equivalent unit, 40 foot container or high cube container.

Due to the unique characteristics of the article of manufacture, it may be used also for noise absorbance and/or temperature isolation.

As used herein, the forms "a", "an" and "the" include singular as well as plural references unless the context clearly dictates otherwise. For example, the term "a support element" includes one or more support elements which may be used in the article of manufacture.

Further, as used herein, the term "comprising" is intended to mean that the composite material includes the recited constituents, e.g. rubber particles, binder and hardener, but is not excluding other materials such as the above mentioned additives. The term "consisting essentially of" is used to define compositions which include the recited elements but exclude other elements. "Consisting of" shall thus mean excluding more than trace amounts of any element other than those recited. Embodiments defined by each of these transition terms are within the scope of this invention.

Further, all numerical values, e.g. when referring the amounts or ranges of the elements or other parameters recited are approximations which are varied (+) or (-) by up to 20%, at times by up to 10% of from the stated values. It is to be understood, even if not always explicitly stated that all numerical designations are preceded by the term "about".

The invention will now be exemplified in the following description of experiments that were carried out in accordance with the invention. It is to be understood that these examples are intended to be in the nature of illustration rather than of limitation. Obviously, many modifications and variations of these examples are possible in light of the above teaching. It is therefore, to be understood that within the scope of the appended claims, the invention may be practiced otherwise, in a myriad of possible ways, than as specifically described hereinbelow.

#### DESCRIPTION OF SOME NON-LIMITING EXAMPLES

### **Example 1: Preparation of the rubber containing composite material (pulp)**

Vulcanized recycled shredded rubber particles which are free of steel and of cotton fluff were obtained at sizes between 0.5mm to 5mm (European Tire Recycling Association (ETRA), Belgium, and France).

The shredded recycled rubber particles (88%) were mixed with 9% w/w of the thermoplastic polyester elastomer binder Hytrel® (DuPont<sup>TM</sup>), with 1.2% v/w silica powder, sawdust (0.6%v/w), and bromide oxide (0.6%w/w) The sawdust was watersprayed, to add to the mixture 0.6% humidity, resulting in a wet but non-dripping.

The above constituents were heated to a temperature of 55°C-65°C while continuously being mixed to obtain a homogonous pulp composite material.

# Example 2: combining rubber with Fiber Reinforced Polyester (FRP) profile

In the tested example, two FRP profiles, having a configuration as illustrated in **Figure 1B**, were placed on a steel casting mold (SCM), such that a space is formed therebetween, with a distance between the two support elements being 10mm. The SCM peripherally encloses the two FRP profiles (i.e. the two support elements) to form voids into which rubber composition may be poured. The SCM was heated to a temperature of about 60°C which caused heating of the FRP profiles to approximately the same temperature. The rubber composite material was then introduced into the voids of the heated profiles.

The heating was stopped and a compression piston was then used to apply a pressure of about 1.2-2 MPa onto the composite material-filled FRP profile.

Pressure by the compression piston was applied until the temperature of the SCM reached  $40^{\circ}$ C.

The resulting article of manufacture comprised  $\sim 30\text{-}40\%$  (w/w) FRP profile and  $\sim 60\text{-}70\%$  (w/w) rubber pulp.

# Example 3: characterization of the Article of Manufacture

A sample of the article of manufacture of Example 2 (dimensions of width: 7 cm, height: 3cm and length: 26cm) was placed on a tensile testing device (such as an hydraulic press)

The distance between the two prisms in the device was set to 235mm and four different loads were applied onto the sample. Table 1 summarizes the different loads and resulting deflections.

**Table 1: sample deflections** 

Test number	Load (Kg force)	Deflection (mm)
1	1168	3.35
2	1433	4.20
3	1650	5.0
4	1890	5.20

A load of 1890kg was set as the upper limit load in which the sample preserved the sample elastic modulus. As shown, at a load of 1890Kg a deflection of 5.2mm was obtained.

Based on the dimensions of the sample, distance between the prisms and the measured deflection, a *bending stretch* of 105MPa and *Elastic modulus* of 6,230MPa were determined for test #4.

#### **CLAIMS:**

- 1. An article of manufacture comprising at least one support element comprising fiber reinforced polyester (FRP), the at least one support element constructed in a form of a base and at least two projections extending from the base, the base and at least two projections forming together at least one compartment which is filled with a composite material comprising rubber particles.
- 2. The article of manufacture of Claim 1, characterized by at least one of:
  - bending strength of between about 50MPa to 120MPa;
  - elastic modulus of at least 3.000MPa.
- **3.** The article of manufacture of Claim 2, wherein the bending strength is between about 80 to 110MPa.
- **4.** The article of manufacture of Claim 2 or 3, characterized by an elastic module of between about 3,000MPa and 7,000MPa.
- **5.** The article of manufacture of Claim 4, characterized by an elastic module of between 6,000MPa-6,500MPa.
- **6.** The article of manufacture of Claim 1 or 2, having a bulk density of between 1,300kg/m³ to 1,400kg/m³.
- 7. The article of manufacture of any one of Claims 1 to 6, wherein the at least two projections extend upwardly from the base.
- **8.** The article of manufacture of Claim 7, wherein the at least two projections are essentially perpendicular to the base.
- **9.** The article of manufacture of any one of Claims 1 to 8, wherein the at least two projections are essentially parallel.
- **10.** The article of manufacture of any one of Claims 1 to 9, comprising a plurality of projections.
- 11. The article of manufacture of any one of Claims 1 to 9, comprising a plurality of support elements having a space therebetween.
- 12. The article of manufacture of Claim 11, comprising composite material filled in the space formed between the plurality of support elements.

- 13. The article of manufacture of any one of Claims 1 to 11, comprising a support element comprising at least one open end compartment.
- **14.** The article of manufacture of Claim 13, comprising composite material filled in the open end compartment.
- 15. The article of manufacture of any one of Claims 1 to 10, comprising at least one support element consisting of a base and three projections.
- 16. The article of manufacture of any one of Claims 1 to 15, wherein the at least one compartment between the base and at least two projections comprise compartment dimensions selected from a compartment height (h) from said base of between 15mm to 50mm and a compartment width (w) between facing surfaces of adjacent projections of between 7mm and 35mm.
- 17. The article of manufacture of Claim 16, comprising two or more compartments having the same or different dimensions.
- 18. The article of manufacture of any one of Claims 1 to 17, wherein the at least one support element comprise a base thickness of between 2 to 5mm, and a projection thickness of between 2 to 5mm.
- **19.** The article of manufacture of any one of Claims 1 to 18, wherein the recycled rubber particles comprise vulcanized recycled rubber.
- **20.** The article of manufacture of Claim 19, wherein the vulcanized recycled rubber particles are tire particles.
- 21. The article of any one of Claims 1 to 20, wherein the ratio between the FRP and the composite material is between 15:85 to 35:65 (v/v).
- **22.** A method of manufacture an article, the method comprising:
  - (a) providing at least one support element comprising fiber reinforced polyester (FRP) constructed in a form comprising a base and at least two projections extending from the base, the base and the at least two projections forming together at least one compartment;
  - (b) placing the at least one support element on a steel casting mold (SCM) while heating the SCM;

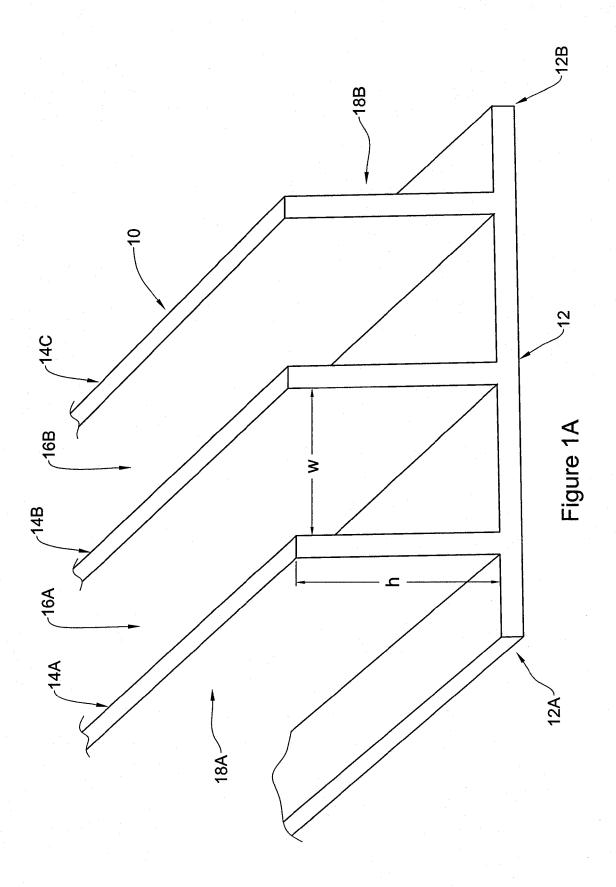
- (c) introducing into the steel casting mold carrying the at least one support element a pulp composite material comprising rubber particles;
- (d) compressing the pulp composite material against the support element;
- (e) allowing the SCM to cool down; and
- (f) releasing compressing, whereby the article of manufacture comprising the at least one support element and the composite material is formed.
- **23.** The method of Claim 22, wherein heating the SCM is to a temperature between 50°C and 80°C.
- **24.** The method of Claim 22, wherein cooling the SCM comprising the support element before releasing the compression is to a temperature of at most 40°C.
- **25.** The method of any one of Claims 22 to 24, wherein the at least two projections extend upwardly from the base.
- **26.** The method of Claim 25, wherein the at least two projections are essentially perpendicular to the base.
- 27. The method of any one of Claims 22 to 26, wherein the at least two projections are essentially parallel.
- **28.** The method of any one of Claims 22 to 27, comprising a plurality of projections forming a plurality of compartments having the same or different dimensions.
- **29.** The method of any one of Claims 22 to 27, wherein a plurality of support elements are placed in the steel casting mold such that a space is formed therebetween.
- **30.** The method of Claim 29, wherein the composite material is introduced into the compartment of each support element and in the space formed between the plurality of support elements.
- **31.** The method of any one of Claims 22 to 30, wherein at least one support element comprises at least one open end compartment.
- **32.** The method of Claim 31, wherein composite material is introduced into the at least one open end compartment.
- 33. The method of any one of Claims 22 to 28, wherein the at least one support element consists of a base and three projections.

- **34.** The method of any one of Claims 22 to 33, wherein the at least one compartment between the base and at least two projections comprise compartment dimensions selected from a compartment height (h) from said base of between 15mm to 50mm and a compartment width (w) between facing surfaces of adjacent projections of between 7mm and 35mm.
- **35.** The method of any one of Claims 22 to 34, wherein the at least one support element comprise a base thickness of between 2 to 5mm, and a projection thickness of between 2 to 5mm.
- **36.** The method of any one of Claims 22 to 35, wherein the rubber particles in the pulp composite material comprise vulcanized recycled rubber particles.
- **37.** The method of Claim 36, wherein the vulcanized recycled rubber particles are tire rubber particles.
- **38.** The method of any one of Claims 22 to 37, wherein the rubber particles are rubber crumbs.
- **39.** The method of any one of Claims 22 to 38, wherein the rubber particles are essentially free of steel and/or cotton fluff.
- **40.** The method of any one of Claims 22 to 39, wherein the rubber particles are at a size between 0.5 mm and 10mm.
- **41.** The method of Claim 40, wherein the rubber particles are of a size between 0.5mm and 5mm.
- **42.** The method of any one of Claims 22 to 41, wherein the composite pulp material comprises a chemical binder.
- **43.** The method of Claim 42, wherein the chemical binder is a thermoplastic and/or a themosetting binder.
- **44.** The method of Claim 43, wherein the chemical binder is a thermoplastic polyester elastomer.
- **45.** The method of any one of Claims 22 to 44, wherein the binder is thermoplastic elastomer selected from a group consisting of a thermoplastic styrenic block copolymer, a thermoplastic polyolefin blend, a thermoplastic blend of polypropylene with

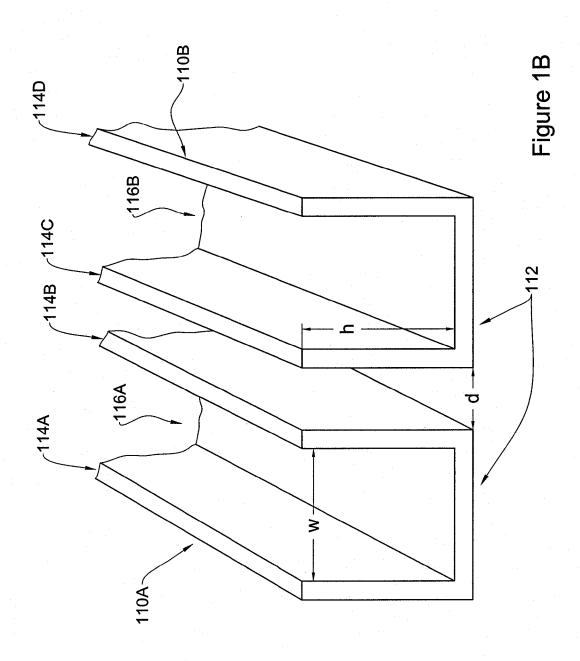
crosslinked thermoplastic vulcanized rubber, a thermoplastic polyurethane, a thermoplastic copolyester and a thermoplastic polyamide.

- **46.** The method of any one of Claims 22 to 45, wherein the composite material comprises a hardener.
- 47. The method of any one of Claims 22 to 46, wherein the hardener is selected from a group consisting of silica powder, quartz silica sand, silica granules.
- **48.** The method of Claim 47, wherein the hardener is silica granules.
- **49.** The method of any one of Claims 22 to 48, wherein the composite material comprises, between 70% to 95% (w/w) rubber particles.
- **50.** The method of any one of Claims 22 to 49, wherein the composite material comprises additives selected from a group consisting of wetted non-dripping sawdust, hydrated magnesium silicate, flame retardant.
- **51.** The method of any one of Claims 22 to 50, wherein the composite material is prepared at a temperature between 55°C and 65°C
- **52.** The method of any one of Claims 22 to 51, wherein the pulp composite material is homogenously mixed prior to being introduced into the at least one compartment.
- 53. The method of any one of Claims 22 to 53, comprising introducing an amount of the pulp composite material to the at least one compartment such that the volume ratio between the FRP and the composite material of between 15:85 to 35:65.
- **54.** The method of any one of Claims 17 to 43, wherein the pulp composite material is added in an amount sufficient to essentially cover at least a portion of projections.
- **55.** The method of Claim 54, wherein the pulp composite material is added in an amount allowing coverage of all projections.
- **56.** The method of any one of Claims 22 to 55, comprises compressing the pulp composite material against the base of the at least one support element.
- **57.** The method of Claim 56, wherein compressing is performed using a compression piston.
- **58.** The method of Claim 56 or 57, wherein the compression comprises applying a pressure of between 1.2MPa and 2.0MPa.

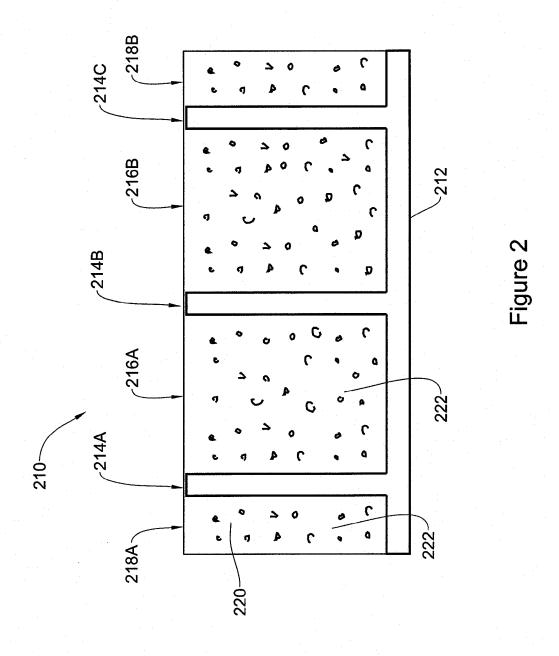
- **59.** The method of any one of Claims 22 to 58, wherein cooling down is to a temperature of at most  $40^{\circ}$ C.
- **60.** An article of manufacture as defined in any one of Claims 1 to 21 or as obtained by the method of any one of Claims 22 to 59, in a form of a laminate.
- **61.** The article of manufacture of Claim 60, in a form selected from the group consisting of flooring, tiles, roofing, ceilings, walls, covering, cladding, boards, fencing plates, railroad ties, noise insulating materials, structure frames, machines and vehicle shield parts, vehicle and road bumpers and bullet-proof shielding.
- **62.** The article of manufacture of Claim 61, for use in container manufacturing, building industry or housing industry.
- **63.** The article of manufacture of Claim 62, wherein said container is a shipping container.



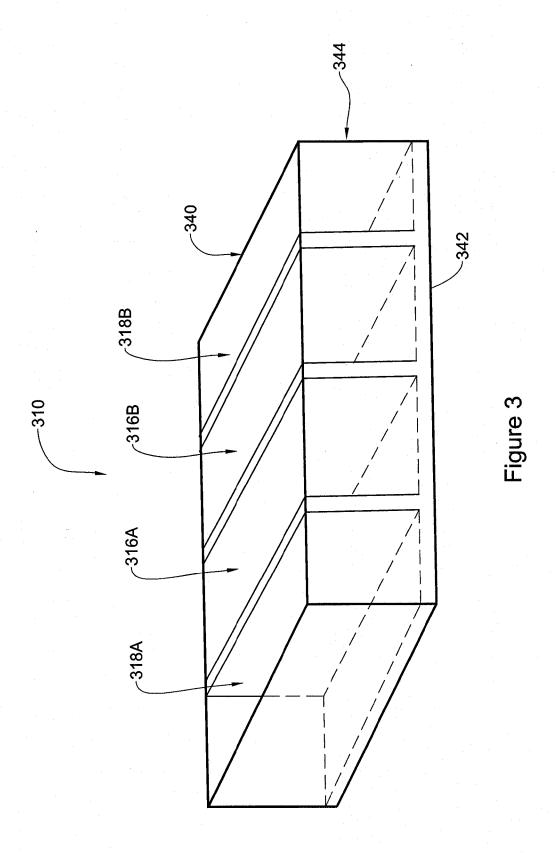
SUBSTITUTE SHEET (RULE 26)



SUBSTITUTE **SHEET** (RULE **26)** 



SUBSTITUTE SHEET (RULE 26)



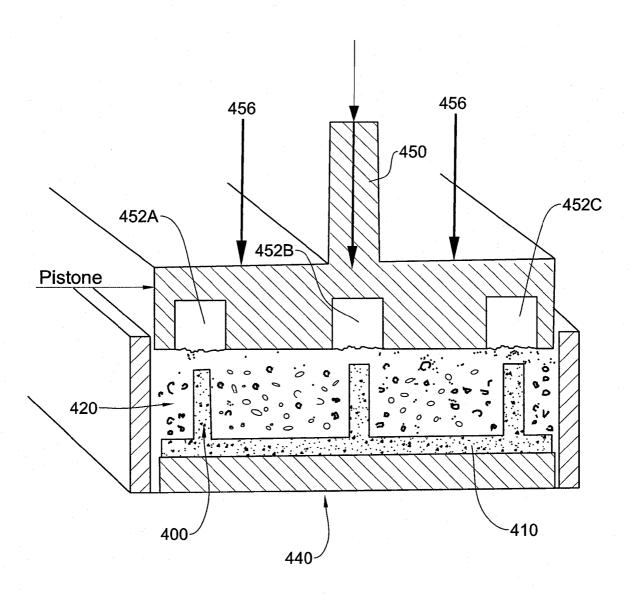


Figure 4

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/IL2012/050322

A. CLASSIFICATION OF SUBJECT MATTER IPC (2012.01) B29C 43/00, B29C 33/40, B29C 70/06, E04C 2/20, E04C 2/22					
According to International Patent Classification (IPC) or to both national classification and IPC					
B. FIELDS SEARCHED					
Minimum documentation searched (classification system followed by classification symbols) IPC (2012.01) B29C, E04C, B29B, B29D					
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) Databases consulted: Esp@cenet, Google Patents, EPODOC Search terms used: preform, prepreg, composite material, rubber, support, reinforcement, compression molding					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where ap	Relevant to claim No.			
X	US 2008098935 A1 Roth et al 01 May 2008 (2008/05/01) Paragraphs: 18-20,55,77-88, 93-96, 106-112, 136-142	1,7-10,15,17,19,20,60-63			
Y	Paragraphs: 18-20,55,77-88, 93-96, 106-112, 136-142	2-6,11-14,16,18,21-59			
Y	US 2006024453 A1 Sester et al 02 Feb 2006 (2006/02/02) Paragraphs: 2,18-25, 55-59, 63-66, 75-84, Fig 1	22-62			
Y	US 3799720 A Fjellman 26 Mar 1974 (1974/03/26) Abstarct	57			
Further documents are listed in the continuation of Box C. See patent family annex.					
* Special categories of cited documents:  "A" document defining the general state of the art which is not considered to be of particular relevance		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention			
"E" earlier application or patent but published on or after the international filing date  "L" document which may throw doubts on priority claim(s) or which is in the formal or after the control of the		"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone			
cited to establish the publication date of another citation or other special reason (as specified)  "O" document referring to an oral disclosure, use, exhibition or other means		"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art			
"P" document published prior to the international filing date but later than the priority date claimed		"&" document member of the same patent family			
Date of the actual completion of the international search 06 Nov 2012		Date of mailing of the international search report  06 Nov 2012			
Name and mailing address of the ISA: Israel Patent Office		Authorized officer ORGAD Yaniv			
The Technology Park, Bldg.5, Malcha, Jerusalem, 96951, Israel Facsimile No. 972-2-5651616		YanivO@justice.gov.il Telephone No. 972-2-5651787			

#### INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/IL2012/050322

Patent document cited search Patent family member(s) Publication date **Publication Date** report 2008098935 A1 US 01 May 2008 ΑU 2005321927 A1 06 Jul 2006 06 Jul 2006 ΑU 2005321927 A2 AU 2005321927 B2 27 Oct 2011 BRPI0516420 02 Sep 2008 2592273 06 Jul 2006 CA A1 CN 101443240 27 May 2009 101443240 22 Jun 2011 CN CN 102285180 21 Dec 2011 200701404 30 Jun 2008 EA 011818 30 Jun 2009 EA В1 EP 1836093 26 Sep 2007 A2 EP 1836093 A4 10 Nov 2010 JP 2008525289 17 Jul 2008 2007007857 A MX 24 Oct 2008 ΝZ 556660 29 Oct 2010 US 2008098935 A1 01 May 2008 US 8181580 B2 22 May 2012 WO 2006071920 A2 06 Jul 2006 WO 2006071920 A3 16 Apr 2009 US 2006024453 A1 02 Feb 2006 ΑU 2003234715 A1 06 Sep 2004 MXPA03006523 A 10 Aug 2004 US 2006024453 A1 02 Feb 2006 WO 2004071740 A1 26 Aug 2004 US 3799720 26 Mar 1974 US 3799720 A 26 Mar 1974 Α