



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

<b>(51) International Patent Classification</b> <sup>6</sup> : <b>B32B 7/08, C08K 3/06, 5/10, 5/32, 5/36, C08L 67/00, 89/04</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/41065</b>  <b>(43) International Publication Date:</b> 19 August 1999 (19.08.99)
<b>(21) International Application Number:</b> PCT/US98/16167  <b>(22) International Filing Date:</b> 3 August 1998 (03.08.98)  <b>(30) Priority Data:</b> 09/022,226      11 February 1998 (11.02.98)      US  <b>(63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Applications</b> US      09/022,226 (CIP) Filed on      11 February 1998 (11.02.98) US      08/843,823 (CIP) Filed on      21 April 1997 (21.04.97) US      08/611,911 (CIP) Filed on      6 March 1996 (06.03.96)  <b>(71) Applicant (for all designated States except US):</b> DEMER CORPORATION [US/US]; P.O. Box 1842, Covington, LA 70434 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> BAYER, John, C. [US/US]; 16461 Bricker Road, Covington, LA 70433 (US). GANDOLFO, Thomas, C. [US/US]; 77060 Highway 25, Covington, LA 70435-5754 (US).	<b>(74) Agent:</b> NEHRBASS, Seth, M.; Garvey, Smith, Nehrbass & Doody, L.L.C., Suite 3290, 3838 N. Causeway Boulevard, Metairie, LA 70002 (US).  <b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>	
<b>(54) Title:</b> THERMOPLASTIC ARTICLES MADE FROM RECYCLED PRODUCTS AND PROCESS FOR MAKING		
<b>(57) Abstract</b>  A process is provided for making thermoplastic-composites from recycled thermoplastics (polyolefins) together with phosphogypsum waste by-product from the phosphate fertilizer wet process or, in an equally preferred embodiment with fluorogypsum waste by-product from fluorine production wet process to produce lumber profiles. The process involves (a) admixing the phosphogypsum (calcium sulphate) or fluorogypsum (calcium fluoride) waste by-product with thermoplastic and a functionalized compound with or without coupling agents to produce a filled thermoplastic-composite composition, and (b) melt processing the composition to produce a filled thermoplastic-composite article. The articles are preferably in the form of railroad cross ties or construction articles such as common lumber profiles, panels, tiles, poles, utility poles, crossarms for utility poles, roofing tiles, pipeline skids, pilings, marine fender-piles (including light-responsive piles), bulkhead, revetments, and are useful for constructing various structures, such as oilfield board roads and equipment mats. The process avoids the accumulation of undesired phosphogypsum/fluorogypsum "stacks" and provides environmentally friendly useful products which require no chemical preservatives to prevent insect infestation or decay from the elements. Tailings from ore processing can also be used as a filler.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## PATENT APPLICATION

## TITLE OF THE INVENTION

5 "THERMOPLASTIC ARTICLES MADE FROM RECYCLED PRODUCTS AND  
PROCESS FOR MAKING"

INVENTORS: BAYER, John C., a US citizen, of 16461 Bricker Rd., Covington, LA  
70433, US, and GANDOLFO, Thomas C., a US citizen, of 77060  
Highway 25, Covington, LA 70435-5754, US

10 APPLICANT (all states but US): DEMER CORPORATION (a Louisiana, US, corporation)

APPLICANTS (US only): BAYER, John C., a US citizen, of 16461 Bricker Rd., Covington,  
LA 70433, US, and GANDOLFO, Thomas C., a US citizen, of  
77060 Highway 25, Covington, LA 70435-5754, US

## CROSS-REFERENCE TO RELATED APPLICATIONS

15 This is a continuation-in-part of co-pending U.S. Patent Application Serial No.  
08/611,911, filed 6 March 1996; this is also a continuation-in-part of co-pending U.S. Patent  
Application Serial No. 08/843,823, filed 21 April 1997; this is also a continuation-in-part of co-  
pending U.S. Patent Application Serial No. 09/022,226, filed 11 February 1998; all of these  
applications are incorporated herein by reference.

20 STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

Not applicable

## REFERENCE TO A "MICROFICHE APPENDIX"

Not applicable

## BACKGROUND OF THE INVENTION

25 1. Field of the Invention

The present invention relates to processes for manufacturing fertilizers and plastic  
articles, and more particularly relates to processes for manufacturing phosphorous containing  
fertilizers and filled plastic articles.

30 The present invention also relates to froth flotation processes and plastic articles, and  
more particularly relates to processes for producing mineral filled thermoplastic composites and  
articles made therefrom.

The present invention also relates to thermoplastic railroad ties and processes for making thereof, and more particularly relates to thermoplastic composite railroad ties and processes for making thereof.

The present invention also relates to protective pilings and processes for making pilings,  
5 and more particularly relates to pilings and processes for making pilings.

## 2. General Background of the Invention

In the fertilizer industry, materials used as sources of calcium and phosphorous are ground in mills and sifted to produce fine particles. For example, phosphate rock is ground to produce phosphate particles to be worked into the soil or for further processing with acids for the  
10 manufacture of fertilizers. A conventional process for using phosphate rock in the fertilizer industry involves a wet process wherein the phosphate rock,  $\text{Ca}_3(\text{PO}_4)_2$ , is contacted with sulfuric acid and a byproduct of calcium sulphate is removed as phosphogypsum( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) or hemihydrate ( $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ ) with residual levels of phosphate in the byproduct. In other words, the wet process waste byproduct typically comprises amounts of calcium sulfate and  
15 smaller amounts of di-calcium phosphate. Additionally, the presence of small amounts of fluorine-containing compounds provides a byproduct that is sometimes referred to as fluorogypsum. The byproducts have had limited commercial utility, and accordingly have been at times stock piled as undesired waste product.

Consequently, there is a need and desire to provide processes which solve the problems  
20 associated with wet process solid waste byproducts. Also, there is a need and desire to provide useful articles comprising these byproducts.

In the mineral industry, mineral ores used as sources of minerals are typically ground in mills near or at the mine site and sifted to produce fine particles which are subjected to froth flotation to produce concentrates of valuable minerals. For example, metallic sulfide ores of  
25 copper, lead, zinc, nickel and molybdenum are ground to produce particles which are subjected to froth flotation where the valuable minerals concentrate in the froth leaving an underflow product as waste. A conventional process for concentrating metallic sulfide ores by froth flotation involves (a) grinding the ore to produce particles, (b) treating the particles with a floatation reagent to render the particulates air-avid and water repellent, (c) vigorously agitating  
30 and aerating the particles in the presence of water to produce a layer of froth containing air-avid particles and (d) collecting the froth. Valuable concentrations may be either in the froth or in the

underflow, but in process involving metallic sulfide ores of copper, lead, zinc, nickel and molybdenum, the valuable minerals concentrate in the froth.

Problems however have been associated with the processes. For example, the tailings from such processes have conventionally been stockpiled and exposed to repeated environmental conditions such as rain. In the case of lead and molybdenum, there has been some concern with the repeated exposure of such tailings containing lead and molybdenum to rain water due to the resulting runoffs.

Consequently, there is a need for improving conventional froth flotation processes and a need to avoid lead and molybdenum contaminated runoff from tailing.

A process is provided for processing ore and for making plastic articles from the solid byproducts therefrom. The process involves (a) providing ore, (b) contacting the ore with reagent in the presence of water to produce coated metallic sulfide particulates, (c) froth flotation of the coated particulates, (d) separating at least a portion of the froth from the underflow to produce a flotation product and a tailing byproduct wherein the tailing byproducts typically comprising calcium carbonate, silica and lead, (d) drying the tailing byproduct to remove water therefrom, (e) admixing the dried tailing byproduct with thermoplastic and a preferably a functionalized compound to produce a filled thermoplastic composition, and (f) melt processing the thermoplastic composition to produce a filled thermoplastic article. The articles are preferably in the form of block shaped articles such as car stops, railroad ties, pilings, poles and timbers suitable for retaining walls and bulkheads. The process avoids the accumulation of undesired tailing byproduct from flotation processes.

In the railroad industry, the railroad tracks comprise metal rails supported on wooden ties. Historically, these wooden ties have exhibited limited useful lives due to their loss of properties upon extended use and extended exposure to environmental elements. The use of composite railroad ties has been disclosed in Neefe U.S. 5,055,350 issued October 8, 1991 which discloses the making of railroad cross-ties from sand and recycled thermoplastic containers by coating the sand with an adhesive substance. The use of sand however can have various problems or disadvantages associated therewith including excessive weight, excessive abrasiveness when used in extrusion processes and when in contact with various processing equipment. Consequently, there is a need and a desire to provide composite railroad ties exhibiting certain enhanced properties.

A composite railroad tie is provided comprising a phosphogypsum filler and a thermoplastic resin. The composite exhibits desirable physical properties for railroad ties. Suitable sources for phospho-gypsum include fertilizer processes involving (a) providing phosphate rock, (b) contacting the phosphate rock with sulfuric acid in the presence of water to produce phosphoric acid and a calcium sulphate, (c) separating at least a portion of the phosphoric acid from the calcium sulphate to produce a phosphoric acid product and a calcium sulphate byproduct, (d) drying the calcium sulphate byproduct to remove water therefrom. The calcium sulphate byproduct (phospho-gypsum) is then admixed with a thermoplastic and a functionalized compound to produce a filled thermoplastic composition. The filled thermoplastic composition is then melt processed (for example injection or compression molded) to produce a filled thermoplastic composite railroad tie. The tie is a useful replacement for wood products having several physical property advantages and being suitably made from recycled plastic and waste byproduct filler.

In the shipping industry, the ships (barges) traveling on narrow waterways such as rivers and bays need to pass under bridges and adjacent to bridge supports and other structures. Historically, these bridge supports have been damaged by accidental ramming and rubbing by heavily loaded ships and barges resulting in undesired damage to the bridges thereby reducing the useful lives of such bridges and structures, and such ships have also been damaged as a result of such undesired contact with the structures. Prior efforts to protect bridges and structure have included the use of protective outer wood pilings which are placed around the structure and banded or bolted together (clustered) to provide a protective outer layer. The use of marine fenders has been disclosed in various patents, see for example Young U.S. Patent 4,281,610 issued August 4, 1981 which discloses a marine fender comprising a sheet of resilient material and an elastomeric core; Nill U.S. Patent 5,037,242 which discloses a dock fender made of PVC pipe; Matthews U.S. Patent 3,950,953 issued April 20, 1976 which discloses a piling fender; Smath U.S. Patent 4,804,296 issued February 14, 1989 which discloses a floatable marine fender device; James U.S. Patent 5,007,363 issued April 16, 1991 which discloses a buoyant marine fender; Watkins U.S. Patent 5,013,272 issued May 7, 1991 which discloses a boat fender made of flexible plastic and having a hollow interior; Stevens U.S. Patent 5,018,471 issued May 28, 1991 which discloses a marine fender for pilings of marine structures, all of which are incorporated herein by reference. These various prior fenders exhibit one or more of the

following problems: (a) they are not easily visible at night (low light conditions) resulting in them not providing warning to the ship (barge) approaching the structure and/or (b) they exhibit floating characteristics, and other characteristics, which make it difficult to use them as pilings or as mostly submerged fenders.

5           Consequently, there is a need and a desire to provide pilings which exhibit certain improved characteristics such as improved visibility and improved density characteristics.

          A composite marine piling is provided comprising (a) a core element comprising filler and a thermoplastic resin and (b) a sheath comprising thermoplastic resin and a light absorbing/emitting material. The filled thermoplastic composition of the core element is melt  
10   processed (for example injection or compression molded) to produce the filled thermoplastic composite marine piling core element. The sheath covers top of the core element to provide the top portion of the piling with a light responsive sheath to enhance the visibility of the piling to ship operators. The piling is a useful replacement for wood pilings and has several physical property advantages and preferably being suitable made from recycled plastic and waste  
15   byproduct filler.

          The following U.S. Patents are incorporated herein by reference:

          U.S. Patent Nos. 3,636,713; 3,995,434; 4,248,760; 5,030,662; 5,344,490; 5,683,616;  
all patents and other references cited herein or in the file histories of any parent patent  
application.

## 20   BRIEF SUMMARY OF THE INVENTION

          The present invention solves the problems confronted in the art in a simple and straightforward manner. What is provided is a process for making fertilizer from phosphate rock and for making plastic articles from the solid byproducts therefrom. The process preferably involves (a) providing phosphate rock, (b) contacting the phosphate rock with sulfuric acid in the  
25   presence of water to produce phosphoric acid and a calcium sulphate, (c) separating at least a portion of the phosphoric acid from the calcium sulphate to produce a phosphoric acid product and a calcium sulphate byproduct, (d) drying the calcium sulphate byproduct to remove water therefrom, (e) admixing the calcium sulphate byproduct with a thermoplastic, preferably a recycled polyolefin, and a functionalized compound to produce a filled thermoplastic  
30   composition, and (f) melt processing (e.g., injection or compression molding) said thermoplastic composition to produce a filled thermoplastic article. The articles are preferably in the form of

construction articles such as plastic lumber, plastic panels, plastic tiles, railroad ties, and marine pilings. The plastic effectively encapsulates (traps, reduces escape of) undesired radon gases and attenuates certain radiation which may be present in the byproduct.

Another embodiment of the present invention is a process for making metallic concentrate  
5 from metallic ore and for making plastic articles from the tailings therefrom. The process preferably involves (a) providing metallic ore, (b) grinding the ore to produce particles, (c) treating the particles with a floatation reagent to render the particulates air-avid and water repellent, (d) vigorously agitating and aerating the particles in the presence of water to produce a layer of froth containing air-avid particles, (e) collecting the froth, (f) collecting the underflow,  
10 (g) removing the tailings from the underflow, (h) drying the tailings to produce a dry particulate material comprising amounts of lead and/or molybdenum, (i) microencapsulating the particulates in a thermoplastic resin to produce a mineral filled composition, and (j) forming a thermoplastic article from the composition. The articles are preferably in the form of elongated blocks suitable as car stops, railroad ties or if utilized in combination as a seawall or sound barrier.

15 The present invention also comprises a composite railroad tie comprising a phosphogypsum filler and a thermoplastic resin. The composite is relatively dense and exhibits desirable physical properties for railroad ties. Suitable sources for phospho-gypsum include the fertilizer manufacturing processes mentioned above.

The present invention also comprises a composite piling (which also functions as a  
20 fender-pile) comprising (a) a core of a composite comprising (i) a filler and (ii) a thermoplastic resin, and (b) an outer layer (sheath) or coating of light absorbing/emitting (light-responsive) material. The composite is dense and preferably exhibits a density of greater than  $1.0 \text{ g/cm}^3$ , and most preferably  $1.4\text{-}1.7 \text{ g/cm}^3$ , though the density can be greater than  $2.0 \text{ g/cm}^3$ . Yet another practical application for this thermoplastic-waste-mineral-tailings-composite material is to  
25 provide a substrate, for example, a pole or piling which will glow-in-the-dark as a result of having photoluminescent material either admixed with the thermoplastic-waste-mineral-tailings-composite prior to extrusion or applied or infused on to the outer surface of the extruded substrate or pole contemporaneously by co-extrusion. Suitable fillers are phosphogypsum (calcium sulfate), fluorogypsum (calcium sulfate) and the tailings from the froth flotation process  
30 discussed above often comprised of: Limestone ( $\text{CaCO}_3$ ), Silica ( $\text{SiO}_2$ ), Fluorspar ( $\text{CaF}_2$ ), Barium Sulfate ( $\text{BaSO}_4$ ), Zinc Sulfate ( $\text{ZnS}$ ), Lead Sulfate ( $\text{PbS}$ ). Phosphogypsum may be obtained from



the fertilizer manufacturing processes mentioned above. An outer layer (sheath) is affixed (adhered) to the core element, and may be created by coextrusion of the core with the outer layer or the outer layer may be separately applied over the core. The outer layer can be melt-mixed with a photoluminescent material (light absorbing/emitting, light responsive).

5 BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

For a further understanding of the nature, objects, and advantages of the present invention, reference should be had to the following detailed description, read in conjunction with the following drawings, wherein like reference numerals denote like elements and wherein:

Figure 1 is a schematic of a wet process for making fertilizer from phosphate rock and  
10 for making plastic articles from the solid byproducts therefrom;

Figure 2 is a perspective view of an extruder;

Figure 3 is a schematic of a froth flotation process for making metallic concentrates and plastic articles from the tailings therefrom;

Figure 4 is a perspective view of an article of the present invention in the shape of a stick  
15 of lumber;

Figure 5 is a perspective view of an article of the present invention in the shape of a sheet;

Figure 6 is a perspective view of an article of the present invention in the shape of a roofing tile;

Figure 7 is a perspective view of a composite railroad tie of the present invention;

Figure 8 is a perspective cutaway view of a railway according to the present invention;  
20 and

Figure 9 is a vertical cross-sectional view of the railroad tie of figure 1;

Figure 10 is a vertical cross-sectional cutaway view of railway of Figure 8;

Figures 11 and 12 show a first alternative embodiment of a railroad cross tie having an  
25 optional longitudinally extending cooling hole;

Figures 13 and 14 show a second alternative embodiment of a railroad cross tie;

Figure 15 is a perspective view of a composite piling of the present invention;

Figure 16 is a perspective view of an alternative embodiment of the composite piling  
of the present invention;

Figure 17 is a perspective cutaway view of a bridge structure having pilings according to  
30 the present invention; and

Figure 18 is a vertical cross-sectional view of the piling of Figure 15;

Figure 19 is a horizontal cross-sectional view of a sheath of a piling according to the present invention;

5 Figure 20 is a perspective view of an article of the present invention in the shape of a car stop;

Figure 21 is a perspective view of an article of the present invention in the shape of a round post;

Figure 22 is a perspective view of an article of the present invention in the shape of a square post; and

10 Figure 23 is a perspective view of an article of the present invention in the shape of a barrier wall, such as a sea wall or a sound barrier wall.

#### DETAILED DESCRIPTION OF THE INVENTION

A process is provided for manufacturing fertilizer and utilizing the byproducts therefrom. The process involves (a) providing phosphate rock, (b) contacting the phosphate rock with sulfuric acid in the presence of water to produce phosphoric acid and a calcium sulphate byproduct, (c) separating at least a portion of the phosphoric acid from the calcium sulphate to produce a phosphoric acid product and a calcium sulphate byproduct, (d) drying the calcium sulphate byproduct to remove water therefrom, (e) admixing the calcium sulphate byproduct with a thermoplastic resin and a functionalized compound to produce a filled thermoplastic composition, and (f) melt processing the thermoplastic composition, preferably a recycled polyolefin resin, to produce a filled thermoplastic article. The thermoplastic composition comprises (a) a thermoplastic resin, (b) a filler comprising a calcium sulphate compound and a phosphate, and (c) a functionalized compound. Articles formed from the compositions are useful in the manufacture of structures, such articles include plastic lumber, plastic panels, plastic tiles, railroad ties, poles, and marine pilings.

25 Manufacturing of fertilizers from phosphate rocks by wet processes are well known. The processes involve (a) providing phosphate rocks and converting (reducing the size of) phosphate rocks into phosphate particulates, preferably by grinding, and preferably involves converting phosphate rocks having weight average diameter particle sizes of greater than 0.1 inches (.254 cm) to small particulates having sizes of less than 0.01 inches (.254mm), more preferably less than 0.005 inches (.013mm), and most preferably less than 0.003 inches (.076mm), for example

into a weight average diameter particulate size of no greater than 60 mesh (.42mm), more preferably no greater than 115 mesh (.22mm), and most preferably no greater than 200 mesh (.13mm). The smaller the particulate size, the greater the effective surface area to volume of the phosphate particulates for contacting with the sulfuric acid in the process. Various grinding and screening systems are suitable for converting phosphate rocks into phosphate particulates having the desired size. Grinding may be achieved by hammer mills, ring roller mills, and ball mills. Screening may be achieved by vibrating screens or other suitable screening devices.

The phosphate solids, preferably in the form of small phosphate particulates, are then contacted with sulfuric acid to the presence of water to form a reaction mass resulting in the production of (formation of) phosphoric acid and a calcium sulphate, as is known in the art. The calcium sulphate typically takes the form of phosphogypsum and/or hemihydrate. The calcium sulphate is then removed from the reaction mass to yield a phosphoric acid product and a calcium sulphate byproduct. Typical calcium sulphate byproducts from this step contain amounts of water and phosphate, and are typically stock piled as an undesired waste product.

In the present process the calcium sulphate byproduct is then dried (dewatered) to produce a calcium sulphate/phosphate product having preferably having less than 1 percent by weight water, more preferably less than 0.5% water, and most preferably less than 0.1% by weight water based on the total weight of the solid byproduct. Drying the product is desirable as it reduces the risk of undesired complications in the extruder (such as explosion of the extruder) due to the presence of high levels of residual water and high temperatures which can cause steam to form inside the extruder.

The process further involves admixing, preferably by melt mixing, (a) the byproduct (calcium sulphate compound/phosphate byproduct (mixture)), (b) a thermoplastic resin and (c) a functionalized compound to produce a filled thermoplastic composition. Optionally, graphite and/or calcium sulphate whiskers may admixed into the composition to provide further reinforcement therein.

The filled thermoplastic resin composition may then be processed to form a thermoplastic article. Suitable articles include thermoplastic-composite lumber, panels, tiles, railroad crossties, utility poles, pilings, bulkheads, marine fender piles, artificial reefs and fish habitat structures.

The thermoplastic composition preferably comprises (a) a polyolefin resin present at a level of from 10 to 99 percent by weight based on the total weight of the composition, (b) a

fertilizer wet process by-product (filler comprising calcium sulphate and trace amounts of phosphate) present at a level of from 1 to 90 percent by weight based on the total weight of the composition, and (c) a functionalized compound present at a level of from 0.5 to 10 percent by weight based on the total weight of the composition.

5           The polyolefin resins include polymers of monoolefins and diolefins, for example polypropylene, polyisobutylene, polybutene-1, polymethylpentene -1, polyisoprene or polybutadiene, as well as polymers of cycloolefins, for instance of cyclopentene or norbornene, polyethylene, for example high density polyethylene, low density polyethylene, linear ultra high density polyethylene, and linear low density polyethylene may be used. Mixtures of these  
10           polymers, for example mixtures of polypropylene with polyethylene and mixtures of different types of polyethylene, may also be used. Also useful are copolymers of monoolefins and diolefins with each other or with other vinyl monomers, such as, for example, ethylene/propylene, linear low density polyethylene and its mixtures with low density polyethylene, propylene/butene-1, ethylene/hexene, ethylene/ethylpentene, ethylene/heptene,  
15           ethylene/octene, propylene/isobutylene, ethylene/butane-1, propylene/butadiene, isobutylene/isoprene, ethylene/alkylacrylates, ethylene/alkyl methacrylates, ethylene/vinyl acetate or ethylene/acrylic acid copolymers and salts thereof and terpolymers of ethylene with propylene and a diene, such as hexadiene, dicyclopentadiene or ethylidene-norbornene, as well as mixtures of such copolymers and their mixtures with polymers mentioned above, or for example  
20           polypropylene/ethylene-propylene-copolymers, low density polyethylene/high density polyethylene, ethylene vinyl acetate. Also suitable are polyvinyl chlorides.

          Most preferably the thermoplastic resin is a recycled polyolefin resin. The preferred recycled thermoplastic resin is a recycled polyolefin, and most preferably is a recycled high density polyethylene.

25           Suitable functionalized compounds include epoxidized oils such as epoxidized esters of unsaturated fatty acid which may be made by reacting alcohols with unsaturated fatty acids to produce esters of unsaturated fatty acids, followed by epoxidizing the esters of unsaturated fatty acids. The epoxidizing may be accomplished by treating the ester of an unsaturated fatty acid with a peroxy organic acid, such as perony acetic acid. Suitable alcohols include mono-ols, diols,  
30           triols such as glycerols, and higher polyols. Suitable unsaturated fatty acids include mono and poly (di, tri, and higher) unsaturated fatty acids such as oleic acid, linoleic acid, linolenic acid,

and arachidonic acid. Naturally occurring esters of unsaturated fatty acids, more particularly glycerides of unsaturated fatty acids, include vegetable oils (chiefly from seeds or nuts), including soybean oil, linseed oil, and cottonseed oil, or alternatively mineral oil. Generally unsaturated fatty acids have from 4 to 24 carbon atoms. The most preferred epoxidized esters of unsaturated fatty acid is epoxidized soybean oil. Soybean oil is predominantly triglycerides of oleic acid, triglycerides of linoleic acid and triglycerides of linolenic acid. Additionally, metal chelates may be present such as titanium chelates to enhance the properties of the filled composition. Examples of titanium chelates are those represented by the general formulas  $(HOYO)_2Ti(OR)_2$  or  $(H_2NYO)_2Ti(OR)_2$  wherein Y and R are selected from hydrocarbon groups, preferably C1 to C20 alkyl groups, and more preferably C2 to C8 alkyl groups and titanium chelates include, but are not limited to octylene glycol titanate and triethanolamine titanate, and most preferably is octylene glycol titanate. Titanium chelates are commercially available, for example a titanium chelate is available from KENRICH Petrochemicals, Inc. A suitable titanium chelate is isopropyl triisostearoyl titanate  $CH_3(CH_3)(CHOTi(OC(O)C_{17}H_{35}))_3$ . The titanium chelate is preferably present at a level of from 1 to 1000 parts per million (ppm) based on the total weight of the composite, more preferably from 2 to 100. Amounts of mineral oil may also be present, and most preferably 2 ppm.

The plastic compositions may optionally contain flame retardants such as halogenated materials, preferably chlorinated or brominated compounds. The filler of the present invention is of a nature containing phosphates which provides the potential additional advantage of added flame retardancy in the composition. Suitable flame proofing additives include low molecular weight bromine compounds, and examples include octabromodiphenyl ethers, tetrabromophthalimide, tribromophenoxy methane, bis(tribromophenoxy)ethane, poly or oligomeric tetrabromobisphenol A, tris(tribromophenyl)triphosphate, trichlorotetrabromotoluene, hexabromocyclododecane and decabromodiphenyl ether.

The process of the present invention allows for the production fertilizer without the undesired stock piling (or solid waste disposal) of solid byproducts. The present process allows the combined production of fertilizer and useful building materials and railroad ties. The presence of the phosphate in the byproduct also provides for possible enhancement in the flame retardancy of the product without the additional expense of purchasing a phosphate flame retardant.

Various other additives such as pigments, dyes, and oxidants, antioxidants, ultraviolet light stabilizers, etc. may be present in the composition or the composition may be free from such additional additives.

5 The thermoplastic compositions may further comprise neutralizers, primary antioxidants, secondary antioxidants and light stabilizers such as hindered amine light stabilizers.

10 The polyolefin resin is preferably present at a level of from 10 to 99 percent by weight based on the total weight of the composition, more preferably from 25 to 80 percent by weight thereof, and most preferably from 40 to 75 percent by weight thereof. The filler (fertilizer waste byproduct or tailing byproduct) is preferably present at a level of from 1 to 90 percent by weight based on the total weight of the composition, more preferably from 20 to 75 percent by weight thereof, and most preferably from 25 to 60 percent by weight thereof. The functionalized compound (epoxidized oil) is preferably present in the composition at a level of from 0.5 to 2 percent by weight based on the total weight of the composition, more preferably from 1 to 5 percent by weight thereof, and most preferably from 2 to 4 percent by weight thereof. The fertilizer waste byproduct known as phosphogypsum used in the present composition with a recycled high density polyethylene provides a filled thermoplastic composition primarily made up of recycled waste products (co-mingled post consumer polyolefins), industrial mineral waste byproduct such as phosphogypsum/fluorogypsum exhibiting suitable physical characteristics for articles such thermoplastic-composite lumber, panels, tiles, railroad crossties, utility poles, pilings, bulkheads, marine fender piles, artificial reefs and fish habitat structures. The composition may further contain graphite and/or calcium sulphate whiskers as reinforcing agents, at levels of from 1 to 20 percent by weight based on the total weight of the composition, more preferably from 2 to 15 percent by weight thereof, and most preferably from 5 to 15 percent by weight thereof. The use of phosphogypsum/fluorogypsum waste byproduct and recycled polyolefins allow the utilization of two waste products, while producing products exhibiting useful physical properties. Thus, the waste by-products, phosphogypsum/fluorogypsum and waste (post-consumer) co-mingled recycled thermoplastics (polyolefins) can be utilized together to produce useful building and marine structural articles. In other words, the present invention provides a solution to waste products from the above processes, while producing building and marine structural articles.

20  
25  
30

The compositions may be used to make thermoplastic-composite lumber, car stops,

roofing tiles, paneling, sheets, pipes, and other types of tiles and load bearing articles such as railroad cross-ties, marine piling systems (e.g., Glow-Pile™), utility poles and cross-arms, bulkheads and retaining walls. For example, thermoplastic-composite lumber can have a length of for example of between 4 feet and 12 feet (1.22m and 3.66m), for example between 6 feet and 10 feet (1.83m and 3.05m), for example about 8 feet (2.44m) in length, and a rectangular cross-section transverse to the above length of for example between 1 inch and 12 inches (2.54cm and 30.5cm), for example between 1.5 inches and 8 inches (3.81cm and 20.3cm), for example between 3 inches and 6 inches (7.62cm and 15.2cm), and a depth of between 0.75 inches and 4 inches (1.91 cm and 10.2cm), for example between 1 inch and 3 inches (2.54cm and 7.62cm), for example between 1.5 inches and 2.5 inches (3.81 cm and 6.35cm), to replicate the dimensions of conventional wood lumber (2" by 4" (5.08cm by 10.2cm), 2" by 6" (5.08cm by 15.2cm), 1" by 4" (2.54cm by 10.2cm), and other cross-sectional dimensions).

As shown in Figure 1, the process of the present invention involves a process for manufacturing fertilizer which utilizes the byproduct thereof, and more specifically involves (a) fertilizer manufacturing system (10) wherein phosphate rock (12) (phosphate rock stream (12)) is fed to a size reducing device (14) (grinder (14)) for reducing the phosphate rock into small size particulates which are then fed as intermediate stream (16) to a first screening unit (18) for separating intermediate phosphate stream (16) into (i) a large particle return stream (20) which is returned to the grinder (14) for further size reduction and (ii) a stream (22) of small particulates. The small particulates are then fed to a reaction vessel (24), and a water feed stream (26) and a sulfuric acid feed stream (28) are also fed to the reaction vessel to form a reaction mass (30). In the reaction mass (30) the phosphate rock and the sulfuric acid react to form liquid (aqueous) phosphoric acid and a solid calcium sulphate (phosphogypsum/fluorogypsum and/or hemihydrate). The liquid phosphoric acid is removed from the vessel (24) as phosphoric acid stream (32) and is retained in a holding container (34) and is used as a fertilizer product, typically after being admixed with other conventional fertilizer elements. The solid calcium sulphate is removed from the vessel (24) as initial calcium sulphate stream (36) which contains undesirably high levels of water (typically in excess of 1 percent by weight based on the total weight of the initial calcium sulphate byproduct). The initial calcium sulphate stream (36) is then fed to a dewatering unit (38) wherein water is removed as water waste stream (40) and a dewatered calcium sulphate stream (42) exits the unit (38). The dewatering unit (38) may be in the form

of a press or a heat drying unit or an air drying system, and preferably the dewatered calcium sulphate (42) has a water content of less than 1 percent by weight based on the total weight of the dewatered calcium sulphate. If the drying unit (38) undesirably causes particulate aggregation, then the system preferably further involves a calcium sulphate grinder (44) for reducing the  
5 particle size of the aggregated calcium sulphate to produce (i) a reduced particle size intermediate calcium sulphate stream (46) which is fed to a screening device (48) for separating the stream (46) into a small particulate (byproduct stream) (50) which is fed to an extruder (or other melt mixing device) (52) and (ii) a return calcium sulphate stream (54) of relatively larger size particles for return to the grinder (44) for size reduction. Alternatively to phosphogypsum, the  
10 filler may be fluorogypsum.

The extruder (52) (see also Figure 2) may be a conventional melt extruder for filled thermoplastics and contains conventional heating and cooling controls for maintaining the extruder within a temperature range suitable for melt processing of the composition. The extruder (52) has an intake throat (53) for receiving the byproduct particulates (50), and for  
15 receiving respective amounts thermoplastic resin by resin stream (56) and functionalized compound (epoxidized oil) by functional compound stream (58). The extruder then melt mixes the particulates, resin and functionalized compound and forces the resulting resin composition through a die or into a mold (60) resulting in a shaped article (62) (final resin product/article stream (62)) or pellets depending upon the cross-sectional configuration of the die (60). The  
20 process may further involve an optional thermoforming unit (64) (such as an injection molding or a compression molding machine) wherein if the die (60) is configured to produce thermoplastic-composite sheet, the sheet may be thermoformed into desired shaped panels or tiles (66) or railroad ties.

The extruder (52) has an output of, for example, 1800 lbs./hr. (817.2kg/hr.) For formula  
25 optimization, the extruder (52) could be, for example, a Berstoff Extruder: Laboratory Compound Twin 25mm; Co-Rotating Intermeshing Screws; Vented; 24:1 Length/Diameter (L/D); Variable Speed High Torque Motor, Multiple Electric Heat Zones/Air Cooled. Laboratory tests were conducted using such an extruder. A commercial extruder (52) with similar features can have an output of, for example, 5,000-10,000lbs./hr (2270-4540kg/hr). Such extruders can  
30 be purchased from Berstoff, Davis & Standard, Cincinnati Milocron, W&P.

Preferred process temperatures for the extruder (52) (see Figure 2) are as follows: Heat



Zone #1 (Z1) - range 140°C - 170°C; Heat Zone #2 (Z2) - range 150°C - 180°C; Heat Zone #3 (Z3) - Range 160°C - 190°C; Heat Zone #4 (Z4) 170°C -200°C; Heat Zone #5 (Z5) 175°C - 205°C; Head Flange Range (60)- 180°C -210°C.

5 The extruder line includes a dry waste storage hopper (151), a waste feeder (152), a polyolefin storage hopper (153), a polyolefin feeder (154), a screw (155), and a vent port (156). A vacuum pump (161) moves gas from the vent port (156) to a HEPA filter (162).

10 The calcium sulphate is present in the byproduct composition at a level of from 50 percent by weight to 99 percent by weight based on the total weight of the byproduct composition, more typically from 60 to 98 percent by weight thereof, and even more typically from 75 to 95 percent by weight thereof. The calcium sulphate may be in the form of calcium sulphate anhydrite or hemihydrate, in other words the calcium sulphate may be in the form of  $\text{CaSO}_4$ ,  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ ,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  or mixtures thereof. The byproduct composition may also contain dicalcium phosphate.

15 As shown in Figure 4, the article (66) may be in the shape of a stick of lumber (68). As shown in Figure 5, the article (66) may be in the shape of a sheet(70) (or panel (70)). As shown in Figure 6, the article (66) may be in the shape of a roofing tile (72).

### EXAMPLES

20 Formulation #1 was made by admixing: Phosphogypsum (a fertilizer process byproduct blend of calcium sulphate and phosphate) 23.5 pounds (10.7kg), recycled high density polyethylene 16 pounds (7.26kg), epoxidized soybean oil 225 grams and a titanium chelate @ 0.45 grams as coupling agent as manufactured by KENRICH Petrochemicals, Inc. The phosphogypsum and recycled high density polyethylene were dry mixed for 5 minutes. The epoxidized soybean oil and the chelate were blended for two minutes. The epoxidized soybean oil and chelate mixture was slowly added to the dry mixture of phosphogypsum and recycled polyethylene while it was mixing in the mixer. The time of mixing all ingredients together was 25 10 minutes (until compound was thoroughly mixed).

30 Formulation #2 was made by mixing: fluorogypsum @ 22.5 pounds (10.2), recycled high density polyethylene @ 16 pounds (7.26kg), epoxidized soybean oil @ 225 grams, titanium chelate @ 0.45 grams. The fluorogypsum and recycled high density polyethylene were dry mixed for 5 minutes. The epoxidized soybean oil and titanium chelate were slowly added to the dry mixture of fluorogypsum and recycled high density polyethylene while it was mixing in the

mixer. The time of mixing all ingredients together was about 10 minutes (until the compound was thoroughly mixed). Both formulas 1 & 2 were then processed into small pellets and then processed through a small extrusion machine and a 2 inch by 2 inch by 12 inch long (5.08cm by 5.08cm by 30.5cm long) sample was produced.

5           The presence of fluorine containing compounds in some fertilizer by products is well known and may be referred to as fluorogypsum. Fluorogypsum may also be generated by other processes such as a byproduct produced from the reaction of fluorspar with sulfuric acid in the production of hydrofluoric acid, see Azar Fluorogypsum Waste Solidification Material U.S. Patent 4,935,211 issued June 19, 1990 which is incorporated herein by reference. Fluorogypsum  
10 contains mostly calcium sulfate anhydrite and calcium sulfate having water chemically combined therewith, plus small quantities of fluorine containing compounds and possibly small concentrations of sulfuric acid. Disposal ponds for fluorogypsum occupy large areas of useful land and commonly require monitoring and maintenance by the owner. The disposal ponds are constantly increasing in size and quantity of fluorogypsum contained as the related production  
15 processes continue. Consequently, there is a problem with the continued accumulation of these byproducts and a need and desire to find a useful product which uses these materials. Fertilizer related processes producing fluorogypsum materials are known, see for example Sardisco et al Recovery of Fluorides From Gypsum U.S. Patent No. 4,060,586 issued November 29, 1977, Johnson U.S. Patent No. 4,175,944 issued November 27, 1979, Gaynor et al U.S. Patent No.  
20 4,402,922 issued September 6, 1983 and Czysch et al Production of Low-Fluorine Gypsum as a By-Product in a Phosphoric Acid Process U.S. Patent No. 4,026,990 issued May 31, 1977, all of which are incorporated herein by reference.

          Instead of phosphogypsum or fluorogypsum as the filler, the filler could be tailings from a process for making metallic concentrate from metallic ore.

25           A process is provided for making metallic concentrate from metallic ore and for making plastic articles from the tailings therefrom. The process preferably involves (a) providing metallic ore, (b) grinding the ore to produce particles, (c) treating the particles with a floatation reagent to render the particulates air-avid and water repellent, (d) vigorously agitating and aerating the particles in the presence of water to produce a layer of froth containing air-avid  
30 particles, (e) collecting the froth, (f) collecting the underflow, (g) removing the tailings from the underflow, (h) drying the tailings to produce a dry particulate material comprising amounts of

lead and/or molybdenum, (i) microencapsulating the particulates in a thermoplastic resin to produce a mineral filled composition, and (j) forming a thermoplastic article from the composition. The articles are preferably in the form of elongated blocks suitable as car stops, railroad ties or if utilized in combination as a seawall or sound barrier.

5           Flotation reagents are referred to as promoters or collectors, and effectively provide the mineral particulates with a coating that either repels or attracts water (water-repellent air-avid coating) and attaches (or adheres) to an air bubble. Suitable reagents for froth floatation of metallic sulfides are xanthates and dithiophosphates. Xanthates may be represented by the formula  $ROC(SNa)(=S)$  where R is an alkyl group preferably having from two to six carbon  
10 atoms. Dithiophosphates may be represented by the formula  $(RO)(RO)P(=S)(SNa)$  where R is an alkyl group preferably having from two to six carbon atoms. The reagent functions by being absorbed onto a metallic sulfide surface and bonding with sulfur atoms. The alkyl moiety effectively repels water thereby providing the particulates with a coating that is water repellent. Typical use ratios of reagents to ore are from 0.01 to 0.2 pounds (4.54g to 91 g) of reagent per ton  
15 (908kg) of ore processed.

The flotation process may utilize a plurality of flotation stages to provide increasing level of concentrate purities at each sequential stage, with the tailings from each intermediate stage being (optionally) recirculated back to an earlier stage in the process for additional froth flotation treatment. Tailing obtained from froth flotation of Galena rock typically yields  
20 undesirably high lead levels.

Froth floatation processes may also be utilized to process calcium fluoride to obtain fluorspar or fluorite, and the tailings therefrom can find utility in some of the articles of the present invention.

The microencapsulating preferably involves melt processing the thermoplastic  
25 composition, preferably a recycled polyolefin resin, to produce the filled thermoplastic article. The thermoplastic composition comprises (a) a thermoplastic resin, and (b) a filler comprising lead (and/or molybdenum), and preferably (c) a functionalized compound. Articles formed from the compositions are useful in the manufacture of block structures, such as railroad ties, car stops, pilings, poles and timbers suitable for retaining walls and marine bulkheads. Other articles, such  
30 as roofing tiles, could also be made.

Conventional tailings from the production of Galen lead have tailing compositions

comprising (a) calcium carbonate ( $\text{CaCO}_3$ ) at a level of from 50 to 70 percent by weight based on the total weight of the composition, (b) silica ( $\text{SiO}_2$ ) at a level of from 10 to 30 percent by weight based on the total weight of the composition, (c) fluorspar ( $\text{CaF}_2$ ) at a level of from 1 to 5 percent by weight based on the total weight of the composition, (d) barium sulfate ( $\text{BaSO}_4$ ) at a level of from 2 to 8 percent by weight based on the total weight of the composition, (e) zinc sulfide ( $\text{ZnS}$ ) present at a level of from 0.05 to 0.3 percent by weight based on the total weight of the composition, and (f) lead sulfide ( $\text{PbS}$ ) at a level of from 0.05 to 0.3 percent by weight based on the total weight of the composition.

The froth floatation process preferably involves (a) providing mineral ore and converting (reducing the size of) the mineral ore into particulates, preferably by grinding, and preferably involves converting mineral ore rocks having weight average diameter particle sizes of greater than 0.1 inches (.254 cm) to small particulates having sizes of less than 0.05 inches (.13mm), more preferably less than 0.01 inches (.254mm), and most preferably less than 0.005 inches (.013mm), for example into a weight average diameter particulate sizes of no greater than 48 mesh (.53mm), more preferably no greater than 65 mesh (.39mm), and most preferably no greater than 80 mesh (.32mm). The smaller the particulate size, the greater the effective surface area to volume of the particulates for contacting with the reagent in the process. Various grinding and screening systems are suitable for converting mineral ore into particulates having the desired size. Grinding may be achieved by hammer mills, ring roller mills, and ball mills. Screening may be achieved by vibrating screens or other suitable screening devices.

The particulates are then contacted with a reagent in the presence of water to form a coated metallic sulfide suitable for separation by floatation. The metallic sulfide particulates are subjected to agitation and aeration in an aqueous medium to cause flotation of the metallic sulfide particulates and separation from the less valuable tailings. Tailings from this step contain amounts of water and lead, and have typically been stock piled as an undesired waste product.

In the present process the tailings (waste byproduct) are then dried (dewatered) to produce a mineral mass product having preferably having less than 1 percent by weight water, more preferably less than 0.5% water, and most preferably less than 0.1% by weight water based on the total weight of the solid byproduct. The byproduct also contains a residual amount of lead and/or molybdenum. Drying the product is preferable and reduces the risk of undesired complications in the extrusion process due to the presence of high levels of residual water and

high temperatures in the presence of ingredients in the composition.

The process further involves admixing, preferably melt mixing, (a) the tailing composition (dried waste byproduct, for example calcium carbonate/silica/lead admixture), (b) a thermoplastic resin, for example high density polyethylene, and (c) a functionalized compound  
5 to produce a filled thermoplastic composition.

The filled thermoplastic resin composition may then be processed to form a thermoplastic article. Suitable articles include block shaped articles having a weight of at least 5 pounds and having a volume of at least one cubic foot. Suitable block shaped articles include car stops, railroad ties, pilings, poles and timbers suitable for retaining walls and marine bulkheads, and  
10 barrier walls such as sea walls and sound barrier walls.

The thermoplastic composition preferably comprises (a) a polyolefin resin (as described above) present at a level of from 10 to 99 percent by weight based on the total weight of the composition, (b) a froth flotation tailing byproduct (filler comprising calcium carbonate and lead) present at a level of from 1 to 90 percent by weight based on the total weight of the composition,  
15 and (c) a functionalized compound present at a level of from 0.5 to 10 percent by weight based on the total weight of the composition.

The process of the present invention allows for the production of valuable mineral concentrations without the undesired stock piling (or solid waste disposal) of solid tailing byproducts containing lead and/or molybdenum. The present process allows the combined  
20 production of valuable mineral concentrations and useful thermoplastic articles.

The mineral tailing waste byproduct comprising calcium carbonate, silica and lead when used in the present composition with a recycled high density polyethylene provides a filled thermoplastic composition primarily made up of recycled waste products exhibiting suitable physical characteristics for articles such as car stops, railroad ties, pilings, poles and timbers  
25 suitable for retaining walls and marine bulkheads, barrier walls and other useful block shaped profiles, even at high loading levels of the waste byproduct in the composition. Thus in a mineral mining setting, the waste product of the froth flotation process can be utilized to produce useful block shaped profiles or articles. In other words, the present invention provides a solution to waste products produced by the froth flotation mineral extraction process.

30 As shown in Figure 3, the process of the present invention involves a process for manufacturing mineral concentrations which utilizes the tailing byproduct thereof, and more

specifically involves (a) froth flotation system (210) wherein metallic mineral ore (112) (lead ore stream (212)) is fed to a size reducing device (14) (grinder (14)) for reducing the ore into small size particulates which are then fed as intermediate stream (216) to a first screening unit (18) for separating intermediate lead stream (216) into (i) a large particle return stream (220) which is returned to the grinder (14) for further size reduction and (ii) a stream (222) of small particulates. The small particulates are then fed to a froth flotation vessel (224), and a water feed stream (226) and a reagent feed stream (228) are also fed to the vessel to form an active mass (230). In the active mass (230) the ore and the reagent interact to form a water repellent and air-avid coating on metallic sulfide particles. The aqueous mass is then agitated and aerated resulting in the coated particles attaching to air bubbles and concentration in the resulting froth. The remaining waste particles sink and accumulate in the underflow. The froth concentrate is removed from the vessel (224) as froth concentrate stream (232) and is retained in a holding container (34) and is used as a concentrated source of metal (for example lead). The underflow is removed from the vessel (224) as underflow stream (236), and is separated into a waste water stream and a tailing stream. The tailing stream contains undesirably high levels of water (typically in excess of 1 percent by weight based on the total weight of the tailing stream). The tailing stream (236) is then fed to a dewatering unit (38) wherein water is removed as a water waste stream (240) and a dewatered tailing stream (242) which exits the unit (38). The dewatering unit (38) may be in the form of a press or a heat drying unit or an air drying system, and preferably the dewatered tailing (242) has a water content of less than 1 percent by weight based on the total weight of the dewatered tailing. If the drying unit (38) undesirably causes particulate aggregation, then the system preferably further involves a grinder (44) for reducing the particle size of the aggregated tailing to produce (i) a reduced particle size intermediate tailing stream (246) which is fed to a screening device (48) for separating the stream (246) into a small particulate (byproduct stream) (250) which is fed to an extruder (or other melt mixing device) (52) and (ii) a return tailing stream (254) of relatively larger size particles for return to the grinder (44) for size reduction.

The tailing byproduct typically comprises (a) a calcium carbonate, (b) silica and (c) lead sulfide. The calcium carbonate is typically present in the byproduct composition at a level of from 20 percent by weight to 90 percent by weight based on the total weight of the byproduct composition, more typically from 40 to 80 percent by weight thereof, and even more typically from 50 to 70 percent by weight thereof. The silica is present in the byproduct composition at

a level of from 1 to 50 percent by weight based on the total weight of the byproduct composition, more typically from 5 to 40 percent by weight thereof, and even more typically from 10 to 30 percent by weight thereof.

As shown in Figure 7, the article (66) may be in the shape of a railroad tie (168). As  
5 shown in Figure 23, the article (66) may be in the shape of a barrier wall (sea wall (470)) (or sound barrier wall (470)). As shown in Figure 20, the article (66) may be in the shape of a railroad crosstie or car stop (472). Figure 21 is a perspective view of an article of the present invention in the shape of a round post 473. Figure 22 is a perspective view of an article of the present invention in the shape of a square post 474.

10 Another embodiment of the present invention involves composite thermoplastic railroad ties and processes for making railroad ties. The thermoplastic railroad ties comprise (a) a thermoplastic resin (b) a filler comprising phosphogypsum/fluorogypsum, and (c) a functionalized compound (for lubrication, such as oil or processing wax). The ties exhibit certain desired and enhanced properties over conventional wooden ties and over sand filled ties. The  
15 filler may be obtained by the fertilizer manufacturing process described above. Other fillers such as fluorogypsum, calcium fluoride, calcium difluoride, fluorspar, barites, barytes, and barium sulphate ( $BaSO_4$ ) may be used as a portion of the inorganic material.

The process further involves admixing, preferably melt mixing, (a) the byproduct comprising, for example, calcium sulphate, (b) a thermoplastic resin and (c) a functionalized  
20 compound to produce a filled thermoplastic composition. Optionally, fiber reinforcing agents may admixed into the composition. These agents may be virgin gypsum fibers or whiskers. The filled thermoplastic resin composition may then be processed to form a thermoplastic filled composite railroad ties. The ties may be then used to support rail in the making of railroad tracks.

25 The thermoplastic composition preferably comprises (a) a polyolefin resin present at a level of from 10 to 99 percent by weight based on the total weight of the composition, (b) a fertilizer wet process byproduct (filler comprising calcium sulphate and phosphate, and optionally other fillers may be utilized comprising calcium fluoride, fluorspar, calcium difluoride or fluorogypsum or tailings from the froth flotation process) present at a level of from 1 to 90  
30 percent by weight based on the total weight of the composition, and (c) a functionalized compound present at a level of from 0.5 to 10 percent by weight based on the total weight of the

composition. If titanate is used, it is preferably used at levels of from 100 ppm to 2000 ppm based on the total weight of the composition. The fertilizer waste byproduct comprising calcium sulphate and phosphate when used in the present composition provides a filled thermoplastic composition exhibiting suitable physical characteristics for railroad ties, even at high loading  
5 levels of the waste byproduct in the composition. When used for railroad ties, the composition may further contain reinforcing fiber, such as graphite and/or calcium sulphate whiskers at levels of perhaps from 1 to 20 percent by weight based on the total weight of the composition, determined by the desired physical properties of the product.

Suitable railroad ties may for example have lengths of from 6 feet to 20 feet (1.83m to  
10 6.10m) and widths of from 8 inches to 12 inches (20.3cm to 30.5cm) and heights of from 5 inches to 10 inches (12.7cm to 25.4cm). The railroad ties (168) (see Figure 7) preferably have two spaced apart rectangular vertical sides (106, 108), a horizontal rectangular top (110) and a horizontal rectangular bottom (112) spaced apart from the top (110), and a pair of vertical rectangular ends (114, 116) extending between the sides (106, 108) and the top (110) and bottom  
15 (112). The weight of the railroad tie may range from 100 pounds to 500 pounds (45.4kg to 227kg) depending on the level of filler in the compound.

As shown in Figure 7, the railroad tie (168) may generally be similar in exterior shape to the shape of a conventional railroad tie. The tie (168) may have various additional features not present in conventional ties, specifically the tie may have holes (100) (two sets of four spaced for  
20 receiving lag (carriage) bolts (timber screws) (78) )extending vertically therethrough. Each set of four holes has two pair spaced apart for being positioned on opposite sides of the rail (76) and adjacent thereto. Figure 8 is a perspective view of a railway (72) which comprises the present ties (168) and rails (76) and rail bolts (78) or other suitable fastening devices for holding the rails (76) in position relative to the ties (168) and relative to the road bed (104) on which the ties (168) are supported. As shown in Figures 8 and 10 the ties are supported on a railbed (104) and are  
25 partially embedded therein for reducing movement of the ties (168). Figure 9 is a vertical cross-sectional view of the railroad tie and shows the optional holes (100) for receiving the bolts (78) for holding the rail in position relative to the ties (168). Figure 10 is a vertical cross-sectional view of the railway (72). Prior railways are disclosed in Tamas et al US Patent 5,163,614 issued  
30 November 17, 1992 and Braitsch, et al US Patent 4,500,037 issued February 19,1985, both of which are incorporated herein by reference. The compositions of the present invention exhibit



desired properties for railroad ties, including tests such as bolt pull tests and compression tests and three-point bend tests (properties). It appears that the crystalline nature of the crystalline filler of the present invention provides enhanced properties in the railroad tie formulations compared to the properties that would be attained by using a filler such as sand. The compositions of the present invention appear to provide a compressional strength in excess of the compression strength of oak, for example a factor of about 10 times the compressional strength of oak as measured by ASTM test, and the retentional strength of the composite is desirable as is required for holding leg-bolts to rails of railroad tracks. The use of the waste byproduct also provides the advantage of finding a desirable use for the byproduct. The present material is also relatively resistant to attack from organisms and does not require the use of preservatives such as creosote.

Figures 11 and 12 show a first alternative embodiment of a railroad cross tie 468 having an optional longitudinally extending cooling hole 469 through the center thereof, extending from one end to the other. Figures 13 and 14 show a second alternative embodiment of a railroad cross tie, tie 478. These embodiments are advantageous because they spread the weight of the track out over a greater area (exemplary dimensions are 10" (25.4cm) wide for the base, 8" (20.3cm) for the top width, and 6" (15.2cm) for the height. The length of the cross ties can be traditional lengths. The tie 468 is preferred because the lower corners 490 of tie 478 have a tendency to chip because they are so thin - in tie 468 the lower corners are truncated.

Conventional railroad crossings have historically been the scene of numerous undesired collisions between trains and automobiles. Consequently, there is a desire to enhance train engineer and automobile driver awareness of the existence of each crossing location. The present invention further involves the use of a yellow colorant (dye or pigment, conventional yellow dyes and pigments for thermoplastics may be used) in the thermoplastic compositions for making of the tie and for use in the process during admixing to provide a yellow colored tie for use at the intersection and before (within 0.5 miles) of the intersection where a road (highway) crosses a railroad track. The bright yellow ties at the intersection provide motorists with additional visual stimuli for the purpose of enhancing awareness of the existence of the crossing, and the yellow ties located at positions before (within 0.5 miles (.81km) of the intersection) provide the engineer with addition warning of the existence of the intersection.

Suitable compositions for use in the manufacture on railroad ties were made and included

admixing 10.5 pounds (4.77kg) of phosphogypsum, 4.5 pounds (2.04kg) of high density polyethylene (RHDPE), 52.08 grams of epoxidized soya oil and 18.75 grams of titanate.

From exposure evaluations (LSU Nuclear Science Department on behalf of the inventors) resulting from the manufacturing and use of phosphogypsum/plastic composite railroad ties, the  
5 MREM/YR for radon was less than 0.1 for railroad construction group, homes 50 feet (15m) from railroad, near stored ties 1 meter away and near stored ties 10 meters away, and nil for the groups of extruder operator, worker near starting material hopper, and railroad passenger because the resin effectively encapsulates the waste byproduct reducing the potential exposure to radon gases from the byproduct.

10 The present invention also comprises composite thermoplastic pilings (protective articles) and processes for making them. The thermoplastic pilings comprise (a) a core element comprising (i) a thermoplastic resin and (ii) a filler, and (b) an outer layer (sheath) comprising (i) a transparent (or translucent or clear) thermoplastic resin and a light responsive material, preferably a photoluminescent material. The composite (and protective article) is dense and  
15 preferably has a density of greater than 1.0 g/cm<sup>3</sup>, and most preferably 1.4-1.7 g/cm<sup>3</sup>, though the density can be greater than 2.0 g/cm<sup>3</sup>.

The filler is preferably phosphogypsum (or fluorogypsum) and may be obtained as a byproduct from the fertilizer manufacturing process mentioned above. A thermoplastic filled composition suitable as the core is made by admixing the calcium sulphate byproduct with a  
20 thermoplastic resin and a functionalized compound. The protective article (and/or core element) may then be manufactured by melt processing (for example injection molding or compression molding or coextrusion) the thermoplastic composition.

The process further involves admixing, by melt mixing, (a) the filler (waste byproduct, such as phosphogypsum or fluorogypsum), (b) a thermoplastic resin such as polyethylene and  
25 preferably (c) a functionalized compound to produce a filled thermoplastic composition suitable as the core element for the piling.

Optionally, graphite and/or calcium sulphate whiskers as reinforcing agents may admixed into the composition. The filled thermoplastic resin composition may then be processed to form thermoplastic filled composite marine pilings and marine safety (Glow-Pile™) fender-pile  
30 system. The pilings may be then used to protect structures and may be used alone or in combination with conventional wood pilings.

Suitable pilings may for example have lengths of from 20 feet to 100 feet (6.10m to 30.5m), more preferably from 30 feet to 50 feet (9.14m to 15.2m), and most preferably about 40 feet (12.2m), and diameters (widths) of from 8 inches to 20 inches (20.3cm to 51cm)), more preferably from 10 inches to 14 inches (25.4cm to 35.6cm) and most preferably about 12 inches (30.5cm). The pilings have a density preferably greater than 1.0 g/cc due to the amount and density of the filler material, and preferably the pilings have a density in excess of 2.0 g/cc, and sometimes as high as 2.5 g/cc (and typically 1.44 g/cc), depending upon the fillers used and the loadings thereof. The weight of the piling preferably ranges from 750 pounds to 4,000 pounds (341kg to 1816kg) depending on the level of filler in the composition and size of the piling, and more preferably ranges from 750 pounds to 2,000 pounds (341kg to 908kg) . The pilings may be cylindrical (preferably) or slightly tapered having a wider diameter bottom than top. Groups of pilings may be banded or bolted together to form a unit. The pilings preferably have the outer layer (sheath, collar) on only the top end (one end) of the piling, for example having only the top half or the top third or top quarter having the outer layer and the bottom half or bottom two thirds or bottom three quarters not having an outer photoluminescent layer. The top portion of the piling is usually the only portion that is primarily out of the water level during use. For example, the bottom portion of the piling may be positioned below the mud level during use, with the top quarter of the piling above the water level (upper surface of the water) and the remaining portion of the piling being between the mud level and the water level. Consequently, the light responsive layer is only needed where it is visible to the ship personnel.

As shown in Figure 1, the process for making the piling of the present invention preferably involves a first step involving a process for making the filler. The filler may be obtained by the process for manufacturing fertilizer described above wherein the byproduct is utilized as the filler for the piling core composite. The process further involves a melt processing unit (64) (extruder) such as a coextruder providing an outer coating layer (sheath, sleeve, collar) about the inner core. The sheath may alternatively be made by injection molding, and the sheath may then be placed on the core element by slipping it over the top of the core element.

The piling (300) may generally be either square, oval or cylindrical. The piling (300) has an outer layer (306) which may also be referred to as a sheath (or coating) (306) which covers a top portion (308) of the piling (300) and is preferably affixed (adhered) to a core element (310) of the piling (300).

Figure 16 is a perspective view of an alternative embodiment of the composite piling of the present invention, piling 400. Piling 400 includes a sheath 406 which may originally be flat and is wrapped around the core element 310 and is riveted thereto with rivets 407.

Figure 17 is a cutaway perspective view of a bridge structure (312) which comprises the present pilings (300). The pilings (300) are in protective position around support columns (314) of the bridge (312) to protect the columns from ship or barge contact. The pilings (300) are preferably banded (or bolted by bolts, forming clusters) together by a band (316) to secure the pilings about the support column (314). The support column supports the weight of the bridge travel surface (bed) (320). The bridge (312) is preferably supported at its ends by abutments (322) and is also supported by upper structural members (324). The support column (314) extends downwardly from bridge travel road bed (320) down to the water surface (326), through the body of water (328), down through the mud surface (river bed) (330), and deep into the mud (332) to provide a stable foundation for the bridge (312). The pilings (300) extend from above the water surface (326) through the body of water (328) and into the mud (332) and may provide the structure with support as well as with protection from ships (barges). The pilings (300) have an outer layer (306) which covers (surrounds) the upper portion (308) of the piling (300). The sheath 306 may optionally be placed on the core (310) by slipping the sheath over the top end of the piling. The sheath may be slightly tapered to match the taper of the upper portion of the piling as best shown in Figure 15.

The sheath (306) comprises a composition of a translucent (but preferable transparent or clear) thermoplastic resin and a light absorbing/emitting (light-responsive) material. The thermoplastic resin may suitably be a transparent polyolefin or may be a polycarbonate resin or a polyvinylchloride resin. The light absorbing/emitting (light-responsive) material is preferably a photoluminescent material, such as the photoluminescent materials disclosed in Lindmayer U.S. Patent 4,812,660 issued March 14, 1989 and Lucky U.S. Patent 3,668,142 issued June 6, 1972, all of which are incorporated herein by reference. As shown in Figure 19, the inner surface of the sheath may have a thin photoluminescent inner coating (340). Coextrusion may be utilized to form the core and the outer layer. The outer layer is formed (extruded) only about a portion (top portion, first portion) of the core so that when the piling is in use, the portion that is above the water level will be coated while the portion below the water level will be un-coated (not coated) to minimize the expense of the coating material.

Conventional pilings have historically been the scene of numerous undesired collisions between ships (barges) and waterway structures (bridges). Consequently, there is a desire to enhance ship operator (captain) awareness of the existence of each such structure and piling. The marine safety fender pile preferably with its photoluminescent coating or sheath provides the ship operator with a visible warning after darkness falls (in the evening hours). Sunlight (solar energy) is stored by the photoluminescent material during daylight hours and then automatically discharges during darkness (some photoluminescent material can discharge light for 10 hours). Also, preferably the photoluminescent material is one which charges with ultraviolet light (such as sunlight), fluorescent light, or incandescent light so that the piling is charged during the day and at night as well when it is irradiated by the light from ships or from other nearby light sources. Such a photoluminescent material is zinc sulfide crystals.

Another suitable filler is fluorogypsum. Fluorogypsum may also be obtained by various processes such as a byproduct produced from the reaction of fluorspar with sulfuric acid in the production of hydrofluoric acid, see Azar Fluorogypsum Waste Solidification Material U.S. Patent 4,935,211 issued June 19, 1990 which is incorporated herein by reference. Fluorogypsum contains mostly calcium sulfate anhydrite and calcium sulfate having water chemically combined therewith, plus small quantities of fluorine containing compounds and possibly small concentrations of sulfuric acid. Disposal ponds for fluorogypsum occupy large areas of useful land and commonly require monitoring and maintenance by the owner. The disposal ponds are constantly increasing in size and quantity of fluorogypsum contained as the related production processes continue. Consequently, there is a problem with the continued accumulation of these byproducts and a need and desire to find a useful product which uses these materials. Processes producing fluorogypsum materials are known, see for example Sardisco et al Recovery of Fluorides From Gypsum U.S. Patent 4,060,586 issued November 29, 1977, Johnson U.S. Patent 4,175,944 issued November 27, 1979, Gaynor et al U.S. Patent 4,402,922 issued September 6, 1983 and Czysch et al Production of Low-Fluorine Gypsum as a By-Product in a Phosphoric Acid Process U.S. Patent 4,026,990 issued May 31, 1977, all of which are incorporated herein by reference.

The sheath covers at least a portion of the core element. The sheath comprises (i) a thermoplastic resin and (ii) a photoluminescent material. The thermoplastic resin is preferably present in the sheath at a level of from 60 to 99 percent by weight based on the total weight of

the sheath, more preferably from 70 to 98 percent by weight thereof, and most preferably from 75 to 95 percent by weight thereof. A suitable thermoplastic resin is polyethylene, polypropylene and other resins that are either translucent or transparent, for example various polyolefins are suitable. The photoluminescent material is preferably present in the sheath at a level of from 1  
5 to 30 percent by weight based on the total weight of the sheath, more preferably from 2 to 20 percent by weight thereof, and most preferably from 3 to 10 percent by weight thereof. The photoluminescent material is preferably a phosphorescent metal sulphide such as zinc, calcium, cadmium or strontium sulphide as disclosed in Gravisse et al US 4,211,813 issued July 8, 1980 which is incorporated herein by reference. The most preferred photoluminescent material is  
10 zinc sulfide, which can be, for example, in the crystal form present in Johnsonite Permalight photoluminescent Safe-T-First products.

In addition to Formulations #1 and #2 for the core material, suitable compositions for use in the manufacture of pilings were made and included admixing 10.5 pounds (4.77kg) of fluorogypsum, 4.5 pounds (2.04kg) of high density polyethylene (RHDPE), 52.08 grams of  
15 epoxidized soya oil and 18.75 grams of titanate.

The present inventors have conducted research using the following different formulations, wherein ESBO is epoxidized soybean oil. When ESBO is used, it can be in the range of 1.0 to 2.0% by weight and when titanate is used, it is preferably in the range of 0.025% to 0.10% by weight.

20 The preferred formulation depends upon the article being made and the physical properties sought for that article. For a crosstie, it might be Formula #5.

Formulas using only RHDPE (recycled high density polyethylene) with no oil or additive:

Formula #1

50% Phosphogypsum and/or fluorogypsum

25 50% RHDPE

Formula #2

60% Phosphogypsum and/or fluorogypsum

40% RHDPE

Formula #3

30 70% Phosphogypsum and/or fluorogypsum

30% RHDPE

Formulas using high and low density polyethylene, with no oil or additive:

Formula #4

50% Phosphogypsum and/or fluorogypsum

40% RHDPE

5 10% RLDPE

Formula #5

60% Phosphogypsum and/or fluorogypsum

30% RHDPE

10% RLDPE

10 Formula #6

70% Phosphogypsum and/or fluorogypsum

20% RHDPE

10% LDPE

Formulas using high density polyethylene and oil and additive:

15 Formula #7

48% Phosphogypsum and/or fluorogypsum

50% RHDPE

1.5% ESBO

0.05% Titanate

20 Formula #8

58% Phosphogypsum and/or fluorogypsum

40% RHDPE

1.5% ESBO

0.05% Titanate

25 Formula #9

68% Phosphogypsum and/or fluorogypsum

30% RHDPE

1.5% ESBO

0.5% Titanate

30 Formulas using high and low density polyethylene and oil and additive:

Formula #10

48% Phosphogypsum and/or fluorogypsum  
40% RHDPE  
10% RLDPE  
1.5% ESBO  
0.05% Titanate

5

Formula #11

58% Phosphogypsum and/or fluorogypsum  
30% RHDPE  
10% RLDPE  
1.5% ESBO  
0.05% Titanate

10

Formula #12

68% Phosphogypsum and/or fluorogypsum  
20% RHDPE  
10% RLDPE  
1.5% ESBO  
0.05% Titanate

15

Formulas using high and low density polyethylene, polypropylene, and oil and additive:

Formula #13

48% Phosphogypsum and/or fluorogypsum  
40% RHDPE  
5% RLDPE  
5% Polypropylene  
1.5% ESBO  
0.05% Titanate

20

25

Formula #14

58% Phosphogypsum and/or fluorogypsum  
30% RHDPE  
5% RLDPE  
5% Polypropylene  
1.5% ESBO

30



0.05% Titanate

Formula #15

68% Phosphogypsum and/or fluorogypsum

20% RHDPE

5 5% RLDPE

5% Polypropylene

1.5% ESBO

0.05% Titanate

Formula #16

10 80% Phosphogypsum and/or fluorogypsum

20% RHDPE

Formula #17

78% Phosphogypsum and/or fluorogypsum

20% RHDPE

15 1.5% ESBO

0.05% Titanate

Formula #18

78% Phosphogypsum and/or fluorogypsum

10% RHDPE

20 5% RLDPE

5% Polypropylene

1.5% ESBO

0.05% Titanate

Formula #19

25 78% Phosphogypsum and/or fluorogypsum

20% RHDPE

10% RLDPE

1.5% ESBO

0.05% Titanate.

30 In the formulas above, although recycled polyolefins are mentioned, virgin polyolefins could be used instead.

The present inventors have also used color pigments and flame retardants. When in production of a finished product the present inventors expect to use UV inhibitors, antioxidants, colors and possibly processing waxes.

5 Calcium sulfate whiskers are commercially available from U.S. Gypsum Corporation in both a hydrated and anhydrous form. The inventors do not know yet which form, hydrated or anhydrous, will be preferred as it depends on the optimum operating temperatures (OOT) of the extruders. If the OOT of the extruders turns out to be high enough to expel the "water of hydration" or the "bound water" it will create steam within the extruder. If the steam cannot be vented fast enough or the steam causes "off-gassing" of volatiles (such as volatile organic  
10 compounds), then it (steam) could become an "environmental problem". So, in that event, it might be advantageous to use the anhydrous form of calcium sulfate whiskers as this would obviate the steam problem. A preferred calcium sulfate filler is CAS-20™-4 brand white anhydrous calcium sulfate filler sold by U.S. Gypsum.

The tailings from the "froth flotation" mineral extraction process contains some very  
15 small traces of zinc sulfate (ZnS). Zinc sulfate is a mineral used to make some photo-luminescent crystals. While there is not enough present to cause fluorescing and it is not in the proper crystalline form, ZnS is very compatible with the composites of the present invention.

Zinc oxide is another mineral used to make photoluminescent crystals.

The "Glow-Pile" technology can use commercially available photoluminescent material.

20 For some time, the present inventors have been looking for the right reinforcing fiber or whisker, as reinforcing fibers are sometimes known, in the event that they need to extend the mechanical properties of the thermoplastic composites of the present invention.

U.S. Patent No. 5,183,594 describes a method of manufacturing zinc oxide whiskers having a novel crystalline form (tetrapod). It appears that the photo-luminescent tetrapod crystal  
25 of U.S. Patent No. 5,183,594 not only fluoresces but could also serve to reinforce the structure of the composite material itself thus serving two desirable functions at once, if it were used in the luminous pilings of the present invention. It is possible that Zinc Sulfate and/or Zinc Oxide in certain crystalline forms, for example, a tetrapod, could both illuminate and reinforce the basic thermoplastic-mineral composites of the present invention.

30 Photoluminescent material can be used throughout the pilings of the present invention so that chipping of the pilings does not result in a loss of luminescence. Alternatively,

photoluminescent material can be used simply in a sheath 406 which can be for example riveted with rivets 407 to an existing pile 310 (see Figure 16). The sheath 406 could be cut from a roll of photoluminescent material.

The composite materials of the present invention can be formed into beach armor (large structures for protecting beaches by absorbing wave energy) or marine blocks. In such a case, one would preferably use more BaSo<sub>4</sub> and PbS to make the armor or marine blocks more dense. The wave absorbing structures have a density of greater than 1.0 g/cm<sup>3</sup> due to the amount and density of the filler material, and preferably the wave absorbing structures have a density in excess of 2.0 g/cm<sup>3</sup>, preferably between 2.5 and 4.0 g/cm<sup>3</sup>.

In some instances, it may be advantageous to use a continuous mixer extruder to produce, for example, crossties of the present invention (and perhaps other products of the present invention as well). Continuous mixer extruders are commercially available from Bandbury, which sells a continuous bath mixer and Farrell, which sells a continuous mixer (which is a newer version).

In operation, the continuous mixer separates the mixing and pressurization functions. All mixing is done in the continuous mixer and the pressurization of the polymer (mix) is accomplished in a short, pumping extruder. In this way each function (mixing and extruding) is optimized for its specific role in the compounding process and mixing can be achieved at the lowest possible energy input levels.

The Farrell Continuous Mixer utilizes self-cleaning, counter-rotating, non-interlocking rotors. During operation it takes a starve feed of multiple ingredients and uses high shear to mix, disperse, and homogenize. The mixer runs in a partially filled condition and does not pressurize the polymer mix. The hot feed extruder receives the discharge from the mixer continuously and pumps the polymer mix through the die into the mold or into the vacuum former for profile production.

All measurements disclosed herein are at standard temperature and pressure, at sea level on Earth, unless indicated otherwise.

The foregoing embodiments are presented by way of example only; the scope of the present invention is to be limited only by the following claims.

## CLAIMS

1. A process for making fertilizer and thermoplastic-composite articles, the process comprising:
  - (a) providing phosphate particulates,
  - 5 (b) contacting the phosphate particulates with sulfuric acid in the presence of water to produce phosphoric acid and a calcium sulphate,
  - (c) separating at least a portion of the phosphoric acid from the calcium sulphate to produce a phosphoric acid product and a calcium sulphate byproduct,
  - (d) admixing the calcium sulphate byproduct with a thermoplastic resin and an oil,
  - 10 (e) melt processing the admixture to produce a thermoplastic-composite composition,
  - (f) forming the thermoplastic-composite composition to produce a thermoplastic-composite article.
2. The process of claim 1 wherein the process comprises dewatering the calcium sulphate byproduct prior to the admixing.
- 15 3. The process of claim 2 wherein the article is in the form of thermoplastic-composite lumber.
4. The process of claim 2 wherein the article is in the form of a sheet.
5. The process of claim 1 wherein the oil is epoxidized soybean oil.
6. The process of claim 1 wherein the thermoplastic resin is a polyolefin.
- 20 7. The process of claim 6 wherein the polyolefin is selected from the group consisting of polyethylene and polypropylene.
8. The process of claim 1 wherein the calcium sulphate byproduct composition comprises a calcium sulphate compound at a level of from 50 to 99 percent by weight based on the total weight of the byproduct composition.
- 25 9. A process for making useful products from byproducts of manufacturing phosphorous fertilizers, the process comprising:
  - (a) providing a calcium sulphate byproduct made by contacting phosphate particulates with sulfuric acid in the presence of water to produce phosphoric acid and the calcium sulphate byproduct, and
  - 30 (b) melt mixing the calcium sulphate byproduct with a polyolefin to produce a thermoplastic-composite composition.

10. The process of claim 9 further comprising forming the thermoplastic-composite composition into a shaped article.
11. The process of claim 10 wherein the article is selected from the group consisting of sheets, lumber, poles, pilings, railroad crossties, car stops, utility pole cross arms, and tiles.
12. An article made by the process of claim 1.
13. An article made by the process of claim 10.
14. An article made by the process of claim 11.
15. A thermoplastic-composite composition comprising:
- 10 (a) a thermoplastic resin, and
- (b) a phosphogypsum (calcium sulphate) composition comprising a calcium sulfate present at a level of from 50 to 99 percent by weight based on the total weight of the calcium sulfate composition.
16. The composition of claim 15 wherein the thermoplastic resin is a polyolefin.
- 15 17. The composition of claim 15 wherein the composition is made with a mixture comprising the thermoplastic resin, the phosphogypsum (calcium sulphate) composition, and an epoxidized oil.
18. The composition of claim 17 wherein the mixture comprises the thermoplastic resin in an amount of from 40 to 75 percent by weight based on the total weight of the mixture, the calcium sulphate composition in an amount of from 25 to 60 percent by weight based on the total weight of the mixture, and the epoxidized oil in an amount of from 0.5 to 2 percent by weight based on the total weight of the mixture.
- 20 19. The composition of claim 15 wherein the filler comprises an amount of a fluoro compound.
- 25 20. The process of claim 1, further comprising:  
separating water from the calcium sulfate byproduct prior to admixing the calcium sulfate byproduct with the thermoplastic resin and the oil, wherein:  
the oil is epoxidized soybean oil, and  
the thermoplastic-composite composition comprises the thermoplastic resin in an amount  
30 of from 25 to 80 % by weight based on the total weight of the composition, the calcium sulfate byproduct being present in an amount of from 20 to 75 % by weight based on the total weight

of the composition, the functionalized oil being present at a level of from 0.5 to 10% by weight based on the total weight of the composition.

21. A process for making metallic concentrates and plastic articles, the process comprising:
- (a) providing metallic ore particulates,
  - 5 (b) contacting the particulates with reagent in the presence of water to produce coated particulates having a water repellent air aoid coating to produce an interaction mass,
  - (c) agitating and aerating the interaction mass to form a (i) froth comprising floating metallic particles and (ii) an underflow comprising water and solid tailings,
  - 10 (d) separating at least a portion of the froth from the underflow,
  - (e) bulk separating the water from the tailings,
  - (f) drying the tailings to produce a tailing composition comprising less than 1 percent by weight water, the tailing composition comprising (i) calcium carbonate, (ii) silica and (iii) lead sulfide,
  - 15 (g) admixing the tailing composition with a thermoplastic resin,
  - (h) melt processing the admixture to produce a thermoplastic article,
22. The process of claim 21 wherein the article is in the form of plastic block.
23. The process of claim 21 wherein the article is in the form of a crosstie or car stop.
24. The process of claim 21 wherein the thermoplastic resin is a polyolefin.
- 20 25. The process of claim 24 wherein the polyolefin is selected from the group consisting of polyethylene and polypropylene.
26. The process of claim 21 wherein the tailing composition comprises (i) a calcium carbonate compound at a level of from 30 to 95 percent by weight based on the total weight of the tailing composition, (ii) a silica at a level of from 1 to 50 percent by weight based on the total weight of the tailing composition, and (iii) a lead sulfide at a level of  
25 from 0.005 to 0.3 percent by weight based on the total weight of the tailing composition.
27. A process for making a thermoplastic composition, comprising:
- (a) contacting ore particulates comprising metallic sulfide particulates with a flotation reagent in the presence of water to produce an interaction mass comprising coated metallic sulfide particulates;  
30
  - (b) aerating the interaction mass to cause flotation of the coated metallic sulfide

particulates thereby producing a froth;

(c) separating the froth from an aqueous underflow comprising tailings, the tailings comprising lead; and

(d) microencapsulating the tailings by melt mixing the tailings with a polyolefin to

5 form a thermoplastic composition.

28. The process of claim 27 further comprising forming the thermoplastic composition into an article.

29. The process of claim 27 wherein the article is a car stop.

30. The process of claim 27, wherein the article is an ocean wave energy absorber.

10 31. An article made by the process of claim 21.

32. An article made by the process of claim 28.

33. A thermoplastic composition comprising:

(a) a thermoplastic polyolefin resin, and

15 (b) a tailing composition comprising (i) a calcium carbonate present at a level of from 30 to 95 percent by weight based on the total weight of the tailing composition, (ii) a silica present at a level of from 1 to 50 percent by weight based on the total weight of the tailing composition, and (iii) a lead sulfide present at a level of from 0.05 to 0.3 percent by weight based on the total weight of the tailing composition.

20 34. The composition of claim 33 wherein the composition is made from a mixture of the thermoplastic polyolefin resin, the tailing composition, and an epoxidized oil.

35. The composition of claim 34 wherein the mixture comprises the thermoplastic resin in an amount of from 40 to 75 percent by weight based on the total weight of the mixture, the tailing composition in an amount of from 25 to 60 percent by weight based on the total weight of the mixture, and the epoxidized oil in an amount of from 0.5 to 2 percent  
25 by weight based on the total weight of the mixture.

36. A railroad tie made by melt processing a thermoplastic composition comprising:

(a) a thermoplastic resin; and

30 (b) a calcium sulphate composition comprising a calcium sulfate present at a level of from 50 to 99 percent by weight based on the total weight of the calcium sulfate composition.

37. The tie of claim 36 wherein the thermoplastic resin is a polyolefin.

38. The tie of claim 36 wherein the thermoplastic composition also includes an epoxidized oil.
39. The tie of claim 36 wherein the thermoplastic composition includes the thermoplastic resin in an amount of from 40 to 75 percent by weight based on the total weight of the thermoplastic composition, the calcium sulphate composition in an amount of from 25 to 60 percent by weight based on the total weight of the thermoplastic composition, and the oil in an amount of from 0.5 to 2 percent by weight based on the total weight of the thermoplastic composition.
40. A process, for making a railroad tie from a fertilizer byproduct and plastic, comprising:
- 10 (a) admixing a fertilizer byproduct comprising a calcium sulphate composition with a thermoplastic resin, the calcium sulphate composition comprising a calcium sulfate present at a level of from 50 to 99 percent by weight based on the total weight of the calcium sulfate composition;
- (b) melt processing the admixture to produce a thermoplastic composition; and
- 15 (c) forming the thermoplastic composition to produce a railroad tie.
41. The process of claim 40 further comprising admixing the fertilizer byproduct and the thermoplastic resin with an epoxidized soybean oil.
42. The process of claim 40 wherein the thermoplastic resin is a polyolefin.
43. The process of claim 42 wherein the polyolefin is selected from the group consisting of polyethylene and polypropylene.
- 20 44. A process for making a railroad track, the process comprising:
- (a) making thermoplastic composite railroad ties from a thermoplastic composition comprising a calcium sulphate, a polyolefin resin, and an epoxidized oil,
- (b) laying the ties on a raised rail bed; and
- 25 (c) placing rail on the ties.
45. The tie of claim 36 wherein the ties include holes for receiving carriage bolts for securing the rail to the ties.
46. The process of claim 44 wherein the composition comprises a yellow colorant.
47. The railroad tie of claim 36, wherein the tie has a top and a bottom, and the bottom is broader than the top.
- 30 48. A marine piling comprising:



(a) a core element comprising a thermoplastic composition comprising a thermoplastic resin and a filler, the core element having an outer surface; and

(b) a photoluminescent material adjacent the outer surface of the core element.

49. A marine piling comprising:

5 (a) a core element comprising a thermoplastic composition comprising a thermoplastic resin and a filler; and

(b) a sheath covering at least a portion of the element, the sheath comprising a second thermoplastic resin and a photoluminescent material.

50. The piling of claim 48 or 49 wherein the thermoplastic resin of the core element is a  
10 polyolefin.

51. The piling of claim 48 or 49 wherein the thermoplastic composition of the core element is made with a mixture which comprises an epoxidized soybean oil.

52. The piling of claim 48 or 49 wherein the filler comprises phosphogypsum (calcium sulfate) and/or fluorogypsum (calcium fluoride) present at a level of from 40 to 99  
15 percent by weight based on the total weight of the composition.

53. The piling of claim 52 wherein the thermoplastic resin of the core element is present at a level of from 40 to 75 percent by weight based on the total weight of the thermoplastic composition, the phosphogypsum (calcium sulphate) or fluorogypsum (calcium fluoride) composition being present at a level of from 25 to 60 percent by weight based on the total weight  
20 of the thermoplastic composition of the core element, and comprising an epoxidized oil present at a level of from 0.5 to 2 percent by weight based on the total weight of the thermoplastic composition of the core element.

54. The piling of claim 49 wherein the sheath comprises a photoluminescent inner coating.

55. The piling of claim 49 wherein the thermoplastic resin of the sheath is transparent.

25 56. The piling of claim 49 wherein the sheath is annular and comprises (i) an admixture of a transparent thermoplastic resin and a photo-luminescent material and (ii) an inner coating of photoluminescent material.

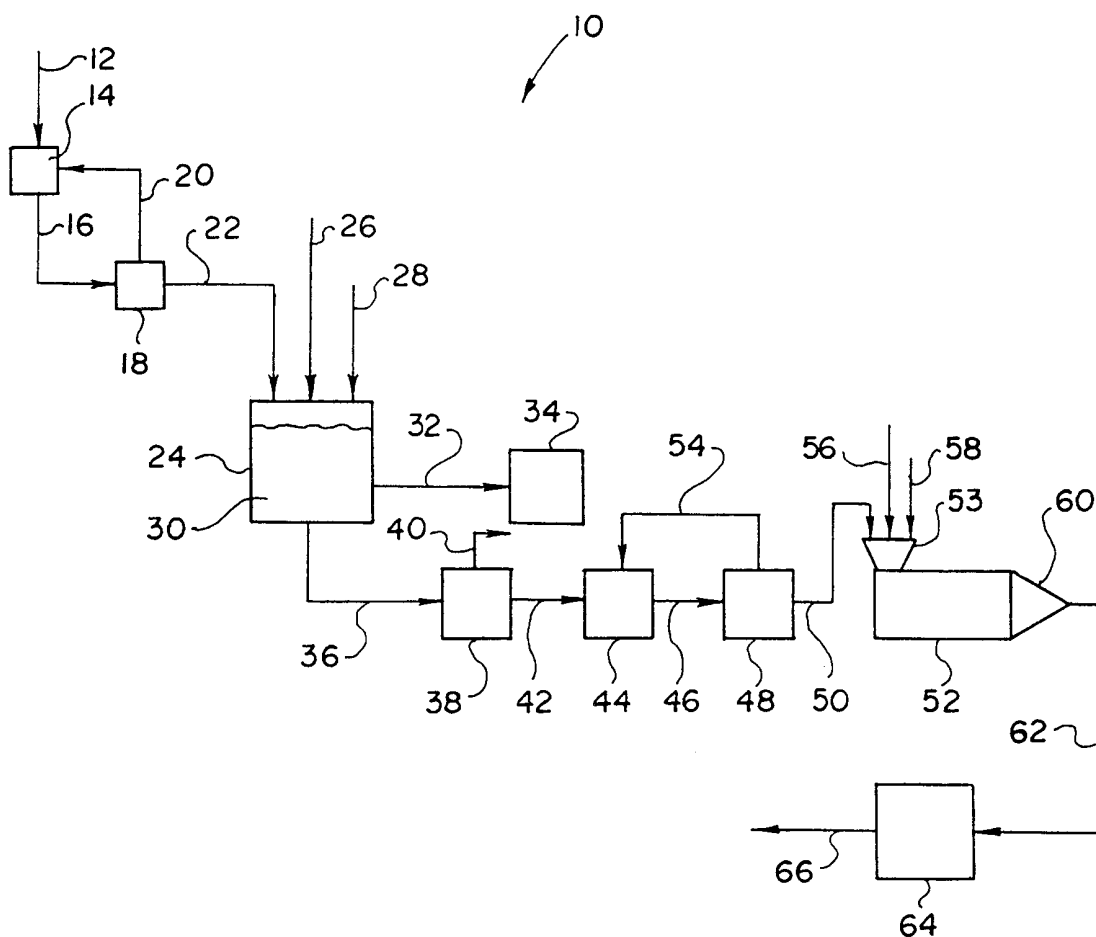
57. The piling of claim 48 or 49 wherein the photoluminescent material is zinc sulfide.

58. The piling of claim 57 wherein the zinc sulfide is in crystal form.

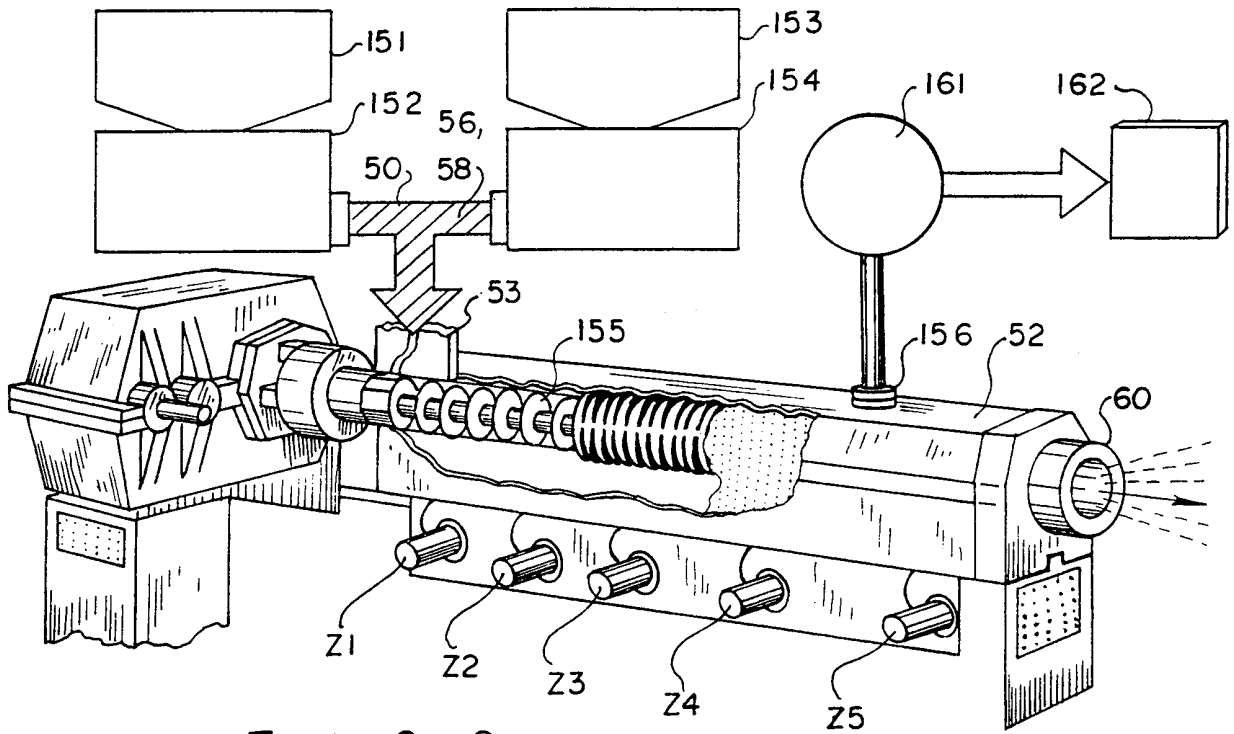
30 59. The piling of claim 57 wherein the photoluminescent material emits light bright enough and long enough that the piling is visible to a normal human eye at a far enough distance to be

useful at night.

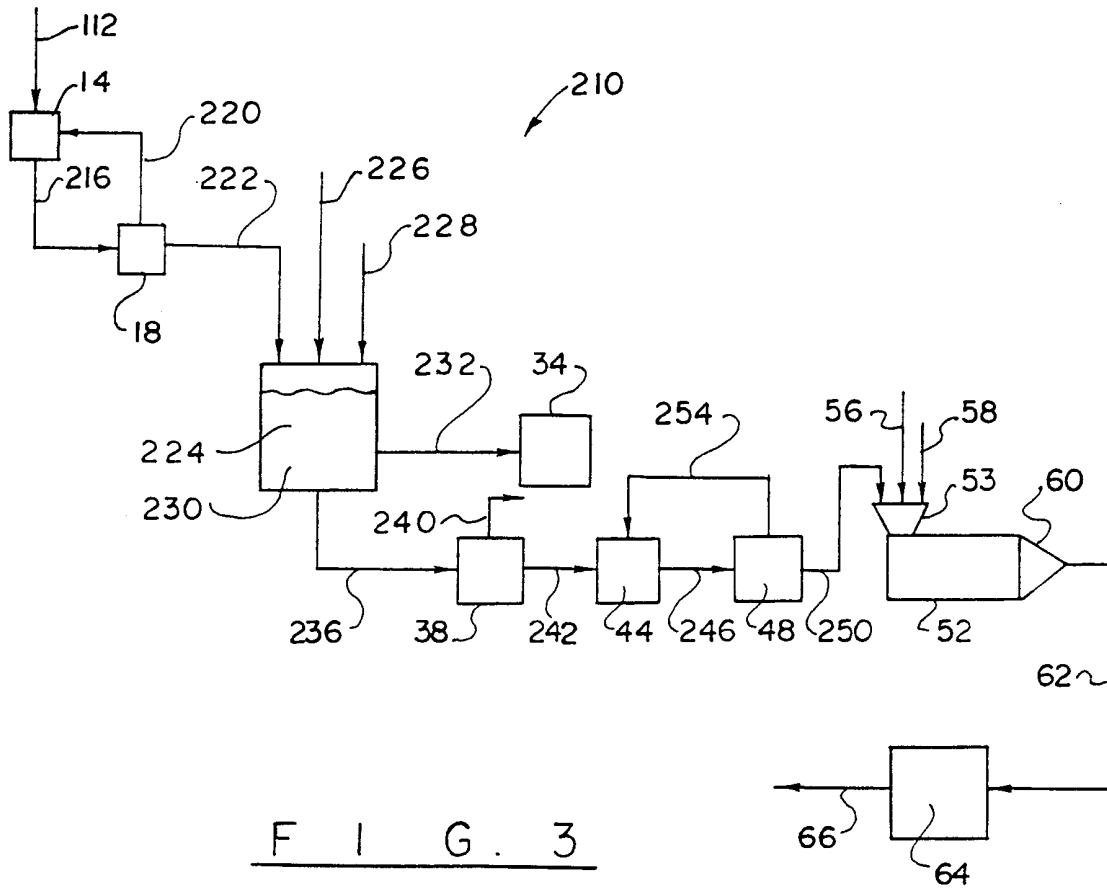
60. The piling of claim 57 wherein the photoluminescent material emits the bright enough light for at least four hours.
61. The piling of claim 57 wherein the photoluminescent material emits the bright enough  
5 light for about 4-10hours.
62. The piling of claim 48 or 49, having a density of at least  $1.0 \text{ g/cm}^3$ .
63. A bridge structure comprising a piling of any of of claims 48-62.
64. A product made by the process of any one of claims 1-11, 20-30, 40-44, and 46.



F I G . 1

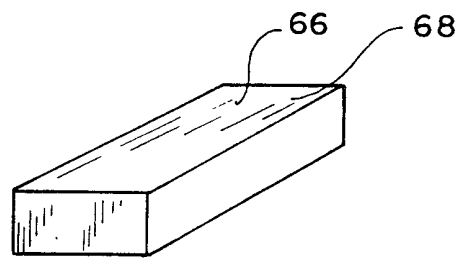


F I G. 2

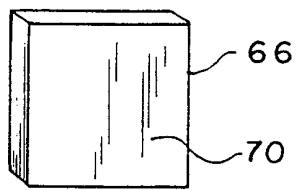


F I G. 3

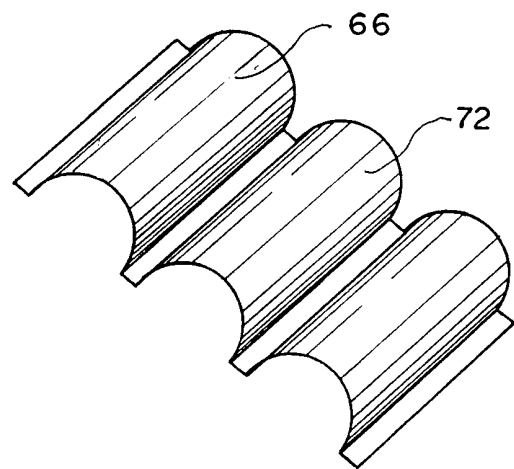
3/8



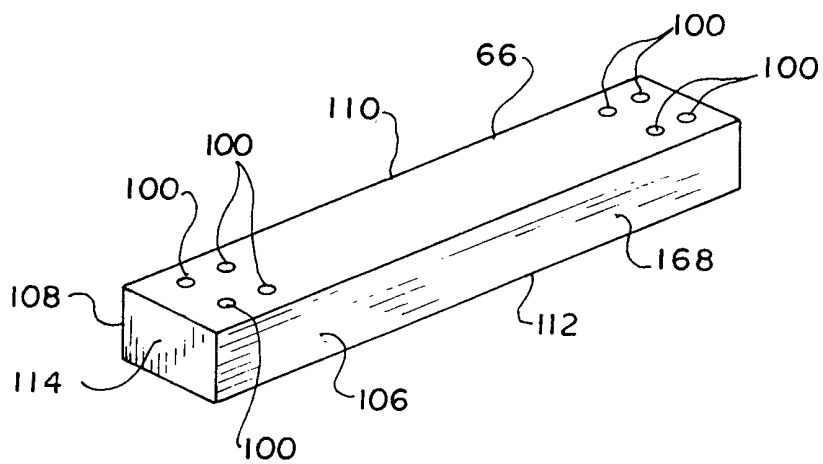
F I G . 4



F I G . 5

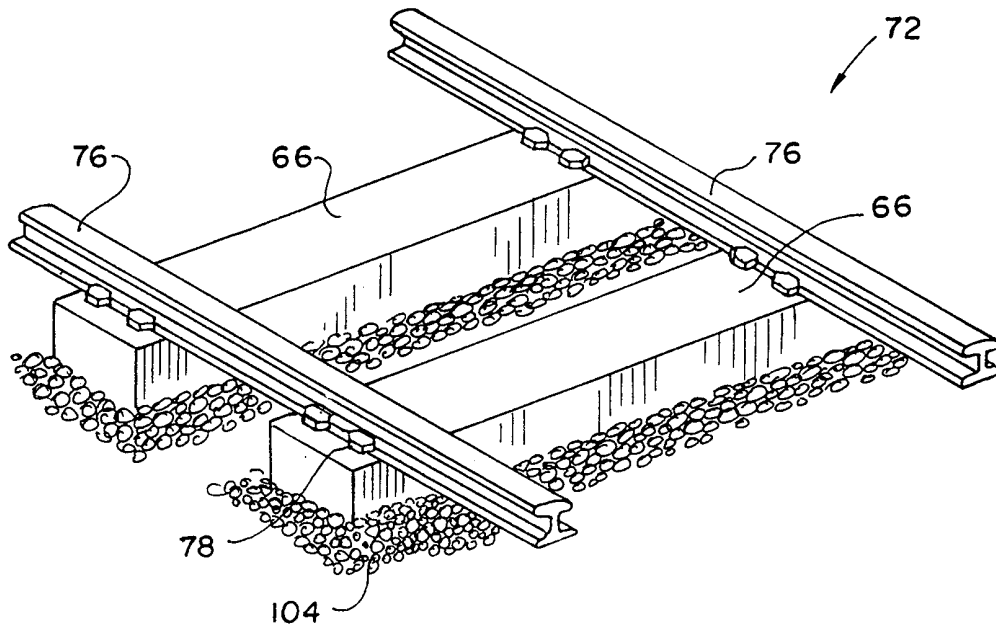


F I G . 6

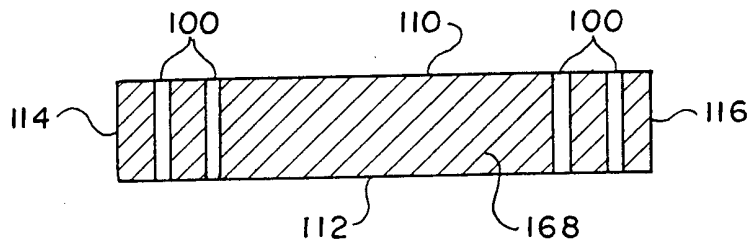


F I G . 7

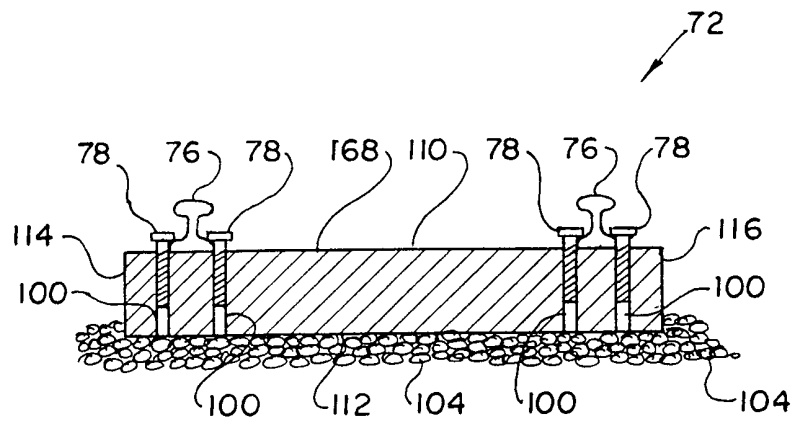
4 / 8



F I G . 8

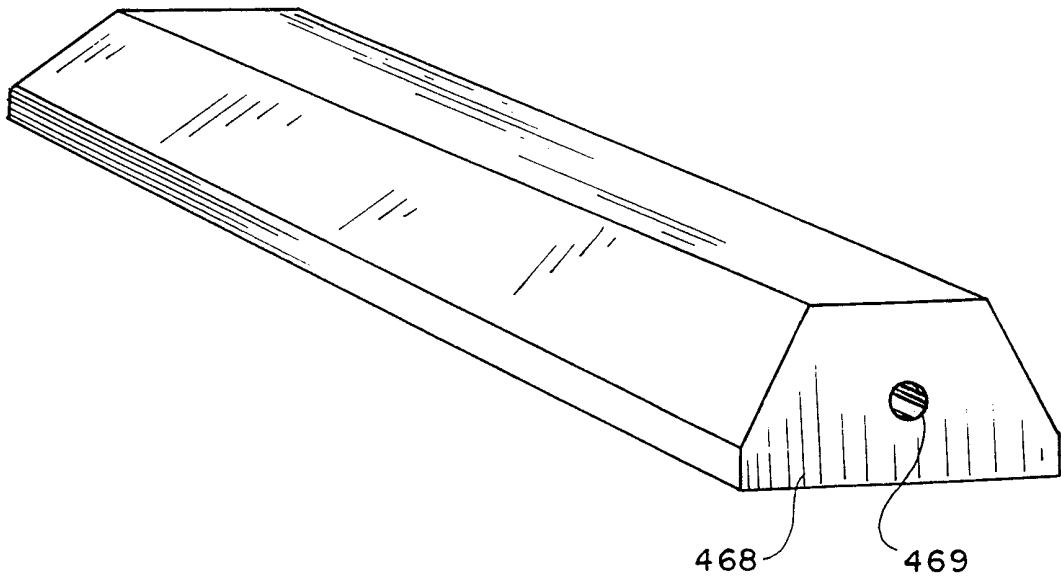


F I G . 9

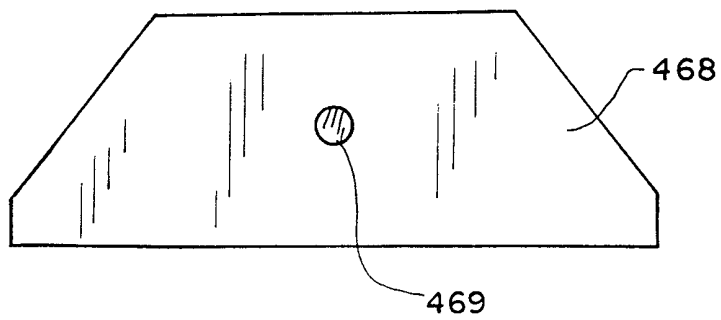


F I G . 10

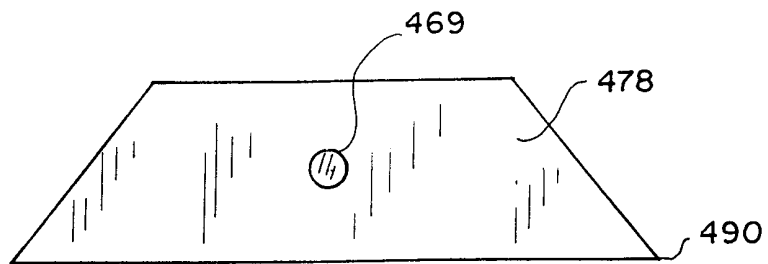
5 / 8



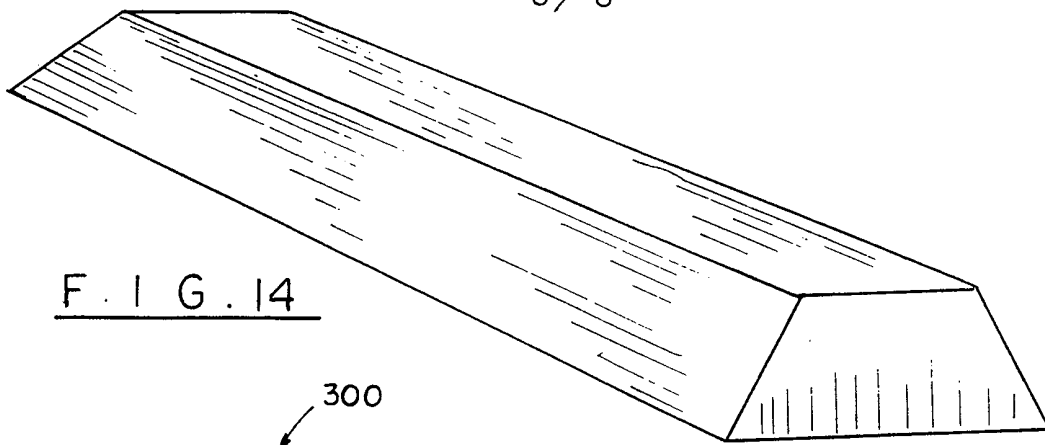
F I G . I I



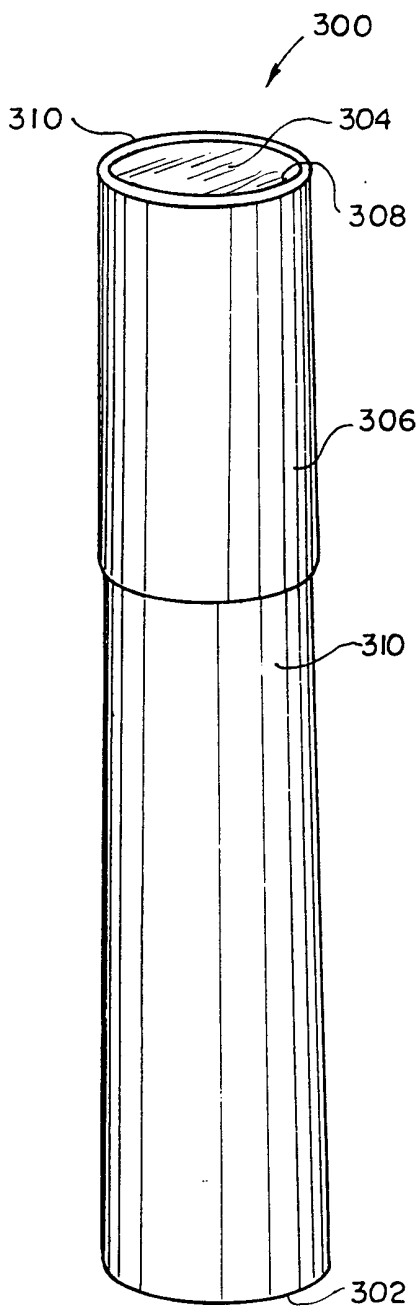
F I G . 12



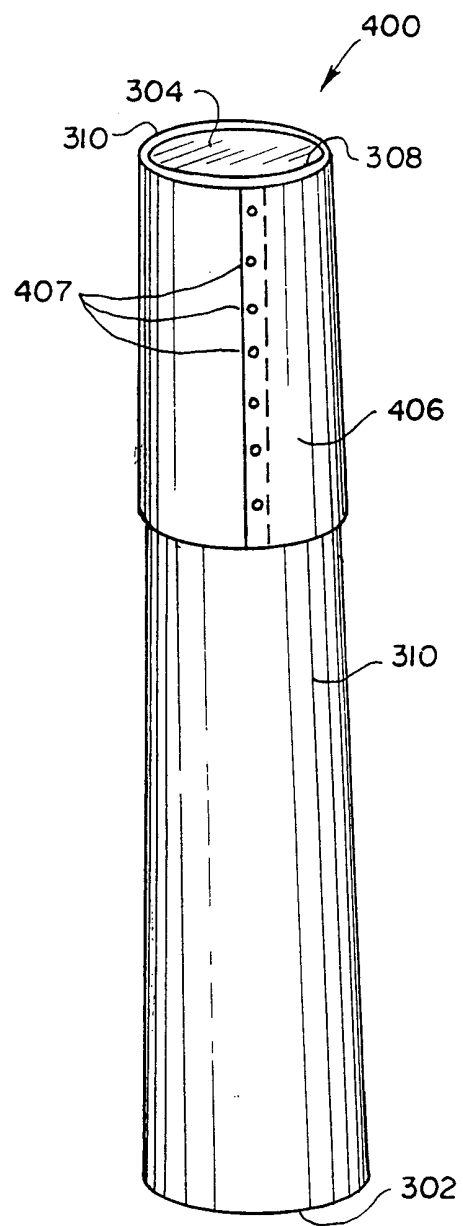
F I G . 13



F I G . 1 4

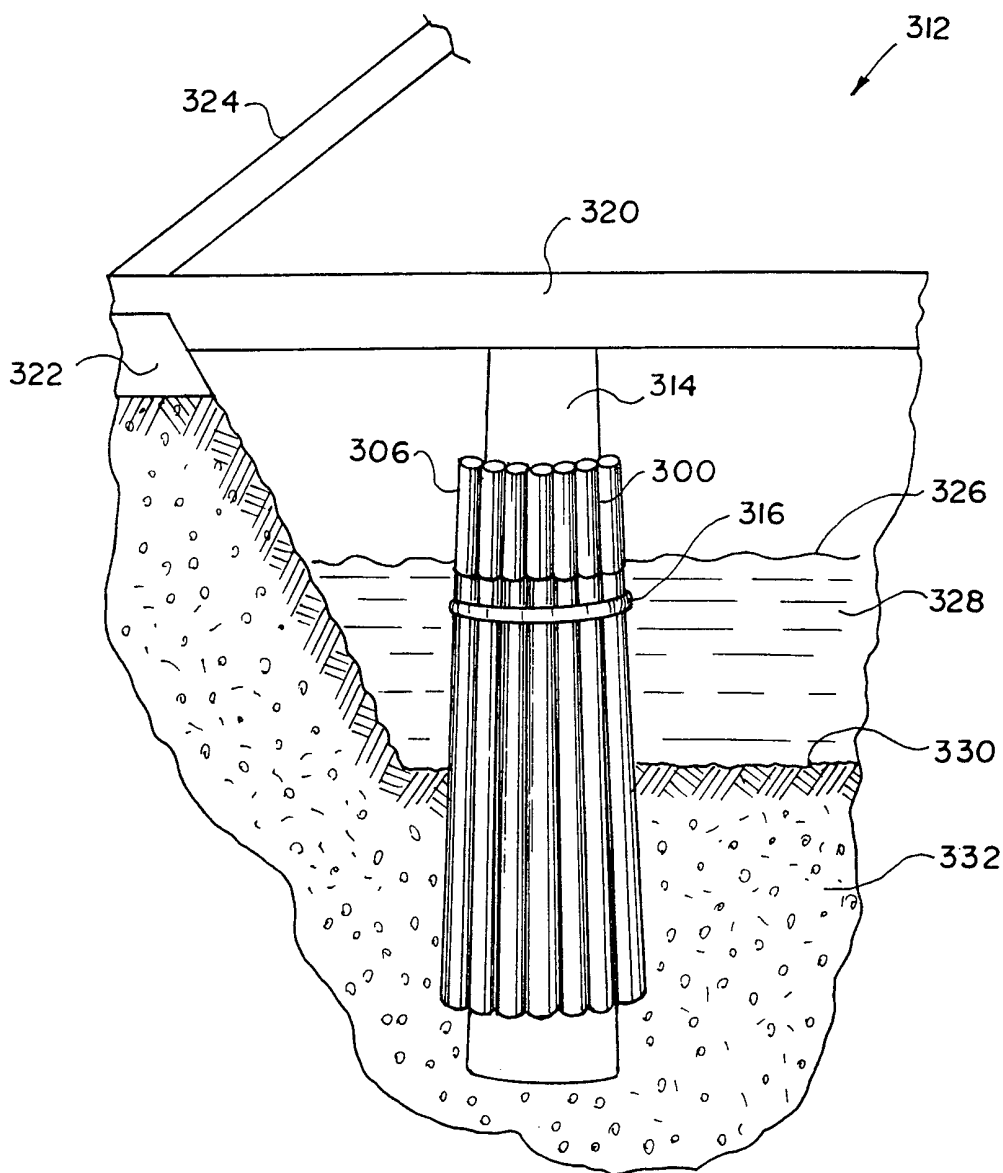


F I G . 1 5



F I G . 1 6





F I G . 17

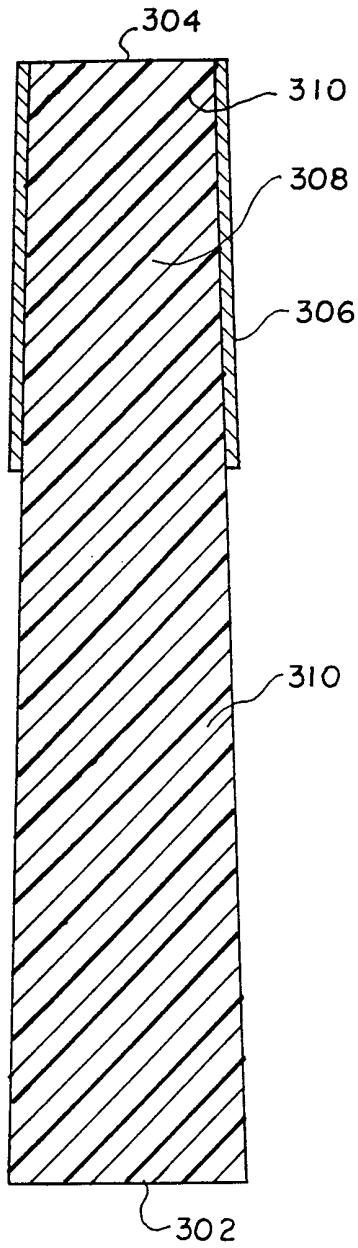


FIG. 18

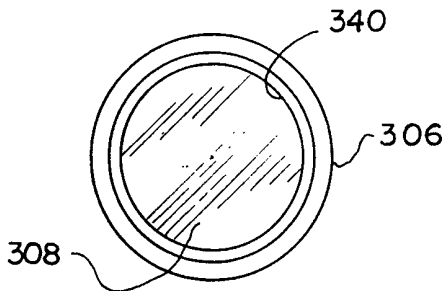


FIG. 19

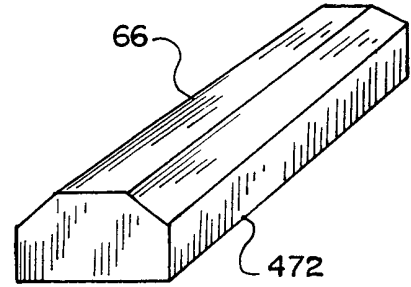


FIG. 20

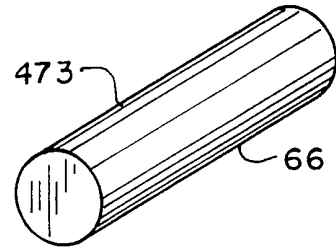


FIG. 21

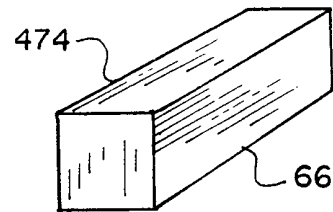


FIG. 22

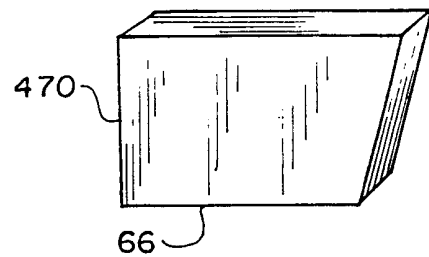


FIG. 23

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/16167

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B32B 7/08; C08K 3/06, 5/10, 5/32, 5/36; C08L 67/00, 89/04  
US CL :423/157.4; 428/221; 523/451, 452; 524/109, 423; 525/122

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)

U.S. : 423/157.4; 428/221; 523/451, 452; 524/109, 423; 525/122

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,128,397 A (HORSEY et al) 07 July 1992, see column 1.	1-64
Y	US 4,165,302 A (ARMENTI et al) 21 August 1979, see column 2.	1-64
Y	US3,933,731 A (MACHI et al) 20 January 1976, see abstract.	1-64
Y	US 2,985,617 A (SALYER et al) 23 May 1961, see entire document.	1-64

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

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"B" earlier document published on or after the international filing date	"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
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Z" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 13 DECEMBER 1998	Date of mailing of the international search report 19 JAN 1999
---	---

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231  
Facsimile No. (703) 305-3230

Authorized officer  
*B. Lipman*  
BERNARD LIPMAN  
Telephone No. (703) 308-0661