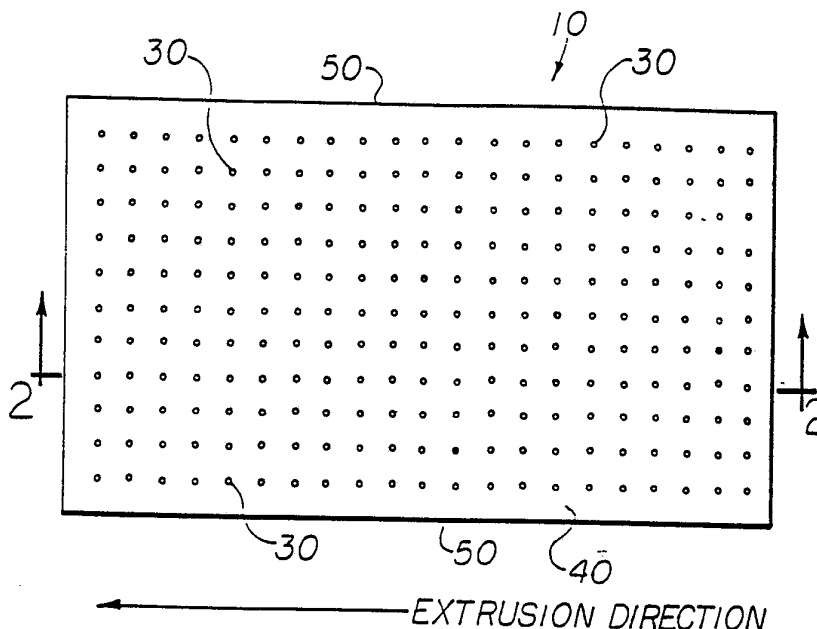




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁵ : B29C 67/20, B32B 3/24</p>	<p>A1</p>	<p>(11) International Publication Number: WO 92/19439 (43) International Publication Date: 12 November 1992 (12.11.92)</p>
<p>(21) International Application Number: PCT/US92/02344 (22) International Filing Date: 24 March 1992 (24.03.92) (30) Priority data: 693,835 30 April 1991 (30.04.91) US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventor: KOLOSOWSKI, Paul, A. ; 3500 Pelham Road, Apartment 96, Greenville, SC 29615 (US). (74) Agent: DEAN, J., Robert, Jr.; The Dow Chemical Company, P.O. Box 515, Granville, OH 43023-0515 (US).</p>		<p>(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), NO, SE (European patent).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>

(54) Title: PERFORATED PLASTIC FOAM AND PROCESS FOR MAKING



(57) Abstract

Disclosed is a closed-cell plastic foam structure comprising a plastic foam (10) defining a multiplicity of channels (30) extending from the surface of the foam into the foam. The channels are free of direction with respect to the longitudinal extension of the foam and preferably extend perpendicularly to the longitudinal extension to the foam structure. The channels are in gaseous communication with the environment outside of the foam structure, and provide enhanced release of blowing agent. Further disclosed is a process for making a plastic foam structure comprising (a) providing the plastic foam and (b) perforating the foam at its surface to form a multiplicity of channels extending from the surface into the foam to form the foam structure.

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PERFORATED PLASTIC FOAM AND PROCESS FOR MAKING

Concern over ozone depletion in the atmosphere has prompted calls for the replacement of chlorofluorocarbon foam blowing agents with blowing agents offering substantially reduced ozone depletion potential such as hydrocarbons.

Hydrocarbons and some other alternative blowing agents present their own unique problems. Chief among these is greater fire hazard in closed-cell foams due to entrapped blowing agent. Other problems however, may include toxicity or environmental incompatibility. The flame retardancy or environmental incompatibility of closed-cell foams may be slow to recover due to the relatively slow permeation of some blowing agents, including hydrocarbons, from the foams.

To address the problem of flame retardancy, it would be desirable to have a closed-cell foam structure which more quickly releases blowing agents, particularly flammable blowing agents. Also desirable would be a process for making such a foam structure.

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According to the present invention, there is a closed-cell plastic foam structure comprising a plastic foam defining a multiplicity of channels extending from the surface of the foam into and preferably through the foam. The channels are free of direction with respect to the longitudinal extension of the foam. The channels are in gaseous communication with the environment outside of the foam structure, and provide enhanced release of blowing agent from the foam structure.

Further according to the present invention, there is a process for making a plastic foam structure comprising (a) providing the plastic foam and (b) perforating the foam at its surface to form a multiplicity of channels extending from the surface into and preferably through the foam to form the foam structure. The channels are free of direction with respect to the longitudinal extension of the foam and in gaseous communication with the environment outside of the foam structure.

The novel features of the present invention and the context within which they are set will be better understood upon reviewing the following specification together with the drawings.

Figure 1 shows a foam structure according to the present invention.

Figure 2 shows a cross-sectional view along line 2-2 of the foam structure of Figure 1.

A closed-cell plastic foam structure of the present invention providing enhanced release of blowing agent is seen in Figures 1 and 2, and is referenced generally by the reference numeral 10. Foam structure

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10 comprises plastic foam 20 and a multiplicity of channels 30 extending into foam 20 from one or both of opposing surfaces 40. Structure 10 also defines opposing surfaces 50, which are generally perpendicular to surfaces 40.

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Plastic materials suitable for the foams of the present foam structure include any known foamable thermoplastic or thermoset material. Suitable plastic materials may include blends of two or more thermoplastic materials, two or more thermoset materials, or thermoset and thermoplastic materials. Suitable plastic materials include polystyrene, polyolefins such as polyethylene and polypropylene, polyurethanes, and polyisocyanurates. Suitable thermoplastic materials may be homopolymers or copolymers of monoethylenically unsaturated comonomers. Useful polystyrene or known derivatives thereof include alphanethylstyrene, butylstyrene, and divinyl benzene. The present invention is particularly useful with polyethylene. Useful polyethylenes include those of high, medium, low, and ultra-low density types. Useful polyethylenes include copolymers thereof such as ethylene-acrylic acid, and ethylene-vinyl acetate.

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The foam of the foam structure may further contain elastomeric components such as polyisobutylene, polybutadiene, ethylene/propylene copolymers, and ethylene/propylene diene interpolymers if desired. Other possible additional components include crosslinking agents if desired. Other additional components may include nucleating agents, extrusion aids, antioxidants, colorants, pigments, etc. if desired.

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The foam of the foam structure may contain one or more permeability modifiers in a quantity sufficient to prevent substantial shrinkage of the structure upon its formation, from premature excessive loss of blowing agent yet allow evolution of the blowing agent from it.

5 Suitable permeability modifiers include fatty acid amides and esters such as stearyl stearamide and glycerol monostearate.

10 The present foam structure is extruded with one or more of any blowing agents known in the art. Suitable volatile blowing agents include halocarbons such as fluorocarbons and chlorofluorocarbons; hydrohalocarbons such as hydrofluorocarbons and

15 hydrochlorofluorocarbons; alkylhalides, such as methyl chloride and ethyl chloride; hydrocarbons such as alkanes or alkenes of three to nine carbon atoms. Other suitable blowing agents include pristine blowing agents such as air, carbon dioxide, nitrogen, argon and water.

20 The blowing agent may comprise a mixture of two or more of any of the above blowing agents. Other suitable blowing agents also include chemical blowing agents such as ammonium and azo type compounds. Such compounds include ammonium carbonate, ammonium bicarbonate,

25 potassium bicarbonate, diazoaminobenzene, diazoaminotoluene, azodicarbonamide, and diazoisobutyronitrile.

30 Preferred blowing agents are hydrocarbons, which include alkanes having from 3 to 9 carbon atoms. Preferred alkanes include butane, isobutane, pentane, isopentane, hexane, isohexane, and heptane. A most preferred blowing agent is isobutane.

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Though the blowing agent may be flammable or nonflammable, the present foam structure is particularly useful with flammable blowing agents because of the accelerated release of blowing agents that it provides. For purpose of this invention, a flammable blowing agent is one that has a lower explosion limit of less than 4 percent by volume in air according to ASTM 681-85 test. Flammable blowing agents include the alkylhalides, alkanes, and alkenes described above.

The present foam structure preferably has a gross density (that is bulk density or densities of the closed-cell foam including interstitial volumes defined by the channels or any voids defined therein) preferably of 1.6 to 160, more preferably of 16 to 48 kilograms per cubic meter.

The present closed-cell foam structure preferably has at least 70 percent of its cells by number being closed-cell according to ASTM D2856-A exclusive of any channels or voids extending through, into, or within the structure.

Channels extend from surfaces into the interior of foam. Channels provide gaseous communication between the interior of foam structure and the environment outside structure to facilitate accelerated release of the blowing agent. The blowing agent permeates from foam into channels to accelerate the rate of release of blowing agent from what the rate would be without channels. Channels are preferably uniformly dispersed over the areas of surfaces. In a preferred embodiment such as in

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Figures 1 and 2, the channels extend through the foam from one surface of the foam to the opposite surface.

Channels 30 have an average width or diameter of preferably 0.05 to 5.1 millimeters (mm) and more preferably 0.5 to 1.5 mm. Channels 30 have an average spacing or distance apart at surfaces 40 of preferably of up to 2.5 centimeters (cm) and more preferably up to 1.3 cm.

The cross-sectional shape of the channels is not critical. For instance, the channels may take on a circular, oval, square, rectangular, or other polygonal cross-sectional shape. Typically however, such shape will take a generally circular form for purposes of convenience. The passageways through the foam defined by the channels are preferably straight and linear, but may also be nonlinear, such as curvilinear.

The prior art relates foam structures of coalesced foam strands having channels directional with the longitudinal extension formed by extrusion from a multiorifice die as seen in U.S. Patent Nos. 3,573,152 and 4,824,720. The present foam structure distinguishes from the prior art structures by having channels free of direction or not directional with respect to the longitudinal extension or extrusion direction of foam structure. Channels 30 of the present structure 10 may be angled toward but not directional with the longitudinal extension. Channels 30 are preferably situated by between 30 and 90 degrees with respect to the longitudinal extension of foam structure 10 and more preferably generally perpendicularly to the longitudinal extension of foam structure 10. Reference to the angle of channels 30 is shown in Figure 2 as angle θ for

channels angled toward the extrusion direction, the reverse extrusion direction, or any direction in between. Both the extrusion direction and the reverse thereof correspond to the longitudinal extension of the structure. Alternatively or additionally, channels (not shown) may extend from surfaces 50 into foam 20 to assist in removal of the blowing agent. As for channels 30 extending into foam 20 from surfaces 40, channels (not shown) extending from surfaces 50 into foam 20 may be angled in corresponding fashion toward but not directional with the longitudinal extension, may be angled toward any direction between the extrusion direction and the reverse extrusion direction, or may extend generally perpendicularly therein with respect to the longitudinal extension. To further assist in the removal of the blowing agent, the foam structure may have additional channels (not shown) directional with the longitudinal extension as seen in U.S. Patent Nos. 3,573,152 and 4,824,720.

There is a process according to the present invention for making plastic foam structure 10 providing accelerated release of blowing agent. The process comprises providing plastic foam 20 and subsequently perforating foam 20 at its surface or surfaces 40 to form channels 30 within foam 20 free of direction with respect to the longitudinal extension of foam 20.

Providing the plastic foam comprises blending of various components, including a resinous melt of a foamable polymer and a blowing agent, under pressure to form a foamable plastic gel and extruding the foamable gel through a conventional die (not shown) to a region of lower pressure to form the foam. The blending of various components of the foamable gel may be

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accomplished according to known techniques in the art, Suitably a mixer, extruder, or other suitable blending device (not shown) may be employed to obtain homogeneous gel. The molten foamable gel is then be passed through conventional dies to form the foam.

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It follows that means for producing foam structures other than extrusion may be employed such as bead molding.

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Perforating the foam comprises puncturing the foam with a multiplicity of pointed, sharp objects in the nature of a needle, pin, spike, or nail. Foam 20 may be perforated by contacting or puncturing surfaces 40 with nails 62 of rack 60 shown in Figure 3 partly through foam 20, or, more preferably, completely through the foam as seen in Figure 2. A mat or bed of nails (not shown) or other device equivalent to rack 60 may be contemplated. It will be obvious that perforating means other than sharp, pointed objects may be employed such as drilling, laser cutting, high-pressure fluid cutting, air guns, or projectiles.

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To further assist in accelerating the release of blowing agent from the present foam structure, the structure may be exposed to elevated temperatures in excess of ambient levels (22°C) for a period of time. Desirable exposure temperatures range from greater than ambient to the temperature below which foam instability will take place. Desirable exposure temperatures may vary due to factors including the properties of the foamed plastic material comprising the structure, the physical dimensions of the structure itself, and the blowing agent employed. The elevated temperature is maintained for a period of time preferably sufficient,

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in conjunction with the perforations in the present structure, to reduce the blowing agent content in the structure to a safe level before it is provided to an end user. The structure might be exposed to elevated temperatures by any suitable means such as an oven, a heating unit or element, or a warehouse having an elevated temperature environment therein.

To further illustrate the present invention, the following nonlimiting examples are provided.

EXAMPLE

Perforated polyethylene foam structures of the present invention were prepared and tested for blowing agent retention as a function of time, temperature, and formulation. The blowing agent retention of the perforated foams was further compared with such retention in solid, non-perforated structures not of the present invention.

Foam structures of 5.1 cm X 25.4 cm cross-section were prepared by extrusion of the foamable gel formulations represented in Table 1. The components of the gel formulations were blended in a 8.8 cm extruder and extruded through a 9.5 cm X 0.3 cm dimension die orifice at a rate of 180 kg/hr and a foaming pressure at the die of 2360 kilopascals. The extruder operated in zones 1-6 at temperatures of 80°C, 140°C, 190°C, 200°C, 225°C, and 225°C, respectively. The foaming pressure and temperature at the die were 2360 kilopascals and 112°C, respectively.

Table 1

Foam Structure Formulations

5 (All proportions are parts by weight unless otherwise indicated.)

	<u>Formulation</u> <u>#1</u>	<u>Formulation</u> <u>#2</u>	<u>Formulation</u> <u>#3</u>
Polyethylene	100	100	100
Permeation 10 Modifier	1.0 (SS)	0.2 (GMS)	0.35 (GMS)
Blowing Agent	11.2 (HCFC-142b)	6.7 (isobutane)	6.7 (isobutane)
Nucleator ¹	0.16	0.25	0.31
Stabilizer ²	0.03	0.03	0.03
15 Foam Density (Kg/m ³)	38	38	38

¹ Hyrocero CF-20 by Boeringer Ingelhiem

² Irganox 1010 by Ciba Geigy

- HCFC-142b = 1, 1, 1 difluorochloroethane

- SS = Stearyl stearamide

20 - GMS = Glycerol monostearate

The foam structures were cut into 2.4 meter lengths, and perforated with 3 mm diameter spikes or nails to form channels generally circular in cross-section extending therethrough between the two large surfaces. The channels were in a square configuration every 1.3 cm or 2.5 cm similar to those seen in Figure 1. Though the structure was perforated with 3 mm spikes, the channels formed upon insertion and withdrawal of the spikes were about 1 millimeter in diameter due to the resiliency or recovery of the foam of the foam structure upon withdrawal.

A 28 cm segment was removed along the longitudinal extension of the foam structure at each time interval of measurement or age, and the sample

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taken from the middle of the structure to ascertain blowing agent content. Blowing agent content was measured by gas chromatography. The blowing agent content of the nonperforated foam structures not of the present invention was ascertained in substantially the same manner.

Table 2

Blowing Agent Retention for Foam Structures of Formulation 1

Foam Structure	21°C ^a		46°C ^a	
	Age (Hours)	Weight Percent 142b	Age (Hours)	Weight Percent 142b
Solid*	1	8.45	1	-
	18	8.40	18	8.29
	168	7.54	168	5.95
	336	6.38	336	4.20
	504	6.46	504	3.83
2.5 cm X 2.5 cm spacing	840	5.99	840	2.69
	1	8.64	-	-
	20	7.43	20	7.46
	44	7.12	44	5.75
	96	6.87	96	4.61
1.3 cm x 1.3 cm spacing	144	6.79	144	3.56
	192	5.92	288	1.80
	188	5.14	384	1.03
	384	4.50		
	1	8.06	1	-
1.3 cm x 1.3 cm spacing	20	6.66	20	4.25
	44	5.28	44	2.92
	96	4.19	96	0.71
	144	3.66	144	0.18
	192	3.16	288	0
	384	1.40	384	0

* Not an example of the present invention
 a Temperature of aging

Table 3

Blowing Agent Retention for Foam Structures
of Formulation 2

5	<u>Foam Structure</u>	<u>21°C^a</u>		<u>46°C^a</u>	
		<u>Age (Hours)</u>	<u>Weight Percent iC₄</u>	<u>Age (Hours)</u>	<u>Weight Percent iC₄</u>
	Solid*	1	5.16	1	-
		40	5.06	15	4.55
		168	4.64	168	2.02
		336	4.39	336	0.89
10	2.5 cm X 2.5 cm spacing	504	3.56	504	0.44
		1	5.30	1	-
		21	4.54	17	3.69
		40	4.49	41	2.52
15	1.3 cm x 1.3 cm spacing	96	3.31	96	0.85
		144	3.25	192	0.27
		192	3.10	228	0
		188	2.05	360	0
20	1.3 cm x 1.3 cm spacing	336	1.72		
		1	4.62	1	-
		20	3.37	15	1.42
		41	2.51	40	0.29
		96	1.26	96	0
		144	0.77	192	0
		192	0.54		
		288	0.24		
		336	0.16		

*-Not an example of the present invention

25 ^a-Temperature of aging
iC₄-Isobutane

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Table 4

Blowing Agent Retention for Foam Structures
of Formulation 1

5	<u>Foam Structure</u>	<u>21°C^a</u>		<u>46°C^a</u>	
		<u>Age (Hours)</u>	<u>Weight Percent iC₄</u>	<u>Age (Hours)</u>	<u>Weight Percent iC₄</u>
	Solid*	1	5.06	1	-
		17	5.16	20	4.88
		168	4.97	336	3.35
		336	4.22	504	2.32
10	2.5 cm X 2.5 cm spacing	1	5.15	1	-
		35	5.03	21	4.79
		96	4.51	37	3.39
		144	4.32	96	2.69
		336	3.60	192	1.59
				228	0.77
				360	0.41
15	1.3 cm x 1.3 cm spacing	1	4.74	1	-
		17	3.95	14	3.49
		35	3.61	36	1.85
		96	2.87	96	0.66
		144	2.55	192	0.09
		192	2.19	288	0
20		288	1.82	360	0
		336	1.38		

*-Not an example of the present invention

a-Temperature of aging

iC₄-Isobutane

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As seen in Tables 2-4, the blowing agent content of the foam structures corresponding to Formulations 1, 2, and 3 was substantially lower as a trend than that of corresponding nonperforated structures for a given age, temperature of ageing, or perforation (channel) spacing. As seen in Tables 2-4, the foam structures corresponding to Formulations 1, 2, and 3 demonstrated substantially faster blowing agent release over time than that of corresponding nonperforated structures for a given temperature of

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ageing or perforation spacing. Further, the foam structures having 1.25 cm spacing demonstrated substantially faster blowing agent release over time than those having 2.5 cm spacing for a given age or temperature of ageing. Further, the foam structures
5 aged at 46°C demonstrated substantially faster blowing agent release over time than those aged at 21°C for a given age or perforation spacing.

10 While embodiments of the foam structure and the process for making have been shown with regard to specific details, it will be appreciated that depending upon the manufacturing process and the manufacturer's desires, the present invention may be modified by
15 various changes by still being fairly within the scope of the novel teachings and principles herein set forth.

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15 1. A method for accelerating the release of
blowing agent from a plastic foam structure comprising
providing a plastic foam, the method being characterized
by perforating the foam at its surface to form a
multiplicity of channels extending from the surface into
20 the foam to form the foam structure, the foam being
perforated to form channels therein free of direction
with respect to the longitudinal extension of the foam.

25 2. The method of Claim 1, wherein the method
is further characterized in that the plastic foam is
provided by extrusion foaming of the plastic with a
blowing agent into a region of lower pressure.

30 3. The method of Claim 2, wherein the blowing
agent is a flammable blowing agent.

 4. The method of Claim 3, wherein the
flammable blowing agent is an alkane having from two to
nine carbon atoms.

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5. The method of Claim 4, wherein the alkane is isobutane.

6. The method of Claim 1, wherein the foam is perforated to form channels therein perpendicular to the longitudinal extension of the foam.

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7. The method of Claim 1, wherein the channels have an average width of 0.05 to 5.1 millimeters.

8. The method of Claim 1, wherein the channels have an average spacing of up to 2.5 centimeters.

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9. A foam structure made according to Claim 1.

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Fig. 1

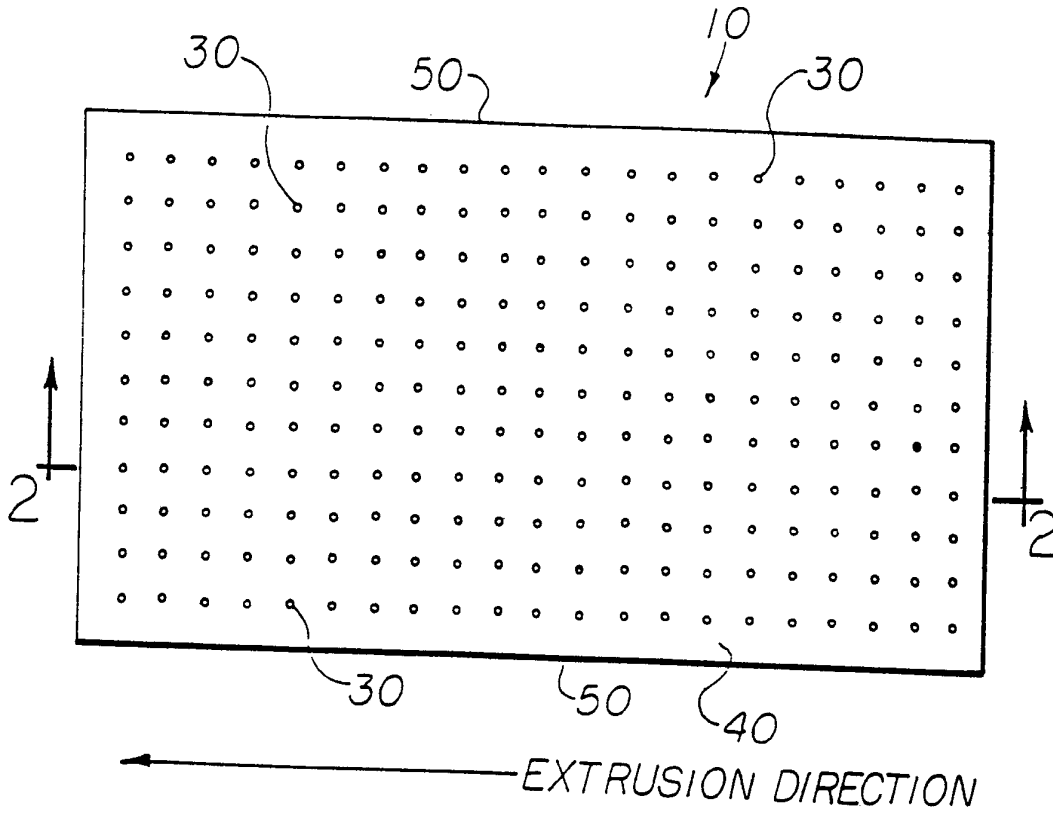


Fig. 2

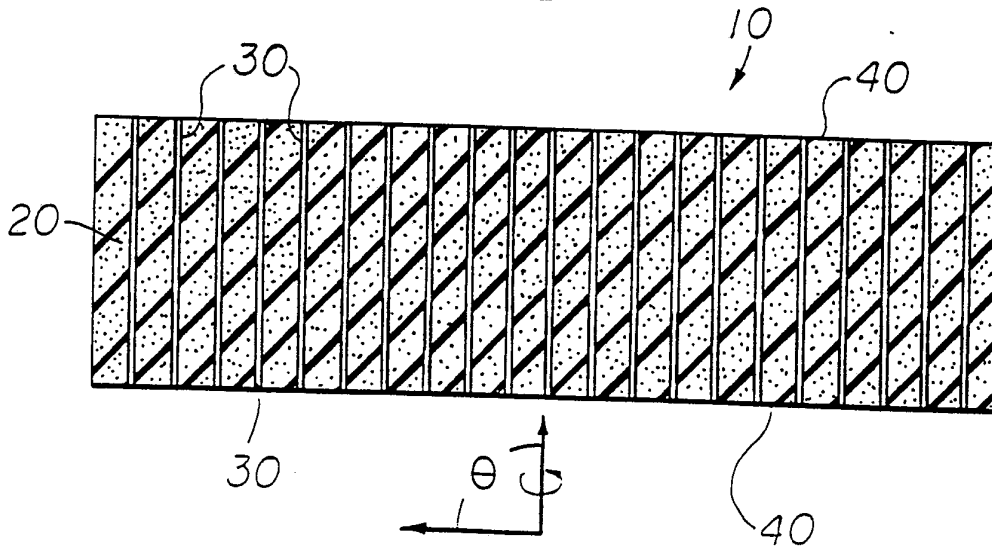
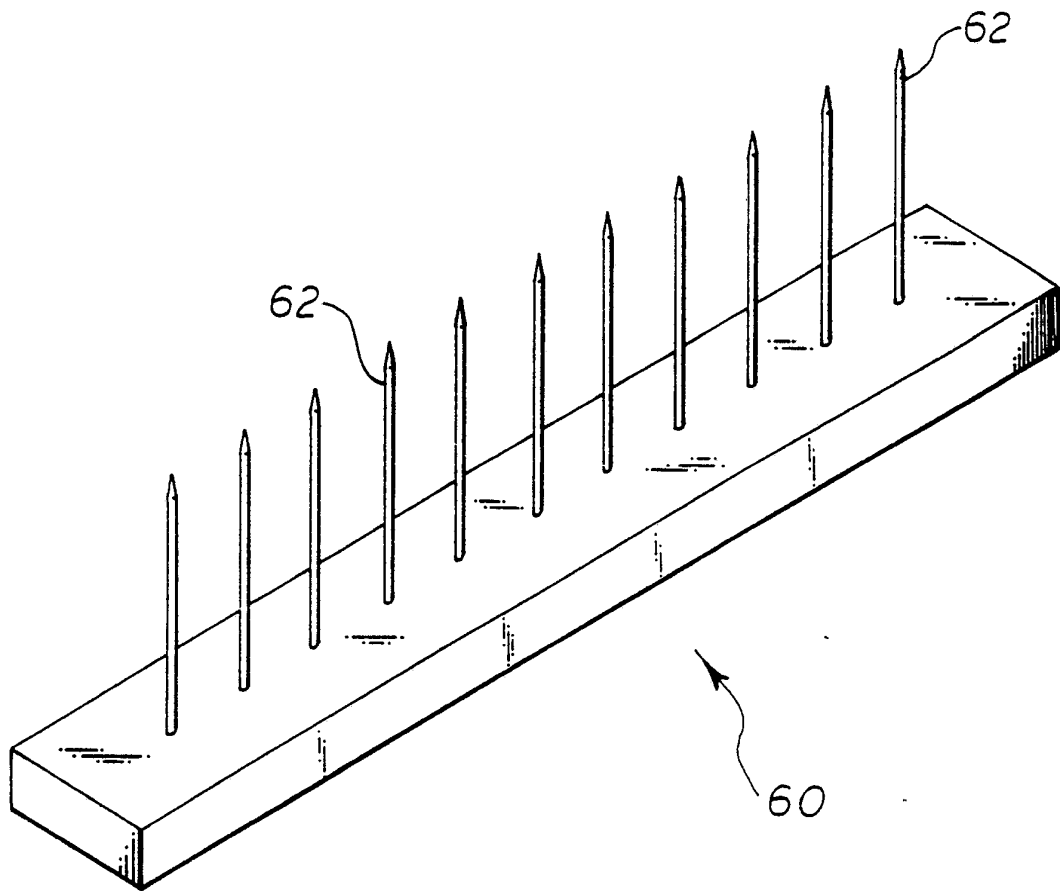


Fig. 3



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/02344

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B29C 67/20; B32B 3/24

IPC: 264/48; 428/131

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. : 428/220, 305.5, 314.4, 304.4; 264/53, 321, 154

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)

APS: Perforate? CPD Foam

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP, A, 63-022631 (KINUGAWA RUBBER IND CO) 30 January 1988 English Abstract	<u>1.2,9.6</u> 3-5,7-8
X Y	US,A, 4,183,984 (BROWERS) 15 January 1980 Column 2, lines 22-35	<u>1.9</u> 6-8
X Y	US,A, 3,966,526,526 (DOERFLING) 29 June 1976 Column 5, lines 10-30	<u>1-9</u> 6-8

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
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Date of the actual completion of the international search 31 JULY 1992	Date of mailing of the international search report 28 SEP 1992
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