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(54) Titre : FEUILLE DE MATIERE PLASTIQUE SANS HALOGENE ET IGNIFUGE

(54) Title: HALOGEN FREE FLAME RETARDANT SHEETING

(57) **Abrégé/Abstract:**

The invention relates to a plastic sheeting which is suitable, in particular, for application in the construction industry. It is obtained by employing thermoplastic elastomers and has good humidity-regulating properties and water impermeability. Flame retardancy in accordance with DIN 4102 B2 is obtained by employing melamine, melamine compounds or melamine condensates in the thermoplastic elastomer composition for the sheeting.

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(21) International Application Number: PCT/NL96/00493 (22) International Filing Date: 20 December 1996 (20.12.96) (30) Priority Data: 1001978 22 December 1995 (22.12.95) NL (71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): GOERTZ, Henricus, Johannes, Jacobus [NL/NL]; Margrietstraat 41, NL-6155 LA Puth (NL). HULSKOTTE, Richerdes, Johanna, Mathilda [NL/NL]; Breijenrode 43, NL-6365 CT Schinnen (NL). BORGGREVE, Reinoldus, Jozef, Maria [NL/NL]; Frank Smitsstraat 1, NL-6336 VG Hulsberg (NL). (74) Agent: ALFENAAR, Marinus; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		(81) Designated States: CA, NZ, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: HALOGEN FREE FLAME RETARDANT SHEETING (57) Abstract The invention relates to a plastic sheeting which is suitable, in particular, for application in the construction industry. It is obtained by employing thermoplastic elastomers and has good humidity-regulating properties and water impermeability. Flame retardancy in accordance with DIN 4102 B2 is obtained by employing melamine, melamine compounds or melamine condensates in the thermoplastic elastomer composition for the sheeting.		

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5 HALOGEN FREE FLAME RETARDANT SHEETING

 The invention relates to flame retardant plastic sheeting especially for use in the construction industry. More specifically the invention relates to flame retardant plastic sheeting for use in the construction industry that is permeable for water vapour but forms a barrier for water. Sheetting having these properties is especially usefull as roofing or as a damp-proof course above for example wooden window and door frames and adjacent brickwork.

 EP-A-167714 and JP-A-0490337 disclose polyetheramide and polyesterester block copolymers as material for construction sheetting. The inventors have found that polyetherester block copolymers and polyurethanes have even better properties for use as sheetting on construction. However requirements are set with respect to flame retardant properties for these sheettings in the construction industry. A very specific requirement for construction sheetting is the DIN 4102 B2 classification. This involves a sheet being suspended vertically and a specified Bunsen burner having a flame length of 20 mm being directed, at an angle of 45 degrees, against the edge or the surface of the sheet. The flame is held against the sheet for 15 seconds, after which the burn time until the flame tip reaches a mark (150 mm above the flame application point) is measured. If this burn time is 20 seconds or longer (measured on 5 samples), the B2 classification is complied with.

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Known flame retardants for use in construction sheeting are combinations of a halogenated organic compound with antimony oxide, as reported, for example, in EP-A-0109928. Quite apart from the drawbacks, corrosivity and potential toxicity, this combination proves unable, according to the invention, even at a high concentration in the sheeting, to conform with DIN 4102 B2. Other known flame retardants for sheeting are metal hydroxides, for example alumina trihydrate and magnesium hydroxide in high concentrations, 60-80 wt%, see US-A-4851463. Owing to the high concentration required of these inorganic materials in the sheeting, the mechanical characteristics are significantly impaired, which means that the use thereof must be avoided.

As even higher requirements will emerge in the future with respect to toxicity and corrosiveness of the smoke and suppression of smoke generation the object of the invention is a flame retardant construction sheeting fulfilling the requirements of DIN 4102 B2 and in which no flame retardants have been incorporated that generate toxic or corrosive gases in case of fire, the sheeting being produced from thermoplastic elastomers chosen from the group of polyurethanes, polyetheresters, polyetheramides and polyesteresters. More specifically the composition should be free from halogen containing compounds.

Very surprisingly the inventors have found that sheeting of the aforementioned thermoplastic elastomers containing from about 5 to about 30 wt.% of at least one compound chosen from the group of melamine, melamine condensates and melamine compounds do fulfill the requirements of DIN 4102 B2.

This finding is very surprising as JP-A-2-88668 discloses that melamine and melamine cyanurate are effective only in polyetherester and polyesterester block copolymer, if combined with a halogenated organic

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compound. In comparative experiment 14 of JP-A-288668 is shown that about 6% of melamine cyanurate has no observable effect on the flame retardancy of polyetherester block copolymer based on polytetramethylene terephthalate and
5 polytetrahydrofuran.

In one aspect, the invention provides a flame retardant, plastic sheeting, suitable for use in the construction industry, permeable for water vapour, consisting of at least one thermoplastic elastomer selected
10 from the group consisting of a polyurethane block copolymer, a polyetheramide block copolymer, a polyetherester block copolymer and a polyesterester block copolymer and containing from about 5 to 30 wt.%, based on the thermoplastic elastomer, of at least one compound selected
15 from the group consisting of a melamine condensate and a melamine compound, with the proviso that the melamine compound is not melamine.

In a further aspect, the invention provides a flame retardant plastic sheeting, suitable for use in the
20 construction industry and permeable for water vapour, consisting of at least one thermoplastic elastomer, having a Shore D hardness of between 30 and 65, selected from the group consisting of a polyurethane block copolymer, a polyetheramide block copolymer, a polyetherester block
25 copolymer and a polyesterester block copolymer, containing from 9 to 22 wt.%, based on the thermoplastic elastomer, of at least one compound selected from the group consisting of a melamine condensate and melaminecyanurate, and wherein the sheeting has a thickness of between 20 μm and 500 μm .

30 Melamine is excluded from being claimed because of the disclosure of melamine in Canadian patent 2017354 as a

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flame retardant additive in films based on thermoplastic polyurethane copolymers.

As noted above, the present application is concerned with water vapour permeable plastic sheetings used in the construction industry, the problem being that the sheetings need to be flame retardant, fulfilling the requirements of DIN 4102 B in which no flame retardants have been incorporated that generate toxic or corrosive gases in case of fire. This problem has been solved with the sheeting according to the invention.

The Canadian patent discloses plastic sheetings based on thermoplastic polyurethane copolymers (PU) and suitable for covering polyurethane foam in car interiors. The problem posed in this patent is to provide a low cost process to provide a plastic sheeting that could be foamed with PU foam systems without problems and without a disadvantageous reaction between the sheeting and the PU foam system. The problem of the present application is not to provide water vapour permeable plastic sheetings containing flame retardant additives per se, but to provide a sheeting that complies with the requirements of DIN 4102 B.

Polyetherester block copolymers, polyetheramide block copolymers, polyesterester block copolymers and polyurethanes block copolymers are known thermoplastic elastomers and are in general all applicable as material for the sheeting of the invention. Preference is thereby given to materials having a Shore D Hardness of between about 30 and 65. Materials that have a too low hardness have generally less good processing characteristics into sheeting, owing to the relatively low crystallinity and

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crystallisation rate. At higher hardnesses, the bending strength and the water vapour permeability decrease unduly.

A comprehensive description of the above polymers and the production thereof can be found for instance in the
5 appropriate Chapters of Encyclopedia of Polymer Science and Technology, Vol. 12, page 76-177 (1985) polyetheresters and polyesteresters, and Kunststoff Handbuch, Teil 7, Ed. G. Oertel, Hanser Verlag (1983) for polyurethanes.

The block copolymers are commercially available
10 under different trade mark names. Pebax, for polyetheramide, Arnitel, Hytrel and Pelprene for polyether- and polyester-ester block copolymers and Pellethane for polyurethane block copolymers. Depending upon the desired mix of characteristics those skilled in the art will be able
15 to choose the most appropriate thermoplastic elastomer. The sheeting according to the invention may further contain the usual additives, for example stabilizers, dyes or pigments, fillers, processing aids etc.

The content of melamine, melamine compound or

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melamine condensation product in the thermoplastic elastomer is between 5 and 30 wt%, based on the thermoplastic elastomer. Preferably, the content is between 7 and 25 wt%, more preferably between 9 and 22 wt%. The content is primarily determined by the desired level of flame retardancy and depends, inter alia, on the thickness of the sheet and the presence or absence of backing.

The particle size of the flame-retarding compound is preferably chosen to be as small as possible, preferably $< 50 \mu\text{m}$, more preferably $< 20 \mu\text{m}$. The best results are achieved with a particle size of $< 10 \mu\text{m}$.

In the case of very thin films for instance $< 50 \mu\text{m}$ a content of $< 5 \text{ wt}\%$ may already suffice to fulfill the DIN 4102 B2 requirement. However reinforcing backing and/or additives adversely effect the flame retardancy so that higher contents i.e. $> 5 \text{ wt}\%$ are preferred.

If required, it is additionally possible to use, in the composition of the flame-resistant sheeting according to the invention, a minor amount of a compound which enhances the flame-retarding effect. Such a compound is chosen from the group of compounds which, in the event of a fire, do not produce corrosive and/or toxic gases. Examples of such compounds are polymers derived from aromatic compounds, for example novolaks and polyphenylene ethers, metal compounds, for example oxides, borates or oxalates, and organic phosphorus-containing compounds. Preferably, the content of these compounds which enhance the flame-retarding effect is smaller than 50 wt%, based on the melamine, the melamine compound or the melamine condensate. However it is experience of the inventors that under normal circumstances no enhancing second flame retarding compound is needed.

In general, melamine will be used only in the

case of sheeting containing a thermoplastic elastomer having a low melting point, preferably in the order of 200°C or less. In the case of higher melting points and concomittantly necessary higher processing temperatures it is possible for fouling of the processing equipment and "bleeding" of melamine to the surface of the sheeting to occur, as a result of the relatively high volatility of melamine. The use of melamine cyanurate and melam is therefore to be preferred.

10 The sheeting according to the invention is obtained by methods known per se from the thermoplastic elastomer. The thermoplastic elastomer is generally obtained by melt blending of the thermoplastic elastomer with the melamine, melamine cyanurate or
15 melamine condensate and, if required, other additives, for example stabilizers. Said melt blending can take place in the customary melt blending equipment, the use of a blending extruder, preferably a twin-screw extruder, being preferable to obtain good dispersion of
20 the flame retardant in the composition. Then the granules obtained after the blending extrusion step are processed in the customary film and sheet production equipment to give the sheeting of the desired thickness, use being made, in general, of sheet
25 extrusion equipment.

 The sheet may have any thickness required, for example between 20 μ m and a few mm. Preferably the thickness of the sheet is less than 1 mm, more preferably less than 0.75 mm, most preferably less than
30 0.5 mm, to be effective as water-vapour permeable medium. The very thin sheeting is generally used in combination with one or more other porous supports which are to ensure the mechanical strength, such as described, for example, in JP-A-0490337.

35 If required, the sheeting is used in combination with a fibrous material which is to ensure the required strength. Examples of such fibrous

materials are organic fibres, for example polyester fibre or fibres of aromatic or aliphatic polyamides, and inorganic fibres, for example glass fibre. Said fibrous material may be present in the form of a woven or as a staple fibre web. The fibre-reinforced sheeting can be obtained, for example, by coextrusion of the woven or the staple fibre web with the thermoplastic elastomer, or by means of compression-moulding the fibre structure with the sheeting.

10 In addition the sheeting may contain various additives to improve the colour and the appearance.

The sheeting according to the invention can be used in highly diverse ways, for example as a component of a roof covering or as an underlay therefor, as protective sheeting above wooden subassemblies, for example door and window frames, as sheeting to drain away any rainwater or condensation water which has penetrated a cavity wall, as a seal between adjoining brickwork, as a wall covering, in which case the accompanying qualities such as elasticity and "soft touch" can be utilized in particular, and many other uses in the construction industry where the qualities of humidity control and water impermeability matter.

25 Although, for the time being, the main applications of the sheeting are to be found within the construction industry, applications outside this sector can also be indicated, for example in furniture upholstery, where good humidity regulation is one of the factors defining comfort and there are requirements regarding flame retardancy.

30 The invention is now explained in more detail with reference to the following examples, without, however, being limited thereto.

35

Materials used:

Arnitel EM 400®: from DSM, the Netherlands; a

- polyetherester block copolymer containing polybutylene terephthalate as hard segments, and soft segments of polytetramethylene oxide, Shore D hardness = 40.
 Arnitel PM 380®: from DSM, the Netherlands; a
 5 polyetherester block copolymer containing polybutylene terephthalate as hard segments, and soft segments of polypropylene oxide end-capped with ethylene oxide, Shore D hardness = 38.
 Pellethane® from BASF, Germany, a thermoplastic
 10 polyurethane block copolymer
 Pebax® MV 1205 from Atochem, France, a polyetheramide block copolymer
 Melamine: from DSM, particle size $d_{99} < 50 \mu\text{m}$
 Melamine cyanurate (Mecy): from DSM, aver. particle
 15 size 50 % $< 2 \mu\text{m}$
 F-2400®: from Dead Sea Bromine, Israel, Br-epoxy polymer compound containing 52 wt% of Br, M = approx. 60,000.
 Sb₂O₃: an 80 wt% masterbatch in PBT, from Campine.
 20 Spinflam MF83®: from Himont, P- and N-containing intumescent flame retardant based on a piperazine salt.
 CDP: from MFC, cresyl diphenyl phosphate
 Chimasorb 944®: from Ciba Geigy, a UV stabilizer based on a hindered amine oligomer.

25

Examples I and II, experiments A-E

- Arnitel PM 380, after drying, was blended in a ZSK 30/33 D twin-screw extruder with the flame retardants listed in Table 1. Screw speed 200 rpm,
 30 throughput 10 kg/h, melt temperature 245°C. The granulate obtained was extruded, to produce a film having a thickness of 0.4 mm, on a Battenfeld 45 mm film extruder at a melt temperature of 216°C and a roller temperature of about 20-25°C and a rolling speed
 35 of 3.13 m/min.

The water vapour permeability, the water absorption after 3 days' immersion in water at 25°C,

and flame retardancy according to DIN 4102 B2 of this film were determined.

The results of these tests are shown in Table 1.

- 5 + means "meets the requirements for roofing sheeting".
++ means "amply meets the requirements for roofing sheeting". "N" is below standard.

Example III

- 10 Example II is repeated, except that 50 % of the melamine cyanurate is replaced by melamine. This composition likewise is found to meet DIN 4102 B2.

Examples IV and V

- 15 Examples I and II were repeated, except that Arnitel EM 400 was used instead of Arnitel PM 380.

Examples VI, VII and VIII

- 20 The compositions of Examples I and IV and V were additionally admixed with 0.5 wt% of Chimasorb 944 FL, and the stability of the sheeting when subjected to UV light was determined by means of an Atlas UVCON apparatus comprising a UV-B313 nm lamp with an exposure, each time, of 4 hours at 60°C, and 4 hours' condensation at 50°C. The breaking elongation of the film was determined by means of a Zwick 1445 instrument, drawing speed 50 mm/min, on an ISO 237 tension test bar ($L_0 = 12$ mm, $b_0 = 2$ mm). The results are reported in Table 2.

30

Examples IX and X

- Example II has been repeated, except Pellethane® and Pebax® MV 1205 were used instead of Arnitel® PM380. These compositions were flame
35 extinguishing after 4 and 12 seconds respectively. Film thicknesses were 0.32 and 0.27 mm respectively.

TABLE 1

	Exp. A	B	C	D	E	Ex. I	Ex. II	Ex. IV	Ex. V	Ex. IX	Ex. X
Arnitel PM 380	93*)	86	78.75	85	95	100	90				
Arnitel EM 400								100	90		
Pellethane										90	
Pebax MV1205											90
Mecy							10		10	10	10
F-2400	5	10	15								
Sb ₂ O ₃	2	4	6.25								
Spinflam MF 83				15							
CDP					5						
water absorption [%]						1.9	1.7	0.75	0.70	-	120
water vapour permeability						++	++	+	+	++	++

5

10

15

	Exp. A	B	C	D	E	Ex. I	Ex. II	Ex. IV	Ex. V	Ex. IX	Ex. X
DIN 4102 B2	N	N	N	N	N	N	com- plies	N	com- plies	com- plies	com- plies

*) composition in parts by weight

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TABLE 2

Arnitel EM 400	100	99.5	89.5	
Arnitel PM 380				89.5
Mecy			10	10
0.5 wt% of Chimasorb		0.5	0.5	0.5
Ageing *) [hours]	95	> 200	> 200	95

*) The measure chosen for ageing under UV light is the time until the breaking elongation has decreased to 250 %.

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CLAIMS:

1. A flame retardant, plastic sheeting, suitable for use in the construction industry, permeable for water vapour, consisting of at least one thermoplastic elastomer
5 selected from the group consisting of a polyurethane block copolymer, a polyetheramide block copolymer, a polyetherester block copolymer and a polyesterester block copolymer and containing from about 5 to 30 wt.%, based on the thermoplastic elastomer, of at least one compound
10 selected from the group consisting of a melamine condensate and a melamine compound, with the proviso that the melamine compound is not melamine.
2. The flame retardant plastic sheeting according to claim 1, wherein the thermoplastic elastomer has a Shore D
15 hardness of between 30 and 65.
3. The flame retardant plastic sheeting according to claim 1 or 2, wherein the at least one compound is melaminecyanurate or melam.
4. The flame retardant plastic sheeting according to
20 any one of the claims 1-3, wherein the thermoplastic elastomer contains from about 7 to 25 wt.% of the at least one compound.
5. The flame retardant plastic sheeting according to any one of the claims 1-4, wherein the thermoplastic
25 elastomer is a polyetherester block copolymer.
6. The flame retardant plastic sheeting according to any one of the claims 1-5, wherein the sheet has a thickness of between 20 μm and 2 mm.

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7. The flame retardant plastic sheeting according to claim 6, wherein the thickness of the sheet is less than 0.75 mm.

8. A flame retardant plastic sheeting, suitable for
5 use in the construction industry and permeable for water vapour, consisting of at least one thermoplastic elastomer, having a Shore D hardness of between 30 and 65, selected from the group consisting of a polyurethane block copolymer, a polyetheramide block copolymer, a polyetherester block
10 copolymer and a polyesterester block copolymer, containing from 9 to 22 wt.%, based on the thermoplastic elastomer, of at least one compound selected from the group consisting of a melamine condensate and melaminecyanurate, and wherein the sheeting has a thickness of between 20 μm and 500 μm .

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