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54 **Wet laid thermoplastic web compositions.**

57 A wet laid fibrous web composition suitable for moulding into a reinforced thermoplastic product comprises the following in parts by dry weight (based on 100 parts of the first, second and third components combined) :

- a) from 3 to 15 parts of a first component being fibers for reinforcing the composition during its manufacture.
- b) a reinforcing amount of a fibrous second component effective for reinforcing the thermoplastic product formed by hot molding the fibrous composition, and
- c) a balance amount of a third component being fibers of a thermoplastic polyester. the first component having a melting or degradation temperature greater than the melting temperature of the third component.

Description

Wet laid thermoplastic web compositions

The invention relates to paper compositions intended especially for forming a reinforced thermoplastic web which can be hot-stamped into a finished product.

This type of sheet is known for example from documents EP-A-39292 or FR-A-2507123, the teaching of which is incorporated here by way of reference.

The compositions intended for forming a web of this type mainly contain fibers for reinforcing the product during manufacture (such as cellulose or the like), fibers for reinforcing the finished product (such as glass fibers or the like), a thermoplastic resin under particulate form, optionally a binder (such as latices in aqueous suspension or the like). The compositions can also contain universal fibers, essentially to reinforce the finished product, by replacing at a lower cost a part of the reinforcing fibers.

The process for the manufacture of the web from the paper composition is a conventional paper-making process such as the one described in the above-mentioned documents, with passage through a paper machine, for example a Fourdrinier machine with a flat table or an inclined wire.

In general the wet process comprises forming an aqueous slurry comprising polymer particles, fibers such as glass fibers which provide reinforcement in the final products, and process aids. The slurry is then laid down in a thin layer on a moving mesh through which the water drains, optionally under negative pressure, to leave a wet web of particles and fibers. The web is then carried through a drying means such as an infra red oven or a hot air jet. The dried, so called wet laid web, is then subjected to densification by hot pressing or moulding to form a (glass) fiber reinforced polymer product.

Up to now, the compositions attempted to meet a certain number of requirements.

The requirements for a good composition, as regards the process are inter alia :

- . to lead to the formulation of a homogeneous and regular web.
- . to authorize the highest possible producing speed.
- . to provide the web with a strength sufficient to permit its drying, its handleability and its transformation.

The requirements for a good composition, as regards transformation of the web thus obtained are :

- . a good capacity of the web to be heated at a temperature higher than the melting temperature of the thermoplastic resin.
- . the highest possible mouldability.

Finally, the requirement for a good composition, as regards the final product produced by transformation of the heated web is, for the current industrial applications, that the components necessary to the manufacture of the web (fibers and process aids) do not impair the required good physical properties of the finished product.

At present, those who industrially transform or utilize plastic products, particularly in the automobile industry, are looking for materials enabling the producing of articles with a good surface appearance.

The requirements for a composition meeting this criterion are :

- . to permit a surface appearance as regular as possible
- . to have a thermal stability adequate for the industrial lines of painting
- . to have the best possible dimensional stability under any weather conditions.

It has been proposed that the appearance be improved by bringing on the surface a sheet or a film on a layer having a composition different from that of the base web but such a solution is limited because it prohibits any complex shape.

The object of the invention is to propose paper compositions meeting all the above-cited requirements and more especially intended for forming a finished product whose appearance satisfies relatively high quality criteria, for example a CLASS A surface finish for visible parts of automobile bodywork.

According to the present invention there is provided a wet laid fibrous web composition suitable for moulding into a reinforced thermoplastic product, comprising fibers for reinforcing the composition during its manufacture, fibers for reinforcing the moulded product, and a thermoplastic resin, said composition comprising the following in parts by dry weight (based on 100 parts of the first, second and third components combined):

- a) from 3 to 15 parts of a first component being fibers for reinforcing the composition during its manufacture,
- b) a reinforcing amount of a fibrous second component effective for reinforcing the thermoplastic product formed by hot moulding the fibrous composition, and
- c) a balance amount of a third component being fibers of a thermoplastic polyester, the first component having a melting point or degradation temperature greater than the melting temperature of the third component.

As will be described hereinafter, the proportions of the first, second and third components may be varied independently within quite wide limits, depending on the balance of properties (mechanical strength of final product, handleability of the wet laid web composition in wet and dry (fused) state, mouldability of composition, water absorbance of moulded product).

In another aspect the invention provides a method for producing a moulded product from such a fibrous web composition which comprises pre-heating the web to a temperature which is lower than the melting or degradation temperature of the first component, but greater than the melting temperature of the third

component, to fuse the third component but retain the reinforcing effect of the first component, and, in a press, moulding the heated web under pressure at a temperature which is lower than the melting temperature of the third component, to form the desired moulded product.

Preferably the preheat temperature is at least 30 degrees C greater than the melting temperature of the third component. The first component serves to provide strength to the fused web during the handling associated with the pressing stage during transfer from the heating zone to the press, which may also be heated to provide improved control over cooling the product.

The fibers for reinforcing the product during manufacture (i.e. the first component) are the mineral or organic fibers with a physical structure identical or close to that of cellulose, i.e. having an irregular shape with a high specific area. Thus, they contribute to the cohesion of the wet and dry web during passage through the paper machine and then during handling and cutting of the dry sheet, and help to prevent the thermoplastic material from shrinking during drying.

According to the invention, the fibers for reinforcing the composition during its manufacture preferably have a melting or degradation temperature at least 20 degrees C greater than the temperature of transformation of the polyester fibres used (for example above 310°C if the thermoplastic material is PETP).

The glass fibers, owing to their structure, also prevent the flowing, i.e. the disorganization of the web and the running of the resin during preheating of a format or a pile of formats from the web, prior to moulding or transforming into a rigid densified plate.

In the context used herein, transformation means the technique by which the web containing the first, second and third fibrous components is converted into the finished thermoplastic product of improved mechanical properties (derived from the second component). Thus typically the web is subjected to an elevated temperature such that the polyester third component melts. It is at this stage, as well as during the wet production process, that the first component shows its value : without the presence of the first component the molten thermoplastic polyester would run and be un-handleable. In the presence of the second component the web maintains its integrity and can be transported to a moulding stage where it is subjected to pressure and cooled, so that the polyester cools into a continuous matrix in which the reinforcing second component fibers are homogeneously dispersed. The moulding can be into a flat sheet (otherwise known as a plaque or blank) which can be used per se or moulded into a more complex shaped article; or the moulding can be directly into a three dimensional shaped article.

It should be understood that the fibrous first and second components provide different reinforcement to the web or final product. Thus the first component serves to hold the second and third component fibers together when in the wet or unfused dry state, and to hold the second component fibers and matrix together when the polyester is in the fused state. For this reason the first component preferably has a fibrillated structure which gives improved entanglement capability. It is preferred that no binder is used in performance of the wet process to produce the web. In contrast the second component fibers are intended to provide reinforcement in the final moulded product and so have a high modulus of elasticity such as is possessed by glass fibres.

It has been found that, in the amounts recommended, cellulose meets these objectives perfectly and is not at all disadvantageous, contrary to the prejudice which is generally not in its favor.

With a cellulose content less than 3% of the fibrous combination, the web has not a sufficient cohesion for its manufacture and its preheating.

Above 150% of the fibrous combination, the composition has a reduced mouldability, and the moulded product becomes wet-sensitive and hence loses dimensional stability.

The fibers for reinforcing the finished product are advantageously glass fibers with a length of less than 50 mm and even preferably less than 25 mm. Preferably the glass fibers are from 6 to 25 mm long. Preferably they are from 9 to 15, more preferably 10 to 12 microns in diameter. Other suitable fibers, above or in combination, and also dispersed in unitary conditions, are carbon fibers, metal or metallized fibers, mineral fibers (rock wool, ceramic, boron, etc.) or organic fibers (carbon, polyaramide, polycarbonate, etc.).

The proportion of second component present in the composition of the invention can be varied in dependence on the balance of mouldability and mechanical strength required of the final product. Thus a high concentration gives good mechanical strength but can impair mouldability, whereas a low concentration gives good mouldability but a diminished mechanical strength. It is a relatively simple task for the person of skill in the art to assess just what will be a reinforcing amount of second component fibers, for any given composition. Preferably the composition comprises from 15 to 40 parts by weight of second component fibers (based on 100 parts of first, second and third components) more preferably from 18 to 27 parts by weight and most preferably from 21 to 26 parts by weight.

The thermoplastic polyester (i.e. the third component) is advantageously either a polyethylene terephthalate (PETP) although other polyalkylene terephthalates and other fiber-forming polyesters may be used. PETP is particularly suitable : its melting point of 240-250°C enables it to withstand the temperatures in the paintshops of automobile production lines, which approach 140°C-160°C.

According to the invention, the polyester in the paper composition is in the form of microfibers or fibers, and preferably fibers 3 to 6 mm long. It has been found noticeably more advantageous to use thermoplastic fibers rather than thermoplastic powders, because the repartition of the resin in the web is more regular. Another advantage is that the draining speed of the suspension during manufacture of the web or the wire, is quite higher, which permits, when compared to a composition with powder, to produce more rapidly and/or to dilute more in order to better disperse the reinforcing fibers. Moreover, unexpectedly, the heated web, although

having with fibers a density less than it would have with powders, and hence a greater "content" of air, exhibits a shorter preheating time under the press, which is indeed surprising when one considers that the air present in the product is a poor conductor of heat.

The compositions of the present invention may therefore be compared with advantage with the compositions taught in WO 87/04476 (Battelle Memorial Institute), which prior art compositions have a heat fusible polymeric component present in the form of particles, rather than fibers.

The amount of polyester in the composition depends on the amounts of the first and second components of course, but is preferably in the range from 45 to 85 parts by weight, more preferably from 58 to 79 and most preferably from 65 to 75 parts by weight (based on 100 parts of first, second and third components combined).

In accordance with the invention the fibers of the first component have a melting or degradation temperature greater than that of the third component, in order to provide strength to the composition in the preheated state immediately prior to final moulding or hot pressing. Preferably the first component has a melting or degradation temperature at least 50 degrees C and more preferably at least 65 degrees C greater than that of the third component.

The composition of the invention may also contain fillers.

According to the invention, the fillers are all the fillers conventionally used in the art, especially carbonates, talc, etc.

Preferably the filler is present, if at all, in an amount up to 45 parts by weight (based on 100 parts of first, second and third components), for example from 20 to 45 parts by weight.

In addition to these basic components, the composition can also contain the additives or aids necessary to the manufacture, the transformation of the web or utilization of the moulded products. Among these, the following may be mentioned : colorants, antioxidants, lubricants, mold release or slip agents, peroxides, antistatic agents, nucleating agents, plasticizers, pigments, flocculants, retention agents, dispersants, flame retardants, water repellants, coupling agents, adhesion primers, UV inhibitors, etc.

Furthermore, it is possible to improve the surface state of the material by adding an IMC (in-mold coating). This in-mold coating technique consists in injecting a coating of varnish (in general a thermoset) into the mold, thereby improving the surface state and permitting the subsequent bonding of coats of paint in the case of, for example, bodywork parts.

Advantages and other aspects of the invention will become apparent on reading Tables I to III attached.

These tables collate the characteristics and measurements of 23 tests performed on different compositions with or without fillers and with the polyester incorporated as powder as in the prior art or fibers according to the invention.

Table I shows the passage characteristics of tests 1 to 23 on a pilot paper machine.

The first column indicates the test number.

The second column indicates the weight of the sheet in g/m².

The third column indicates the position of the water line by reference to the corresponding chain line, this number being, for a same dilution, all the higher as the composition drains less.

The fourth column indicates the dilution, namely the rate at which water has to be supplied in order to keep the water line in its given position.

The combination of these two columns makes it possible to compare the draining speed of the different compositions.

The fifth and sixth columns indicate the amount of dry matter present at the head of the machine and in the white water respectively.

The seventh column gives the wet porosity on entering the dry end, measured in ml/min on a Bendsten porosimeter.

The eighth column gives the dryness of the sheet on leaving the wire, before drying.

The preferred way of heating being by means of traversing hot air, the higher the values indicated in these last two columns, the better the composition permits a high manufacture speed and/or a high weight/m² of the web.

Finally the last column indicates the web density after drying for 15 min in a chamber at 80°C.

Table II refers to the conversion of the sheets by preheating between the platens of a hot press at 300°C.

The first column indicates the test number.

The next four columns relate to the conditions of the preheating test and respectively indicate the number of piles, the total number of formats, the size of the format (either rectangular and 15 x 11 cm² or round and 18 cm in diameter) and their total weight.

The sixth column indicates the calculated pressure on the piles of heated formats.

The seventh column shows the preheating time required to reach 290°C at the core of the formats.

The last column sets out observations, where appropriate, on the flow noted during preheating.

Finally, Table III relates to a plate molding tests. Two types of mold were used : the mold shown as no. 1 in the second column is a straight-edged plate mold with a circular rib on the bottom, and mold no. 2 is an ordinary hollow plate mold.

The third column shows information on the stack formats used to produce the plates.

The fourth column relates to the visual appearance of the surface of the molding (homogeneity and evenness).

The fifth column indicates the thickness of the plate, the sixth its density and the seventh the percentage of

ash. The last three columns respectively indicate the tensile and flexural stresses and flexural modulus. Two values are indicated for the compositions with fillers, these corresponding respectively to the percentage of ash for the fillers and for the glass fibers.

Tests 1 to 10 relate to compositions without fillers and tests 11 to 20 relate to compositions with fillers.

1. COMPOSITIONS WITHOUT FILLERS

1.1. Compositions with cellulose

Tests 1 to 6 involve compositions with cellulose, containing the following in parts in dry weight :

Cellulose fibers 10

Glass fibers 21.5

PETP 68.5

The glass fibers are R18DX9 fibers marketed by OWENS CORNING FIBERGLAS EUROPE, with a length of 6 mm and a diameter of 11 micrometers.

In a preferred embodiment, the aqueous suspension is prepared in a chest in the following manner :

The cellulose fiber, refined beforehand to between 15 and 65 degrees SR, particularly about 50, is introduced at a concentration of the order of 10 to 50 g/l, particularly about 30 g/l, with agitation ;

- the polyester fiber in the commercial form is added to the cellulose ;

- this is followed by the dispersant for the glass fiber, namely, for the fibers used, a cationic dispersant based on fatty acids -Cartaspers DS1 (registered trademark of SANDOZ) - at a rate of 10% of the commercial product, relative to the dry glass fiber ;

and

- finally, the glass fiber is added last in the commercial form.

1.1.1. Tests with PETP fibers

Test no. 1

The PETP is the T 100 polyester from RHONE-POULENC, in the form of 6 mm fibers of 3.3. dtex.

Test no. 2

The PETP is the T 100 polyester from RHONE-POULENC, in the form of 3 mm fibers of 17 dtex.

Test no. 3

The PETP is the GRILON NV2 polyester from GRILENE, in the form of 6 mm fibers of 3.3 dtex.

1.1.2. Comparative tests with PETP powder

Test no. 4

The PETP is the T 100 polyester from RHONE-POULENC, in the form of powder with a particle size of less than 300 micrometers.

Comparison with test no. 1 in Table I shows the very distinct advantage of the composition with fibers as far as draining is concerned. The porosity is similar, however, which is surprising.

Furthermore, despite the fact that the density of the composition of test no. 1 indicates a greater air "content" than in the case of test 4. Table II shows that the preheating time is shorter, which is both surprising and advantageous.

On the other hand, the mechanical characteristics of the plate (Table III) are comparable in test 1 and test 4, which is normal insofar as the polyester has been melted and is therefore no longer dependent on the form in which it was initially introduced.

Test no.5

The PETP is the 6438 polyester from Eastman Kodak, with a mean particle size of 200 micrometers. This test confirms the preceding one.

Table I shows that the draining is very slow, Table II shows that the preheating time is very long and Table III shows that the percentage of ash is high, indicating that the PETP in powder form has a low retention, which may justify the relatively inferior characteristics. Finally, the poor appearance of the molded plate should be noted, this being related to the very long preheating time which results in surface degradation of the material.

Test no. 6

The PETP is a polyester supplied by ENKA, ground to a particle size of less than 300 micrometers. Features to note are the slow draining and the longer preheating time than in the case of the fibers, which results in substantial browning on the surface of the molded plate.

The percentage of ash is again fairly high.

The use of thermoplastic fibers instead of powders allows a better capacity to be produced in machine, a higher productivity and a transformation made much easier.

1.2.1. Compositions without cellulose (for comparison)Test no. 7

R18DX9 glass fibers, 6 mm, 11 micrometers 23.9 parts

T 900 PETP fibers from Rhône-Poulenc, 3.3 dtex, 3mm 76.1 parts

This type of composition leads to a product which is impossible to draw satisfactorily through an industrial paper machine with a wet and a dry end, due to the lack of cohesion and the high shrinkage during drying.

Moreover, Table II indicates very significant flow : the material flows and makes it necessary to fold the assembly into a ball ; the material cools. The process is not industrial.

This significant flow is explained by the absence of cellulose, which provided the preheated product with necessary cohesion.

The characteristics observed in Table III are somewhat better than with the compositions containing cellulose (see test 10), but not as much as might have been hoped, especially in view of the high proportion of glass fibers. This confirms that cellulose is not of a disadvantageous nature.

Test no. 8

In order to obviate the lack of cohesion of the web due to the absence of cellulose, the test no.7 is carried out again by adding as fibers with a high specific area, a synthetic polyolefin pulp.

Glass fibers (as in test 7) 22.4 parts

PETP (as in test 7) 71.2 parts

PULPEX EA polyethylene pulp marketed by HERCULES 6.4 parts.

Table II indicates that the preheating had to be stopped before reaching 290°C because of very significant flow. The PULPEX EA used had fiber length from 0.2 to 1.3 mm and diameter from 10 to 20 microns.

Test no. 9

The composition is the same as in test 8 but the preheating conditions are altered in an attempt to overcome the problem encountered in the previous test.

Despite the significant flow which persists, we somehow managed to mold a plate. The final appearance is found to be very poor, rough and heterogeneous with dull specks due to exudation of the polyolefin on the surface as a consequence of its melting point being too low. Polyolefin pulps cannot therefore be used to replace cellulose in the applications of the invention and it is necessary to use, as fibers reinforcing the product during its manufacture, fibers having a melting temperature higher than the transformation temperature.

1.2.2. Compositions with cellulose:Test no. 10

For the purpose of comparison with test 7, the composition of test 10 contains cellulose and the same T 900 PETP polymer as in test 7. The composition is as follows :

Cellulose 10 parts

Glass fibers 21.5 parts

PETP 68.5 parts

The slightly branched T 900 polymer is an inferior grade of polymer to the linear T 100 in terms of the mechanical strengths, which largely explains the drop in the characteristics compared with test no. 1.

2. COMPOSITIONS WITH FILLERS

These correspond to the following formula (parts by weight) :

Cellulose 14

Glass fibers 26

PETP (fibers or powder) 60
 Filler 43

2.1. Compositions with PETP fibers

The filler used is a Millicarb carbonate marketed by OMYA. 5

In the preferred embodiment, the mineral filler is introduced into the refined cellulose before the polyester. In this case, a customary retention agent has to be added at the head of the machine in order to ensure a good retention of the said filler. Good results were obtained with a high-molecular poly-acryamide at a rate of 0.2% relative to the dry materials. 10

A mixture of this type is then diluted to the desired concentration to enable it to pass satisfactorily through the paper machine.

Tests no. 11 and 12.

The fibers are the T 100 PETP from Rhone-Poulenc, 6 mm, 17 dtex. 15

The final appearance of the plates shows fewer wrinkles than for a composition without a filler.

Test no. 13

The fibers are the T 100 PETP from Rhone-Poulenc, 6 mm, 3.3 dtex. 20

As in test 11, fewer wrinkles are found on the plates than in the case of the compositions without fillers.

Test no. 14

The fibers are a PTEP from MONTEFIBRE, with a length of 6 mm. 25

The reduction in wrinkles is less substantial than with the PTEP from Rhône-Poulenc and the percentage of ash in the fillers indicates a problem of filler retention.

Test no. 15

The fibers are DACRON PETP fibers from DUPONT DE NEMOURS, D157N, 6 mm, 7 dtex. 30

There were again found to be fewer wrinkles than in the case of the compositions without fillers.

Thus the addition of carbonate improves the surface appearance. 35

2.2. Comparative tests with PETP powder.

Test no. 16

The powder is the T 100 PETP from Rhône-Poulenc, with a particle size of less than 300 micrometers. 40

This test shows, with the fibers, a surface appearance improved in comparison to test no. 4, but with a noticeable reduction of the draining and a preheating time increased in comparison to test no. 11.

Test no. 17

The powder is the 64-38 PTEP from Kodak, with a mean particle size of 200 micrometers. 45

The wrinkles are analogous to those obtained with the compositions with Rhône-Poulenc fibers, but there are more dull specks.

This test also confirms the advantage of compositions with PETP fibers since in this case, the shorter preheating time is to allow for the smaller amount of material. 50

2.3. Compositions with other fillers

Taking into account the above comparative tests, and according to the invention, other mineral fillers have been tested with a PETP being in the form of T 100 PETP fibers from Rhône-Poulenc, 3mm, 17 dtex. 55

Test no. 18

The filler is OMYA Millicarb carbonate with a mean particle size of 1 to 2 micrometers. 60

Test no. 19

The filler is B038 carbonate from Blanc Minéraux de Paris, with a particle size of 10 to 12 micrometers. 65

In these last two tests, a few wrinkles are found to be present on the molded plates.

Test no. 20

The filler is no. 2 talc (hydrated magnesium silicate) from Talcs de Luzenac, with a means particle size of 12 micrometers.

The surface appearance is still better than in the case of the compositions with carbonates.

3. MOLDABILITY STUDY

The more complicated the articles, the more difficult is filling of the mold. For this reason, it may be useful to minimize the proportion of non-thermoplastic material. The fibers for reinforcing the finished product are essential, so it is of course preferable to reduce the proportion of reinforcing fibers necessary for manufacture.

Thus tests were carried out on compositions without mineral fillers for the purpose of evaluating the minimum proportion of cellulose fibers which has to be introduced in order to permit satisfactory production on a conventional paper machine or during the handling operations prior to molding, without detracting from the moldability.

From all these tests, we used the T 100 PETP polyester from Rhône-Poulenc, in the form of 6 mm fibers of 17 dtex, and R18DX9 glass fibers marketed by OWENS CORNING FIBREGLASS EUROPE, 6 mm, 11 micrometers.

Test no. 21

This is carried out with 10 parts by weight of cellulose, i.e. in parts by dry weight :

Cellulose fibers 10

Glass fibers 21.5

PETP 68.5

Test no. 22

This is carried out with 5 parts of cellulose :

Cellulose fibers 5

Glass fibers 21

PETP 74

Test no. 23 (comparative)

This is carried out with 2 parts of cellulose :

Cellulose fibers 2

Glass fibers 21

PETP 77

As regards the conditions of passage through the pilot machine and handling of the dry sheet, the composition with 5 parts of cellulose is found to have a very distinct advantage over the composition with 2 parts. The latter gives a sheet with very weak wet and dry cohesion and results in very significant flow of the thermoplastic material during preheating. This significant flow and the poor cohesion of the molten material make it impossible to densify it into a rigid sheet or to manipulate this material for placing it in the stamping mold. This type of composition is thus not industrial.

The composition with 5 parts of cellulose permits correct passage through the paper machine and is sufficiently strong to allow handling, cutting of the dry sheet and preheating without the material flowing.

In these three tests, we tested the ability of the material to fill a mold during the stamping operation. This involves the "ear mold" test which is well known in the composite materials trade.

The moldability values collated in Table III represent the distance, in degrees, travelled by the material in a circular direction. The attached diagram shows the plate 1 of which one edge 2 can extend circumferentially, during molding, to form an ear 3, the length of which is measured by a graduated scale 4 on the mold.

No difference in moldability is found between 2 and 5 parts of cellulose, which is surprising.

However as mentioned, compositions with cellulose fiber concentration less than about 3 parts by weight generally have inadequate handling strength during preheating prior to hot pressing.

These results justify our lower limit of the proportion of cellulose within the range of compositions given.

With regard to the upper limit of cellulose fiber content, this is set by the value which leads to a generally unacceptable water absorbance in the final product, i.e. about 15 parts by weight. Also at this value, the compositions become less readily mouldable, especially into parts of complicated shape.

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TABLE I
PASSAGE THROUGH PILOT MACHINE

Test no.	Weight (approx.) (g/m ²)	Water line (1)	Dilution (l/min)	Head (g/l)	White water (g/l)	Wet porosity on entering dry end (ml/min)	Dryness on leaving wire (before drying) (%)	Density after drying for 1/4 h at 80°C g/cm ³
1	800	18	24			6000	46.4	0.23
2	800	18	22					0.22
3	800	20	20					
4	800	18	5			6000	45.5	0.26
5	800	23	4	5.96	0.07			0.29
6	800	22	10					0.28
7	800	15	25		0.02			
8	800	17	25		0.02			
9	800	17	25		0.02			
10	800	15	20		0.02			
11	800	15	13			3750	50	0.21
12	800	15	13			3750	50	0.21
13	800	17	14	7.7	0.24			
14	800	15	13			6000	39.2	
15	600/800	8	8					
16	800	23	8		1.1	3300	48	0.30
17	800	20	5					0.36
18	300/400	14	22		0.8			
19	300/400	14	22		0.5	3825	47.4	
20	300/400	14	27			3715	47	
21	400	14	15					
22	400	10	27					
23	400	10	27					

Notes:

(1) The figures refer to the chain line at which the water line stops.

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TABLE II

CONVERSION BY PREHEATING BETWEEN PLATENS AT 300°C UNDER A PRESSURE OF 40 BAR

Test no.	Test conditions				Pressure on the samples (daN/cm ²)	Preheating time to reach 290° (at the core)	Observations
	A	B	C	D			
1	2	13 or 14	15 x 11	250 g	2.4	2 min 50 s	
2	1	12	d 18	250 g	3.2	5 min 55 s	
3	1	13	d 18	250 g	3.2	6 min 50 s/ 7 min 20 s	
4	2	16 or 17	15 x 11	250 g	2.4	3 min 50 s	
5	1	13	d 18	250 g	3.2	7 min 40 s/ 9 min 25 s	
6	1	13	d 18	250 g	3.2	7 min	
7	1	18	15 x 11	250 g	4.8	4 min to 4 min 15 s	very significant flow
8	1	18	15 x 11	250 g	4.8	stopped before 290°C	very significant flow
9	4	18	15 x 11	250 g	1.2	1 min	significant flow
10	1	18	15 x 11	250 g	4.8	7 min 40 s to 8 min 45 s	
11	2	18	15 x 11	270 g	2.4	3 min 10 s/ 3 min 20 s	
12	2	27	15 x 11	340 g	2.4	5 min 40 s to 6 min	
13	2	20	15 x 11	250 g	2.4	4 min 40 s	
14	2	21	15 x 11	250 g	2.4	3 min 30 s	
15	2	30	15 x 11	340 g	2.4	6 min to 6 min 30 s	
16	2	27	15 x 11	340 g	2.4	8 min/9 min	
17	2	18	15 x 11	270 g	2.4	3 min 50 s/ 4 min 10 s	
18	2	68	15 x 11	340 g	2.4	7 min 20 s	
19	2	57	15 x 11	340 g	2.4	7 min 10 s	
20	2	57	15 x 11	340 g	2.4	5 min 30 s/ 5 min 40 s	
21	2	43	15 x 11	340 g	2.4	5 min 30 s	
22	2	42	15 x 11	340 g	2.4	5 min	
23	2	51	15 x 11	340 g	2.4	not measurable	very significant flow

A: number of piles

C: size of the format in cm

D: total weight

B: total number of formats

d: diameter in cm (circular format)

TABLE III

Molding at 160°C under a pressure of 106 daN/cm² for 1 min 30 s

Test no.	Mold no.	Stack formats	Final appearance of the molded plates	Thickness (mm)	Density (g/cm ³)	CHARACTERISTICS OF THE PLATE			
						Ash (%)	Tensile stress (MPa)	Flexural stress (MPa)	Flexural modulus (MPa)
1	2	15 x 11	HO; RF	2.45	1.59	GLASS 21.7 - 23	60	125	7007
2	2	d 18	HO; RF	2.45	1.58	22.5 - 24.8	51	115	6390
3	2	d 18	HO; RF	2.45			50	136	7705
4	2	15 x 11	HO; RF	2.45		23 - 24.3	65	128	7012
5	2	d 18	HT; RF	2.35		30	44	110	6294
6	2	d 18	HO; RF	2.34		26.9	67	153	7632
7	2	ball	HO; RF	2.20		24.6	69	135	7752
8	2	-	(a)						
9	2	deformed	(b)						
10	2	15 x 11	HO; RF	2.45		23.3	63	127	6105
						FILLER/GLASS	44	97	6118
11	1	15 x 11	HO; RF	2.1	1.6	19.1 - 21.8	66	138	9352
12	1	15 x 11	RF to RF						
13	2	15 x 11	HO; RF	2.3	1.58	20.1 - 21.4	71	132	8126
14	2	15 x 11	RF to RF	2.3	1.54	11.3 - 22.4	78	159	8463
15	1	15 x 11	HO; RF	3.2	1.67	27.2 - 18.9	76	153	8597
16	1	15 x 11	RF	3.16	1.66	24.6 - 21.5	58	150	9199
17	1	15 x 11	RF	2.2	1.65	21.5 - 24	55	143	8930
18	1	15 x 11	HO; RF			10 - 24	47	135	8274
19	1	15 x 11	HO; RF	3.3	1.60	17.5 - 23	48	125	8265
20	1	15 x 11	HO; RO	3.1	1.64	24.7 - 19.4	54	117	8773
						GLASS			
21	1	15 x 11	HO; RF	3.65	1.53	28.8			
22	1	15 x 11	HO; RF	3.74	1.54	22.5			
23	1	15 x 11	HT; RF	3.77	1.50	21			

MOLDABILITY TESTS

90 degrees
160 degrees
160 degrees

HO: homogeneous appearance
HT: heterogeneous appearance
RF: tendency to form wrinkles
Rf: slight tendency to form wrinkles
RO: no apparent wrinkles

(a): no molding

(b): deformed formats: heterogeneous; rough; dull specks

d: diameter in cm (circular format)

Claims

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1. A wet laid fibrous web composition suitable for moulding into a reinforced thermoplastic product, comprising fibers for reinforcing the composition during its manufacture, fibers for reinforcing the moulded product, and a thermoplastic resin, said composition comprising the following in parts by dry weight (based on 100 parts of the first, second and third components combined) :

a) from 3 to 15 parts of a first component being fibers for reinforcing the composition during its manufacture.

b) a reinforcing amount of a fibrous second component effective for reinforcing the thermoplastic product formed by not molding the fibrous composition, and

c) a balance amount of a third component being fibers of a thermoplastic polyester, the first component having a molting or degradation temperature greater than the melting temperature of the third component.

2. A composition according to claim 1 which comprises from 4 to 8 parts, preferably from 4.5 to 6 parts by weight of the first component.

3. A composition according to claim 1 or 2 wherein the first component comprises cellulose.

4. A composition according to anyone of the preceding claims which comprises from 15 to 40 parts by dry weight of the second component.

5. A composition according to claim 4 which comprises from 18 to 27, preferably from 21 to 26 parts by weight of the second component.

6. A composition according to anyone of the preceding claims wherein the second component comprises glass fibers.

7. A composition according to claim 6 wherein the glass fibers have a length of from 6 to 50 mm, preferably from 6 to 25 mm.

8. A composition according to anyone of the preceding claims which comprises from 45 to 85 parts by weight of the third component.

9. A composition according to claim 8 which comprises from 58 to 79, preferably from 65 to 75 parts by weight of the third component.

10. A composition according to anyone of the preceding claims wherein the third component comprises polyethylene terephthalate.

11. A composition according to claim 1 which comprises from 3 to 15 parts of the first component from 18 to 17 parts of the second component and from 58 to 79 parts of the third component.

12. A composition according to anyone of the preceding claims wherein the melting or degradation temperature of the first component is at least 50 degrees C, preferably 65 degrees C greater than the melting temperature of the third component.

13. A composition according to anyone of the preceding claims which additionally includes a filler.

14. A composition according to claim 13 which contains from 20 to 45 parts by dry weight filler, based on 100 parts by dry weight of the first, second and third components combined.

15. A reinforced thermoplastic product comprising a fibrous composition according to anyone of the preceding claims, which has been subjected to a temperature of at least the melting temperature of the third component for a time sufficient to fuse the third component, followed by cooling under applied pressure.

16. A product according to claim 15 having a surface coating of a varnish, preferably a thermoset, thereon.

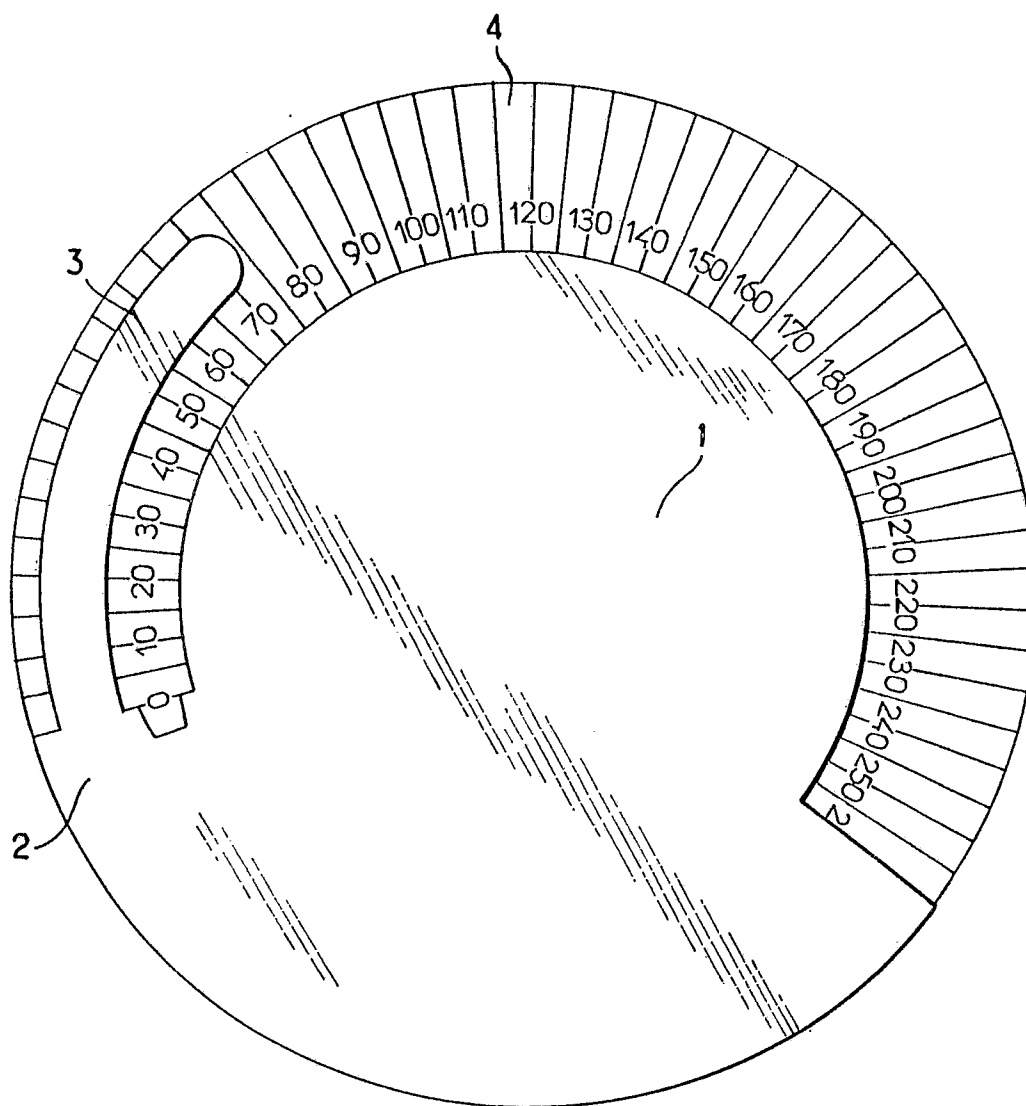
17. A method of producing a product according to claim 15 which comprises

1) pre-heating a fibrous web according to anyone of claims 1 to 14 to a temperature which is lower than the melting or degradation temperature of the first components, but greater than the melting temperature of the third component, to fuse the third component but retain the reinforcing effect of the first component, and

2) moulding the heated web under pressure and at a temperature which is lower than the melting temperature of the third component, to form the desired moulded product.

18. A method according to claim 17 wherein the web is preheated to a temperature at least 30 degrees C greater than the melting temperature of the third component.

19. A moulded article produced from the product according to claim 15 or 16 or by method of claim 17 or 18.





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,X Y	FR-A-2 507 123 (ARJOMARI-PRIOUX) * Claims 1-5,9,10; example 3 *	1,4,6-9 ,12,13, 15,17- 19	D 21 H 5/12 D 21 H 3/78 C 08 J 5/04
P,X Y	--- ABSTRACT BULLETIN, vol. 58, no. 4, 4th October 1987, page 563, abstract no. 5163, Appleton, WI, US; & JP-A-79 82 287 (JAPAN INORGANIC FIBER INDUSTRY CO., LTD) 13-04-1987 * Abstract *	1,3-6,8 ,11	
Y	--- GB-A-1 200 342 (IMPERIAL CHEMICAL INDUSTRIES) * Page 1; page 2, lines 9-30; examples II,III *	1,4,6, 10,15, 17-19	
Y	--- GB-A- 572 962 (SYLVANIA INDUSTRIAL CORP.) * Page 2, line 16 - page 5, line 79 *	1,3,6, 15,17- 19	
Y	--- FR-A-2 346 520 (IMPERIAL CHEMICAL INDUSTRIES) * Pages 1,2 *	1,3,12, 13,15, 17-19	TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 08 J D 21 H
A	--- EUROPEAN PLASTICS NEWS, vol. 3, nos. 7/8, July/August 1976, pages 25-27; "Thermoplastic polyesters- glass reinforced PBT leads the way" * Whole article, in particular page 27, left-hand column, paragraph 1 *	15-19	
A	--- EP-A-0 113 279 (SOCIETE CHIMIQUE DES CHARBONNAGES) * Page 1 *	16	
A	--- GB-A-2 070 092 (W.R. GRACE) --- -/-		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14-11-1988	Examiner NESTBY K.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D, A	WO-A-8 704 476 (BATTELLE MEMORIAL INSTITUTE) ---		
D, A	EP-A-0 039 292 (ARJOMAN-PRIOUX) ---		
A	EP-A-0 151 448 (MISHIMA PAPER) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14-11-1988	Examiner NESTBY K.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			