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(54) Title: BALLISTIC-RESISTANT ARTICLES AND METHOD OF MANUFACTURE THEREOF (57) Abstract A ballistic-resistant article of manufacture which comprises an agglomerated web of two types of discrete fibers. The first type is a fiber formed from polyolefin filament having, in the case of polyethylene filament, a weight average molecular weight of at least about 500,000, a tensile modulus of at least about 300 g/denier and a tenacity of at least about 15 g/denier, and in the case of polypropylene filament, a weight average molecular weight of at least 750,000, a tensile modulus of at least about 160 g/denier and a tenacity of at least about 8 g/denier. The second type is a high density polyolefin fiber having an average fiber length substantially shorter than the first type. The article has a sufficient thickness to absorb the energy of a projectile.		

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BALLISTIC-RESISTANT ARTICLES
AND
METHOD OF MANUFACTURE THEREOF

BACKGROUND OF THE INVENTION

5 The present invention relates to ballistic-resistant articles of manufacture, as well as to a method of manufacture thereof. The ballistic-resistant articles of the present invention comprise high strength polyolefin fibers.

10 Ballistic-resistant articles formed from high strength polyolefin fibers are known from a series of U.S. Patents assigned of record to Allied Corporation. These are:

	<u>Harpell et al</u>	U.S. Patent No. 4,403,012
15	<u>Harpell et al</u>	U.S. Patent No. 4,457,985
	<u>Harpell et al</u>	U.S. Patent No. 4,501,856
	<u>Harpell et al</u>	U.S. Patent No. 4,623,574
	<u>Harpell et al</u>	U.S. Patent No. 4,650,710; and
	<u>Harpell et al</u>	U.S. Patent No. 4,681,792.

20 Another Allied Corporation patent directed to high strength polyethylene fiber is Kavesh et al, U.S. Patent No. 4,413,110.

 These patents describe ballistic-resistant articles of manufacture comprising a flexible network
25 of polyolefin fibers having, in the case of polyethylene filament, a weight average molecular weight of at least about 500,000, a tensile modulus of at least about 300 g/denier and a tenacity of at least about 15 g/denier, and in the case of polypropylene
30 filament, a weight average molecular weight of at least

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750,000, a tensile modulus of at least about 160 g/denier and a tenacity of at least about 8 g/denier, said fibers being formed into a network of sufficient thickness to absorb the energy of a projectile.

5 As will be discussed hereinafter, the filament described in the above patents is a preferred ingredient for use in forming the ballistic-resistant articles according to the present invention. Accordingly, the disclosure of the above patents is
10 hereby expressly incorporated by reference, to the extent not inconsistent herewith.

Other patents of general interest with respect to ballistic-resistant articles include Zeglen, U.S. Patent No. 604,870, and Hawkinson, U.S. Patent No.
15 4,428,998.

The Harpell et al patents listed above are directed to ballistic-resistant articles formed by winding a continuous filament of the high strength polyethylene around a steel plate to form a network of
20 parallel fibers. This construction was found to be superior to KEVLAR (trademark of Dupont for aramid yarn) in arresting projectile penetration.

There remains a need, however, for ballistic-resistant articles capable of arresting projectile
25 penetration more effectively than those discussed above at a given basis weight of ballistic-resistant material, or, correspondingly, that are equally as effective at a lower basis weight.

SUMMARY OF THE INVENTION

30 A major object of the present invention is to provide ballistic resistant articles of manufacture that offer improved penetration resistance as compared to ballistic-resistant articles of the prior art.

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Another object of the invention is to provide a method for manufacturing such ballistic-resistant articles that is easily adapted to an industrial scale, preferably by modifying conventional processing apparatus.

A further object of the present invention is to provide ballistic resistant articles that offer penetration resistance equal to articles of the prior art, but at significantly lower material basis weight, thereby greatly expanding the useful applications for such articles.

These and other objects according to the present invention are accomplished by ballistic resistant articles having as a principal ingredient the high strength polyolefin filament discussed above, but in which that filament has been converted to discrete fibers of a much shorter and definite length, and in which those discrete fibers have been formed into an agglomerated web together with a minor amount of much shorter polyolefin fibers.

The ballistic resistant articles according to the present invention are preferably formed by conventional papermaking techniques. In this manner, a uniform web of the high strength fibers can be readily generated, and the process can be carried out on an industrial scale without extensive original plant design.

It has been found that an agglomerated web of the high strength Allied fiber alone does not offer significantly improved penetration resistance. Instead, it is necessary to form the web with a minor amount of a much shorter, high density polyolefin fiber such as that marketed commercially under the trademark PULPEX (trademark of Hercules Inc., a Delaware Corporation, for high density polyethylene pulp having

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an average fiber length of 0.6 - 1.2 mm, made water-dispersible with polyvinyl alcohol treatment).

Accordingly, the present invention relates in one aspect to ballistic resistant articles of manufacture comprising an agglomerated web of discrete fibers formed from (1) polyolefin filament having, in the case of polyethylene filament, a weight average molecular weight of at least about 500,000, a tensile modulus of at least about 300 g/denier and a tenacity of at least about 15 g/denier, and in the case of polypropylene filament, a weight average molecular weight of at least 750,000, a tensile modulus of at least about 160 g/denier and a tenacity of at least about 8 g/denier; and (2) high density polyolefin fibers having an average fiber length of about 0.5 to about 1.5 mm; said article having a sufficient thickness to absorb the energy of a projectile.

In another aspect, the present invention relates to a process for making such ballistic-resistant articles, in which an aqueous slurry of the two types of fibers is de-watered on a wire screen, to form the agglomerated web according to the invention.

BRIEF DESCRIPTION OF THE DRAWING

The Figure of the drawing graphically depicts the experimental results of Table 1.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE PRESENT INVENTION

A high strength polyolefin filament such as that described in the aforementioned Allied patents is converted, for use in the present invention, to fibers having a length from about 0.5 to about 1.5 inches,

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preferably from about 0.5 to about 1 inch, and optimally about 0.75 inch (referred to hereinafter as "long fiber"). This fiber is then formed into an aqueous slurry together with a lesser amount of high density polyethylene fiber having an average fiber length of about 0.5 to about 1.5 mm, preferably about 0.6 to about 1.2 mm (referred to hereinafter as "short fiber"). The slurry is then converted to an agglomerated web, for example by using a Fourdrinier wire and appropriate suction rolls.

Experimentation with the relative amounts of long fiber and short fiber, as will be set forth hereinafter, has revealed the optimum composition to be one containing from about 75 to about 85% long fiber and from about 15 to about 25% short fiber. Compositions containing from about 65 to about 95% long fiber and from about 5 to about 35% short fiber, however, are also within the scope of the invention. Moreover, because various additives may be included in the formulations according to the invention, the optimum ratio of long fiber to short fiber may also be expressed as preferably 65 to 95 parts long fiber to 35 to 5 parts short fiber, more preferably 75 to 85 parts long fiber to 25 to 15 parts short fiber.

The ballistic-resistant articles according to the invention are formed using conventional papermaking techniques, such as passing an aqueous slurry of the admixed long and short fibers onto an endless wire screen, followed by dewatering and drying of the thus-formed sheet. The sheet is then heat-treated with or without pressure as is known to those skilled in the paper-making art. The heat treatment is generally of sufficient temperature and pressure to melt or sinter the short fiber, which results in a bonding of the long

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fibers. It will be appreciated that in such process, what might otherwise be a conventional technique interacts with the materials employed to form a resultant product having properties of penetration
5 resistance that could not have been predicted from the starting materials and technique alone.

It is also contemplated to form the agglomerated web by a hydroentangling process. Hydroentangling is a process for producing nonwoven fabrics by impinging a
10 plurality of fine columnar streams of a fluid, such as water or air, onto a fibrous web carried by an apertured or patterned conveying means. There is thus produced a felt-like material in which even relatively short fibers can be mechanically intertwined without
15 the damaging effects of needling. One example of a patent describing hydroentangling is U.S. Patent No. 3,485,706, the disclosure of which is hereby expressly incorporated by reference, to the extent not inconsistent herewith. In this patent, an apertured
20 hydroentangled fabric is produced wherein the apertures in the fabric correspond to knuckles in the wire screen used to support and convey the fibrous web. Patterned supporting means are disclosed for imparting to the resulting hydroentangled fabric a desired ornamental
25 appearance.

A series of experimental handsheets were prepared, whose formulations were both within and without the scope of the present invention, and subjected to ballistic testing to determine their
30 penetration resistance. The handsheets were prepared by dewatering an aqueous slurry of the constituent ingredients, to form an agglomerated web, followed by drying on a steam-heated drum and bonding in a 130°C oven for ten minutes. The handsheets thus formed

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measured 8 inches by 8 inches square, and were formed so as to have a basis weight of 60 pounds per 3000 square feet. The basis weight of a specimen to be subjected to ballistic testing could easily be increased 2, 4 or 8 times by folding one of these sheets once, twice or three times, respectively. The specimens tested thus tend to have basis weights increasing by multiples of eight, because the basis weight of a specimen was generally increased by adding an additional 8 inch by 8 inch sheet that had been folded three times.

The specimens tested were backed either by plywood or by clay. The first tests were run with plywood as the backing. When plywood backing was used, the plywood had a hole formed where the bullet was expected to pass (or not pass, depending on whether the specimen stopped the bullet). Clay backing was also used, primarily since modeling clay is the backing used for determining the ballistic resistance of body armor (U.S. Department of Justice - National Institute of Justice, NIJ Standard 0101.03).

The firing was done with a .22 caliber rifle using Winchester high velocity .22 caliber long rifle bullets. According to literature published by Winchester, the muzzle velocity of these bullets is about 1440 feet per second. The target was located about three feet from the muzzle of the rifle.

The results of these experiments are listed in Table 1 below. In Table 1, the term "Spectra" is a trademark of Allied Corporation for high strength polyethylene as described in the Harpell et al patents, whereas the term "Pulpex" is a trademark of Hercules Corporation for their short fiber polyethylene synthetic pulp. The Pulpex was used in its

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commercially available form, whereas the Spectra filament was modified by chopping it to form fibers having an average length of about 0.75 inch. All number entries are percent by weight, except for

5 "Basis Weight", which is in units of lb/3000 ft², and refers to the basis weight of the specimen tested.

TABLE 1

	Ex.	Spectra	Pulpex	Other Additives	Basis Weight	Pene- tration
10	1	50	25*	25 Albacel ¹	2880	N
	2	"	"	"	2400	N
	3	"	"	"	1920	P
	4	"	50	-	1440	P
	5	"	"	-	1920	P
15	6	"	"	-	3360	P
	7	"	"	-	3840	P
	8	"	"	-	4800	N
	9	"	"	-	5760	N
	10	60	40	-	1440	P
20	11	"	"	-	1920	P
	12	"	"	-	2400	P
	13	"	"	-	2880	P
	14	"	"	-	3840	P
	15	"	"	-	4800	N
25	16	"	20	20 CA ²	1920	N
	17	"	"	"	1440	P
	18	64	21	15 CA	1920	N
	19	"	"	"	1440	N
	20	68	22	10 CA	1920	N
30	21	"	"	"	1440	P
	22	70	30	-	1440	P, P, N, N
	23	"	"	(dry)	1680	N
	24	"	"	(wet)	1680	P
	25	"	"	dry, heat pressed	1680	N

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	26	"	"	wet; heat pressed	1680	P
	27	"	"	add'l 20% EL ³	1440	P
	28	"	"	"	1920	P
	29	"	"	"	1440	P
5	30	"	"	"	1688	P
	31	"	"	"	1920	P
	32	70	25*	5 AL	1920	N
	33	"	"	"	1440	P
	34	"	25	5 AP ⁴	960	P
10	35	"	"	"	1440	N
	36	"	"	5 KF ⁵	960	P
	37	"	"	"	1440	N
	38	"	10*	20 AL	1920	N
	39	"	"	"	1440	N
15	40	"	"	"	960	P
	41	"	20*	10 AL	1920	N
	42	"	"	"	1440	N
	43	"	22*	3 AL, 5 M ⁶	1440	N
	44	"	25	5 CA	1440	N,P
20	45	"	"	5 M	1440	P,N
	46	"	30	SC ⁷	1920	P
	47	"	"	"	1680	P
	48	"	"	"	1440	P
	49	71	24	5 CA	1440	N
25	50	"	"	"	960	N,P,P
	51	75	25	-	1440	N
	52	"	"	-	960	P
	53	80	20	-	1440	N,N,P
	54	"	"	-	960	P,P,N
30	55	85	15	-	1440	N
	56	"	"	-	960	P,P

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57	90	10	-	1440	P,P,N
58	"	"	-	1920	N
59	"	"	-	960	P
60	"	"	-	480	P

- 5 Notes: * Pulpex grade A321 - "bondable" pulp, treated to have increased hydrogen bonding;
otherwise, Pulpex grade ED (unmodified)
- 10 1. Albacel southern softwood kraft pulp
2. Cellulose acetate fibrit (Celanese Corp'n)
3. Elastoplast resin added as saturant, about 20% pick up
4. Apyeil (Japanese aramid fibrid)
- 15 5. Kevlar Fibrid
6. Microfibrillated cellulose from ITT
7. Caschem - a surfactant based on a castor oil soap (glycerol monoricinolate CAS-1323382),
- 20 0.5 g/handsheet added for formation improvement

In the above table, "N" indicates that the bullet was stopped by the specimen, whereas "P" indicates that the bullet passed through the specimen. Where more than one designation appears, it indicates that the testing was performed a plurality of times. When a clay backing was used, the bullet would sometimes penetrate fairly deeply into the clay backing, yet fail completely to rupture the paper-like structure of the specimen. Nevertheless, if the bullet penetrated more than 0.75 inch into the clay backing, the result was judged "P". The results of these tests are somewhat qualitative, because the clay backing appeared to

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improve slightly the performance of the specimen.

The data of Table 1, for handsheets containing mixtures of Spectra type fiber and Pulpex fiber, may be represented graphically, as is shown in the accompanying Figure, by plotting increasing long fiber/decreasing short fiber percentage on the abscissa, and total basis weight of specimen on the ordinate. From this Figure, it appears that a composition range of 75-85% long fiber to 15-25% short fiber is optimum for use in the invention.

A number of interesting observations can be made from the above table. If the tensile strength of varying long fiber/short fiber compositions is calculated, it appears that specimens with a very high tensile strength required a much higher basis weight per specimen to display penetration resistance, as compared to specimens with a much lower tensile strength. This is shown below in Table 2, where there are listed the minimum basis weights at which each of a variety of long fiber/short fiber compositions displayed penetration resistance.

TABLE 2

	Long Fiber/ short fiber	50-50	60-40	70-30	80-20	90-10
25	Bullet Penetration	NO	NO	NO	NO	NO
	Total basis weight	4800	4800	1440	960	1440
	Tensile, lb/in	2800	2850	567	256	144
30	Basis weight long fiber	2400	2880	1008	778	1296

It is indeed surprising how poorly the 50-50 composition fared in penetration resistance, as it has

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has the highest tensile strength of the specimens listed. This is entirely contrary to the teaching of the prior art, notably the Harpell et al patents and Kevlar ballistic-resistant articles, where high
5 tensile strength is taught to be directly related to increased penetration resistance.

The explanation for these discrepant results is that the present invention operates on an entirely different principle than the prior art discussed above,
10 owing to its unique structure and attendant properties. In the Harpell et al patents, and in woven Kevlar fabrics, when a bullet strikes the wound or woven filament, the kinetic energy of the bullet causes the filament to rupture. By contrast, in the present
15 invention, the filament is present as relatively short fibers in a randomly oriented paper-like agglomeration. When a bullet strikes this structure, the predominant mechanism is one in which the relatively short fibers are caused not to rupture, but rather to be pulled out
20 from the entangled paper-like structure. It has been found that more kinetic energy is consumed by pulling a fiber out of an entangled structure than by rupturing a fiber.

This can be demonstrated by a kinetic energy
25 calculation comparing a specimen according to the present invention (identical to Example 22 of Table 1, but having a slightly higher total basis weight of 1488 lb/300 ft²) with the best performing fabric disclosed in Harpell et al, U.S. Patent No. 4,650,710, as well as
30 a another ballistic article prepared according to the teaching of this same patent. The fabrics from Harpell '710 are those designated Examples F-1 and F-5, appearing in Table 1B at column 9, lines 20-30. It should be further noted that the data used for the wet

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laid nonwoven structure of the present invention is for no bullet penetration, while the data of Harpell et al is for 50% bullet penetration.

Calculations

- 5 1. Ballistic resistant article according to the present invention:

Specimen basis weight = 1488 lb/ream or 2.427 kg/m²

10 Long fiber basis weight = 1041 lb/ream or 1.7 kg/m²

Velocity, no penetration = 1250 ft/s = 381 m/s

Bullet = 40 grains = 2.592 g = 0.002593 kg

Kinetic energy = $\frac{1}{2} mv^2 = (0.5)(0.002593)(381)^2$
= 188 kg m²/s²

15 Kinetic energy/specimen basis weight = 188/2.427
= 78 Joules/(kg/m²)

Kinetic energy/long fiber basis weight = 188/1.7
= 111 Joules/(kg/m²)

- 20 2. Example F-1 according to Harpell '710 (best-performing):

Fabric basis weight = 1079 lb/ream or 1.76 kg/m²

Velocity, 50% penetration = 1318 ft/s = 402 m/s

Bullet = 19 grain fragment = 0.0012312 kg

25 Kinetic energy = $\frac{1}{2} mv^2 = (0.5)(0.0012312)(402)^2$
= 99.4 kg m²/s²

Kinetic energy/fabric basis weight = 99.4/1.76
= 56 Joules/(kg/m²)

- 30 3. Example F-5 according to Harpell '710:

Fabric basis weight = 3008 lb/ream or 4.95 kg/m²

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Bullet = 19 grain fragment = 0.0012312 kg

$$\text{Kinetic energy} = \frac{1}{2} mv^2 = (0.5)(0.0012312)(406^2)$$
$$= 101.6 \text{ kg m}^2/\text{s}^2$$

Kinetic energy/fabric basis weight = 101.6/4.95

$$5 = 21 \text{ Joules}/(\text{kg}/\text{m}^2)$$

The above comparison shows that a given basis weight of the same type of filament as used in the Harpell et al patents, when present as relatively short fibers in a paper-like agglomeration according to the present invention, absorbs nearly twice the kinetic energy as the most preferred use disclosed by the teaching of the prior art.

While the present invention has been described in connection with various preferred embodiments thereof, it will be appreciated that it should not be construed to be limited thereby. Modifications remain possible, without departing from the scope and spirit of the appended claims.

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CLAIMS:

1. A ballistic-resistant article of manufacture, comprising an agglomerated web of discrete fibers including (1) a first type of fiber formed from
5 polyolefin filament having, in the case of polyethylene filament, a weight average molecular weight of at least about 500,000, a tensile modulus of at least about 300 g/denier and a tenacity of at least about 15 g/denier, and in the case of polypropylene
10 filament, a weight average molecular weight of at least 750,000, a tensile modulus of at least about 160 g/denier and a tenacity of at least about 8 g/denier; and (2) a second type of fiber, comprising high density polyolefin fibers having an average fiber length
15 substantially shorter than said first type; said article having a sufficient thickness to absorb the energy of a projectile.

2. The ballistic-resistant article of Claim 1, wherein said first type of fiber has an average length
20 of about 0.5 to about 1.5 inches (about 12.7 mm to about 38.1 mm).

3. The ballistic-resistant article of Claim 2, wherein said first type of fiber has an average length of about 0.5 to about 1 inch (about 12.7 mm to about
25 25.4 mm).

4. The ballistic-resistant article of Claim 3, wherein said first type of fiber has an average length of about 0.75 inch (19.05 mm).

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5. The ballistic-resistant article of Claim 1, wherein said second type of fiber has an average length of about 0.5 to about 1.5 millimeters.

6. The ballistic-resistant article of Claim 5, wherein said second type of fiber has an average length of about 0.6 to about 1.2 millimeters.

7. The ballistic-resistant article of Claim 1, comprising about 65 to about 95 % by weight of said first type of fiber, and about 5 to about 35 % by weight of said second type of fiber.

8. The ballistic-resistant article of Claim 7, comprising about 75 to about 85 % by weight of said first type of fiber, and about 15 to about 25 % by weight of said second type of fiber.

9. The ballistic-resistant article of Claim 2, comprising about 65 to about 95 parts by weight of said first type of fiber, and about 5 to about 35 parts by weight of said second type of fiber.

10. The ballistic-resistant article of Claim 9, comprising about 75 to about 85 parts by weight of said first type of fiber, and about 15 to about 25 parts by weight of said second type of fiber.

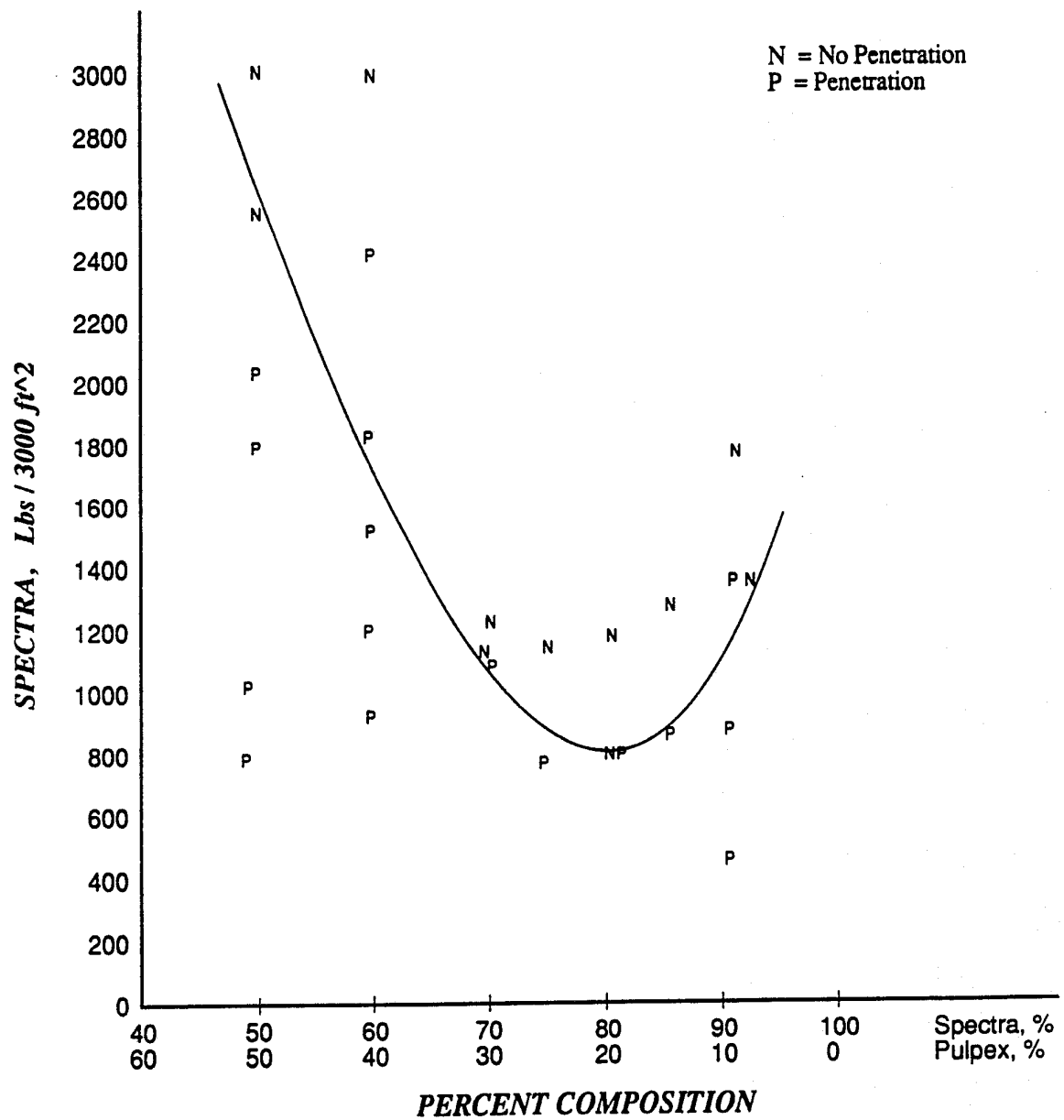
11. A process for making the ballistic-resistant article of Claim 1, comprising de-watering an aqueous slurry of said first and second types of fibers on a wire screen, thereby to form the said agglomerated web.

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12. The process of claim 11, wherein the agglomerated web is heat-treated to sinter or melt the second type of fiber to thereby result in a bonding of the first type of fiber.

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Figure



SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/05137

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. (5): B32B 27/34		
U.S. CL. 428/288, 296, 911		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
U.S.	428/288, 296, 911	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 4,808,467 (SUSKIND) 28 FEBRUARY 1989 See the entire document.	1-12
<p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
11 NOVEMBER 1990	26 DEC 1990	
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