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(54) COPOLYAMIDES CONTAINING CAPROLACTAM,
 LAURICLACTAM AND 11-AMINOUNDECANOIC ACID

(71) We, PLATE BONN GESELLSCHAFT MIT BESCHRANKTER
 HAFTUNG, a body corporate organised under the Laws of Germany, of 53 Bonn,
 Dransdorfer Weg 21, Federal Republic of Germany, do hereby declare the invention,
 for which we pray that a patent may be granted to us, and the method by which it is
 to be performed, to be particularly described in and by the following statement:—

This invention relates to copolyamides containing caprolactam, lauric lactam and
 11-aminoundecanoic acid together with further polyamide-forming components as
 basic units, to a process for producing these copolyamides and to their use for heat-
 sealing.

Copolyamides of the basic units caprolactam, lauric lactam and 11-aminoundecanoic
 acid are known from German Offenlegungsschrift No. 1,595,591. In melt form, these
 ternary polyamides show high bond strength which is used in the textile industry
 for heat-sealing fabrics. In addition to high bond strength, these copolyamides show
 high resistance to solvents of the kind used for dry-cleaning textiles, and to the washing
 temperatures of up to about 80° C. normally encountered in the textile industry.
 Unfortunately, this resistance is largely governed by a high content of lauric lactam
 and/or 11-aminoundecanoic acid. Although the resistance of the copolyamides to wash-
 ing at elevated temperatures increases with increasing content of these basic units, their
 melting temperature is also increased with the result that conventional copolyamides
 cannot be used for heat-sealing temperature-sensitive substrates such as leather, tem-
 perature-sensitive natural and/or synthetic materials, non-woven fabrics, felts, tufted
 fabrics and the like. Substances melting below about 115° C., below 110° C. or even
 below 105° C., are required for heat-sealing temperature-sensitive substrates of this kind

The object of the invention is to find substances which are suitable for heat-sealing
 temperature-sensitive substrates, show high bond strength at low sealing temperatures and
 during subsequent cooling and which nevertheless are highly resistant to chemical
 cleaning agents.

The invention relates to copolyamides containing units derived from caprolactam,
 lauric lactam, 11-aminoundecanoic acid and a unit derived from a hexamethylene diamine
 salt of an aliphatic dicarboxylic acid of the formula



in which n is the number 4, 7, 8, 10 or 11, the monomers being incorporated in the
 copolymer by polymerisation in the following proportions:

caprolactam	20—40% by weight
lauric lactam	20—35% by weight
11-aminoundecanoic acid	15—35% by weight
hexamethylene diamine salt of the acid of formula (I)	15—40% by weight

The invention also relates to a process for producing such copolyamides dis-
 tinguished by the fact that the aforementioned monomers and, as additional comonomer

a hexamethylene diamine salt of an aliphatic dicarboxylic acid, corresponding to the formula (I) in which n is 4, 7, 8, 10 or 11, are polymerised under pressure at elevated temperature in the following quantitative proportions:

5	caprolactam	20—40% by weight	
	laurilactam	20—35% by weight	5
	11-aminoundecanoic acid	15—35% by weight	
	hexamethylene diamine salt of the acid of formula (I)	15—40% by weight	

by methods known per se.

10 The copolyamides defined above are used for heat-sealing. Surprisingly, they have an extremely low melting point of below 110° C., generally below 100° C. and, in some cases, even below 90° C. Despite these low melting points, they show extremely high bond strength after heat-sealing at elevated temperature and, on the other hand, a high resistance to chemical cleaning agents, i.e. solvents and cleaning agents of the kind added to aqueous cleaning solutions. Accordingly, substrates heat-sealed with the copolyamides according to the invention show high resistance to water-containing cleaning agents, even at elevated washing temperatures.

15 Accordingly, the copolyamides according to the invention can be used with advantage for heat-sealing temperature-sensitive substrates.

20 Copolyamides of the kind whose monomers are incorporated in the copolymer in the following proportions:

	caprolactam	25—35% by weight	
	laurilactam	~30% by weight	
	11-aminoundecanoic acid	18—25% by weight	
25	hexamethylene diamine salt of the acid of formula (I)	15—30% by weight	25

are preferred for the purposes of the invention. The following quantitative proportions are particularly preferred:

	caprolactam	~30% by weight	
30	laurilactam	~30% by weight	30
	11-aminoundecanoic acid	~20% by weight	
	hexamethylene diamine salt of the acid of formula (I)	~20% by weight	

The acids of general formula (I) have the following names:

35	$n=4$, adipic acid	35
	$n=7$, azelaic acid	
	$n=8$, sebacic acid	
	$n=10$, dodecane dicarboxylic acid	
	$n=11$, brassylic acid.	

40 The acids of formula (I) in which n is 4, 7, 8 or 10 are particularly preferred for the purposes of the invention, acids in which n is 7 or 8 being most particularly preferred because they are readily available commercial products and lead to copolyamides which can be used with particular advantage for heat-sealing.

45 According to the invention, the copolyamides are produced by methods known per se. As in the production of C12-polyamide from laurilactam, temperatures of from 280 to 300° C., preferably of about 290° C., and pressures of from 10 to 50 atms, preferably from 15 to 30 atms, are generally used. Polymerisation is continued for several hours under these conditions and is preferably followed by after-condensation for a few hours, preferably for 1 to 3 hours, at 250 to 300° C. The catalysts, chain terminators and/or other additives and the process conditions normally used for the polymerisation of laurilactam are employed. More particularly, polymerisation is best carried out in the absence of air, i.e. in an inert gas atmosphere. The copolyamides according to the invention are preferably used for heat-sealing in the form of fine powders which are applied to the substrates to be bonded. A suitable viscosity of the copolyamide where it is used for the production of films is best in the range from

1.4 to 1.5. This number denotes the relative viscosity of a 0.5% wt/vol solution of the copolyamide in *m*-cresol at 25° C.

The copolyamides used in accordance with the invention can contain other additives, for example dyes, in the usual way.

The copolyamides used in accordance with the invention are copolymers which are formed during the polymerisation of a mixture of the polyamide formers. The basic units are condensed into the polymer chain in statistical distribution. The surprising effects described are not obtained in cases where the polyamide formers are polymerised separately and then melted together.

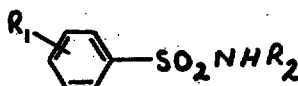
The copolyamides according to the invention can also have small quantities of other polyamide formers condensed into them.

For reasons of ready accessibility and satisfactory reproducibility of production to form copolyamides with uniform properties, it is generally not advisable to add further polyamide formers.

It is possible by means of the copolyamides according to the invention to bond substrates of many different kinds, particularly temperature-sensitive substrates to substrates of the same or different type. A copolyamide according to the invention is preferably introduced in the form of powder between the surfaces to be bonded. The copolyamide can of course also be used in the other forms, for example films, filaments or chopped filaments. The substrates are then pressed at elevated temperature. The pressing temperature is governed primarily by the temperature-sensitivity of the substrate. Since the copolyamides according to the invention develop outstanding bond strength even at very low sealing temperatures of, for example, from about 100 to 130° C. or up to 150° C. in dependence upon their melting range, it is possible to apply extremely low sealing temperatures. Cooling to room temperature is accompanied by hardening so that the bonded substrates are firmly united. There is no need for drying or evaporation of solvents.

The copolyamides according to the invention in the form of powders can be applied to a substrate to be bonded, for example by the powder coating machines normally used in the coating industry. In this connection, it is also possible to coat only selected areas of the substrate surface with the copolyamide powder according to the invention. Examples of substrates to be bonded include textiles of natural materials and/or synthetic materials such as wool, silk, cotton and polyesters or polyamides. Other temperature-sensitive substrates such as leather and plastics films can also be heat sealed using the copolyamides according to the invention.

The copolyamides according to the invention can be mixed with plasticisers before they are used. Examples of suitable plasticisers are sulphonic acid derivatives corresponding to the following formula



II

in which R_1 represents hydrogen or methyl and R_2 represents hydrogen, an alkyl group containing 1 to 6 carbon atoms or cyclohexyl group.

Benzene or toluene sulphonic acid ethylamide is particularly preferred. Corresponding commercial products are available. These commercial products are, for example, mixtures of *p*- and *o*-toluene sulphonic acid alkylamides. Phenolcarboxylic acid or alkylesters thereof can also be used for plasticisation. Examples of plasticisers of this kind are butyl-*p*-hydroxybenzoate, lauryl-*p*-hydroxybenzoate, *p*-hydroxybenzoic acid, octyl-*p*-hydroxybenzoate. Bisphenol A and similar compounds can also be used as plasticisers. It is of course necessary to employ plasticisers of the kind which are compatible with and suitable for the particular copolyamides used, as any expert will know. The plasticisers can be incorporated in the copolyamides by mixing them with the copolyamides, followed by heating to temperatures above the melting point. They can be extruded for example at these temperatures in order to obtain suitably shaped articles such as filaments, films and the like. Powders can also be prepared.

In cases where the copolyamides are used in the form of powders, it is of advantage in some cases to disperse these copolyamide powders in aqueous dispersions, to apply the resulting dispersions, for example, to textiles to be bonded with one another, more especially interlinings for articles of clothing, for example by point coating, subsequently to dry, sinter and fix the textiles thus coated and to heat-seal them with the fabrics to be bonded, for example by ironing the textiles with irons or with ironing

presses (cf. for example German Patent No. 2,007,971 and German Auslegeschrift No. 2,229,308). The dispersions generally contain thickeners and stabilisers for producing stable dispersions. It is possible to use thickeners and stabilisers of the kind known to any expert, for example polymeric organic acids and long-chain fatty acids containing up to 34 carbon atoms. The dispersions are preferably made weakly alkaline. In cases where dispersions of this kind are used, it is particularly preferred to add the plasticisers as an additional component to the dispersions, rather than to melt them with the copolyamides, as described above.

In either case, the plasticisers can be used in a quantity of up to 50% by weight of the total quantity of copolyamide and plasticiser. It is particularly preferred to use the plasticiser in a quantity of up to 25% by weight, based on the total quantity of copolyamide and plasticiser.

It has already been pointed out that the copolyamides according to the invention can also contain dyes or other usual additives. In this respect, the copolyamides can contain, for example, conventional antioxidants, flameproofing agents and, in particular, optical brighteners and agents which impart fluorescence. A large number of agents of this kind, which are available as commercial products, are known to the expert. It is of course necessary to use additives of the kind which are stable at the heat-sealing temperatures applied.

EXAMPLE 1.

300 parts by weight of caprolactam, 200 parts by weight of 11-aminoundecanoic acid, 300 parts by weight of laurilactam, 200 parts by weight of AH-salt (adipic acid hexamethylene diamine salt) and 12 parts by weight of adipic acid as polymerisation-degree regulator, are weighed into an autoclave equipped with stirring mechanism, a gas inlet and a gas outlet. The atmospheric oxygen present inside the autoclave is removed by repeated rinsing under pressure with purified nitrogen.

The reaction mixture is heated to 290° C. and the increasing pressure inside the autoclave limited to 25—30 atms by correspondingly setting the valve. The reaction mixture is stirred for 3 hours under these conditions. The pressure is then reduced to normal pressure over a period of 2 hours.

The reaction mixture is then aftercondensed with stirring for 2 hours in the absence of pressure under a gentle stream of nitrogen.

On completion of the pressure-free aftercondensation phase, the temperature is lowered to 160—180° C. and the melt spun through a nozzle in the form of a monofil by means of a gear pump, cooled and granulated.

The resulting granulates have a melting range of from about 90 to 95° C., as measured on a KOFLER heating-stage microscope.

EXAMPLE 2.

The following polyamide-forming monomers are reacted under the polycondensation conditions described in Example 1: 200 parts by weight of caprolactam, 250 parts by weight of 11-aminoundecanoic acid and 250 parts by weight of laurilactam, 300 parts by weight of 6,10-salt, 12 parts by weight of adipic acid. The resulting copolyamide has a melting range of from about 85 to 90° C., as measured on a KOFLER heating-stage microscope.

EXAMPLE 3.

A copolyamide is prepared from the following components in the same way as described in Example 1: 250 parts by weight of caprolactam, 250 parts by weight of 11-aminoundecanoic acid, 250 parts by weight of laurilactam, 250 parts by weight of the salt of azelaic acid and hexamethylene diamine, 12 parts by weight of adipic acid. A copolyamide with a melting range of from about 84 to 88° C. is obtained.

EXAMPLE 4.

The following monomer combination: 350 parts by weight of caprolactam, 200 parts by weight of 11-aminoundecanoic acid, 300 parts by weight of laurilactam, 150 parts by weight of 6,12-salt and 12 parts by weight of adipic acid, gives a copolyamide with a melting range of 95 to 105° C. under the same polycondensation conditions as in Example 1.

EXAMPLE 5.

A copolyamide with a melting range of 90 to 100° C. is obtained from the following components under the same polycondensation conditions as in Example 1: 300

parts by weight of caprolactam, 300 parts by weight of 11-aminoundecanoic acid, 200 parts by weight of laurilactam, 200 parts by weight of 6,13-salt, 12 parts by weight of adipic acid.

EXAMPLES 6 to 21.

Copolyamides were prepared from the starting components specified in Table 1 below in accordance with the procedure described in Example 1. The following abbreviations were used:

5	6	=	caprolactam	5
	11	=	11-aminoundecanoic acid	
10	12	=	laurilactam	10
	6,6	=	AH-salt (adipic acid hexamethylene diamine salt)	
	6,9	=	hexamethylene diamine azelaic acid salt	
	6,10	=	hexamethylene diamine sebacic acid salt	
	6,12	=	hexamethylene diamine dodecane dicarboxylic acid salt	
15	6,13	=	hexamethylene diamine brassylic acid salt	15

The melting temperatures of the copolyamides obtained are also shown in Table 1.

In the individual Examples, the quantities in which the basic units are used can generally be varied by about $\pm 3\%$ or at least by 1.5% without adversely affecting the properties of the resulting copolyamides to any appreciable extent.

TABLE 1

Example	Monomer composition								Melting range °C
	% 6	% 11	% 12	% 6,6	% 6,9	% 6,10	% 6,12	% 6,13	
6	35	35	20	10	—	—	—	—	100 — 105
7	35	20	30	15	—	—	—	—	103 — 108
8	30	30	20	20	—	—	—	—	98 — 104
1	30	20	30	20	—	—	—	—	90 — 95
9	25	40	20	15	—	—	—	—	105 — 110
10	25	25	25	25	—	—	—	—	95 — 100
11	20	25	25	—	30	—	—	—	83 — 89
3	25	25	25	—	25	—	—	—	84 — 88
12	30	20	30	—	20	—	—	—	88 — 95
13	30	15	20	—	35	—	—	—	85 — 90
14	35	35	20	—	—	10	—	—	100 — 108
15	35	20	30	—	—	15	—	—	97 — 107
16	30	20	30	—	—	20	—	—	90 — 95
17	30	25	25	—	—	20	—	—	82 — 90
18	30	30	20	—	—	20	—	—	90 — 95
19	25	25	25	—	—	25	—	—	85 — 90
2	20	25	25	—	—	30	—	—	86 — 91
20	30	20	30	—	—	20	—	—	95 — 100
21	35	20	30	—	—	15	—	—	95 — 105
4	35	20	30	—	—	—	15	—	95 — 105
5	30	30	20	—	—	—	—	20	90 — 100

COMPARISON TEST.

In this comparison test, the bond strength of a copolyamide according to the invention is compared with that of a copolyamide containing only the basic units caprolactam, 11-aminoundecanoic acid and lauric lactam.

A copolyamide is prepared as described in Example 1 from the following monomer constituents: 25% by weight of caprolactam, 25% by weight of 11-aminoundecanoic acid, 25% by weight of lauric lactam, 25% by weight of azelaic acid hexamethylene diamine salt and 2% by weight of azelaic acid as polymerisation-degree regulator. A transparent polyamide melting at 80 to 90° C., as measured on a KOFER heating-stage microscope, and having a melt index at 130° C. of 22, as measured in accordance with DIN 53 735, is obtained.

For comparison, a ternary copolyamide is prepared from the following constituents: 34% by weight of caprolactam 33% by weight of 11-aminoundecanoic acid, 33% by weight of lauric lactam and 1.5% by weight of azelaic acid as polymerisation degree regulator. A copolyamide melting at 110 to 115° C. and having a melt index of 22, as measured in accordance with DIN 53 735, is obtained.

The polyamides were each ground while cooling and separated by sifting into a fraction of 0 to 200 μ m.

The two powder fractions were applied to a conventional interlining material in an 11-mesh pattern in an amount of 16 ± 1 g per m^2 by means of a powder pointing machine of the kind normally used in the coating industry.

The coated interlinings thus obtained were ironed with a polyester/cotton fabric under a constant pressure of 350 p/cm² in an electrically heated ironing press of the kind commonly used in the garment industry, both the plate temperature and the contact time being varied.

The delamination strengths of 2.5 cm wide laminate strips were measured with a tension tester.

The delamination strengths (p/2.5 cm) specified in Table 2 were measured:

TABLE 2

Contact time (seconds)	Plate temperature of the ironing press (°C)							
	110	120	130	140	150	160	170	
6	300	400	500	700	1000	900	900	Invention
	—	—	100	200	400	300	300	Comparison
10	400	500	800	1100	1000	1100	1600	Invention
	—	—	200	300	400	500	500	Comparison
15	450	700	900	1200	1400	1400	1300	Invention
	—	—	250	350	500	700	600	Comparison
18	600	900	900	1300	1500	1400	1700	Invention
	—	—	300	600	500	600	750	Comparison

It can be seen from the Table that extremely good adhesion is obtained even at very low plate temperatures of the ironing press, i.e. at very low sealing temperatures of 110 and 120° C., whereas no adhesion is obtained with the conventional copolyamide at these sealing temperatures. The conventional copolyamide only produces firm adhesion at higher sealing temperatures.

WHAT WE CLAIM IS:—

1. Copolyamides containing units derived from caprolactam, lauric lactam, 11-



COMPARISON TEST.

In this comparison test, the bond strength of a copolyamide according to the invention is compared with that of a copolyamide containing only the basic units caprolactam, 11-aminoundecanoic acid and laurilactam.

A copolyamide is prepared as described in Example 1 from the following monomer constituents: 25% by weight of caprolactam, 25% by weight of 11-aminoundecanoic acid, 25% by weight of laurilactam, 25% by weight of azelaic acid hexamethylene diamine salt and 2% by weight of azelaic acid as polymerisation-degree regulator. A transparent polyamide melting at 80 to 90° C., as measured on a KOFLER heating-stage microscope, and having a melt index at 130° C. of 22, as measured in accordance with DIN 53 735, is obtained.

For comparison, a ternary copolyamide is prepared from the following constituents: 34% by weight of caprolactam 33% by weight of 11-aminoundecanoic acid, 33% by weight of laurilactam and 1.5% by weight of azelaic acid as polymerisation degree regulator. A copolyamide melting at 110 to 115° C. and having a melt index of 22, as measured in accordance with DIN 53 735, is obtained.

The polyamides were each ground while cooling and separated by sifting into a fraction of 0 to 200 μ m.

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The coated interlinings thus obtained were ironed with a polyester/cotton fabric under a constant pressure of 350 p/cm² in an electrically heated ironing press of the kind commonly used in the garment industry, both the plate temperature and the contact time being varied.

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TABLE 2

Contact time (seconds)	Plate temperature of the ironing press (°C)							
	110	120	130	140	150	160	170	
6	300	400	500	700	1000	900	900	Invention
	—	—	100	200	400	300	300	Comparison
10	400	500	800	1100	1000	1100	1600	Invention
	—	—	200	300	400	500	500	Comparison
15	450	700	900	1200	1400	1400	1300	Invention
	—	—	250	350	500	700	600	Comparison
18	600	900	900	1300	1500	1400	1700	Invention
	—	—	300	600	500	600	750	Comparison

It can be seen from the Table that extremely good adhesion is obtained even at very low plate temperatures of the ironing press, i.e. at very low sealing temperatures of 110 and 120° C., whereas no adhesion is obtained with the conventional copolyamide at these sealing temperatures. The conventional copolyamide only produces firm adhesion at higher sealing temperatures.

WHAT WE CLAIM IS:—

1. Copolyamides containing units derived from caprolactam, laurilactam, 11-



aminoundecanoic acid and a unit derived from a hexamethylene diamine salt of an aliphatic dicarboxylic acid corresponding to the formula



in which n stands for the number 4, 7, 8, 10 or 11, the basic units being incorporated in the copolymer in the following proportions:

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caprolactam	20—40% by weight
laurilactam	20—35% by weight
11-aminoundecanoic acid	15—35% by weight
hexamethylene diamine salt of the acid of formula I	15—40% by weight

2. Copolyamides as claimed in claim 1, wherein the basic units are incorporated in the copolymer in the following proportions:

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15

caprolactam	25—35% by weight
laurilactam	~30% by weight
11-aminoundecanoic acid	18—25% by weight
hexamethylene diamine salt of the acid of formula I	15—30% by weight

3. Copolyamides as claimed in claim 1, wherein the basic units are incorporated in the copolymer in the following proportions:

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20

caprolactam	~30% by weight
laurilactam	~30% by weight
11-aminoundecanoic acid	~20% by weight
hexamethylene diamine salt of the acid of formula I	~20% by weight

25

25

4. A process for producing copolyamides according to claim 1 wherein caprolactam, laurilactam and 11-aminoundecanoic acid and a hexamethylene diamine salt of an aliphatic dicarboxylic acid corresponding to the formula



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in which n stands for the number 4, 7, 8, 10 or 11, are polymerised under pressure at elevated temperature in the following quantitative proportions:

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35

caprolactam	20—40% by weight
laurilactam	20—35% by weight
11-aminoundecanoic acid	15—35% by weight
hexamethylene diamine salt of the acid of formula I	15—40% by weight

5. A process as claimed in claim 4, wherein the comonomers are polymerised in the following quantitative proportions:

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caprolactam	25—35% by weight
laurilactam	~30% by weight
11-aminoundecanoic acid	18—25% by weight
hexamethylene diamine salt of the acid of formula I	15—30% by weight

6. A process as claimed in claims 4 or 5, wherein the comonomers are polymerised in the following quantitative proportions:

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caprolactam	~30% by weight
laurilactam	~30% by weight
11-aminoundecanoic acid	~20% by weight
hexamethylene diamine salt of the acid of formula I	~20% by weight

7. A process as claimed in any of claims 4 to 6, wherein polymerisation is carried out at a temperature of 280 to 300° C. under a pressure of from 10 to 50 atms.

8. A process as claimed in any of claims 4 to 7, wherein aftercondensation is carried out for 1 to 3 hours under normal pressure at 250 to 300° C.

9. A process for the heat-sealing together of materials comprising applying to at least one of the surfaces to be sealed a copolyamide according to claim 1 and heating the materials to be sealed to a temperature sufficient to melt the copolyamide and cooling the sealed surfaces.

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