

PATENT SPECIFICATION

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(54) COPOLYAMIDES CONTAINING CAPROLACTAM, LAURICLACTAM AND HEXAMETHYLENE DIAMINE ADIPATE

(71) We, PLATE BONN GESELLSCHAFT MIT BESCHRANKTER HAF-
TUNG, a body corporate organised under the
Laws of Germany, of 53 Bonn, Bransdorfer
Weg 51, 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:—

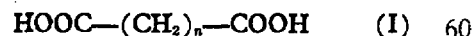
This invention relates to copolyamides con-
taining caprolactam, lauric lactam and hexa-
methylenediamine adipate together with other
polyamide-forming components as basic units,
to a process for producing these copolyamides
and to their use for heat-sealing.

British Patent Specification No. 1,172,427
discloses shaped articles having highly adhe-
sive surfaces at elevated temperatures, which
articles are made from copolyamide compris-
ing from 80 to 20% by weight of units de-
rived from lauric lactam and, correspondingly,
20 to 80% by weight of units derived from
one or more additional polyamide-forming
substances. It is particularly preferred to use
for this purpose copolyamides lauric lactam
and, preferably, caprolactam and/or hexa-
methylenediamine adipate or hexamethylenediamine
sebacate. These known copolyamides
into which two or three polyamide-forming
monomers are incorporated by condensation
as basic units, are widely used in the garment
industry for heat-sealing textiles, especially
woven fabrics. Unfortunately, the copoly-
amides described in British Patent Specifica-
tion No. 1,172,427 have a relatively high melt-
ing point which is above 110°C, with the
result that they cannot be used for heat-sealing
temperature-sensitive substrates such as
leather, temperature-sensitive natural and/or
synthetic woven fabrics, non-woven fabrics,

felts, tufted fabrics and the like. Substances
with melting temperatures of below 115°C,
if possible below 110°C or even below 105°C,
are required for heat-sealing temperature-sen-
sitive substrates of this kind.

We have sought to provide substances which
are suitable for heat-sealing temperature-sen-
sitive substrates, show a high bond strength
at low sealing temperatures and after cooling
and which nevertheless are highly resistant
to chemical cleaning agents.

Accordingly the present invention provides
a copolyamide containing caprolactam, lauric-
lactam and hexamethylenediamine adipate as
basic units, distinguished by the fact that it
contains as additional basic unit a hexamethyl-
ene diamine salt of an aliphatic dicarboxylic
acid corresponding to the formula



in which n is the number 7, 8, 10 or 11, the
basic units being incorporated into the co-
polymer in the following proportions:

caprolactam	25 to 30% by weight	
lauric lactam	24 to 40% by weight	
Hexamethylene		
diamine adipate	8 to 25% by weight	
hexamethylene		
diamine salt of		
the acid of		
formula (I)	10 to 40% by weight	

The invention also provides a process for the
production of a copolyamide containing capro-
lactam, lauric lactam and hexamethylenediamine
adipate as basic units which is distin-
guished by the fact that the aforementioned
basic units and, as an additional basic unit,
a hexamethylene diamine salt of an aliphatic

dicarboxylic acid corresponding to formula (I) are polymerised in the above proportions under pressure at elevated temperatures by methods known *per se*.

- 5 The copolyamides defined above are used for heat-sealing. The copolyamides according to the invention surprisingly show a very low melting point of below 110°C, extremely high bond strength at elevated temperature, so that they can be used with advantage for heat-sealing temperature-sensitive substrates, and a high resistance to chemical cleaning agents.

- 10 Copolyamides of the kind whose basic units are incorporated into the copolyamide by polymerisation in the following proportions are preferred for the purposes of the invention:

	caprolactam	30% by weight
	laurilactam	30 to 40% by weight
20	hexamethylene diamine	
	adipate	10 to 15% by weight
	hexamethylene diamine salt of the acid of formula (I)	15 to 30% by weight,
25		

the total percentage by weight of the basic units being 100 percent by weight.

- 30 It is particularly preferred for the copolyamide to contain the hexamethylene diamine salt of the dicarboxylic acid of formula (I) in a quantity of from 20 to 30% by weight.

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

- 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 stands for the number 7, 8 or 10 are particularly preferred for the purposes of the invention, acids in which n is 7 or 8 being 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 a temperature of 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. Polymerisation is preferably followed by after condensation for a few hours, preferably for 1 to 3 hours, at a temperature of 250 to 300°C. The catalysts, chain terminators and/or other additives and the process conditions known for the polymerisation of laurilactam are employed. The process is best carried out in the absence of air, i.e. in an inert gas atmosphere. The co-

polyamides 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 preferred viscosity for the copolyamide when it is used for the production of films is from 1.4 to 1.5. This figure denotes the solution viscosity of a 0.5% solution of the copolyamide in *m*-cresol at 25°C.

The copolyamides used in accordance with the invention can be mixed with 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 basic units. The basic units are condensed into the polymer chain in static distribution. The surprising effects described are not obtained when the polyamide basic units are polymerised separately to form the homo-polyamides and subsequently mixed together in the molten state.

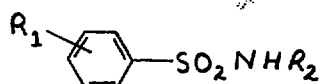
The copolyamides according to the invention can also have small quantities of other polyamide basic units condensed into them. However, for reasons of ready accessibility and satisfactory reproducibility of production to form copolyamides with uniform properties, it is generally not advisable to add further polyamide basic units.

It is possible by means of the copolyamides according to the invention to bond substrates of many different kinds with particular advantage temperature-resistant substrates to substrates of the same or different type. A copolyamide according to the invention is preferably introduced in the form of a powder between the surface to be bonded. The copolyamide can of course also be used in the form of films, filaments and chopped filaments. The substrates are then pressed with the polyamide according to the invention at elevated temperatures. 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 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 and 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



in which R_1 represents hydrogen or methyl and R_2 represents hydrogen, a lower alkyl group or cyclohexyl group.

Benzene or toluene sulphonic acid ethylamide is particularly preferred. Corresponding commercial products are available. These commercial products are, for example, mixture 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* - hydroxybenzoate acid, octyl - *p* - hydroxybenzoate. Bisphenol A can also be used as a plasticiser. 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 and films. 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 DT-PS 2,007,971 and DT-AS 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. 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 be mixed with dyes or other usual additives. In this respect, the copolyamides can be mixed with, 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.

350 parts by weight of caprolactam, 150 parts by weight of adipic acid hexamethylene diamine salt, 350 parts by weight of lauric-lactam, 150 parts by weight of azelaic acid hexamethylene diamine salt (6,9-salt), 12 parts by weight of adipic acid as polymerisation-degree regulator and 100 parts by weight of distilled water, are weighed into an autoclave equipped with stirring mechanism. The atmospheric oxygen inside the autoclave is removed by repeated rinsing under pressure with pure nitrogen. The reaction mixture is heated to 290°C and the pressure inside the autoclave limited to 25 to 30 atms by suitably adjusting the valve. The reaction mixture is exposed to the aforementioned pressure and temperature conditions for a period of 3 hours during which it is stirred. The pressure is then reduced to normal pressure over a period of 2 hours. The reaction mass is then after-condensed while stirring for 2 hours in the absence of pressure under a gentle stream of nitrogen.

On completion of the pressure free after-condensation phase, the temperature is reduced to 180° to 200°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 95 to 102°C, as measured on a KOFER heating-stage microscope, and a relative solution viscosity of 1.45, as measured in 0.5% solution in *m*-cresol at 25°C by means of an Ostwald viscosimeter.

The azelaic acid hexamethylene diamine salt used in this Example was prepared as follows from a commercial-grade azelaic acid known as EMEROX 1144; (the word "Emerox" is a Registered Trade Mark).

1 mol (190.0 g) of EMEROX 1144 are dissolved under reflux in isopropanol, fol-

lowed by the addition while stirring off 1.02 mol (118.5 g) of hexamethylene diamine, also dissolved in isopropanol. The white deposit formed is filtered off and dried. The resulting azelaic acid hexamethylene diamine salt (6,9-salt) melts at 150 to 152°C and has a pH-value of 7.6, as measured in a 1% aqueous solution.

EXAMPLE 2.

300 parts by weight of caprolactam, 100 parts by weight of AH-salt (hexamethylene diamine adipate), 300 parts by weight of laurilactam, 300 parts by weight of azelaic acid hexamethylene diamine salt, 12 parts by weight of adipic acid as polymerisation-degree regulator and 100 parts by weight of distilled water, are reacted under the polycondensation conditions described in Example 1.

The product is a copolyamide melting at 90 to 95°C, as measured on a KOFER heating-stage microscope.

EXAMPLE 3.

A copolyamide at 85 to 90°C is prepared from the following components in the manner described in Example 1: 300 parts by weight of caprolactam, 150 parts by weight of AH-salt, 400 parts by weight of laurilactam, 150 parts by weight of sebacic acid hexamethylene diamine salt (6,10-salt) and 12 parts by weight of adipic acid.

EXAMPLE 4.

300 parts by weight of caprolactam, 150 parts by weight of AH-salt, 400 parts by weight of laurilactam, 150 parts by weight of dodecane dicarboxylic acid hexamethylene diamine salt (6,12-salt), 12 parts by weight of adipic acid and 100 parts by weight of distilled water, are reacted under the polycondensation conditions describe in Example 1.

A copolyamide melting at 95 to 102°C is obtained.

The 6,12-salt used is prepared from the commercially available components described in Example 1.

EXAMPLE 5.

A copolyamide melting at 100 to 110°C is prepared from the following components under the polycondensation conditions described in Example 1: 300 parts by weight of caprolactam, 150 parts by weight of AH-salt, 350 parts by weight of laurilactam, 135.5 parts by weight of brassylic acid (C₁₃-dicarboxylic acid), 64.5 parts by weight of hexamethylene diamine, 12 parts by weight of adipic acid.

EXAMPLES 6 to 15.

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:

6	=caprolactam	
12	=laurilactam	
6,6	=AH-salt	
6,9	=hexamethylene diamine azelaic acid salt	65
6,10	=hexamethylene diamine sebacic acid salt	
6,12	=hexamethylene diamine dodecane dicarboxylic acid salt	70
6,13	=hexamethylene diamine brassylic acid salt	

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 changed by about $\pm 3\%$ or at least by 1.5% without adversely affecting the properties of the copolyamides obtained to any appreciable extent.

TABLE 1

Example	Monomer composition							Melting range °C
	% 6	% 12	% 6,6	% 6,9	% 6,10	% 6,12	% 6,13	
6	25	35	20	20	—	—	—	95 — 100
7	30	20	20	30	—	—	—	98 — 106
8	30	30	20	20	—	—	—	95 — 100
2	30	30	10	30	—	—	—	92 — 98
9	30	35	15	20	—	—	—	90 — 100
10	30	40	15	15	—	—	—	90 — 95
11	30	40	10	20	—	—	—	101 — 107
1	35	35	15	15	—	—	—	95 — 102
12	30	35	15	—	20	—	—	85 — 91
13	30	30	10	—	30	—	—	91 — 99
3	30	40	15	—	15	—	—	85 — 90
14	30	30	10	—	—	30	—	95 — 103
15	30	35	15	—	—	20	—	96 — 103
4	30	40	15	—	—	15	—	95 — 102
5	30	15	15	—	—	—	20	100 — 100

COMPARISON TEST.

5 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, lauric lactam and AH-salt.

10 The copolyamide of Example 13 which has a melt viscosity of 3000 poises at 140°C, is used as the copolyamide according to the invention.

15 A copolyamide of the following polyamide-forming basic units is based as the comparison copolyamide: 30% of caprolactam, 45% of lauric lactam and 25% of AH-salt.

This copolyamide has a melting temperature of from 110 to 120°C and a melt viscosity of 2000 poises at 140°C.

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

The two powder fractions were applied to a conventional interlining material in an 11-mesh pattern in a weight of 16 ± 1 g per m² by means of a powder pointing machine of the kind commonly 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 on 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 by means of a tension tester.

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

25

30

35

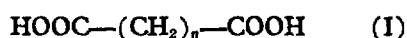
TABLE 2

Contact time (seconds)	Plate temperature of the ironing press (°C)					
	110	120	130	140	150	
6	400	700	600	800	900	Invention
	—	—	100	200	200	Comparison
10	500	900	900	900	1200	Invention
	—	—	200	300	400	Comparison
15	700	1100	1100	1200	1200	Invention
	—	—	300	400	700	Comparison
18	700	1200	1000	1100	1600	Invention
	—	—	350	500	800	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 sealing temperatures as low as these. The conventional polyamide only produces firm adhesion at higher sealing temperatures.

WHAT WE CLAIM IS:—

1. A copolyamide containing caprolactam, lauricactam and hexamethylene diamine adipate as basic units, wherein it contains as an additional basic unit a hexamethylene diamine salt of an aliphatic dicarboxylic acid corresponding to the formula



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

caprolactam 25 to 35% by weight
lauricactam 20 to 40% by weight
hexamethylene diamine adipate 80 to 25% by weight
hexamethylene diamine salt of the acid of formula I 10 to 40% by weight

2. A copolyamide as claimed in Claim 1, wherein the basic units are incorporated in the copolymer by polymerisation in the following proportions:

caprolactam 30% by weight
lauricactam 30—40% by weight
hexamethylene diamine adipate 10—15% by weight
hexamethylene diamine salt of the acid of formula I 15—30% by weight

the total percentage by weight of the basic units being 100 percent by weight.

3. A copolyamide as claimed in claim 1 or 2, wherein the basic unit hexamethylene diamine salt of the dicarboxylic acid of formula I is incorporated in the copolymer in a quantity of from 20 to 30% by weight.

4. A copolyamide as claimed in any of claims 1 to 3, wherein n in formula I stands for the number 7, 8 or 10.

5. A copolyamide as claimed in any of claims 1 to 3, wherein n in formula I stands for the number 7 or 8.

6. A copolyamide as claimed in claim 1 substantially as described with reference to any one of the Examples.

7. A process for the productions of a copolyamide containing caprolactam, lauricactam and hexamethylene diamine adipate as basic units, wherein the aforementioned basic units and, as additional basic unit, a hexamethylene diamine salt of an aliphatic dicarboxylic acid corresponding to the formula



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

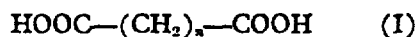
TABLE 2

Contact time (seconds)	Plate temperature of the ironing press (°C)					
	110	120	130	140	150	
6	400	700	600	800	900	Invention
	—	—	100	200	200	Comparison
10	500	900	900	900	1200	Invention
	—	—	200	300	400	Comparison
15	700	1100	1100	1200	1200	Invention
	—	—	300	400	700	Comparison
18	700	1200	1000	1100	1600	Invention
	—	—	350	500	800	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 sealing temperatures as low as these. The conventional polyamide only produces firm adhesion at higher sealing temperatures.

WHAT WE CLAIM IS:—

1. A copolyamide containing caprolactam, lauric-lactam and hexamethylene diamine adipate as basic units, wherein it contains as an additional basic unit a hexamethylene diamine salt of an aliphatic dicarboxylic acid corresponding to the formula



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

caprolactam 25 to 35% by weight
 lauric-lactam 20 to 40% by weight
 hexamethylene diamine adipate 80 to 25% by weight
 hexamethylene diamine salt of the acid of formula I 10 to 40% by weight

2. A copolyamide as claimed in Claim 1, wherein the basic units are incorporated in the copolymer by polymerisation in the following proportions:

caprolactam 30% by weight
 lauric-lactam 30—40% by weight
 hexamethylene diamine adipate 10—15% by weight
 hexamethylene diamine salt of the acid of formula I 15—30% by weight

the total percentage by weight of the basic units being 100 percent by weight.

3. A copolyamide as claimed in claim 1 or 2, wherein the basic unit hexamethylene diamine salt of the dicarboxylic acid of formula I is incorporated in the copolymer in a quantity of from 20 to 30% by weight.

4. A copolyamide as claimed in any of claims 1 to 3, wherein n in formula I stands for the number 7, 8 or 10.

5. A copolyamide as claimed in any of claims 1 to 3, wherein n in formula I stands for the number 7 or 8.

6. A copolyamide as claimed in claim 1 substantially as described with reference to any one of the Examples.

7. A process for the productions of a copolyamide containing caprolactam, lauric-lactam and hexamethylene diamine adipate as basic units, wherein the aforementioned basic units and, as additional basic unit, a hexamethylene diamine salt of an aliphatic dicarboxylic acid corresponding to the formula



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



- | | | | | |
|----|---|---------------------|--|----|
| | caprolactam | 25 to 35% by weight | 11. A process as claimed in any of claims 7 to 9, wherein n in formula I stands for the number 7 or 8. | |
| | lauriclactam | 20 to 40% by weight | 12. A process as claimed in any of claims 7 to 11, wherein polymerisation is carried out at a temperature of from 280 to 300°C under a pressure of 10 to 50 atms. | 35 |
| 5 | hexamethylene diamine adipate | 8 to 25% by weight | 13. A process as claimed in any of claims 7 to 12, wherein aftercondensation is carried out for 1 to 3 hours under normal pressure at 250 to 300°C. | 40 |
| | hexamethylene diamine salt of the acid of formula I | 10 to 40% by weight | 14. A process as claimed in claim 7, substantially as described with reference to any one of the Examples. | |
| 10 | 8. A process as claimed in claim 7, wherein the basic units are polymerised in the following quantitative proportions: | | 15. A copolyamide whenever prepared by a process as claimed in any of claims 7 to 14. | 45 |
| | caprolactam | 30% by weight | 16. A process for the heat-sealing together of materials comprising applying to at least one of the surfaces to be sealed is coated with a copolyamide according to claim 1, heating the materials to be sealed to a temperature sufficient to melt the copolyamide and cooling the sealed surfaces. | 50 |
| 15 | lauriclactam | 30 to 40% by weight | 17. A process as claimed in claim 16 substantially as herein described. | 55 |
| | hexamethylene diamine adipate | 10 to 15% by weight | | |
| | hexamethylene diamine salt of the acid of formula I | 15 to 30% by weight | | |
| 20 | the total percentage by weight of all the basic units being 100 per cent by weight. | | | |
| | 9. A process as claimed in claim 7 or 8 wherein the basic unit hexamethylene diamine salt of the dicarboxylic acid of formula I is incorporated in the copolymer in a quantity of from 20 to 30% by weight. | | | |
| 25 | 10. A process as claimed in any of claims 7 to 9, wherein n in formula I stands for the number 7, 8, or 10. | | | |
| 30 | | | | |

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