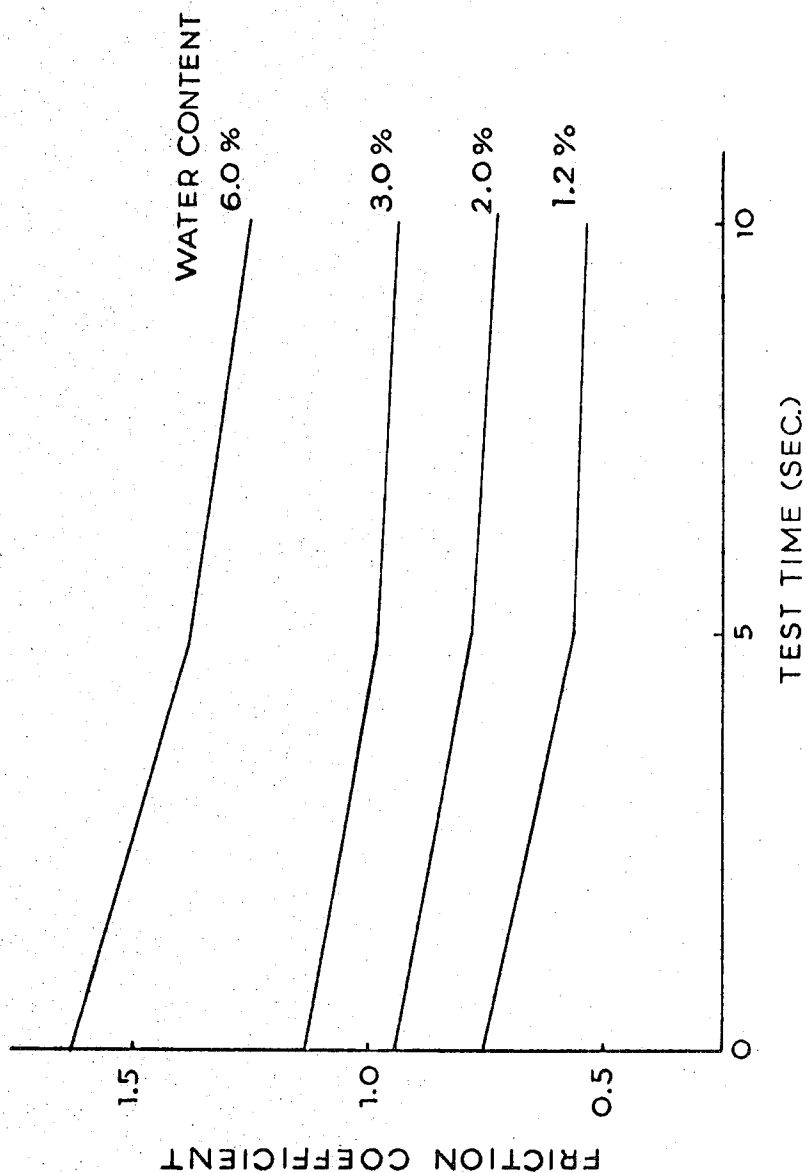


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PROCESS FOR PREPARING DRAWN POLYAMIDE FILMS
AND FILMS PRODUCED THEREBY
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1

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PROCESS FOR PREPARING DRAWN POLYAMIDE FILMS

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10 Claims

ABSTRACT OF THE DISCLOSURE

Polyamide film is processed by adding 1 to 6% by weight water, preheating and then biaxially drawing at a temperature at least 5° C. higher than the preheating temperature. During preheating a substantial difference in water content between the interior and surface of the film is created. The films made by this process have a relatively low friction coefficient.

Processes for the production of polyamide films involving the simultaneous longitudinal and transverse drawing of a substantially amorphous polyamide film has recently been proposed. In such processes, drawing is effected in both the longitudinal and transverse directions at a draw speed of from 6,000 to 100,000 percent/min. and at a temperature within the range of from 70° C. to 180° C., which is at least 35° C. below the melting point of the film. The ratio of the longitudinal to transverse draw speeds is generally from 2:1 to 0.5:1, and the draw ratio from 16:1 to 4:1. The polyamide films obtained according to these methods have various advantageous properties such as improved tensile strength, and optical clarity for general industrial uses. Although they have a very even surface, high transparency and beautiful luster, they do however have several disadvantages in use. Such films, for example, have a high friction coefficient with themselves or with printing machines when they are processed e.g. for printing, bag making, adhesion and various other purposes.

Moreover, operational efficiency may be impaired due to their high adherent properties. It is an object of the present invention to provide improved polyamide films having low friction coefficient, and low adherent properties.

SUMMARY OF INVENTION

According to the present invention there is provided a process for drawing a polyamide film which comprises treating the polyamide film with water, preheating the film to produce a difference of water content between the surface and the interior of the film and drawing the film simultaneously in the longitudinal and transverse direction.

According to the process of the invention it is possible to obtain a polyamide film having uneven reticulated fine projections on its surface, and a low friction coefficient. Moreover, blocking characteristics are reduced and the processability of the film is improved. The film obtained also has a uniformity of properties.

According to the present invention, better results may be achieved by drawing the film simultaneously and biaxially in an atmosphere having a higher temperature than that of the preheated film. The present invention gives particularly advantageous results when drawing conditions are controlled so that the draw speed of the polyamide film is conveniently 6,000–100,000 percent/

2

min., and especially good results can be obtained at a draw speed ranging from about 10,000–60,000 percent/min. At any point on the surface of the polyamide film during drawing the ratio of draw speeds, the ratio of the speed of stretching in the longitudinal and transverse directions is preferably from 2:1 to 0.5:1. The draw ratio should preferably be in the range of from 16:1 to 4:1.

The expressions "draw speed," "ratio of draw speeds" and "draw ratio" used herein have the following meanings:

(1) "Draw speed" can be defined by the following formula:

$$\text{draw speed} = d_1/d_2 \times 100 \text{ (percent/t)}$$

wherein d_2 is thickness of the drawn film, d_1 is thickness of the film before drawing, and t is the time in minutes necessary to draw the film.

(2) "Ratio of draw speeds" can be defined as follows:

$$\text{ratio of draw speeds} = \frac{\text{longitudinal draw speed}}{\text{transverse draw speed}}$$

in which the longitudinal draw speed and transverse draw speed show respectively normal values or mean values of draw speeds in longitudinal and transverse directions from the begin of drawing to an optional point reached in the drawing process. Draw speeds are measured at the said point.

In other words, when a film having a length of L_1 and width of H_1 is drawn, the longitudinal draw speed and transverse draw speed can be defined respectively as follows:

$$l_t/L_1 \times 100 \text{ percent/t and } h_t/H_1 \times 100 \text{ percent/t}$$

wherein l_t and h_t are respectively the length in the transverse direction and width of the drawn film, which are measured after t minutes from the beginning of the drawing at an optional point on the film track.

(3) In industrial practice of biaxial and simultaneous drawing, it is preferred to define the "draw ratio" as d_1/d_2 , in which d_2 is the thickness of a drawn film and d_1 is the thickness of said film before drawing.

The film obtained has unevenly reticulated fine projections (or webs) on the surface and an improved friction coefficient.

The method of giving a film a difference of water content between its surface and interior is preferably as follows. A film having the desired water content is preheated in the shortest possible time to a suitable temperature in order to achieve a difference of water content between the surface and the interior. It is then drawn simultaneously in the longitudinal and transverse directions in a drawing zone where the temperature of the atmosphere is higher than the temperature of the preheated film, so that the surface of the preheated film is heated during drawing to evaporate water from its surface and provide a large difference of water content between the surface and the interior. As used herein, the term "polyamide films" includes films made from linear polyamides, for example, poly-ε-caproamide, poly-hexamethylene-adipamide, poly-hexamethylene-sebacamide, poly-11-aminoundecanamide, copolymerized polyamide, etc. The water-content of the polyamide film is preferably from 1 to 6% by weight before preheating. Preferred amounts of water which are added in the pretreatment of the polyamide films vary according to the types of

polyamide film and may for example be within the following approximate ranges:

Polyamide	Water content (percent by weight of film)
Poly-ε-caproamide	1-6
Polyhexamethylene-adipamide	1-6
Polyhexamethylene-sebacamide	1-5
Poly-11-amino-undecanamide	1-3

These values may however vary according to the temperature and other conditions under which the film is treated. The relationship between the water content of the polyamide film before drawing and the surface properties of the films obtained may be as follows:

(1) Raw film having too high a water content may give rise to a drawn film having uneven reticulated fine projections (webs) on its surface which may grow gradually and simultaneously result in a decrease of their heights. The friction coefficient of the film may increase as the water content in the raw film increases.

(2) Low water contents of the raw film before drawing may give rise to a lower friction coefficient in the drawn film.

According to the present invention, the absorption of water onto the raw film is effected prior to the drawing step, and water is added to the undrawn film, for example, by the use of a water bath, water spray, etc. in order to give a uniform water content to the raw film which may be drawn uniformly. As a result, it is possible to obtain a uniformly undulating surface on the drawn film.

The water content is preferably uniformly distributed throughout the film before drawing, for example, by passing the film through an atmosphere maintained at the correct temperature and humidity. A film having the correct water content is then preheated to a suitable temperature and drawn simultaneously in the longitudinal and transverse directions whilst maintaining a difference of water content between the surface and the interior of the film during a drawing process.

Improper heating may give rise to an incorrect difference in water content between the surface and the interior of the film. It is therefore necessary to use the shortest possible time to heat the film to the temperature required for drawing. Suitable heating times and temperatures may be determined empirically according to types and dimensions of the raw films.

Better results may be obtained by preheating the surface of a raw film, 50-500μ thick, for several seconds, e.g. 0.5 to 30 seconds, in an atmosphere having a temperature from about 70° to 35° C. below the melting point of the film. Furthermore, it is preferred that the temperature of the atmosphere in the drawing zone be maintained at least 5° C. above the temperature of the preheated film but at a temperature not higher than 30° C. below the melting point of the film. This is required in order that the surface of the preheated film is heated to evaporate water from its surface and thereby achieve a larger difference of water content between the surface and the interior of the film. To achieve the improvements obtainable from the present invention, it is necessary to impart a large difference in the water content of the film between its surface and interior at the initial stage of drawing. Generally the surface of the film at this stage will be substantially dry.

The film may preferably be drawn, at least in part, in a zone where the temperature of the atmosphere is at least 5° C. above the temperature of the preheated film, before the film is drawn such that the ratio between the average thickness of the drawn film and the undrawn film is 0.5:1. The temperature of the atmosphere may be maintained by any suitable method, for example, using hot air, infra-red radiation, etc. After drawing of the film, it may be heat-set for example by heating at a temperature not higher than 10° C. below the melting point

of the film with the film maintained under tension such that the transverse direction remains substantially constant.

In use, the most advantageous water content of the raw film may be determined by drawing raw films having various water contents simultaneously in the longitudinal and transverse directions and inspecting the surface of the resultant film. A suitable method of inspection is by the photographic determination of drawn polyamide film. For example a photographic enlargement (×70) has been prepared showing the surface of a simultaneously longitudinally and transversely drawn polyamide film prepared from a raw poly-ε-caproamide film having a thickness of 200μ and a water content of 1.2% by weight of film, and obtained by pre-heating the raw film to 80° C. for several seconds, and drawing simultaneously in the longitudinal and transverse directions with an elongation of 3×3, with a draw speed of 24,000 percent/min., and a draw ratio of about 1 in an atmosphere having a temperature of 160° C. Uneven reticulated fine projections (webs) which are very closely spaced can be observed.

Similar photomicrographs have been produced which show the surface of drawn films obtained from a similar raw film except that the water contents of the films were 2% and 3% by weight respectively. As the water content of the raw film increases, the uneven reticulated fine projections (webs) become more uniformly distributed. However, uneven mesh-like projections (webs) appear to slowly expand and at the same time the height of these meshes decreases.

In a film obtained from the similar raw film having a water content of 6.0%, it is apparent from the photomicrograph that this film has an even and smooth surface.

An enlarged photographic appearance of the glycerin-coated surface of a drawn poly-ε-caproamide film obtained by simultaneous drawing in the longitudinal and transverse directions of a similar raw film having a water content of 1.2% by weight shows the difference between the inner and outer structures of the drawn film. It may be seen that the inner structure of the drawn film is similar to that of the transparent film obtained from a raw film which had a water content of 6.0% by weight.

The densities of both low and high friction films after drying are similar and have an approximate value of 1.144. These observations lead one to the conclusion that the inner parts of the film are uniformly drawn, and that the uneven areas of cracks only occur on the surface.

DRAWING

The accompanying drawing graphically represents the friction coefficient of the films obtained under the conditions described above at various water contents. It is apparent from these figures that the friction coefficient decreases as the absorbed water content decreases.

The friction coefficient was measured using a commercial instrument designed for measuring the friction coefficient of textile materials (available from Toyo Sokuki, K.K., Japan) with a slide speed of 0.50 cm./sec., a load of 100 grms. the width of the test strip being 0.50 cm. and the contact length of 2.0 cm., the film surfaces being in contact with each other. A satisfactory method for obtaining improved biaxially drawn polyamide films having a low friction coefficient has not been previously reported. Biaxially drawn polyamide films having low friction coefficients have been obtained by the present invention and the improved polyamide films have a friction coefficient of less than three.

The following examples are given by way of illustration only:

Example 1

Substantially amorphous films of poly-ε-caproamide (relative viscosity 3.0 at 25° C. in 96% sulphuric acid)

5

having an average thickness of 200μ are pretreated with water to give the films a water content of about 3% (measured by Karl Fischer's method) and density of 1.130. Samples of the films were preheated to 70°C ., 80°C ., 100°C ., 110°C ., 140°C and 160°C respectively by passing them through a preheating zone, in which the atmosphere was maintained at 170°C for a suitable time e.g. 3 to 6 seconds. The preheated films were then simultaneously drawn in the longitudinal and transverse directions with a draw speed of about 24,000 percent min. for about 2.2 seconds by passing through a drawing zone about 0.9 m. in length, where the atmospheres were respectively maintained at 140°C ., 130°C ., 120°C ., 115°C ., 160°C and 180°C to draw the films with a magnification of about 3 in both the longitudinal and transverse directions at a ratio of draw speeds of about 1~1.2. Two films drawn as described above and designated C_1 was prepared for comparison purposes except that the temperature of the preheated films was 100°C and the temperature of the atmosphere in drawing zone 80°C . The temperatures of the films were measured by using a "Radiation Pyrometer" and the atmospheric temperatures measured 10 mm. above the films, were thermocouples. The static friction coefficient of the film (average thickness about 22μ) obtained under the conditions above are shown in Table 1.

Table 1 illustrates the low static friction coefficient of films prepared by the present process as compared with film wherein the draw temperature was lower than the preheat temperature.

TABLE 1

Test No.:	Temperature of preheated raw film, $^\circ\text{C}$.	Temperature of atmosphere in drawing zone, $^\circ\text{C}$.	Static friction coefficient
1.....	70	140	1.5
2.....	80	130	1
3.....	100	120	2
4.....	110	115	3
5.....	140	180	1.5
6.....	160	180	1
C_1	100	80	20

Example 2

Substantially amorphous films (average thickness 160μ ; density—1.128) of poly- ϵ -caproamide (relative viscosity 3.0 measured at 25°C in 96% sulphuric acid) were pretreated with water to give the films a water content of about 1.2, 3, 4.5 and 6.0% respectively.

The films were preheated to 70°C by passing through a preheating zone, where the atmosphere was maintained at 130°C for a residence time of about 4 seconds. The preheated films were then simultaneously drawn in the longitudinal and transverse directions with a draw speed of about 30,000 percent/min. in a drawing zone, where the atmosphere was maintained at 140°C ., to draw the films with a magnification of 3 in the longitudinal direction and 3.5 in the transverse direction at a ratio of draw speeds of about 0.6 to 1.0.

For comparison purposes, two biaxially drawn films designated C_2 and C_3 were prepared under similar conditions to those described above except that the water content of the films was about 0.5% and 8.0% respectively.

The static friction coefficient of the film (average thickness about 15μ) obtained under the conditions described above are shown in Table 2 which illustrates the significance of the water content in the practice of the present invention.

6

TABLE 2

Test No.:	Water content, percent by weight	Static friction coefficient
7.....	1.2	0.7
8.....	3	1.2
9.....	4.5	1.5
10.....	6.0	2.0
C_2	0.5	(¹)
C_3	8.0	18.0

¹ Not measured.

Example 3

Poly- ϵ -caproamide (relative viscosity 2.7 at 25°C in 96% sulphuric acid) was extruded by means of a conventional screw extruder having a diameter of 45 mm. to give a raw film having a thickness of 200 microns. The raw film was left in a vessel, in which the atmosphere was kept at 20°C and the relative humidity was 65%, to provide a film with a water content of about 3% (measured by Karl Fischer's method). The film was preheated to 60°C in an atmosphere having a temperature of 130°C by conventional infra-red heaters for a period of 4 seconds.

The preheated film was then simultaneously drawn in the longitudinal and transverse directions with a draw speed of about 24,000 percent/min. in an atmosphere having a temperature of 150°C to provide a film having a magnification of about 3 in both the longitudinal and transverse direction at a ratio of draw speeds of 1 to 1.2. The drawn film was heat-set by heating for 10 seconds at 190°C under tension so that its transverse dimensions would be kept constant to give a film 22μ in thickness. Microscopic observation of the surface of a drawn film showed that throughout the surface numerous fine uneven webs (of a height of about 1~2 microns) were formed thereon. The static friction coefficient of the drawn film measured by this method was about 1.0, and the film obtained had improved antiblocking characteristics and its machinability was improved. The film transparency measured at $450\text{ m}\mu$ was 80%.

Another raw film was preheated and drawn for comparison purpose in the same manner as described above except that the raw film had a water content of about 8%. The drawn film in comparison with that of this example had an even surface and various practical disadvantages, for example, blocking, bad machinability, etc.

Example 4

A substantially amorphous film (density 1.030; thickness 200μ) of poly-11-amino-undecanamide (relative viscosity 2.8 at 25°C in 96% sulphuric acid) was left in a vessel, in which the atmosphere was kept at a temperature of 35°C and a relative humidity of 65%, to give a film having a water content of about 1.2% (measured by Karl Fischer's method).

The film was pre-heated to about 70°C by conventional infra-red heaters in an atmosphere maintained at 100°C for a period of 2.7 seconds. The preheated film was then simultaneously drawn in the longitudinal and transverse directions with a draw speed of about 36,000 percent/min. in an atmosphere maintained at 120°C to draw a film with a magnification of about 3 in both the longitudinal and transverse directions at a ratio of draw speeds of 0.9 to 1.2. The drawn film was heat-set for 10 seconds at 150°C under tension such that its dimensions would be kept constant in a transverse direction to give a film 22μ in thickness. The polyamide film obtained had unevenly reticulated fine projections on its surface, and a static friction coefficient of less than 0.8.

The film had improved antiblocking characteristics and processability.

Example 5

A substantially amorphous film (density 1.125; average thickness 150μ) of poly- ϵ -caproamide (relative viscosity 3.2 at 25° C. in 96% sulphuric acid) was extruded at a speed of 10 m./min. by means of a conventional T-die process using a 90 mm. extruder, and immediately immersed in a water bath, maintained at 40° C. This provided an average water content for the film of about 3%. The film was then passed through a vessel, in which the atmosphere was maintained at a temperature of 50° C. and a relatively humidity of 60%.

The film was then immediately pre-heated to about 75° C. by passing it through a pre-heating zone 1 m. in length at a through-put speed of 10 m./min. where the atmosphere was maintained at 90° C. by conventional infra-red heaters. The pre-heated film was then simultaneously drawn in the longitudinal and transverse directions with a draw speed of about 24,000 percent/min. through a drawing zone, where the atmosphere was maintained at 150° C. to draw a film with magnification of about 3 in the longitudinal direction and 3.4 in the transverse direction at a ratio of draw speeds of 0.6 to 1.0.

The drawn film was heat-set for 10 seconds at 190° C. under tension, in order that its dimensions would be kept constant in a transverse direction, to give a film 15μ in thickness. The polyamide film obtained had unevenly reticulated projections on its surface, and a static friction coefficient of 0.7. It had improved antiblocking characteristics and processability.

Example 6

Poly- ϵ -caproamide (relative viscosity 3.0 at 25° C. in 96% sulphuric acid) was extruded with a conventional screw extruder having a diameter of 65 mm. to give a raw film density—1.128—having a thickness of 215 microns. The raw film was dipped into a water bath, which was maintained at 40° C. to provide an average water content of the film of about 3%. The film was then passed through a vessel, in which the atmosphere was maintained at a temperature of 50° C. and a relative humidity of 60% and then pre-heated to 90° C. by passing it through a preheating zone 1 m. in length at a through-put speed of 10 m./min. the atmosphere being maintained at 120° C. by conventional infra-red heaters. The pre-heated film was immediately drawn simultaneously in the longitudinal and transverse directions with a draw speed of about 30,000 percent/min. through a drawing zone, where the atmosphere was maintained at 120° C. by conventional hot air heaters, to draw a film having a magnification of about 3 in both the longitudinal and transverse directions at a ratio of draw speeds of 1 to 1.2. The drawn film was heat-set for 10 seconds at 200° C. under tension in order that its dimension in the transverse direction be kept constant to give a film 24μ in thickness. The polyamide film obtained had unevenly reticulated fine projections on its surface, and a static friction coefficient of 1.0 with improved antiblocking characteristics and processability.

Example 7

A substantially amorphous film (density 1.128; average thickness 135μ) of poly- ϵ -caproamide (relative viscosity 3.0 at 25° C. in 96% sulphuric acid) was dipped into a water bath maintained at 35° C. to give a film having an average water content of about 2.5%. The film was pre-heated to about 90° C. for approximately 5 seconds in an atmosphere at 120° C. using conventional infra-red heaters in order to provide a large difference of water content between the surface and the interior of the film.

The pre-heated film was immediately drawn simultaneously in the longitudinal and transverse directions with a draw speed of about 30,000 percent/min. through a drawing zone, in which the atmosphere was maintained at 120° C. by conventional hot air heaters, to draw a film

having a magnification of about 3 in both the longitudinal and transverse directions at a ratio of draw speeds of 0.9 to 1.2. The draw film was heat-set for 8 seconds at 200° C. under tension in order that its dimensions would be kept constant in a transverse direction to provide a film 15μ in thickness.

The static friction coefficient of the polyamide film was 1.2 and it had improved antiblocking characteristics and processability.

Example 8

A substantially amorphous film of polyhexamethylene sebacamide (average thickness— 160μ ; density—1.057) was pretreated with water to give the film a water content of about 3%. The film was preheated to 130° C. by passing through a preheating zone, where the atmosphere was maintained at 180° C. The preheated film was then simultaneously and biaxially drawn in the longitudinal and transverse directions with a draw speed of about 30,000 percent/min. in a drawing zone, where the atmosphere was maintained at 140° C. to draw the film with a magnification of 3 in the longitudinal direction and 3.5 in the transverse direction at a ratio of draw speeds of about 0.6 to 1.0. The drawn film was heat-set by heating for 10 sec. at 190° C. under tension so that its transverse dimension would be kept constant whereby to yield a film having a thickness of 15μ . The static friction coefficient of the drawn film was about 2.5. It was observed that the obtained film had improved antiblocking characteristics and machinability.

Various modifications can be made to the instant invention. For example, a suitable additive may be added to the water absorbed by the film so as to enhance its heat transmission without adverse effect on the film properties.

Having described the present invention that which is sought to be protected is set forth in the following claims.

What is claimed is:

1. A process for drawing a polyamide film which comprises:

(a) treating the polyamide film with water so that it contains 1 to 6% of water by weight (based upon the weight of the film);

(b) preheating said film for 0.5 to 30 seconds to a temperature which is 70° to 35° C. below the melting point of the film so as to impart a substantial difference in water content between the surface and interior of the film, and

(c) drawing the film simultaneously in the transverse and longitudinal directions at a temperature at least 5° C. higher than said preheat temperature but not higher than 30° C. below the melting point of the film at a draw ratio from 16:1 to 4:1.

2. The process of claim 1 wherein the polyamide film is selected from a member of the group consisting of poly- ϵ -caproamide, poly-hexamethylene-adipamide, poly-hexamethylene - sebacamide, poly-1-aminoundecanamide, poly-laurinamide, a copolymerised polyamide or a mixture of two or more thereof.

3. A process as claimed in claim 1 in which the said film is a film of poly-hexamethylene-sebacamide and from 1 to 5% of water by weight (based upon the weight of the film) is absorbed.

4. A process as claimed in claim 1 in which the said film is a film of poly-11-aminoundecanamide and from 1 to 3% of water by weight (based upon the weight of the film) is absorbed.

5. The process of claim 1 wherein the polyamide film passes through a zone with an atmosphere at a temperature at least 5° C. above the temperature of the pre-heated film before drawing to a point where the ratio of average thickness of the drawn film to average thickness of the undrawn film is 0.5:1.

6. The process as claimed in claim 1 in which the said

9

film is drawn at a speed of from 6000 to 100,000 percent/min.

7. A process as claimed in claim 1 in which the ratio of the longitudinal and transverse draw speeds is from 2:1 to 0.5:1.

8. The process of claim 1 wherein the film is drawn at a speed of 6000 to 100,000 percent/min., the longitudinal and transverse draw speeds range from 2:1 to 0.5:1 and the draw ratios are from 16:1 to 4:1.

9. The process of claim 1 wherein the film is preheated for a period of 3 to 6 seconds.

10. A process as claimed in claim 1 in which the drawn film is heat-set at a temperature not higher than 10° C. below the melting point of the film with the film maintained under tension such that the transverse direction remains substantially constant.

10

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