

ALIEN PROPERTY CUSTODIAN

POLYAMIDE ARTICLES

Wilhelm Wehr, Ellenburg, Germany; vested in
the Allen Property Custodian

No Drawing. Application filed March 8, 1941

My present invention relates to polyamide articles, and more particularly to an improved process for preparing articles wholly or partly consisting of polyamides.

It is already known that polyamide articles can be produced by stretching, blowing, pressing, sawing, cutting, stamping or the like materials of synthetic linear polyamides. In contrast with celluloid, cellulose acetate and the vinyl polymers which thermoplastic materials can be molded within a rather large range of temperature, the polyamides are not thermoplastic in a strict sense for they melt i. e. they form a fused mass of high viscosity within few degrees of temperature. Moreover, the range or plasticity of the really thermoplastic substances lies below 100°C and all mechanical apparatus correspond to this relatively low working temperature whereas the polyamides do not form a melt till they have reached temperatures far above 100°C. Owing to this fact the working up of raw materials wholly or partly consisting of polyamides according to the methods usual celluloid, cellulose acetate and other known thermoplastic materials is pretty difficult.

It is an object of my present invention to overcome these disadvantages. Other objects will become apparent from the reading of the detailed description of the invention.

These objects are accomplished by extending the range of becoming liquid of the polyamides towards the low temperatures. The invention is based on the observation that polyamides the melting point of which is between 160 and 300°C can be made sufficiently plastic and capable of being treated in the usual apparatus for working up celluloid already at temperatures below about 110°C by adding a certain percentage of swelling agents.

As swelling agents such liquids are suited which are incapable of dissolving polyamides at ordinary temperature but become capable to dissolve either on increasing temperature or on adding other liquids having a latent dissolving capacity. The most important swelling agents according to the invention are the alcohols and other liquids containing in their molecule hydroxyl conveniently diluted with water. With strongly hydrophilic polyamides it generally suffices to impregnate the polyamide only with water as the swelling agent.

Although no limit is set the addition of swelling agents amounts to at most 25% by weight of the polyamide in general. The optimum quantity of swelling agent to be added depends on the nature of the polyamide and can readily be de-

termined by a preliminary test. The optimum range of temperature below about 110°C in which the polyamide mass is molded most conveniently is dependent on the constitution of the polyamide as well as the percentage of the swelling agent. The higher this percentage is the lower the molding temperature lies below 110°C in general. Moreover, other factors are able to influence the optimum range of temperature as, for instance, the pressure used for stretching. All these factors can be determined by simple tests without difficulty. Since furthermore the degree of impregnation can easily reproducibly be adjusted it is possible to work up the polyamide material continuously and under optimum conditions.

The adjustment of the degree of impregnation may be effected in several ways. When foils produced from solutions or celluloid-like pastes of polyamide by adding swelling agents are the starting material, the desired degree of impregnation is conveniently adjusted by stopping the drying of the foils at a determined percentage of swelling agent. In using foils prepared in a precipitating bath the drying is likewise stopped when they still contain a certain amount capable of swelling of solvent and precipitating agent. Foils formed in the dry way are placed in the bath containing swelling agent and reach the desired effect. In the same way as described above polyamide materials shaped otherwise may also be moistened with swelling agents.

By the invention a displacement of the range of temperature is effected without the product falling off in quality whereas the range of temperature for the molding of thermoplastic substances has chiefly hitherto been determined by structural factors and the properties of the end product are simultaneously impaired if the range of temperature is displaced. After the desired polyamide article has been molded the swelling agent is removed from the polyamide by drying it for a short time. The polymer then again exhibits its original high melting point. The swelling agent is more quickly removed in this drying procedure than it is in treating cellulose derivatives such as nitrocellulose or cellulose acetate plastified with gelatinizing agents.

The following examples set forth certain well defined instances of the application of this invention. They are, however, not to be considered as limitations thereof since many modifications may be made without departing from the spirit and scope of this invention.

Example I

A sheet of an interpolyamide from hexamethylenediamine, adipic acid, and ϵ -aminocaproic acid prepared according to my copending U. S. Application corresponding with the German Application D 81 720 IVc/39b is dried at 40°C to obtain a polymer still having about 10% of swelling agent and then cut into pieces adapted to the stretching apparatus. The polyamide pieces are heated, for instance, by putting the apparatus in a water bath, to the plastifying temperature of about 50 to 60°C whereupon they are molded. Thus one obtains hemispheres which are then agglutinated with or without stiffened intermediate layers according to the intended use. In order to agglutinate the hemispheres, it suffices to apply a solvent for polyamide as, for instance, ethylenechlorohydrin to the connecting surfaces and press them together. The thus resulting balls are subsequently dried at 40°C. The duration of drying depends upon the thickness of the material. After drying the balls exhibit a softening point of about 160°C. Small cases, boxes, for instance, for soaps and brushes, handles of brushes, toy of different kind and the like may also be produced in this way.

Example II

The polyamide material necessary for the production of dolls and the like in the blowing method is employed in the form of plates and tubes. As steam is generally available or this molding process polyamide plates, for instance, composed in the manner described in Example I are used which contain about 6% of moisture of the swelling agent. If sheets made as mentioned in Example I according to the Celluloid method are worked up the moisture content is reached by drying. If, however, dolls produced from the melt of the polyamide by rolling are to be employed the moisture content is adjusted by placing the sheets in ethanol of 50% strength. The time of imbibition is dependent upon the thickness of the material and the temperature. The sheets thus treated are then blown in the same way as in the production of Celluloid dolls with steam

or warm compressed air in metal molds to form parts of dolls. Already during this plastification at about 100°C a portion of the moisture is removed from the polymer article. It is, therefore, only necessary shortly to after-dry the material subsequently so as to obtain an article the polyamide of which has its original melting point.

In the same way tubes may be worked up into umbrella handles and the like.

Example III

A sheet consisting of a polyamide prepared from hexamethylenediamine and adipic acid and containing about 12% of methanol (having 1% of hydrogenchloride) as the swelling agent or a sheet consisting of an interpolyamide from hexamethylene-diamineadipate and caprolactam and containing about 12% of water as the swelling agent are molded at 20 to 30°C under a pressure of about 100 atmospheres into packing collars, combs, spectacle frames and the like. The articles thus obtained are dried at 50 to 60°C for about two days. Since the softening point of the polyamide is above 160°C the collars of polyhexamethylenediamine-adipate may, for instance, be used as packing materials in apparatus in which there are hot solvents.

Example IV

A polyamide sheet is swollen in ethanol of 70% strength up to a moisture of about 18%. After the plate has been heated to 50-60°C, the polyamide is applied to wooden stools or poles, metal tubes and the like. By subsequently drying at about 40 to 50°C the ethanol is removed and the polyamide mass is contracted so as to form a strongly adhering protective layer.

It is also possible to seal bottles or other containers in the way described above. For this purpose it is convenient to employ polyamides having a relatively great hydrophily. The polyamide is laid in water for a short time, then applied to the containers and finally dried at an elevated or ordinary temperature, whereby shrinking is reached.

WILHELM WEHR.