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POLYMERIC MATERIALS

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This invention relates to synthetic filaments, films, sheets, ribbons and the like, and more particularly to novel coated products of this kind.

This application is a continuation-in-part of my application Serial Number 222,941, filed August 3, 1938.

This invention has as an object a method for obtaining coated objects of the above mentioned kind which are characterized by novel effects in the applied surface coating or in the object as a result of the surface coating. A further object is the manufacture of new and useful coated synthetic materials in the form of useful shaped objects. Other objects will appear hereinafter.

These objects are accomplished by the following invention which comprises coating a synthetic polymeric substance of the kind referred to below which is capable of being cold drawn, but which is undrawn or only partly cold drawn and which is in one of the forms indicated above, with a solid film-forming material which is not capable of cold drawing or at least not capable of being permanently elongated by cold drawing to the same extent as said polymeric substance, and then cold drawing whereby novel effects are obtained. The surface coating may be an elastic substance which may be stretched to the extent to which the polymeric substance is cold drawn but which tends to retract to its original length when the cold drawing force is removed.

The synthetic polymeric materials which are capable of being cold drawn and to which the present invention is applicable are best exemplified by the synthetic linear condensation polymers, and particularly by the polyamides which are obtainable by condensation polymerization from amino acids or from diamines and dibasic carboxylic acids as described in Patents 2,071,250, 2,071,253, and 2,130,948. These polymers, after being extruded as filaments or ribbons either from melt or from solutions, can be cold drawn three to six times their original length, a procedure which profoundly modifies their physical character. The filaments, for instance, after drawing are considerably improved in strength and in flexibility and show by X-ray examination orientation along the fiber axis. By coating such filaments before they are fully drawn with material not capable of being cold drawn or at least not capable of permanent drawing to the same extent, including elastic materials, novel effects are obtained that cannot be obtained with artificial filaments such as cellulosic filaments which cannot be cold drawn. Coating the fiber with rubber or any other elastic material and then cold drawing it results in curled or coiled fibers due to contraction of the rubber or elastic material. This is because the cold drawing of the synthetic linear polymers results in a permanent elongation whereas the stretching of rubber does not. Coating the polymer with a film of resinous material, or other material incapable of being temporarily or permanently stretched, and then drawing usually results in cracking the sheath leaving the surface roughened by the adhering particles, shreds, scales or the like. In some cases the applied coating may fail to adhere to the fiber when it is cold drawn but will break away in small cylinders giving a beaded thread. Some materials applied in this way modify the dyeing characteristics of the fibers or act as delusterants, or give the filament a woolly appearance. Application of certain materials with binders, e. g. particles of the polymer from which filament is made, yield novel roughened surfaces when the filaments are subsequently cold drawn. Coatings of polymeric or resinous materials applied to filaments of synthetic linear polymers may be either plasticized or unplasticized. The results obtained may be profoundly affected by introduction or omission of plasticizer in the coating. For example, if the coating is unplasticized polymeric methyl methacrylate, it will break off into adhering particles during cold drawing and produce a straight filament with a rough surface. However, if the coating is a properly plasticized polymeric methyl methacrylate, it will be elastic, and if the filament is not cold drawn beyond the elastic limit of the coating, a crimped filament with a smooth surface will be obtained.

The present invention is applicable not only to the synthetic linear condensation polymers mentioned above but also to other synthetic polymers capable of being cold drawn, that is permanently elongated under application of stress in the solid state. An example of an additional synthetic material of this kind is the solid polymer of ethylene made as described in U. S. Patent No. 2,153,553 by subjecting ethylene to high pressure, preferably not less than 1000 atmospheres, and to moderately elevated temperatures as, for instance, 150°–250° C.

The following examples are illustrative of methods for practicing my invention:

Example I

A smooth undrawn filament of polyhexamethylene adipamide of 15 mils diameter was coated with a film of unplasticized cellulose acetate

from a chloroform solution. The filament was cold drawn about 400% before all the solvent had evaporated from the coating. The coating broke up into small areas during the cold drawing but these areas of coating showed good adhesion to the filament. By virtue of these intermittent areas of cellulose acetate coating, the cold drawn filament had a roughened surface.

Example II

Undrawn filaments of polyhexamethylene adipamide of intrinsic viscosity 0.9 were coated with pigment-size particles of a lower molecular weight polyhexamethylene adipamide (intrinsic viscosity 0.45) by passing the filaments through an aqueous suspension of the particles. After passing through the suspension of particles the filaments were dried in the air and then baked at 240° for 15 minutes to improve the adhesion of the particles to the filaments. The filaments were then cold drawn about 400% at room temperature yielding a product with a rough surface.

Example III

A skein of partially drawn yarn made from polydecamethylene adipamide was dipped into a suspension of 0.1% titanium dioxide pigment in an aqueous solution of partially deacetylated chitin, centrifuged, and dried at 100° C. for 15 minutes. On completing the cold drawing, the resultant dull yarn yielded a product which was still somewhat dull but which had better luster than the original coated yarn.

Example IV

A filament of undrawn polyhexamethylene adipamide was dipped into a toluene alcohol solution of unplasticized polymeric methyl methacrylate and the coating dried in the air. Repeating the operation gave a coating of considerable thickness. When the dried coated filament was cold drawn 300%, it developed a beady surface appearance.

Example V

A filament, 30 cm. long, of polyhexamethylene adipamide was coated with rubber, applied in the form of vulcanized latex, and then cold drawn about 300%. The drawn filament when released showed a marked crinkle or curl because of the retractive force of the rubber coating.

Example VI

A filament of polyhexamethylene adipamide was cold drawn 100%. It was then coated with plasticized polymerized methyl methacrylate by passing it through a 10% solution of polymerized methyl methacrylate in toluene containing 4% of butyl Cellosolve phthalate. When the filament was cold drawn further amounts up to 100% and released, it assumed a crimped form due to the retraction force of the polymeric methyl methacrylate resulting from its stretching during the cold drawing of the polyhexamethylene adipamide.

Example VII

The procedure of Example VI was repeated except that the coating solution used was one made up by mixing 50 grams of a 5% solution of polymeric methyl methacrylate in toluene with 50 grams of a 5% solution of polyvinyl butyral in ethanol and adding 1.5 grams of butyl Cellosolve phthalate. The results were essentially the same as those in Example VI.

Example VIII

A filament of undrawn polyhexamethylene adipamide was coated with a rubbery polymer obtained by reacting hexamethylenediamine, pentaglycol ($HOCH_2C(CH_3)_2CH_2OH$), and sebacic acid in such proportions that the resulting interpolymer is 95% polyester and 5% polyamide. The coating of the polyhexamethylene adipamide was accomplished by passing the filament through a 13% solution of the above interpolymer in chloroform. When the coated filament was cold drawn and released, it took on an excellent spiral crimp.

Example IX

A filament of polyhexamethylene adipamide was coated with plasticized cellulose acetate by passing it through a 10% solution of cellulose acetate containing 4% of methyl Cellosolve phthalate. When the coated filament was cold drawn, the coating broke into non-adhering cylinders, giving a beaded effect.

As already indicated, this invention is applicable broadly to the coating of synthetic polymeric products which can be formed into shaped objects, such as filaments, bristles, yarns, fabrics, sheeting, ribbons, and the like, and which can be cold drawn in these forms. To be useful in obtaining the novel effects previously mentioned, however, it is necessary that the polymeric product be capable of undergoing at least 25% cold drawing. In other words, to secure the desired effect according to the process of this invention, the coated filament, sheet, or the like should be cold drawn until its length is at least 1.25 times its original length. To obtain the most marked effects, however, the coated article should be cold drawn at least 100%, which necessarily means that the material coated, i. e. the core, must be capable of undergoing at least 100% cold drawing. Certain polymeric materials, and particularly the synthetic linear polymers obtained by condensation referred to above, can be cold drawn several hundred per cent. In view of the high degree of cold drawing which these products can undergo, it will be apparent that they are especially adapted to the process of this invention. It will be apparent also that the novel effects obtainable by this invention can be secured by applying a coating to a partially drawn filament or sheet of these polymers and then further cold drawing the same. As examples of representative synthetic linear polymers obtainable by condensation which are useful in the process herein described may be mentioned polyesters, polyethers, polyacetals, ester-amide interpolymers, e. g. those obtainable from the condensation polymerization of a diamine, dibasic acid and a glycol. Examples of such polymers are given in Patent 2,071,250 referred to above. As already indicated, certain other types of synthetic polymers, e. g. ethylene polymers, can be cold drawn and can therefore serve in making the shaped articles which are to be coated and cold drawn according to the process of this invention. As examples of other polymers which are of limited utility in the process of this invention may be mentioned polystyrene, polyvinyl chloride, and polyacrylic acid derivatives, and polymethacrylic acid derivatives. These polymers are much less satisfactory than the synthetic linear condensation polymers, however, because they cannot be elongated so readily and because they tend to retract considerably after

elongation. This may be because these polymers unlike the linear condensation polymers are plastic rather than crystalline.

As applied to filaments the novel effects previously mentioned can be obtained most conveniently by subjecting the coated filament to cold drawing. Novel effects can also be obtained by cold rolling, which is a procedure intended in this application to be included by the term "cold drawing." In the case of cold rolling the polymeric material, e. g. ribbon or sheeting, is squeezed between rollers and thereby permanently extended to larger dimensions. This procedure, which can be used to effect elongation both longitudinally and laterally, is particularly well adapted to ribbons and sheet material.

In the practice of this invention the surface coating may be applied in a variety of ways. Typical methods of application are dipping the shaped article into or spraying it with a solution or suspension of the coating composition. In some cases the coating can be applied in the molten condition. Transfer rolls are also useful in applying the coating.

The thickness of the coating which is applied to the shaped article to be cold drawn will depend on the nature of the article and the effect desired. For filaments and films the thickness of the solid coat prior to drawing may vary from a fraction of the diameter of the filaments up to equality with the diameter of the filaments, or even greater.

The coating material includes resinous materials, and particularly the synthetic resins, as for instance vinyl resins, phenol-formaldehyde resins, polyacrylic resins, polymethacrylic resins, polyether resins, and polyhydric alcohol-polybasic acid resins. Other useful coating materials are cellulose and its derivatives, such as its ethers, e. g. ethyl cellulose and benzyl cellulose, and cellulose esters, e. g. the acetate and nitrate; and natural and synthetic rubbers or any elastic material, e. g. polymerized chloro-2-butadiene-1,3, polymerized butadiene-1,3, amide-ester interpolymers, e. g. those obtained from aminoacids and hydroxyacids or from glycols including ethylene glycol, 2,2-dimethyl propane diol-1,3, 2-methyl, 2-ethyl propane diol-1,3, 2-methyl, and 2-propyl propane diol-1,3, diamines including hexamethylenediamine, pentamethylenediamine, and decamethylenediamine, and dibasic acids including adipic, sebacic, and terephthalic acids, preferably containing more than 65% polyester. Other elastic coating materials which may be used are properly plasticized resins such as polymeric methacrylates, polymeric acrylates, polyvinyl butyral, vinyl chloride-vinyl acetate interpolymers, certain cellulose derivatives, or suitable mixtures of the above resins. Synthetic linear polymers which are not capable of undergoing so high a degree of cold drawing as the shaped article to be cold drawn can also be used as the coating.

The unusual roughed, scaled, delustered, or other coating effects obtained by the practice of this invention are not only useful because of their novelty effects, but also because these effects actually enhance the utility of the product for various purposes. For instance, the novel surface effects obtained on the polymer filaments may be used to advantage in plying such yarns with natural or artificial yarn, e. g. silk, wool, cotton, and rayon. Desired effects are also obtained if the treated polymer yarn is cut into staple, then spun and woven into fabrics either alone or mixed with other fibers and yarns. The rough surface on the staple or its crimp makes it easier to spin into yarns and gives the yarns a more woolly character. The rough surface or crimp also modifies the felting characteristics of the fibers. Colored coatings, aside from dyes, such as bronze powder, colored pigments, etc., offer other possibilities for novel effects. Yarns so prepared may be plied with other yarns or used separately. Or the yarn from polymer filaments may be dyed, then coated and drawn afterward to secure novel effects. Novel fabrics may be made from yarn prepared by this process by combination with other yarns as indicated above. Novel effects are also obtained by making fabrics from polymer yarn which has been coated with one or more different kinds of coating on the same or separate threads followed by cold drawing. Such fabrics as draperies, decorated fabrics, pile fabrics, upholstery goods, woven and knitted wear offer additional opportunities for novel effects, especially for the beaded type described in Examples IV and IX.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A process which comprises applying a solid, continuous coating to a shaped article comprising a synthetic polymer which is capable of being cold drawn with substantially permanent increase in length of said article, said coating being a substance incapable of being cold drawn with permanent increase in length to the extent to which said polymer is capable, and then cold drawing said shaped article beyond the extent to which said coating is capable of being cold drawn with permanent increase in length.

2. A process which comprises applying a solid, continuous substantially non-elastic coating to a shaped article comprising a synthetic linear polymer which is capable of being cold drawn with substantially permanent increase in length of said article, and then cold drawing said shaped article to an extent which breaks the coating and imparts to the article a discontinuous surface covering.

3. A process which comprises applying a continuous coating of elastic material to a filament comprising a synthetic linear polymer which is capable of being cold drawn with substantial permanent increase in length of said filament, cold drawing said filament to stretch said coating, and then relaxing the filament to permit retraction of the coating.

4. The process set forth in claim 1 in which said polymer is a crystalline synthetic linear polymer.

5. The process set forth in claim 2 in which said polymer is a polyamide.

6. The process set forth in claim 3 in which said polymer is a polyamide.

7. The process set forth in claim 1 in which said article is a filament of a polyamide obtainable by condensation polymerization from a diamine and a dibasic carboxylic acid.

8. The process set forth in claim 1 in which said article is a filament of a polyamide obtainable by polymerization of a monoaminomonocarboxylic acid.

9. A shaped article which comprises a synthetic linear polymer exhibiting molecular orien-

tation and which has a solid pellicular coating broken into small areas over the surface of the polymer, said article presenting a roughened surface of intermittent areas of said polymer and coating, said shaped article being obtained by coating a synthetic polymer capable of being cold drawn to substantial increase in length with a continuous non-elastic coating, and then cold drawing the coated polymer.

10. A filament which comprises a synthetic linear polymer exhibiting permanent orientation along the filament axis and which has a solid pellicular coating broken into small areas over the surface of the filament, said filament presenting a roughened surface of intermittent areas of said polymer and coating, said shaped filament being obtained by coating a filament of synthetic polymer capable of being cold drawn to substantial increase in length with a continuous non-elastic coating, and then cold drawing said filament.

11. A shaped article which comprises a synthetic linear polymer exhibiting molecular orientation and which has on the surface of the polymer a solid continuous coating of elastic material under tension.

12. A filament which comprises a synthetic linear polyamide exhibiting permanent orientation along the filament axis, and which has on its surface a solid continuous coating of elastic material under tension.

13. A crimped filament which comprises a synthetic linear polymer exhibiting orientation along the filament axis, and which has on its surface a solid continuous film of elastic material under tension.

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