Aug. 19, 1941. W. H. BRADSHAW 2,252,689

PRODUCTION OF FILAMENTS, RIBBONS, AND THE LIKE

Filed March 10, 1938

Fig. 1.

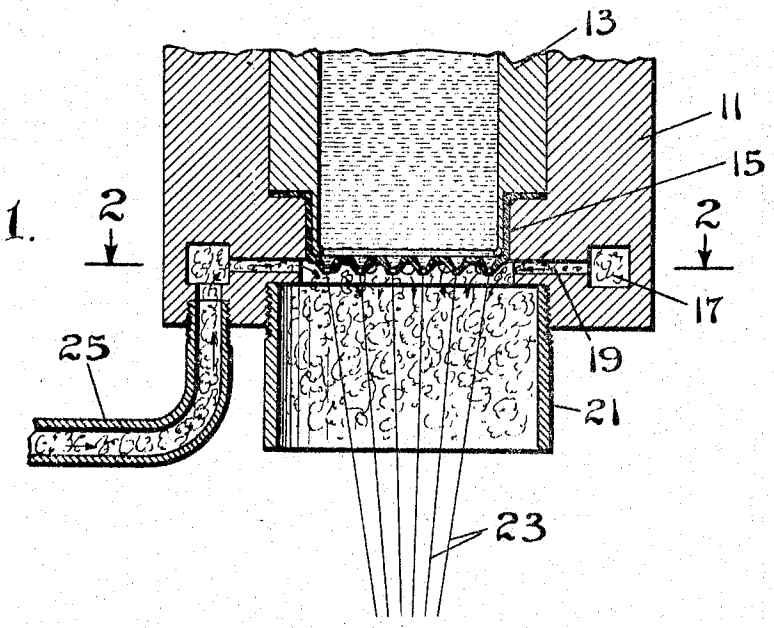
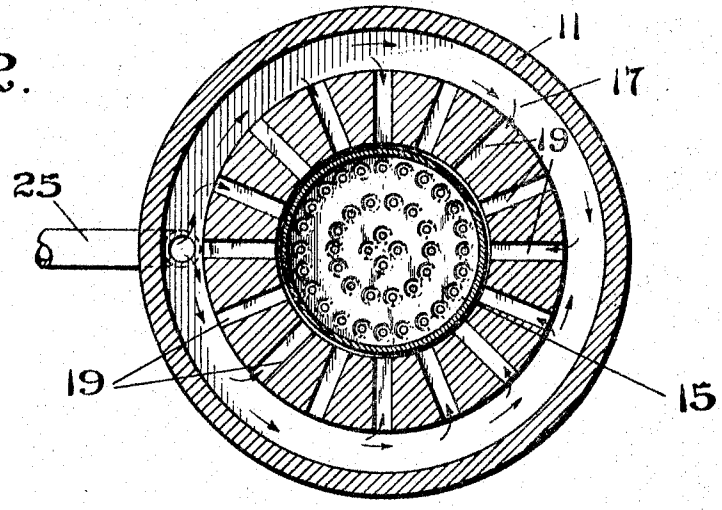


Fig. 2.



INVENTOR.
William Henry Bradshaw
BY
Louis Allis
ATTORNEYS.

Patented Aug. 19, 1941 2,252,689

UNITED STATES PATENT OFFICE

2,252,689

PRODUCTION OF FILAMENTS, RIBBONS, AND THE LIKE

William Henry Bradshaw, Buffalo, N. Y., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

Application March 10, 1938, Serial No. 195,042

12 Claims. (Cl. 18—8)

This invention relates to the production of filaments, ribbons and the like, and more particularly, it relates to the melt spinning of organic filaments. This invention has been found to have particular utility in the melt spinning of filaments, ribbons, and the like from synthetic polyamide compositions in that it is adapted to reduce very materially the objectionable "flicking" of the molten extruded filaments at the face of the spinneret.

Heretofore, a great deal of difficulty has been experienced in spinning filaments from molten synthetic polyamide compositions due to the interruption of the spinning by a turning back of the filamentary streams of molten material to the face of the spinneret. This phenomenon will, for convenience, be hereafter referred to as "flicking."

It is an object of the present invention to provide an improved method and apparatus for the melt spinning of filaments from organic filament-forming compositions which have a tendency to flick during the spinning thereof.

It is another object of this invention to provide a method and apparatus for the melt spinning of filaments from organic filament-forming compositions having a tendency to flick, which method and apparatus will materially reduce the flicking of said compositions.

It is a specific object of this invention to provide a method and apparatus for the melt spinning of filaments from synthetic linear condensation polyamide filament-forming compositions, which method and apparatus will materially reduce the flicking of said compositions.

Other objects of the invention will appear hereinafter.

The objects of the invention may be accomplished, in general, by spinning the molten organic filament-forming composition through a spinneret, the face of which is blanketed with a gas which is substantially inert to the filament-forming composition.

The details of the invention, and the objects thereof, will be easily understood by reference to the following detailed description taken in connection with the accompanying illustration, in which:

Figure 1 is a side elevational sectional view of the lower portion of a melt spinning apparatus.

Figure 2 is a sectional top plan view taken along the lines 2—2 of Figure 1.

Referring to the illustration, reference numeral 11 designates the outer rigid shell of a melt spinning apparatus. A spinneret 15 is held in position against the shoulder of the shell 11 by means of a sleeve element 13. An annular passage 17 is provided in the shell 11 in such a manner as to surround the spinneret 15. A plurality of radial passages 19 connect the passage 17 with the spinneret face. An annular shield 21 is fitted into the lower portion of the shell 11 so that the filaments 23 passing from the orifices of the spinneret pass through the space enclosed by the shield 21. The annular passage 17 is connected by means of a conduit 25 to a source of a gas which is inert to the filament-forming composition. As the spinning of the molten material takes place, a substantially oxygen-free gas such as nitrogen, hydrogen, methane or the like is passed through the conduit 25, the passage 17, and the radial passages 19 to the face of the spinneret and outwardly along the shield 21.

It is preferred, in accordance with the present invention, that the spinneret be constructed with a plurality of cone-like protrusions for the individual orifices. It has been found that the combination between the spinneret with individual coned orifices, together with the shielding device, will produce exceptionally desirable results. However, very satisfactory results are obtained by spinning from a flat face spinneret in accordance with this invention.

This invention is applicable, broadly, to the spinning of molten organic filament-forming compositions having a tendency to flick. It is, however, particularly valuable in the spinning of molten synthetic linear condensation polyamides and for this reason, it will described with particular reference to these materials.

As indicated in U. S. 2,071,250 and 2,071,253, valuable artificial fibers can be prepared from high molecular weight synthetic linear condensation polyamides, therein referred to as superpolyamides. These superpolyamides are of two types: Those derived from polymerizable monoaminomonocarboxylic acids or their amide-forming derivatives, and those derived from the reaction of suitable diamines with suitable dicarboxylic acid or amide-forming derivatives of dibasic carboxylic acids.

Although the filament-forming synthetic linear condensation polyamides have fairly high melting points, generally between 175 and 300° C., their thermal stability is such that they can be spun from melt, i. e., the molten polymer can be extruded into filaments and the like without the use of solvent or plasticizer. While this is a very desirable method of spinning, it presents certain difficulties. Among the principal difficulties is

the tendency of the filaments to flick and foul the spinneret during spinning. It is believed that usually the flicking occurs gradually, i. e., the distortion of the filament from its linear path becomes progressively worse until finally the filament touches the spinneret face. However, the flicking may occur within a few minutes after spinning starts. Spinning can be resumed by wiping the face of the spinneret with a swab which indicates that flicking is the result of external fouling. Attempts to overcome flicking by increasing the jet velocity, by coating the face of the spinneret with a lubricant and by using spinnerets in which the orifices are located in cone-like protrusions extending outward from the delivery side of the spinneret have decreased the interruption to the spinning considerably but have not overcome it sufficiently to be considered an entirely satisfactory solution.

Surprisingly, it has now been discovered that flicking can be overcome in the melt spinning of polyamides by blanketing the face of the spinneret with a gas which is inert toward the polyamide. It is particularly important to exclude free oxygen. It is desirable that the gas contain less than 0.03% free oxygen. Thus, if an atmosphere of substantially oxygen-free nitrogen, methane, helium, argon, hydrogen, carbon dioxide or the like is maintained at the face of the spinneret, spinning can be continued almost indefinitely without flicking. It is desirable that the gas used be substantially insoluble in the filament-forming composition. The advantages of this invention are particularly pronounced when spinning at relatively low jet velocity.

This discovery indicates that flicking is in some way associated with the presence of oxygen. This is very surprising for although polyamides do show some tendency to oxidize at elevated temperatures, the filamentary streams of molten polymer leaving the spinneret do not oxidize appreciably during the short time they are exposed to air while hot. Apparently, however, the small amount of molten polymer which creeps back on the spinneret face does oxidize. By blanketing the spinneret face with an oxygen-free gas, the molten polymer which creeps back on the spinneret face does not oxidize and therefore does not induce flicking.

According to the present invention, molten polyamides are spun through a spinneret, preferably a spinneret of the cone type, under such conditions that the delivery side of the spinneret is blanketed with a gas which is substantially free from oxygen or other reactive gas. Nitrogen is a good gas for blanketing the spinneret, since it has practically the same density as air and is therefore readily maintained at the spinneret face. While ordinary commercial nitrogen is helpful, it is much more advantageous to use nitrogen which has been freed from substantially the last traces of oxygen by scrubbing with an oxygen absorbent, such as pyrogallol or "silver salt" (sodium salt of beta-anthraquinone sulfonic acid), or by passing the nitrogen over heated copper preferably in the presence of a small amount of hydrogen. However, other inert gases or mixtures of inert gases may also be used.

In melt spinning, the spinneret is generally placed so that the filaments fall vertically from the spinneret. It is therefore a simple matter to provide the spinneret face with a shield which will aid in maintaining an inert atmosphere at the spinneret face. The shield may take the form of a hollow tube, one end of which is joined to or surrounds the spinneret. The shield being open at its lower end provides a free passage for the filaments to the wind-up device. The inert gas can be introduced into the space adjacent the spinneret face through the open lower end of the shield or through outlets on the side or near the top of the shield. The rate of flow of the gas required to maintain a substantially oxygen-free condition at the spinneret face will naturally vary with the physical properties of the gas used and with the details of the shield, if any. It is preferred to employ a minimum rate of flow of the gas.

The following example illustrates the preparation of filaments according to the process of this invention; it is to be understood, however, that the invention is not to be limited thereby.

Example

Polyhexamethylene adipamide of intrinsic viscosity 0.9 and melting point 263° C. was spun from melt at about 290° C., using a constant volume delivery pump. The spinneret employed contained 10 orifices each of 0.0088" diameter, situated at the bottom of truncated cone-shaped protrusions extending outward from the delivery side of the spinneret. Each cone-like protrusion had a height of 0.063" and the sides of the cone formed an angle of about 60°. The spinneret had been dressed with a polymerized isobutylene lubricant. Adjacent the spinneret face and extending downward for about 2 inches so as to protect the filements, as indicated in the attached diagram, was a metal sleeve or shield. Oxygen-free nitrogen was introduced through the conduit and passages leading to this shield at a rate of 730 cc. per minute and the gas was distributed at the spinneret face at the base of the cone-shaped protrusions. The rate of spinning was 1,500 ft. per minute, i. e., the 10-filament yarn (denier 50) was collected on a bobbin placed below the spinneret and shield at a rate of 1,500 ft. per minute. The pump rate was 2.6 grams per minute. After 8 hours of continuous spinning without interruption, the current of nitrogen introduced at the spinneret face was discontinued and air was introduced at the same rate. Within 15 minutes, the filaments were deformed from their linear path and the spinnerets became badly fouled due to flicking. This clearly illustrates the importance of having an oxygen-free gas at the spinneret face. If no nitrogen is introduced and no shield is employed, fouling usually occurs within a few hours under these conditions.

The foregoing example illustrates the melt spinning of a synthetic linear condensation polyamide derived from hexamethylenediamine and adipic acid. It will be apparent that this invention is applicable to other fiber-forming materials which are capable of being spun from melt but which tend to foul the spinneret, by reason of oxidation and, as a consequence, interrupt the spinning. Since the rate of oxidation increases with temperature, this process is particularly important in the spinning of high melting products, e. g., products melting above 175° C.

The method of spinning herein described is also useful in making filaments from polyamides which have been modified with other materials, such as pigments, resins, dyes, plasticizers, luster modifying agents, etc. It is, of course, applicable also to mixed polyamides and to inter-polyamides.

While this invention is most useful in the preparation of filaments, particularly filaments of the type used in making fibers or yarns for fabric

manufacture, it is also applicable to the preparation of large filaments, e. g., bristles, and to ribbons and the like.

It will be apparent that various methods can be employed in maintaining an inert substantially oxygen-free atmosphere at the spinneret face. While a shield is not absolutely necessary in practicing this invention, it is most expedient and economical to use one in maintaining the inert gas at the spinneret face. The design of the shield may obviously take a variety of forms without departing from the spirit of this invention. It will be apparent also that various types of inert gases may be used to blanket the spinneret face. Any polymerized hydrocarbon, e. g., metastyrene and polymerized olefines may be used as the spinneret lubricant.

This invention is in no way limited by the means employed in melting the filament-forming compositions, in bringing about spinning of the filaments, or in treating the filaments after they are spun. The essential part of this invention is that an inert oxygen-free atmosphere is maintained at the spinneret face.

This invention provides an improved method for the preparation of filaments and the like from oxygen-sensitive molten filament-forming compositions, particularly synthetic linear condensation polyamides. This improvement very materially reduces and, to a large extent, overcomes spinneret fouling thus making it possible to spin filaments from molten filament-forming compositions, e. g., synthetic polyamides, almost indefinitely without interruption. This is an important contribution to the art, for melt spinning, when free from spinneret fouling, is a much more rapid and economical method for producing filaments than spinning from solution.

Since it is obvious that many changes and modifications can be made without departing from the nature and spirit of the invention, as above described, it is to be understood that the invention is not to be limited except as set forth in the appended claims.

I claim:

1. In an apparatus capable of spinning a molten organic filament-forming composition substantially without flicking, a spinneret, a lubricating composition on the external face of said spinneret, an annular shield surrounding the external face of said spinneret, and a plurality of conduit means substantially in the plane of the external face of the spinneret for introducing an inert substantially molecular oxygen-free gas adjacent to the external face of said spinneret.

2. In an apparatus capable of spinning a molten organic filament-forming composition substantially without flicking, a spinneret, an annular shield surrounding said spinneret, and a plurality of conduit means substantially in the plane of the external face of the spinneret for uniformly introducing an inert substantially molecular oxygen-free gas around the external face of said spinneret.

3. In an apparatus capable of spinning a molten organic filament-forming composition substantially without flicking, a spinneret provided with a plurality of conical protrusions having orifices therein, an annular shield surrounding said spinneret, and a plurality of conduit means substantially in the plane of the external face of the spinneret for uniformly introducing an inert substantially molecular oxygen-free gas around the conical protrusions on external face of said spinneret.

4. In a process for the formation of filaments by extruding, into a gaseous medium, a molten organic filament-forming composition, the freshly formed filamentary streams of molten composition being subject to flicking in the presence of oxygen, the step of eliminating flicking of the freshly formed filamentary streams which comprises surrounding the freshly formed filamentary streams immediately after they are extruded with a sufficient quantity of an inert substantially molecular oxygen-free gas to maintain said streams in a substantially oxygen-free condition.

5. In a process for the formation of filaments by extruding, into a gaseous medium, a molten organic filament-forming composition, the freshly formed filamentary streams of molten composition being subject to flicking in the presence of oxygen, the step of eliminating flicking of the freshly formed filamentary streams which comprises surrounding the freshly formed filamentary streams immediately after they are extruded with substantially molecular oxygen-free nitrogen.

6. In a process for the formation of filaments by extruding, into a gaseous medium, a molten organic filament-forming composition, the freshly formed filamentary streams of molten composition being subject to flicking in the presence of oxygen, the step of eliminating flicking of the freshly formed filamentary streams which comprises surrounding the freshly formed filamentary streams immediately after they are extruded with substantially molecular oxygen-free methane.

7. In a process for the formation of filaments by extruding, into a gaseous medium, a molten synthetic linear condensation filament-forming polyamide composition the freshly formed filamentary streams of which are subject to flicking in the presence of oxygen, the step of eliminating flicking of said freshly formed filamentary streams which comprises surrounding the freshly formed filamentary streams immediately after they are extruded with a sufficient quantity of an inert substantially molecular oxygen-free gas to maintain said streams in a substantially oxygen-free condition.

8. In a process for the formation of filaments by extruding, into a gaseous medium, a molten synthetic linear condensation filament-forming polyamide composition the freshly formed filamentary streams of which are subject to flicking in the presence of oxygen, the step of eliminating flicking of said freshly formed filamentary streams which comprises surrounding the freshly formed filamentary streams immediately after they are extruded with an inert substantially molecular oxygen-free nitrogen.

9. In a process for the formation of filaments by extruding, into a gaseous medium, a molten synthetic linear condensation filament-forming polyamide composition the freshly formed filamentary streams of which are subject to flicking in the presence of oxygen, the step of eliminating flicking of said freshly formed filamentary streams which comprises surrounding the freshly formed filamentary streams immediately after they are extruded with substantially molecular oxygen-free methane.

10. In a process for the formation of filaments by extruding, through a spinneret, into a gaseous medium, a molten synthetic linear condensation filament-forming polyamide composition, the

freshly formed filamentary streams of which are subject to flicking in the presence of oxygen, the step of eliminating flicking of the freshly formed filamentary streams which comprises surrounding the external face of the spinneret with a sufficient quantity of an inert substantially molecular oxygen-free gas to maintain said spinneret face in a substantially oxygen-free condition.

11. In a process for the formation of filaments by extruding, through a spinneret, into a gaseous medium, a molten synthetic linear condensation filament-forming polyamide composition, the freshly formed filamentary streams of which are subject to flicking in the presence of oxygen, the step of eliminating flicking of the freshly formed filamentary streams which comprises surrounding the external face of the spinneret with substantially molecular oxygen-free nitrogen.

12. In a process for the formation of filaments by extruding, through a spinneret, into a gaseous medium, a molten synthetic linear condensation filament-forming polyamide composition, the freshly formed filamentary streams of which are subject to flicking in the presence of oxygen, the step of eliminating flicking of the freshly formed filamentary streams which comprises surrounding the external face of the spinneret with substantially molecular oxygen-free methane.

WILLIAM HENRY BRADSHAW.