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SPINNERETS COATED BY METAL EVAPORATION

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This invention relates to spinnerets. More particularly, it relates to an improved spinneret for the spinning of artificial filaments from synthetic filament-forming compositions and to the method of forming the improved spinneret. Still more particularly it relates to an improved method for dry spinning dimethyl formamide solutions of acrylonitrile polymers.

In the shaping of structures, such as filaments, from acrylonitrile polymers dissolved in dimethyl formamide by the dry or evaporative method, considerable difficulty is encountered in starting up spinning positions. When the common type dry spinning nozzles, such as nickel spinnerets, are used, the solutions have a tendency to wet the faces of the spinnerets thereby fouling the spinneret holes and developing deposits in and around the holes in relatively short times. The usual means for avoiding these difficulties, such as wiping the face of the spinneret with gasoline to get the spinning solution completely and uniformly started through the spinneret orifices, do not prevent irregularities which occur quickly and which soon result in off-denier filaments, a reduced number of filaments in the yarn due to blocked holes and yarn that has but little commercial value. While these difficulties are not encountered to any appreciable extent using certain other solvents, such as tetramethylene cyclic sulfone, dimethyl formamide is a particularly good solvent for acrylonitrile polymers and its utilization is desired.

It is, therefore, an object of this invention to provide a spinneret suitable for the spinning of synthetic filament-forming substances, and especially useful for the dry or evaporative spinning of dimethyl formamide solutions of acrylonitrile polymers. Other objects will be apparent from the following description.

These objects are accomplished by dry spinning dimethyl formamide solutions of acrylonitrile polymers through a spinneret prepared by subjecting a spinneret prepared from nickel or other workable metals, such as stainless steel, brass, and aluminum, to a coating operation involving metal evaporation carried out in a high vacuum whereby a thin coating of chromium is deposited on the spinneret. The spinneret as prepared is chromium-surfaced not only on the face of the spinneret but in and around the outer openings of the spinneret orifices without blocking the small holes or distorting them sufficiently to affect their usefulness. Further, the surfaces are advantageously converted to non-wettable surfaces. Dimethyl formamide solutions of

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acrylonitrile polymers are spun through these chromium-surfaced spinnerets with surprising facility.

This invention may be better understood by reference to the following example and description which are given for illustrative purposes and are not to be construed as limitative.

Example

A spinneret of suitable size, depending on the number of holes desired which are suitably spaced one from the other, is prepared from nickel, stainless steel alloys or the like. The holes may, for example, be of about 0.15 mm. diameter and the minimum spacing between holes about 7 mm. A spinneret of about 2¼ inches diameter across the face accommodates comfortably about 40 holes. If a larger number of holes is desired, the spinneret is made somewhat larger in face diameter. This spinneret, after suitably preparing the holes with the desired inside countersinks and then polishing and carefully cleaning, is given a thin coating of chromium all over the outside face. This is accomplished by following the method described in U. S. Patent 2,079,784. If a film is to be prepared, the orifice is in the form of a slot. The chromium coating is accomplished in the same manner. Coatings in the range from 200 to 1,000 or more angstrom units in thickness are made and the corresponding spinnerets are used with excellent results. When the coating is very much less than 400 or very much more than 600 angstrom units, it tends to be worn off rather quickly. Appreciable flaking occurs when the coatings are too thick. Accordingly, coatings having a thickness of from 300 to 700 angstrom units are generally preferred. When dimethyl formamide solutions of acrylonitrile polymers are spun through spinnerets prepared in this manner, spinning is accomplished more easily and yarn of better quality is obtained. For example, an uncoated nickel spinneret is corroded within five minutes as shown visibly by the frosting that appears on the polished surface. On the other hand, the coated spinnerets of this invention are still uncorroded after sixty hours of spinning. Further, the yarn produced using the spinnerets of this invention have higher tenacities and elongations and are more uniform, both in these physical properties and in contour.

While this invention has been illustrated particularly in reference to polyacrylonitrile, it encompasses the use of acrylonitrile polymers containing a major portion of acrylonitrile in the polymer. Thus, copolymers and interpoly-

mers prepared using small amounts of such monomers as vinyl esters, vinyl halides, vinylidene halides or other ethylenic compounds such as ethylene or the butadienes may be employed. For example, vinyl acetate, vinyl chloride, vinyl pyridine, esters or other derivatives of acrylic or methacrylic acids, styrene, and isobutylene may be used in the preparation of the polymers. However, for the final yarn to possess the desirable properties of polymerized acrylonitrile (such as resistance to acids and common solvents), it is necessary that the polymer contain a major portion of acrylonitrile, and those polymers that are prepared from at least 85 parts of acrylonitrile and no more than 15 parts of another polymerizable substance are preferred.

The solutions of the above polymers in dimethyl formamide may be prepared as described in Latham, U. S. 2,404,714. The solutions utilized commercially generally contain from about 5% to 25% of the acrylonitrile polymer. The solids content is not limited thereto and may be greater or less, if desired. Any of the conventional spinning conditions may be used in the extrusion of the polymer solutions through the apparatus of this invention. For example, those conditions disclosed in U. S. Patent 2,404,714 may be employed. While the spinnerets of this invention are particularly useful in dry spinning of acrylonitrile polymer solutions, they may also be used in wet-spinning procedures such as those disclosed in U. S. 2,426,719.

The acrylonitrile polymers which are generally used commercially for the preparation of the shaped articles described in this invention must, of course, be of a sufficiently high molecular weight to possess film- or filament-forming properties. The polymers employed possess an average molecular weight within the range of 25,000 to 750,000 or even higher and preferably between the range of 40,000 to 250,000 as calculated from viscosity measurements by the Staudinger equation:

$$\text{Molecular weight} = \frac{N_{sp}}{K_m C}$$

wherein:

$K_m = 1.5 \times 10^{-4}$

$N_{sp} = \text{specific viscosity} = \frac{\text{viscosity of solution}}{\text{viscosity of solvent}} - 1$

and

C = concentration of the solution expressed as the number of moles of the monomer (calculated) per liter of solution.

It is to be understood, however, that acrylonitrile polymers having molecular weights below or above the range indicated may be subjected successfully to the process of this invention.

This invention has been described with particular reference to dimethyl formamide solutions of acrylonitrile polymers. It may also be used with good results in the extrusion of any dry spinning solution of acrylonitrile polymers or for the spinning of other synthetic filament-forming materials, such as other filament-forming vinyl polymers. However, the dimethyl formamide solutions of acrylonitrile polymers are particularly difficult to handle in dry spinning and generally no specially prepared spinneret is needed for dry spinning other solutions.

As pointed out above, the difficulties encountered in dry spinning dimethyl formamide solutions of acrylonitrile polymers are in starting the spinning. The solutions wet the face of conventional spinnerets; polymer deposits are formed; holes are blocked; and yarn irregularities are produced. Simple mechanical means are not available to prevent these difficulties. Likewise, substitution of spinnerets made of other metals does not provide the solution to the problem. Thus, spinnerets made of brass, silver, copper, iron, and zinc, among others, are not satisfactory. Attempts to fabricate chromium spinnerets failed because of the non-workability of the metal. Further, electroplating of nickel spinnerets with chromium is unsatisfactory because the fine orifices are either closed partially or completely and can not be re-opened in a satisfactory manner.

It was indeed surprising to discover that when a spinneret was prepared from nickel or other workable metal or metal alloy and then subjected to a coating operation by metal evaporation carried out in a high vacuum, a relatively thin but very satisfactory coating of chromium could be applied, not only on the face of the spinneret, but in and around the outer openings of the spinneret orifices without blocking the holes or distorting or changing them sufficiently to affect their usefulness. The coating that occurs in and around the orifices is of definite value since this coating prevents the plugging that usually occurs within the orifices and since this coating converts an otherwise wettable surface to a non-wettable one.

By coating on this very thin layer of chromium, the desired surface characteristics are obtained without building up sufficient chromium in or around the holes to alter their diameter noticeably and, if the surface of the spinneret is properly cleaned and prepared before the coating is applied, the chromium sticks tenaciously to the base metal. That the chromium vapor penetrates the fine orifices and deposits itself in and on the walls thereof is indeed surprising and, even though the deposition of metal on the orifice walls is probably somewhat thinner than on the face of the spinneret, the variation in thickness is of no significance in view of the very thin coating applied.

It was subsequently found that when a 20% solution of polyacrylonitrile dissolved in dimethyl formamide was extruded through this type spinneret by an evaporative spinning process, the startability of spinning was excellent, and spinning of high quality yarn could be continued uninterrupted over extended periods of time. It was found that the hole spacing in the spinneret could be made somewhat closer than had been possible in the case of nickel or stainless steel spinnerets and still give good startability and continuity of spinning. This is a very definite advantage for the spinning of yarns comprised of a large number of filaments, since the spinneret can be made smaller in diameter. This greatly increases the ease of stringing up.

While the coating of the spinneret can be made by metal evaporation, the so-called technique of sputtering may also be used for similarly depositing chromium in an exceedingly thin layer on spinnerets. In this connection see the book "Procedures in Experimental Physics" by John Strong, Prentice Hall, 1942, pp. 159 to 187.

As described above, this invention provides for outstanding advantages in spinnability and in yarn quality. In dry spinning by the process of this invention, the lower wettability of the chromium-surfaced spinneret permits self-starting at the beginning of spinning. There is no troublesome corrosion during spinning. Further, occa-

sional solvent cleaning of the spinneret is all that is necessary to continue satisfactory spinning over extended time periods rather than the usual firing, lapping, reaming and polishing. Still further, it is not necessary to coat the spinneret completely. While spinnerets completely coated on all sides and within the orifices can be prepared and used advantageously in the process of this invention, it is preferred to coat only the outside face of the spinneret and the surfaces of the orifices nearest it. The solution side need not be coated, because, for some reason, corrosion and depositions do not occur on this side of the spinnerets or on the orifice walls nearest this side. The partially coated spinneret can be used with eminently satisfactory results and with a substantial saving in materials and in time of preparing the spinnerets of this invention. That the coating extends well in and around the outer openings of the spinneret orifices is an important advantage. The deposits within the holes are avoided and there is no blocking of the holes either partially or completely. Another advantage resides in the fact that the spinnerets of this invention have non-wettable surfaces. Not only are deposits on the outer face avoided, but the filaments no longer tend to become joined and a filament is obtained for every orifice present. Yarn quality is greatly improved and spinning proceeds more uniformly and for longer time periods without interruption.

Any departure from the above description which conforms to the present invention is intended to be included within the scope of the claims.

I claim:

1. In the process of dry spinning dimethyl formamide solutions of acrylonitrile polymers containing a major portion of acrylonitrile, the improvement comprising spinning without the development of polymer deposits and blocked holes by extruding the said solutions through chromium-surfaced spinnerets.

2. In the process of dry spinning dimethyl formamide solutions of acrylonitrile polymers containing a major portion of acrylonitrile, the improvement comprising spinning without the development of polymer deposits and blocked holes by extruding the said solutions containing from 5% to 25% of said polymers through chromium-surfaced spinnerets.

3. A method for improving the spinnability of dimethyl formamide solutions of acrylonitrile polymers containing a major portion of acrylonitrile which comprises spinning without the development of polymer deposits and blocked holes by extruding said solutions through chromium-surfaced spinnerets.

4. A metallic spinneret, the surface and orifice walls of which are coated with chromium.

5. A spinneret in accordance with claim 4 in which the chromium coating is from 200 to 1000 angstrom units in thickness.

6. A nickel spinneret, the surface and orifice walls of which are coated with a layer of chromium from 200 to 1000 angstrom units in thickness.

7. A nickel spinneret, the surface and orifice walls on the outside face being coated with a layer of chromium from 200 to 1000 angstrom units in thickness.

8. A metallic spinneret, the surface and orifice walls of which are coated with chromium, the coating being about 300 to about 700 angstrom units in thickness.

9. A spinneret in accordance with claim 6 in which the said thickness is from about 300 to about 700 angstrom units.

10. A spinneret in accordance with claim 7 in which the said thickness is from about 300 to about 700 angstrom units.

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REFERENCES CITED

The following references are of record in the file of this patent:

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2,404,714	Latham	July 23, 1946
2,496,961	Schneider	Feb. 7, 1950