This invention relates to a process for the preparation of yarns, films, ribbons, etc., from acrylonitrile polymers, which possess a high tenacity, a desirable elongation, a lustrous appearance, and are substantially free of voids. Acrylonitrile polymers can be dissolved in certain volatile organic solvents, such as are disclosed in U. S. Patents 2,404,714--2,404,727 inclusive, to form solutions suitable for extrusion into shaped articles such as yarns. Wet-spinning processes for the preparation of yarns from these solutions are described in U. S. Patents 2,426,719, 2,451,420 and 2,467,553. These yarns are emissarily suited for use in the textile art. In fact, there is a great demand in the textile industry for a yarn having the outstanding properties, such as high tenacity, good outdoor durability, and the insolubility in and insensitivity to common organic solvents, possessed by polyacrylonitrile yarns.

While the wet-spinning techniques described in U. S. 2,426,719, U. S. 2,451,420 and U. S. 2,467,553 yield high tenacity, dense, lustrous shaped articles, such as yarn, from acrylonitrile polymers, the spinning speed and productivity are limited. The dense structures produced are the result of gradual rather than rapid coagulation. A top speed of 100 yds./min. was obtained with glycerol as the coagulating bath. With the less expensive aqueous salt solution as the coagulating bath, the spinning speeds were more in the order of 50 yds./min. From the standpoint of production economy, it is desirable to spin a large number of filaments at high rates of speed into an inexpensive coagulating bath, such as water, from which the polymer solvent can be readily recovered. However, this results in yarns having varying degrees of porosity, depending upon the spinning conditions. These porous yarns lack strength and luster, and their use in the textile art is extremely limited.

It is an object of this invention to provide a method by which porous shaped articles, such as wet-spun acrylonitrile polymer yarns are converted into articles that possess a sufficiently high tenacity and elongation to render them suitable for use in the textile art, have a lustrous appearance and are substantially free of voids. A particular object of this invention is to provide a process for healing or closing the voids in acrylonitrile polymer yarns prepared by wet-spinning an organic solvent solution of the polymer into an inexpensive aqueous coagulating bath at high speed. Other objects will become apparent from the description of the invention which follows.

The objects of this invention are accomplished in general by a process which comprises drawing the wet, solvent-free, porous acrylonitrile polymer yarn at least twice its as-spun length and then passing the oriented yarn while still wet through a fluid bath heated to a temperature exceeding the temperature of the wetting material. More specifically, the fluid bath comprises a material which is liquid at ordinary temperatures and immiscible with the wetting material.

The ability to heal a yarn, i. e., to convert a porous yarn to a solid yarn, depends upon the degree of porosity, which in turn is a function of the spinning conditions, particularly the rate of coagulation. If the rate of coagulation is high, a skin forms on the polymer structure and the structure cannot collapse properly during coagulation to form a solid yarn. The compactness of the structure can be shown by determining the area ratio of the yarn obtained. The term "area ratio" refers to the ratio of the measured cross-sectional area of the individual filaments of an acrylonitrile polymer yarn to the theoretical cross-sectional area of those filaments as calculated from the denier of the yarn and the known density of the polymer.

When this area ratio is less than 3.1, the voids in the yarn are small and well distributed so that the yarn is healed or becomes completely solid during subsequent normal drawing. The strength of such yarns as expressed in terms of tenacity will generally be in the order of at least 3 g. p. d. and may reach as high as 6.5 g. p. d. depending upon the spinning conditions. The porosity may not be removed or diminished appreciably by simple orientation for the voids are merely elongated going from nearly round holes to tubular channels. In fact, a highly porous yarn, say of 3.3 porosity, will actually increase in porosity due to bulging on expansion of the gas in the yarn.

As described in a copending case, Serial No. 172,620, filed July 7, 1950, when the area ratio is greater than 3.1 an additional process step is required to convert the white, opaque, porous yarn to a solid, clear yarn. This can be accomplished by treating the wet, porous yarn at a temperature of 100° C. or greater while exerting a lateral pressure on the yarn surface, such as by a hot roll. Naturally, each additional process step is reflected in the cost of the yarn. It is desirable, therefore, to simplify each required process step.
and minimize its cost. Wet, porous, oriented acrylonitrile polymer yarns having an area ratio of about 3.3 or less can be converted into more useful solid yarns by passing them through a bath of hot fluid immiscible with water. The hot fluid treatment eliminates the voids in a few seconds and involves less expense than hot roll equipment. In addition, the yarn when heated by the fluid bath treatment of this invention will crimp spontaneously upon relaxation.

The invention may be better understood by referring to the following examples, which are to be construed as illustrative and not limitative and in which parts and percentages are by weight unless otherwise specified.

**Example I**
A solution of 20 parts of a copolymer, containing 94% acrylonitrile and 6% 2-vinylpyridine and possessing an average molecular weight of approximately 78,000, in 80 parts of N,N-dimethyl formamide (DMF) is extruded at a temperature of 100° C. through a 960-hole spinmeret (hole diameter of 0.003") into a spinning bath consisting of 19% DMF and 81% water heated to a temperature of 85° C., the solutions being delivered to the spinmeret at the rate of 200 gms./min. The yarn formed is led through the bath for a total distance of 28", the yarn being subjected during its travel to a tension by means of a snubbing guide mounted at a distance of 10" from the spinmeret face. On leaving the bath the yarn is passed without slippage about a positively driven feed roll possessing a peripheral speed of 100 yds./min., the yarn being subsequently collected at the same rate. This yarn was washed free of dimethyl formamide and its degree of porosity was defined by an area ratio of about 3.0. This yarn was then drawn 3.5 times its original length in a tube containing steam under 40 lbs./sq. in. pressure. The drawn yarn was then led through a boiling xylene bath without longitudinal shrinkage during which process the voids were completely eliminated. The resulting yarn had a tenacity of 2.3 g. p. d. dry and an elongation of 35%. Its loop tenacity was 1.7 g. p. d. at an elongation of 28%. High-tensile yarns are readily prepared by increasing the draw ratio used in the spinning drawing step. The present sample of yarn, however, was to be used in the preparation of staple whereby a tenacity of greater than 2 g. p. d. is highly satisfactory. When staple fibers cut from the yarn prepared in the manner of this experiment were placed in boiling water, they developed spontaneously a crimp suitable for processing.

**Example II**
A solution of 20 parts of polyacrylonitrile, possessing an average molecular weight of 70,000, in 80 parts of dimethyl formamide was spun in the manner described in Example I using a delivery to the spinmeret of 230 gms./min. with a snubbing guide in the bath 5½" from the spinmeret. The yarn after passing without slippage around a feed roll having a peripheral speed of 100 yds./min. was collected by dropping into a rotating collecting can. This yarn without washing was drawn 4 times its length through steam at 30 lbs./sq. in. pressure. It was then washed in water at room temperature and possessed a degree of porosity defined by an area ratio of about 3.3. A portion, air dried, was very dull in luster and of rather harsh handle, and a porosity of 2.2. A second portion of the wet yarn was placed in the form of a skein in the saturated vapors of boiling xylene according to this invention. Relatively rapid removal of the water in the yarn took place and the yarn became transparent and non-porous in appearance, the area ratio being 1.2. This yarn after the residual xylene was removed was lustrous, strong and dense showing no porosity in filament cross-sections viewed at 500 diameters magnification. Physical properties of the yarn which had a denier per filament of 3.4, were 1.8 g. p. d., tenacity and 23% elongation.

**Example III**
A third portion of the drawn washed yarn of Example II was similarly treated except that saturated vapors of toluene were utilized instead of the xylene. The treated yarn was likewise dense and lustrous having a measured porosity of 1.2 and only minute traces of porosity in cross-sections observed at 500 diameters.

**Example IV**
A fourth portion of the drawn washed yarn of Example II was similarly treated but vapors of boiling benzene were used. The resultant yarn had a degree of porosity being readily visible in the filament cross-section observed at 500 diameters magnification. In order that the voids may be eliminated from moderately porous acrylonitrile polymer yarns by the fluid bath treatment of this invention the residual solvent contained by the wet spun yarn must be substantially removed. There is reason to believe that the surface tension of the shrinking liquid film on the yarn pores contributes to the healing of the pores by the hot fluid bath treatment. Solvents for acrylonitrile polymer are generally miscible with water and will reduce the surface tension of the water in the pores of the yarn. This probably accounts also for the fact that the fluid bath for healing the yarn pores must comprise a material immiscible with water or the liquid wetting the yarn.

The solvent-free yarn must be oriented by drawing at least twice its as-spin length. Stretch applied during spinning will not satisfy this requirement unless orientation accompanies the stretching. Since rapid coagulation in a wet spinning bath leads to wet weak porous yarn, it is usually necessary to orient the yarn by means of a subsequent drawing operation. This is best performed by passing the as-spin yarn either before or after complete solvent removal through a tube containing steam at atmospheric or slightly greater pressure and collecting the yarn at least twice as fast as it enters the steam tube. As pointed out below, the desired orientation may be accomplished at the time of spinning or formation of the article. Further, the orientation may be accomplished in any convenient manner, as by the use of steam baths, hot water baths or spin baths. The drawing may be accomplished before or after applying the wetting agent.

As mentioned previously, the fluid bath for healing the yarn pores must comprise a material immiscible with the peripheral solvent of the yarn. The wetting agent may be water or similar polar substance, such as the alcohols, like ethyl alcohol, dioxane, etc. and in general substances which have a slight swelling action on the polymers. Since for the sake of economy the yarn will generally be wetted with water, the preferred healing baths will comprise hydrocarbons and water immiscible derivatives thereof which boil at temperatures ranging from about 100°-
2,677,590

200° C. Such materials are, for example, toluene, xylene, p-cymene, ethyl benzene, n-octane, nonane, cumene, diisooamy, pseudocumene, p-methane, chlorobenzene, chlorotoluene, mono-halides of pentane, hexane and heptane, ethylene bromide, tetrachloroethene, tetrachloroethylene, perfluorobutlyne and the like. Still further metallic substances such as Wood’s metal or mercury may be used. Also, oily materials such as silicon oils may be employed. The fluid bath may be liquid or substantially saturated vapor heated to a temperature of 100° C. or over. The preferred temperatures for heating are in the range of 125°-165° C. Temperatures lower than 100° C. may be used on occasion depending upon the materials involved, but in general, a temperature of 100° C. or higher is preferred because the polymers have better plasticity at those temperatures.

The wet, porous, oriented acrylonitrile polymer yarn may be converted to solid yarn by the fluid bath treatment either while under tension or in a relaxed condition. The treatment may be akin-wise in batch form or performed continuously in the running. If the spinning is carried out while the yarn is in relaxed condition, the yarn will develop a substantial crimp in the process. The best crimp is obtained, however, by heating the yarn pores under tension, subsequently drawing the yarn to maximum orientation and finally relaxing the yarn in boiling water. An excellent crimp develops spontaneously in the hot water relaxation.

It is essential in the operation of this invention that the yarn being heated be thoroughly wet. The heating takes place only while the yarn is drying. It is not essential that water be the wetting liquor but water certainly is the easiest to handle and the most economical. It is thought that the heating actually takes place in addition to the effect of the surface tension of the shrinking liquid film because a slight vacuum is developed as the vaporized liquor leaves the yarn and this vacuum collapses the porous structure.

In preparing the yarn, the polymer can be dissolved in any suitable solvent. However, it is preferred that the solvent comprises a volatile organic substance. The term “volatile organic solvent” as used in this specification is meant to include those organic substances that are capable of forming stable homogeneous solutions with an acrylonitrile polymer and that can be distilled without decomposition at atmospheric pressure. This class of substances is exemplified in U. S. Patent Nos. 2,404,714-2,404,727, inclusive.

The preferred concentration of the spinning solution is, of course, dependent upon the average molecular weight of the polymer employed, it generally being desirable to use more dilute solutions in the spinning of polymers of high molecular weight. It has been found that the viscosity of the spinning solution has an appreciable effect on the degree of porosity of the spun yarn. Solutions of acrylonitrile polymers in dimethyl formamide having a viscosity of from 30-90 poises at 125° C. result in the formation of the least porous yarns when spun into aqueous baths, particularly at spinning speeds in the range of 100-200 yds./min.

Since the severity of the heating operation required depends upon the degree of porosity of the as-spun yarn, the yarn to be prepared should be thermally treated to have a minimum as-spun porosity. When spinning acrylonitrile polymer solutions into aqueous coagulating baths at speeds of 100 yds./min. and higher, the porosity is also minimized by submitting the freshly coagulated yarn to a snubbing tension in the coagulating bath. The snubbing tension guides may be placed between 4 and 15’ from the spinmeret face in order to minimize the porosity. If the snubbing tension guides are placed more than 15’ from the spinmeret face, the degree of porosity is not affected but the size of the pores is decreased. This is similar to the effect obtained by drawing the as-spun yarn.

The coagulating baths used may be water or aqueous solutions which gelatinize adducts rapidly. Otherwise, the spinning speed must be low and productivity is limited. The preferred coagulating baths are aqueous solutions containing from 20-50% of the polymer solvent being used. The solvent can be readily recovered from such aqueous solutions and spinning speeds up to 300 yds./min. can be used without developing more porosity than can be handled. The temperatures of the coagulating bath is preferably in the range of 50°-100° C., although other temperatures may be employed. The bath temperature should, of course, be below the boiling point of the solvents employed in the spinning solution.

It is generally preferred to employ a bath travel of the order of 20-60’. However, this is not essential and bath travels as short as 6” can be used if desired. One of the advantages of this invention is that large bundles of filaments intended for conversion into staple fibers can readily be spun into the relatively short aqueous coagulating baths. The porosity developed in such a process can readily be healed by the process of this invention. In the preparation of yarns having an area ratio of less than 2.1, as described in U. S. 2,426,719 and U. S. 2,451,420, it is indicated that much longer bath travels of the order of 100-200 inches are to be used in the spinning of heavy denier yarn or large bundles of filaments. The shaped articles which may be treated by the process of this invention are prepared in general from acrylonitrile polymers containing a major portion of acrylonitrile. These include polyacrylonitrile and copolymers of acrylonitrile with such monomers as styrene, methyl vinyl ketone, butadiene and other vinyl, acryloyl methacrylic and diolefin compounds including vinyl halides, vinylidene halides, esters of acrylic and methacrylic acid, 5-vinyl-2-methylpyridine, 5-ethyl-2-vinylpyridine, etc. The shaped articles of these compositions that contain at least 65% of acrylonitrile are preferred and are used more extensively than those containing smaller amounts of acrylonitrile, say from 55% to 80% acrylonitrile. The process of this invention makes it possible to convert dull, moderately porous and weak acrylonitrile polymer yarns, prepared by rapid coagulation of filaments in an economical spinning bath, into strong lustrous yarns substantially free of voids. The development of a good spontaneous crimp in the solid yarns prepared by the process of this invention recommends the process particularly for use in staple yarn production. If the process is applied to wet-spun acrylonitrile polymer yarns having an area ratio greater than about 3.3, microporous yarns are obtained which can be made into light weight, absorbent fabrics. The shaped process of the invention can be operated at inexpensive equipment and broadens the utility of cheaply prepared yarns having the interesting properties of a polymer
containing a major portion of acrylonitrile units in its linear chain.

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

We claim:
1. A process for converting a porous filamentary article, derived from an acrylonitrile polymer containing a major portion of acrylonitrile and substantially free of any solvent for said polymer, to a substantially non-porous condition, which comprises stretching said porous article to at least twice its original length; wetting the resultant article with a volatile liquid non-solvent for said polymer; and contacting the resultant wet article with a fluid immiscible with said non-solvent, said fluid being also a non-solvent for said polymer and being heated to a temperature below the thermal decomposition point of said polymer and at least 100°F, which will evaporate the volatile liquid non-solvent from the article and render the article substantially non-porous.
2. The process of claim 1 in which said filamentary article is a yarn.
3. The process of claim 1 in which said liquid non-solvent used in said wetting is water.
4. The process of claim 1 in which said polymer is the homopolymer, polyacrylonitrile.
5. The process of claim 1 in which said polymer is a copolymer.
6. The process of claim 1 in which said polymer is a copolymer of acrylonitrile and a vinylpyridine.
7. The process of claim 6 in which said vinylpyridine is 2-vinylpyridine.
8. The process of claim 1 in which said immiscible fluid is a hydrocarbon.
9. The process of claim 1 in which said immiscible fluid is xylene.
10. A process for converting a porous yarn, derived from an acrylonitrile polymer containing a major portion of acrylonitrile and substantially free of any solvent for said polymer, to a substantially non-porous condition, which consists of stretching said porous yarn to at least twice its original length; wetting the resultant stretched yarn with water; and contacting the resultant wet yarn with a water-immiscible fluid heated to a temperature of about 100°F to about 165°F and incapable of dissolving said polymer.
11. The process of claim 10 in which said water-immiscible fluid is xylene.

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