

- [54] CONDUCTIVE NYLON SUBSTRATES AND METHOD OF PRODUCING THEM
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[57] **ABSTRACT**
A method for providing nylon substrates with a durable, adherent silver coating and product by electroless deposition from a plating bath comprising silver salt, ammonia, anionic surfactant, formaldehyde, and sufficient acid to bring the pH to about 8.4–9.4. The substrates are sensitized with stannic chloride solution.

4 Claims, No Drawings

CONDUCTIVE NYLON SUBSTRATES AND METHOD OF PRODUCING THEM

This application is a division of our copending U.S. application Ser. No. 76,245, filed Sept. 28, 1970 now abandoned.

DESCRIPTION OF THE INVENTION

This invention relates to a method for plating nylon with silver. The plating of metals such as silver onto a nylon substrate has been known for some time and can be effected with relative ease. For many purposes a minimum of adherence of the silver to the substrate is sufficient for the intended use of the plated substrate. In some instances, however, it is critical that the silver plating be extremely durable and adherent. It is extremely difficult to obtain such a durable and adherent coating on a consistent and readily reproducible basis by the techniques of the prior art.

It has now been found that a process involving a series of carefully controlled process steps can provide nylon substrates with a durable and adherent coating without significantly altering the basic mechanical characteristics of the product.

The process of the present invention is applicable to nylon substrates irrespective of the substrate form. Thus, it is effective in the silver plating of monofilaments, nylon fabrics, including both knit and woven fabrics, bundles of filaments in yarn form, nylon staple and nylon films. Somewhat more massive nylon forms may also be treated by the process of the present invention, but the need for the exceptional characteristics provided by the present invention are less commonly required for such articles. The term "nylon" is used in its broadest sense to cover fiber-and/or filmforming polyamides; the invention is of particular use, however, in the silver plating of polycaprolactam and polyhexamethylene adipamide.

As is customary in the art, any finishes on the substrate which tend to interfere with the plating process should be cleansed from the substrate prior to the process. Typically, fabrics and fibers may have some sort of finish or lubricant which might interfere with the process; generally, these can be removed by treatment of the material with suitable surface active agents and/or solvents.

The substrate is customarily "sensitized" by treatment with a water soluble salt having a polyvalent metal cation. For example, an aqueous solution of stannous chloride is commonly used for this purpose. Such solutions can also be used for the purposes of the present invention to the extent that suitable penetration of the sensitizer into the substrate surface can be effected and to the extent that interfering ions and/or precipitates can be removed by simple washing procedures prior to the silver deposition. In the preferred and quite superior practice of the present invention, a stannic salt such as stannic chloride is utilized instead of the stannous salt, and a water-soluble organic solvent for the stannic salt is used instead of water to form a solution of the sensitizing agent. For example, lower molecular weight alcohols such as ethanol and isopropanol are quite effective. Methanol offers no real advantage over water insofar as improving the activity of the sensitizing agent, although the use of methanol alone or in combination with the other sensitizer solvents can be em-

ployed as necessary to the particular practice contemplated.

In order to obtain a product having the desired characteristics for the purposes of the present invention, careful control of the silvering solution is essential. In the normal practices of the prior art, silvering solutions prepared with a slight deficiency of ammonia, i.e., less than the two equivalents of ammonia required to form the silver-ammonia complex, is utilized. In accordance with the practice of the present invention at least three mols of ammonia up to 4 mols of ammonia per mol of silver nitrate or its equivalent are incorporated in the silver plating bath. If less than this amount is included in the bath, the silver plating solution is insufficiently stable for effective deposition without bath decomposition. If greater than this amount is used, the process proceeds too slowly, if at all, and it is difficult to obtain a good silver coating in a reasonable time. Preferably, the bath incorporates less than about 3.5 mols of ammonia per mol of silver nitrate.

The silvering bath should contain a small amount of anionic surfactant to stabilize the system and thereby to insure that the plating occurs essentially only on the sensitized surface without seriously affecting the metal of the silver coating applied to the substrate. Typically, 0.01% up to about 0.1% defines the operable concentration of sodium lauryl sulfate. At the higher end of the range, this surfactant tends to destroy the boiling water resistance of the coating, while at the lower end of the range, the amount of surfactant present is not sufficient to give the necessary bath stabilization. In general, optimum results are obtained if the bath contains the equivalent of 0.025% of sodium lauryl sulfate.

With the large quantities of ammonia recommended for the practice of the present invention, the pH of the bath is in excess of 10, e.g., about 10.4. It has been found that if the pH is not reduced, the bath tends to decompose before the nylon substrate is silvered. More importantly, if the bath is not adjusted to a pH of about 9.4 or lower, the silver coating that does result is not particularly resistant to boiling water. However, if the pH is lowered to about 8.0, a good coating is not obtained. Accordingly, it has been found necessary to maintain the pH of the silvering bath at a value from about 8.4 up to about 9.4 to obtain results necessary for many substrate uses.

The ammonia can be introduced into the solution, e.g., as ammonium hydroxide, in which case it is necessary to add an acid to reduce the pH to the desired level. Acetic acid is a typical acid useful for this purpose. It should be understood, however, that the ammonia stabilization and pH maintenance of the bath can be accomplished by other essentially equivalent means. Thus, e.g., amines and/or certain ammonium salts may be used in place of ammonium hydroxide in which case the need for acid adjustment to obtain the desired pH may be minimized and/or eliminated. It is to be understood that such methods are contemplated as included within the scope of introducing ammonia and acid into the silvering solution to provide an amount of ammonia and acid in the silvering bath corresponding to the values previously described.

In accordance with the practices of the present invention, the sensitized nylon substrate is introduced into the silvering bath together with the customary reducing agents such as formaldehyde. The reaction is standard and well known in the art and leads to the de-

position of silver on the nylon substrate. The resulting product is a silvered nylon in which the silver coating is extremely durable and adherent as well as electrically conductive. The resulting product further possesses essentially all of the mechanical characteristics of the substrate despite the penetration, as shown by photomicrographs, of the silver into the surface of the substrate.

In the examples which follow, the durability and adherence of the silver plating on nylon is tested, inter alia, by a boiling water test. In that test, a portion of the silvered nylon article is placed in a beaker of boiling deionized water for 30 minutes and dried by patting the excess water from the specimen with a paper towel. Silvered portions of the specimen are placed across electrodes spaced 1.5 inches apart and the electrical resistance measured (e.g., using a Kiethley Electrometer Model 610C, or a Mura Corporation Model 80M Multimeter). Samples are considered non-conductive if their resistances is greater than a million ohms. In the examples which follow, the substrate which was silvered was a knit nylon sleeve. For these articles, a section at least two inches long was cut from the sleeve and several cut filaments were unravelled from different parts of the section (generally about ten) and tested in the manner just described. Other tests are described in the examples.

The invention is described with regard to the preferred practices of the invention which include use of the stannic salt-ethanol sensitizer and the treatment of knit fabrics. In its broadest scope, however, the invention is not limited thereto and is broadly useful in the manner described earlier herein. An interesting facet of the invention is that the silvering of fabrics such as knitted and woven fabrics can be effected in a manner such that the silver coating on fibers removed from the fabric is continuous and does not apparently change at the fiber crossover points which were present in the fabric during the plating thereof. The individual conductive filaments are basically nylon having the same modulus characteristics as the uncoated filaments. Filamentary materials can be uniformly silvered irrespective of the physical form of the filament, i.e., irrespective of whether the filament has been crimped, false twisted, or otherwise textured.

EXAMPLE I

A silvering bath was prepared, by dissolving in 14,200 ml. of deionized water, 362 ml. of 1% aqueous sodium lauryl sulfate solution, 700 ml. of a solution of 37.0 grams of silver nitrate in deionized water, 325 ml. of 2.17N ammonium hydroxide and sufficient 1N acetic acid to reduce the pH to 9.0.

A sensitizing solution was prepared by dissolving 15 grams of stannic chloride in 1500 ml. of denatured (one-half gallon of benzene per 100 gallons of 95% ethanol) alcohol. A three-inch diameter sleeve was knit from a 15-denier nylon monofilament. A 94 gram sample of the nylon sleeve was placed in the sensitizing solution for five minutes, then drained and washed with running water and placed in a bath of deionized water. To the silvering solution were then added 725 ml. of 2.4% formaldehyde solution. The nylon sleeve, after squeezing to remove water, was then fed into the silvering solution and allowed to stand therein for 90 minutes with periodic agitation. The sleeve was then removed from the silvering bath, rinsed with water, and dried for

2 hours at 65°C. in a circulating air oven. The dried sleeve weighed 105.7 grams and 10 filaments removed thereof had an average resistance of 490 ohms per 1.5 inch length. After being subjected to the boiling water treatment described previously herein, the ten filaments had an average resistance of 600 ohms per 1.5 inch length. The average resistance of 15 denier nylon filament which has not been silvered is greater than the upper limit of the test machine employed which is 10^{14} ohms.

EXAMPLE II

A 100-gram sample of nylon sleeve of the type described in Example I was scoured with t-octylphenoxypoly(9) ethoxyethanol and sodium tri-polyphosphate to remove the finish therefrom. The scoured sample was then placed in 2000 ml. of a sensitizing solution comprising 20.0 grams of anhydrous stannic chloride in denatured alcohol (as described in Example I). The sleeve was soaked for five minutes, withdrawn from the sensitizing solution and passed under two water spray heads, passed through a aqueeze roll and then stored in 2,000 ml. of deionized water. A silvering bath was prepared by adding in sequence, to 6,300 ml. of water, 1.58 grams of sodium lauryl sulfate, 625 ml. of 0.30N silver nitrate solution, 612 ml. of 1N ammonium hydroxide, 160 ml. of 1N acetic acid (to bring the silvering bath pH to 9.0) and 371 ml. of 2.4% formaldehyde solution. The nylon sleeve was removed from the deionized water, squeezed to remove excess water, and placed in the silvering bath. The sleeve was retained in the bath for 165 minutes with occasional stirring and then removed from the bath, rinsed with water to remove the silvering solution, and dried. Fibers (about 10) removed from the sample had an average resistance of 860 ohms per 1.5 inch length. After being subjected to the boiling water test described previously, the sample had an average resistance of 570 ohms per 1.5 inch length. No non-conductive filaments were found in any of the samples.

The products obtained by the present invention can be used for any of the purposes for which silvered nylon has been employed in the past. In particular, however, the process provides an excellent method for the production of silvered fabrics, including films, for use as electrical components of various electronic devices. The individual fibers can be used in such various items as women's apparel, including stockings and panty hose, and in carpeting and other like uses wherein it is desired to reduce the static charge accumulated on the article of which the silvered filament is a part. In view of the extreme resistance of the silvered fiber to boiling water, it is particularly useful for incorporation in carpets in place of metal fibers employed in the past. Yarns prepared containing the silvered nylon may be subjected to the usual dyeing operations and scouring operations characteristic of carpet industry practice without substantial loss of the static-reducing conductivity. The fact that the fiber is basically nylon and has the same modulus characteristics as the rest of the filaments in the yarn bundle permits use of the silvered filament in this manner without significantly changing the physical characteristics of the yarn bundle other than the tendency to build up a static charge. Metal fibers used in this manner tend to be less durable in service due to the tendency of the metal filaments to break. Previously silvered nylon filaments lacked the durabil-

ity and silver adhesion to permit treatment of the filament in dyeing, scouring, and like operations.

Accordingly, the preferred products obtained by the practice of the present invention can be subjected to 30 minutes treatment at 180°F, in an aqueous bath containing 0.5 weight percent of sodium lauryl sulfate and sufficient sodium tripolyphosphate, trisodium phosphate or tetrasodium pyrophosphate to provide a pH of 9, followed by two hours in a boiling acetic acid solution at a pH of 5 without the electrical resistance increasing beyond 10,000 ohms/inch. In general, the resistance will be less than about 1,000 ohms/inch.

A significant feature of the process defined herein is that both a nylon monofilament and a nylon multifilament yarn, whether crimped or uncrimped, can be processed to provide a silver-coated nylon monofilament or yarn having the desired electrical conductivity and resistance. The yarn can be silvered as a warp proceeding from a beam in a manner similar to that used in slashing. The monofilament or yarn can suitably be pre-textured or not, as desired, to provide a package, i.e., a bobbin, spool, cone, pirn, tube, etc., of silvered monofilament or yarn in continuous form, i.e., in continuous lengths greater than 100 yards long.

The process can also be utilized with nylon staple fiber to provide a silvered staple fiber having the previously described characteristics. A staple fiber yarn can be produced from the silvered staple fiber to provide a staple fiber yarn having conductivity characteristics consistent with those earlier defined.

What is claimed is:

1. A process for producing a silver-coated fibrous nylon substrate which comprises subjecting a fibrous nylon substrate to a sensitizing polyvalent metal salt bath, then washing the substrate with water, subjecting it to a bath of deionized water, removing it from the deionized water and squeezing excess water out of it, then

allowing the resulting wet fibrous substrate to stand, with periodic agitation, within an aqueous solution consisting essentially of water, a silver salt dissolved therein, 3 to 3.5 mols of ammonia per mol of silver salt, 0.025 to 0.1 percent, based on the solution, of an anionic surfactant, formaldehyde, and sufficient acid to bring the solution to a pH of about 8.4 to about 9.4 prior to introduction of the substrate, rinsing the silver-coated fibrous substrate, and drying it, the time of the silvering step being sufficient to deposit a substantially continuous coating of silver on the substrate fiber without changing the modulus characteristics of the fiber.

2. A method in accordance with claim 1 wherein said anionic surfactant is sodium lauryl sulfate.

3. A method in accordance with claim 1 wherein said nylon substrate is sensitized with an alcohol solution of a stannic salt.

4. A process for producing a silver-coated fibrous nylon substrate which comprises subjecting a fibrous nylon substrate to a sensitizing ethanol solution of a stannic salt, then washing the substrate with water, subjecting it to a bath of deionized water, removing it from the deionized water and squeezing excess water out of it, then allowing the resulting wet fibrous substrate to stand, with occasionally stirring within an aqueous solution consisting essentially of water, silver nitrate, 3 to 3.5 mols of ammonia per mol of silver nitrate, 0.025 to 0.1 percent, based on the solution of sodium lauryl sulfate, formaldehyde in an amount sufficient to reduce the silver nitrate to metallic silver, and sufficient acid to bring the solution to a pH of about 8.4 to about 9.4 prior to introduction of the substrate, rinsing the silver-coated fibrous substrate, and drying it, the time of the silvering step being sufficient to deposit a substantially continuous coating of silver on the substrate fiber without changing the modulus characteristics of the fiber.

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