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DYEING OF TEXTILE FIBERS

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The present invention relates to a method of dyeing acrylic fiber.

In recent years there has been developed a new synthetic fiber known as "acrylic fiber" which name is derived from the fact that the fiber is prepared from polymeric acrylonitrile or copolymers of acrylonitrile and related vinyl compounds. The fiber is currently sold under a variety of tradenames including Orlon, Dynel and Acrilan. With the advent of the new fiber it has been necessary to develop new methods of dyeing since it was found very early in the development of the new synthetic that the older, more conventional methods of dyeing were incapable of giving satisfactory penetration and depth of color.

Probably the most widely used and most successful of the new dyeing methods for acrylic fiber is known as the "cuprous ion" method. This method consists in adding a cupric salt and a reducing agent to a bath containing the fiber and an acid dye and maintaining the bath at or very near the boiling point during the dyeing operation. It is known that in this method the copper sulfate and the reducing agent react within the bath to produce copper in the cuprous valence state. It is theorized that the cuprous copper is then absorbed by the acrylic fiber thereby creating an affinity for acid dyes. Despite the success of this method it has several disadvantages. The greatest disadvantage results from the fact that the addition of the reducing agent to the dye bath is very critical and as a result it has been necessary to devise rather elaborate methods for controlling the addition of the reducing agent. One such control is discussed in the American Dye Stuff Reporter, vol. II, No. 3, pgs. 76 to 80, wherein there is presented a brief review of the cuprous ion method of dyeing. It can be seen from this publication that the cuprous ion method is undesirably complicated and that close control is required in order to obtain satisfactory results.

In view of the difficulties in practicing the cuprous ion method, it is an object of the present invention to provide a method for dyeing acrylic fiber which does not require the complex controls of the former method.

It is a further object of the invention to provide a method for dyeing acrylic fiber which is considerably faster than the previously known cuprous ion method.

It is still another object of the invention to provide a method for dyeing acrylic fiber which does not require the addition of a reducing agent to the dye bath.

The method of the present invention is based on the discovery that a bath containing an acid dye and a cupric salt can be rendered suitable for dyeing acrylic fiber by passing an alternating electric current through the dye bath prior to the actual dyeing operation.

In the process of this invention, a bath containing an acid dye and a cupric salt is subjected to the passage of an alternating electric current. After the passage of the alternating current for a certain length of time, which will vary with the volume of the dye bath, the ingredients of the bath, the temperature of the bath and the amperage of the current, the bath is then ready for the actual dyeing operation which may be performed in conventional manner and which usually comprises the mere immersion of the fiber in the dye bath for the requisite length of time until the desired depth of color has been obtained. Preferably, as in most cases of dyeing with an acid dye, the bath is maintained at or near the boiling temperature of the bath.

It has been found that the passage of the alternating current after a certain point is no longer essential and that it may be discontinued after the dye bath has been properly prepared. However, if it is desired to utilize the heating effect of the alternating current, it is, of course, permissible to continue the passage of the current during the dyeing operation.

The process is applicable to staple fiber prepared from various polymers and copolymers of acrylonitrile. The copolymers from which the fiber can be prepared include copolymers of acrylonitrile with such compounds as, for example, vinyl acetate, vinyl chloride, esters or other derivatives of acrylic or methacrylic acids, styrene, methyl vinyl ketone, or other similar polymerizable monomers. In general, the copolymers contain not more than 15% of the aforesaid monomers.

The dyes which can be satisfactorily applied in the practice of this invention include all of those known as acid dyes. These are a well recognized class of dyes which are commercially available and which are characterized by their application from an acidic dye bath. Such dyes include, for example, Anthraquinone Blue Sky (C. I. 1088), a Anthraquinone Green GN (C. I. 1078), Orange II (C. I. 151), Quinoline Yellow PN (C. I. 802), Anthraquinone Blue RA (Du Pont), Anthracene Blue WR (1, 2, 4, 5, 6, 8-hexahydroxyanthraquinone), as well as many other dyes. Suitable acid dyes are also sold under various tradenames such as Roracyl Orange R (Du Pont), Roracyl Dark Green B (Du Pont), Pontacyl Fast Red AS (C. I. 176), Pontacyl Rubine R (C. I. 179), and Roracyl Violet 2R (Du Pont).

In practicing the invention it is first necessary to provide a suitable dye bath which is done by dissolving predetermined amounts of an acid dye and a cupic salt in water. The concentration of the dye in the solution is not critical and almost any amount of dye can be employed. Generally, however, it is preferred to dissolve an amount of dye equal to from about 0.5% to about 20% by weight of the material in accordance with conventional dyeing practice. The amount of cupric salt to be employed is dependent upon the amount of dye in the bath. Thus, within fairly critical limits, the amount of cupric salt should be equal to from about 40 to about 70% by weight of the dye in the bath. Amounts of cupric salt above the stated range are unsatisfactory because during the later dyeing operation the yarn will acquire a coppery tint and an undesirable stiffness. Amounts of cupric salt below the stated range are not particularly harmful but there will not be obtained during the dyeing operation the desired exhaustion of the dye. It is mentioned at this point that the amount of cupric salt will vary somewhat within the above range depending on the particular dye that is being used and on the particular cupric salt that is being employed. With many dyes the optimum amount of cupric salt to be used is about 65% by weight of the dye and with other dyes the amount of cupric salt can easily be determined by simple experimentation.

Good dyeing can be obtained with almost any cupric salt that is water-soluble. By far the best results from the standpoint of shade and penetration can be obtained using copper sulfate and for this reason it is preferred to employ this compound. Satisfactory dyeings can also

be obtained, however, by the use of such cupric salts as copper nitrate, copper acetate and cupric chloride.

After the solution of ingredients in the bath, it is prepared for the dyeing operation by the passage of an alternating electric current therethrough. The passage of the alternating current is conveniently accomplished by immersing electrodes in the dye bath and connecting one of the electrodes to a suitable source of alternating current and grounding the other electrode. The best results in the present invention are obtained using copper electrodes but the material of which the electrodes are made does not seem to be especially critical.

The principal variable affecting the amperage of the alternating current to be employed is the volume of the dye bath. It has been found that the amperage varies in direct proportion to the volume of the liquid. For example in a bath containing about 125 gallons of liquid it has been found that amperages between 100 and 1000 amperes can be used although for a bath of this size it is preferred to employ an amperage between about 300 and 500 amperes. From this knowledge it is possible to calculate directly the amperage which will be required for a bath of almost any other size. Assuming, for example, that the bath contains approximately one-half of 125 gallons, then approximately one-half of the amperage required for a 125 gallon bath will be needed. The only exception to this rule is in the case of small baths of laboratory size, i. e., from about ½ to 5 gallons, wherein currents of from about 10 to 40 ameres are preferred.

The amperage will also vary with the number of electrodes. Thus, if there is provided a plurality of electrodes arranged in a sandwich fashion with the outermost electrodes being connected for a flow of alternating voltage and the inner electrodes being merely suspended between the outer electrodes, the amperage required will be reduced in inverse proportion to the number of cells. For example, a series of three electrodes will provide two cells and there will be required only one-half the number of amperes that would be required for a system having only two electrodes. It is believed that the reason for this phenomenon is the fact that the greater the number of electrodes and consequently the greater the number of cells, the greater will be the degree of ionization of the ingredients of the dye bath.

The preparation of the dye bath by the passage of an alternating electric current therethrough is preferably performed at or near the boiling point of the dye bath since at the boiling point of the dye bath the time of passage of the alternating current is materially reduced, the length of time required for the electrical preparation of the bath being a function of the temperature of the bath.

The duration of the passage of the alternating current is also a function of the volume of the dye bath and the amperage. It is, therefore, not possible to establish definite periods of time which will accomplish the necessary preparation of the dye bath in all instances. However, it has been found that for a dye bath of commercial size, i. e., about 125 gallons, passage of the alternating current for about two hours while the dye bath is at its boiling point is sufficient. Under the same conditions in laboratory size vessels of approximately one gallon, about ten minutes suffices for the passage of the alternating current.

In determining the duration of the passage of the alternating current, it has been found that the passage of the current is accompanied by a lowering of the pH of the dye bath. For example, in a dye bath containing Roracyl Dark Green B and copper sulfate, the pH is lowered from about an initial 3.5 to about 2.6 at which point the preparation of the dye bath is complete. The pH measurement, therefore, affords a convenient method for determining the moment when the dye bath is properly prepared for the dyeing operation. However, the pH varies according to the ingredients of the bath and the pH figures stated above are applicable only to the combination of Roracyl Dark Green B and copper sulfate. The actual pH change for each different dye bath can best be determined by the experimental dyeing of yarn samples after varying periods of alternating current passage. In this manner, a pH change for each dye bath can be established and there is thus provided a simple and convenient method of control which can be employed in all subsequent dyeings with the same bath.

After the dye bath has been subjected to the passage of an alternating current for the required length of time in accordance with the considerations mentioned above, the bath is ready for the actual dyeing operation. In this operation no special precautions are necessary and satisfactory dyeings can be obtained quite rapidly by merely immersing the yarn or fabric to be dyed in the boiling dye bath and sufficient yarn can be dyed to substantially exhaust the bath. Any of the customary and conventional pieces of apparatus that are presently employed in the dyeing of staple yarn or fabric can be employed. The length of time for the immersion of the yarn or fabric is subject to many considerations and will vary according to the temperature of the dye bath, and the depth of shade desired.

Very little is known of the mechanism by which the alternating current modifies the dye bath so that it is rendered suitable for the subsequent dyeing operation. However, it is known that satisfactory dyeing cannot be obtained without the preliminary treatment with the alternating current so that it is reasonably certain that a chemical change of some kind occurs within the bath. It has also been determined that direct current is completely unsuitable in the method of this invention since the use of direct current invariably results in a deposition of copper in the bath and on the fiber.

Various conventional dyeing assistants, surface active agents, or the like, may be added to the dye bath if desired. For example, in some instances improved results may be obtained by adding a carrier of the type conventionally employed in the dyeing of acrylic fibers, as illustrated by p-phenylphenol, o-phenylphenol, diphenyl and benzoic acid.

In order to illustrate the invention and its attendant advantages, the following examples are given.

Example 1

A dye bath was made up by dissolving the following ingredients in 500 ml. of water:

	Grams
Roracyl Dark Green B (Du Pont)	1
Anthraquinone Blue SWF (150%) (Pr. 12)	0.2
Du Pont Orange RO (C. I. 161)	0.1
Copper Sulfate	3

The bath was then heated to its boiling point (approximately 213° F.) and two copper electrodes, each having an area of about 10 square inches, were immersed in the bath. A sixty cycle alternating current (10 amperes) was then passed between the electrodes for a period of ten minutes while the bath was maintained at its boiling point. The current supply was then shut off and the electrodes were removed. During the passage of the current the pH of the bath was lowered from 3.5 to 2.1.

A skein of orlon staple yarn which had been previously scoured was then immersed in the dye bath with constant stirring, still maintaining the temperature of the dye bath at the boiling point. After an immersion time of about 5 minutes, the yarn had acquired an excellent black color. The penetration of the dye was also excellent. The color was fast to repeated washings.

Example 2

A dye bath was made up by dissolving the following ingredients in 4 liters of water:

	Grams
Roracyl Dark Green B (Du Pont)	40
Anthraquinone Blue SWF (150%) (Pr. 12)	10
Du Pont Orange RO (C. I. 161)	3.75
Copper sulfate	37.5

Two copper electrodes, each having an area of about 32 square inches, were immersed in the bath with a space about ⅛ inch between electrodes. A sixty cycle alternating current was passed between the electrodes to give an amperage of 35 amperes and with the aid of external heating elements the temperature of the bath was raised to the boiling point of approximately 213° F. After passage of the electric current for ½ hour at the boiling point of the dye bath, the pH of the bath dropped from about 3.5 to about 2.1.

A package or orlon staple yarn weighing about 1 lb. which had been previously scoured was then dyed in the bath using a 1 lb. package dyeing machine, a conventional piece of equipment in the industry. During the dyeing operation the passage of the alternating current was continued and the heat therefrom was utilized to help maintain the bath at the boiling point. After approximately 30 minutes on the machine the yarn was dyed a good black; the penetration of the dye was excellent and the color was fast to washing.

Example 3

The procedure of Example 2 was followed substituting copper nitrate for the copper sulfate. Again a good dyeing was obtained but the penetration of the dye was somewhat poorer than in Example 2.

Example 4

The procedure of Example 2 was followed except that a series of six electrodes in which the four central electrodes were suspended between the two outer electrodes was employed in place of the pair of electrodes used in Example 2. This enabled the amperage of the alternating current to be reduced to about ⅕ of the amperage employed in Example 2. The dyeing of the yarn was performed as in Example 2 and an excellent shade of black was obtained.

The foregoing examples demonstrate the simplicity of the process of the present invention and its advantages. It is to be noted particularly that no extensive controls are necessary during the dyeing operation and that the dyeings are fairly rapid.

We claim:

1. A method for dyeing acrylic fiber which comprises subjecting to the passage of an alternating electric current an aqueous dye bath containing an acidic dye and an amount of a water-soluble cupric salt equal to about from 40 to 70% by weight of the dye, and thereafter dyeing acrylic fiber in the dye bath.

2. A method according to claim 1 in which the cupric salt is copper sulfate.

3. A method for the dyeing of acrylic fiber which comprises subjecting an aqueous dye bath containing an acidic dye and a cupric salt in an amount equal to from about 40 to about 70% by weight of the dye to the passage of an alternating electric current, the amperage of the alternating current being based on the volume of the aqueous solution and being equivalent to from about 100 to 1000 amperes for a bath of 125 gallons and thereafter dyeing acrylic fiber in the bath.

4. A method according to claim 3 in which the cupric salt is copper sulfate.

5. A method according to claim 3 in which the entire process is carried out at a temperature approximating the boiling point of the bath.

6. The method for preparing a dye bath capable of dyeing acrylic fibers without the addition thereto of a reducing agent which method comprises subjecting an aqueous dye bath containing an acidic dye and an amount of a water-soluble cupric salt equal to about 40% to 70% by weight of the dye to the passage of an alternating electric current.

7. A method according to claim 6 wherein the amperage of the alternating current is from about 100 to 1,000 amperes for each 125 gallons of dye bath.

8. A method according to claim 7 wherein the dye bath during the passage of the electric current is at a temperature approximating the boiling point of the bath and the bath is subjected to the alternating current for a period of about at least 2 hours.

9. The method of claim 8 wherein the cupric salt is copper sulfate.

References Cited in the file of this patent

UNITED STATES PATENTS

1,333,700 Bloom ---------- Mar. 16, 1920

OTHER REFERENCES

Du Pont Technical Bulletin, vol. 7, No. 1 (March 1951), pp. 45–52.