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## BLEACHING POLYACRYLONITRILE FIBERS

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This invention relates to the bleaching of fibers and particularly to an improved method for bleaching polyacrylonitrile fibers.

Polyacrylonitrile fibers, including textiles in the form of cloth, yarns, threads and the like, produced from such fibers, are relatively difficult to bleach. The usual bleaching methods employing aqueous hydrogen peroxide are ineffective. Methods employing bleaching agents more powerful than hydrogen peroxide, for example, the hypochlorites or chlorites, are unsatisfactory in that they either do not produce a permanent bleach or they seriously damage the fiber. Insofar as I am aware, no really satisfactory method has been available heretofore for bleaching polyacrylonitrile fibers.

It is an object of the invention to provide an improved bleaching procedure. A particular object is to provide an improved method for bleaching polyacrylonitrile fibers. A further object is a method for rapidly bleaching such fibers to a whiteness approaching that of bleached cotton with maximum whiteness retention of stability to color reversion. A still further object is to provide a method for bleaching such fibers without substantial damage thereto or change in their qualities of "hand" or finish. Other objects will be apparent from the following description.

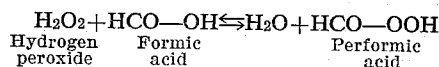
The above objects are accomplished in accordance with the invention by subjecting polyacrylonitrile fiber to the action of a solution comprising performic acid or hydrogen peroxide in a solvent comprising concentrated formic acid, i. e. at least 75% formic acid by weight. It has been found that the use of performic acid or hydrogen peroxide in a solvent comprising concentrated formic acid is essential to the attainment of effective bleaching.

The term "polyacrylonitrile fiber" is employed herein to designate synthetic fibers, including textiles in the form of cloth, yarns, threads, fibers and the like, produced from homopolymers of acrylonitrile or from copolymers thereof with other monomeric unsaturates, such as vinyl chloride, vinylidene chloride, vinyl acetate, butadiene, methyl acrylate, methyl methacrylate, acrylic acid, methacrylic acid and the like, which are copolymerizable by known methods with acrylonitrile. Fibers produced from such copolymers which do not contain acrylonitrile units equal to at least 30% by weight of the polymer molecule, are intended, however, to be excluded by the term, since they are not effectively bleached by the present method. Accordingly, the term is employed to designate synthetic fibers produced from acrylonitrile polymers containing from 30 to 100% acrylonitrile units by weight, as well as textile materials made from such fibers. Preferably, the fiber will have been produced from a polymer containing at least 85% acrylonitrile units. Generally, the lower the acrylonitrile content of a copolymer from which the fibers are produced, the lower will be the final brightness obtained when bleached by the present method. However, the initial brightness also will generally be lower the lower the acrylonitrile content so that even when the latter is as low as 35–40%, substantial and worthwhile bleaching will be obtained.

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The bleaching agent, i. e. performic acid or hydrogen peroxide, must be used in a solvent comprising at least 75% formic acid, based on the weight of the solvent. The effectiveness of the bleaching agent in such a solvent is unique since performic acid in other solvents, such as ethanol or glacial acetic acid, is ineffective. Moreover, peracetic acid in glacial acetic acid, and perpropionic acid in glacial propionic acid, were also found to be ineffective. The reason for the excellent results obtained using solutions of the bleaching agent in concentrated formic acid is not entirely clear. It appears, however, that a solvent comprising at least 75% formic acid by weight acts to swell and penetrate polyacrylonitrile fibers sufficiently to permit effective bleaching. When the solvent is formic acid of less than 100% strength, the constituent other than formic acid is preferably water, but may be any solvent constituent which is substantially inert to the material being bleached and does not destroy the active oxygen content of the bleach bath.

The bleach solution may be formed by adding either hydrogen peroxide, preformed performic acid, or both, to concentrated formic acid. If hydrogen peroxide is added, it reacts with the formic acid to produce performic acid; conversely, the addition of preformed performic acid will usually result in the formation of some hydrogen peroxide, all in accordance with the following known reversible reactions:



Because the above reversible reactions occur rapidly even in the absence of such catalysts such as strong acids, e. g.  $\text{H}_2\text{SO}_4$ , it can generally be assumed that both hydrogen peroxide and performic acid will be present in the bleach solution. It is not certain in view thereof whether the active bleaching agent is hydrogen peroxide or performic acid; perhaps both are active. But whatever the active bleaching agent may be, effective bleaching is obtained in accordance with the invention by supplying the active oxygen required to the bleach solution either as hydrogen peroxide, performic acid or both. It will, of course, be obvious to those skilled in the chemistry of peroxygen compounds that peroxygen compounds which yield either hydrogen peroxide or performic acid under the conditions of use can be employed as the original source of active oxygen. Examples of such compounds are sodium peroxide, sodium perborate, sodium percarbonate, sodium perphosphate, urea peroxide and peracids other than performic acid, e. g., peracetic acid, perpropionic acid and the like. Most conveniently, the bleach solution will be formed by adding to concentrated formic acid, aqueous hydrogen peroxide solutions containing 25–70%  $\text{H}_2\text{O}_2$  by weight.

Regardless of how the bleach solution is formed, the free formic acid content of the solvent in the bleach solution should be at least 75% based on the weight of the solvent. At substantially lower formic acid concentrations, bleaching does not occur to any practical extent. The preferred formic acid concentrations are in the range 85–100%.

The active oxygen content of the bleach solution can be varied considerably depending upon the degree of bleaching desired and the conditions employed. Ordinarily, the active oxygen content will be at least 0.1%, calculated as  $\text{H}_2\text{O}_2$ , based upon the weight of the bleach solution. At lower concentrations, the bleaching effect is generally too small for most purposes. Concentrations equivalent to 1.0–3.0%  $\text{H}_2\text{O}_2$  give excellent results and will most generally be used. Concentrations as high as 10% may be desirable in some instances. Ordinarily no additional bleaching results from the use of concentrations greater than about 5–10%.

Temperatures ranging from around 20° C. to about 90° C. will generally be used. Temperatures below about 20° C. can be used but are not recommended because of the longer time required. Temperatures above about 90° C. are conducive to color reversion and are not recommended. The preferred temperature range is 55° to 75° C. Within this range effective bleaching is usually secured in about 0.5 to 4 hours.

The invention is illustrated by the following examples:

#### Example 1

To 100 ml. of a commercial aqueous formic acid solution containing 85–90% formic acid by weight there was added 4.4 ml. of an aqueous hydrogen peroxide solution containing 35%  $\text{H}_2\text{O}_2$  by weight. The resulting solution, if allowed to stand for 1–2 hours at room temperature, will contain from 2–2.5% performic acid by weight due to reaction between the formic acid and hydrogen peroxide. Immediately after the solution components were mixed, there was immersed in the solution a 7-inch square of a polyacrylonitrile cloth made from a polymer containing essentially 100% acrylonitrile units. This cloth had been previously desized with warm water and scoured in a solution containing 0.2% by weight of a commercial alkoxylated aryl polyether alcohol nonionic wetting agent for 0.5 hr. at 75° C. After 3 hours at 55° C. the cloth was removed from the bleach bath and rinsed successively in cold water, in a cold solution containing 5% by weight sodium bicarbonate, and then again in cold water. The bleached cloth, after being ironed dry with a household iron in the rayon temperature range, had a brightness value of 82% as measured on a Hunter Reflectometer. The brightness value before bleaching but after the scouring treatment was 76%.

#### Example 2

To 100 ml. of commercial 98–100% formic acid there were added 0.7 ml. of concentrated sulfuric acid and 4.4 ml. of aqueous hydrogen peroxide containing 35%  $\text{H}_2\text{O}_2$  by weight. The procedure of Example 1 was repeated employing the resulting mixture as the bleaching solution. The final brightness value of the bleached cloth was 82.4%.

#### Example 3

The general procedure of Example 1 was repeated except that the bleaching temperature was 75° C. and the time 0.5 hour. The final brightness value was 82.2%.

#### Example 4

The procedure of Example 1 was repeated except that the desizing and scouring pretreatments were replaced by a treatment with a 1% oxalic solution at 75° C. for 0.5 hour to give a brightness of 73% following which the pretreated cloth was bleached for 4 hours at 55° C. in 130 g. of a peracetic acid solution in glacial acetic acid containing, by analysis, 2.7% peracetic acid and 1.4%  $\text{H}_2\text{O}_2$  by weight. The final brightness value of the bleached cloth was only 76.5%.

#### Example 5

The procedure of Example 4 was repeated except bleaching was effected during 3 hours at 55° C. in 130 g. of a perpropionic acid solution in glacial propionic acid analyzing 6.7% of the peracid by weight. The final brightness value of the bleached cloth was only 76.0%.

#### Example 6

A performic acid solution was prepared by allowing a mixture of 17.6 ml. of aqueous hydrogen peroxide containing 35%  $\text{H}_2\text{O}_2$  by weight and 100 ml. of a formic acid solution containing about 88% of the acid to stand for about 2 hours at which time the solution contained 6.5% performic acid by weight. A bleach solution was then prepared by mixing 20 ml. of the above solution with 50 ml. of glacial acetic acid. A prescoured 7-inch square of polyacrylonitrile cloth (from a polymer containing es-

entially 100% acrylonitrile units) was immersed in this bleach solution for 0.5 hr. at 75° C. After rinsing and ironing as described in Example 1, the cloth had a brightness of 76.8% as compared with an initial brightness of 73%.

#### Example 7

A bleach solution was prepared by adding to 55 ml. of anhydrous ethanol 19 ml. of a 7.9% (by weight) solution of performic acid prepared by the method indicated in Example 6. The resulting solution contained 2.1% performic acid and about 25% formic acid by weight, the balance being essentially ethanol. The bleaching trial of Example 6 was repeated using this solution, except that the bleaching time was 40 min. The final brightness of the cloth was only 75.5%.

#### Example 8

Commercial unwoven fibers produced from a copolymer containing about 40% acrylonitrile and 60% vinyl chloride units by weight were bleached for 0.5 hour at 75° C. in a bleach bath consisting of a formic acid solution containing 91% formic acid and active oxygen equivalent to 1.3%  $\text{H}_2\text{O}_2$  by weight. The brightness of the fibers was increased from 55% to 70% by the treatment.

#### Example 9

Spun fiber produced from a copolymer of the composition indicated in Example 8 was bleached as described in that example except that the temperature was 55° C. and the time 3 hours. The brightness was increased from 43% to 66%.

#### Example 10

Polyacrylonitrile filament fiber produced from a copolymer containing 90% acrylonitrile unit was bleached by the procedure of Example 8. The brightness was increased from 57.6% to 74.6%.

In some of the examples the materials were desized or scoured prior to the bleaching treatment. Such pretreatments are not essential and can be omitted if desired. In all of the examples, the bleaching treatments employed did not adversely affect the hand or feel of the goods. The bleaches obtained in the concentrated formic acid bleach baths showed good stability towards reversion in ultraviolet light.

The method of the invention can be practiced employing equipment constructed of any material resistant to the bleach solution under the conditions of use. Examples of such materials are glass and stainless steel, e. g., stainless steels of A. I. S. I. Nos. 304, 316, 317, 321 and 347.

I claim:

1. The method of bleaching polyacrylonitrile fiber comprising subjecting the fiber to the action of a bleach solution comprising an agent from the group consisting of performic acid, hydrogen peroxide and mixtures thereof, dissolved in a solvent containing at least 75% formic acid by weight.

2. The method of claim 1 wherein the temperature of the bleach solution is in the range 20 to 90° C.

3. The method of claim 1 wherein the active oxygen content of the bleach solution is equivalent to 0.1 to 10%  $\text{H}_2\text{O}_2$  by weight.

4. The method of claim 1 wherein the formic acid content of the solvent is 85 to 100% by weight.

5. The method of claim 1 wherein the bleach solution is formed by adding hydrogen peroxide to concentrated formic acid.

6. The method of bleaching polyacrylonitrile fiber comprising subjecting the fiber to the action of a bleach solution comprising an agent from the group consisting of performic acid, hydrogen peroxide and mixtures thereof, dissolved in a solvent containing at least 75% formic acid by weight, at a temperature of 20 to 90° C.,

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said bleaching solution having an active oxygen content equivalent to 0.1–10%  $\text{H}_2\text{O}_2$  by weight.

7. The method of claim 6 wherein the active oxygen content of the bleach solution is equivalent to 1.0–3.0%  $\text{H}_2\text{O}_2$  by weight.

8. The method of claim 6 wherein the formic acid content of the solvent is 85–100% by weight.

9. The method of claim 8 wherein the temperature is 55 to 75° C.

2,077,103  
2,347,434  
2,432,447  
2,432,448  
5 2,512,640  
2,526,839

918,532  
10 581,046

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

1,075,663 Meerbott ----- Oct. 14, 1913

## 6

Franz ----- Apr. 13, 1937  
Reichert ----- Apr. 25, 1944  
Scheiderbauer ----- Dec. 9, 1947  
Richards ----- Dec. 9, 1947  
Greenspan ----- June 27, 1950  
Aston ----- Oct. 24, 1950

##### FOREIGN PATENTS

France ----- Feb. 1, 1947  
Great Britain ----- Sept. 30, 1946