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METHOD OF ENHANCING THE DYEABILITY OF VINYLIDENE CYANIDE INTERPOLYMER FIBERS WITH ORGANIC AMINES AND PRODUCTS RESULTING THEREFROM

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This invention relates to methods for enhancing the dyeability of certain types of synthetic fibers, and more particularly relates to a pre-dye treatment of vinylidene cyanide interpolymer fibers with a dilute aqueous amine solution.

Vinylidene cyanide fiber-forming interpolymers are described in U.S. Patents Nos. 2,615,865 to 2,615,880, 2,628,954, 2,650,911, 2,654,724, 2,654,728, 2,657,797, 2,716,104, 2,716,105, 2,716,106 and in copending applications, Serial Nos. 402,823, filed January 7, 1954, now U.S. Patent No. 2,786,046, and 407,595, filed February 1, 1954, now abandoned. As described therein, synthetic fibers spun from such interpolymers possess unusually high strength and other desirable properties.

To be of value to the trade, however, any synthetic fiber produced must be readily and successfully dyeable, preferably with the dyes and techniques currently in use. Like many hydrophobic synthetic fibers and filaments, those made from vinylidene cyanide interpolymers have slick, smooth surfaces and are resistant to penetration by ordinary dyestuffs. Further, these polymeric fibers offer a minimum of points or molecular groups to which dye molecules may become affixed.

One approach to the problem, used with fibers made of cyano-containing polymers of the polyacrylonitrile type, has been copolymerization with monomers containing basic groups. This procedure fails with polymers based on vinylidene cyanide, however, for this monomer, as demonstrated in the art, homopolymerizes under polymerization conditions when basic groups or water are present, even in small amounts.

Another expedient to encourage dye penetration is to open the fiber structure by the action of a swelling agent. Swelling agents are often applied to the fibers in liquid form before the fibers are immersed in the dye bath, or they may be added directly to the dye bath. Phenyl phenol, benzoic acid and monochlorobenzene have been used in pre-dye treatments. Swelling agents useful for incorporation into the dye bath include: aromatic amines such as aniline, p-chloroaniline, a-naphthylamine and m-toluidine, nitroaromatic compounds such as p-nitrotoluene, nitrobenzene, m-dinitrobenzene and p-nitrodiphenyl as well as salicylic acid, chlorosalicylic acid, quinoline, isoquinoline, acetophenone, chloroacetophenone, N,N-diphenyl formamide, N,N-diphenyl acetamide and benzaldehyde. The use of these and similar materials, however, results in increased costs and requires extra care in handling to avoid the effects of odious and toxic vapors.

It has also been proposed that synthetic fibers containing cyano groups be immersed in concentrated solutions of amines such as ethanolamine at elevated temperatures of approximately 100° C. The so-treated fibers are said to accept acid dyeing much more readily than when untreated, but this procedure results in problems of dye uniformity and degradation of the physical properties of the fiber. If an amine compound and an acid such as sulfuric acid or paratoluene sulfonic acid are added to the dope before spinning the polymer, improvement in dyeability of the spun filaments has been found. The acid seems to stabilize the dope against degradation while the amine acts as a basic agent to be attached to the polymer. However, when sufficient acid is used to prevent

degradation, the desirable action of the amine is severely impaired. This process is quite expensive since much of the amine is lost to the spinning bath; it is potentially a toxicity hazard and still does not provide fibers dyed with the uniformity and light, heat and laundry fastness of natural fibers such as wool.

It has now been discovered that a simple, economical pre-dye aqueous amine treatment avoids the failures and inconveniences of the prior art and allows fibers spun from vinylidene cyanide interpolymers to be dyed with acid and acetate dyes to depths and fastness of shades comparable to those obtained when using hydrophyllic fibers such as wool.

An object of this invention is to provide an economical process for pretreating vinylidene cyanide interpolymer fibers to render them readily dyeable with acid and acetate dyes. Another object is to provide a pretreating process that will not require expensive materials, high temperatures, or potentially toxic concentrations of chemicals.

Another object is to provide vinylidene cyanide interpolymer fibers, filaments, yarns and fabrics, which are dyeable with standard, commercially available, acid dyes; which possess, when so dyed, light, cleaning and laundering fastness comparable to dyed woolen fibers and fabrics, and which also possess improved flex abrasion resistance, improved electrostatic properties, improved resistance to solvents and a higher softening point.

These and other objects are attained according to this invention by the process of treating vinylidene cyanide interpolymer fibers with a dilute aqueous solution of an amine for a time and at a temperature sufficient for the amine to react with a significant proportion of the non-basic cyano groups in the vinylidene cyanide interpolymer structure to convert them into basic groups which are receptive to acid dyes. The vinylidene cyanide interpolymer fibers may be treated with the amine immediately after the fibers are formed, as by spinning a solution of the polymer through a spinnerette and then passing the filaments so formed through a heated bath of the dilute amine solution. Alternatively, the treatment with dilute amine may be applied to the fibers, or yarns or fabrics made therefrom, at any other desired time. For example, yarns or fabrics may be immersed in a heated bath solution of the dilute aqueous amine before passing them to the standard dye bath. Heat is not essential in either process if a long enough immersion time is allowed, the essential feature of the invention being that the treating conditions permit a significant degree of reaction between the dilute amine and the cyano groups of the interpolymer.

Any of the various water-soluble primary and secondary amines may be used to prepare the aqueous amine solution, but primary alkylene di- and polyamines are preferred. These include, for example, ethylene diamine, trimethylene diamine, tetramethylene diamine, hexamethylene diamine, 1,2-propylene diamine, 1,8-octamethylene diamine, diethylene triamine, triethylene tetramine, pentaethylene tetramine, tetraethylene pentamine, and the like, with ethylene diamine being the one most preferred.

Primary mono-aliphatic amines which are water-soluble such as methyl-, ethyl-, propyl- and n-butylamine and water-soluble secondary aliphatic amines such as dimethyl, diethyl and dipropyl amine may also be used. Still other amines that may be employed in the practice of this invention include water-soluble secondary heterocyclic amines such as piperidine, piperazine, morpholine, and the like, with piperazine the most preferred of this latter class.

The concentration of the amine in the aqueous solution is somewhat critical to the success of the process, as are the conditions of treatment. Amine solution concentra-

tions from 0.25 weight percent to 30 weight percent may be used, with 0.5 percent to 15 percent being generally preferred for reasons of economy. Temperatures above room temperature and below the boiling point of the amine used are preferred at atmospheric pressures, though higher temperatures may be employed at higher pressures. The time of treatment is inversely proportional to temperature, but treatment times of ten minutes to ten hours are generally used. Different amines will require the use of different operating times and temperatures, but these can be readily found by those skilled in the art, in the light of the attached examples.

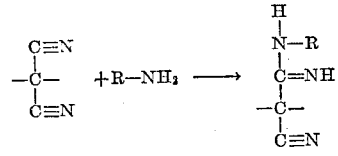
In general, treatments with any of the amines are preferably those which are substantially equivalent, in terms of reaction at the cyano groups, to treatments with 10 to 15 weight percent of ethylene diamine solutions for five to ninety minutes at a temperature of 100° to 120° C.

Any vinylidene cyanide interpolymer may be used. Such interpolymers contain



groups in their structure, and the preferred interpolymers are bicomponent interpolymers in which the vinylidene cyanide residue shown alternates in 1:1 molar ratio with the residue of the comonomers. Specific vinylidene cyanide interpolymers which may be used are disclosed in the patents set forth in the second paragraph hereof, the disclosures of which are incorporated herein by reference. The most preferred interpolymer is the 1 to 1 molar interpolymer of vinylidene cyanide with vinyl acetate.

As indicated hereinabove, when fibers or fabrics made from these interpolymers are exposed to dilute amines at elevated temperatures, the following reaction occurs:



The vinylidene cyanide interpolymer fibers seem to concentrate the small amount of amine out of solution into attachment on the fiber, and, at least, with vinylidene cyanide based fibers, if not with other cyano-containing synthetic fibers, hydrolysis of the amidine group by the water present, is minimized. When the comonomer with vinylidene cyanide contains groups such as Cl that are also reactive, the amine, of course, also attaches to the polymer at these reactive points.

When a pure undiluted amine is used, the reaction sites developed are not distributed uniformly throughout the cross section of the fiber, but are concentrated in the outer layer which results in erratic ring dyeing and poor flex abrasion resistance of the dyed fiber. It is possible by the practice of this invention to get reaction sites uniformly distributed through the fiber cross section when a dilute aqueous amine solution is employed.

Advantages which may be cited for the synthetic materials dyed by the process of this invention include complete penetration of the dye into the fiber, improved flex abrasion resistance of the fiber, less tendency to static charge build up, no change in hand or feel of the fabric, and, most unexpectedly, improved resistance to organic solvents and higher safe ironing temperatures of the fabric.

The examples given below are intended only to illustrate the striking advantages of this invention and are not to be construed as a limitation upon the scope thereof, for there are, of course, numerous possible variations and modifications that will be apparent to those skilled in the art. In the examples all parts are by weight.

EXAMPLE 1

Samples of 100 percent vinylidene cyanide-vinyl acetate interpolymer yarn and 100 percent vinylidene cyanide-vinylidene chloride interpolymer yarn, prepared as described in U.S. Patents 2,615,866 and 2,615,870, and a sample of commercially available polyacrylonitrile fiber modified to accept acid dyes, are treated for two hours at 100° C. in 4.4 weight percent aqueous solution of ethylene diamine, scoured for 15 minutes in a boiling wash solution of the sodium salt of N-methyl-oleoyl taurate, dried one hour at 110° C. and then dyed with 5 percent on weight of fabric (owf.) of a standard acid dye, Fast Light Red 4BA, and 6 percent owf. formic acid at a bath ratio of 40 parts dye liquor to 1 part fiber.

Parallel dyeings are run using untreated 100 percent vinylidene cyanide-vinyl acetate yarn, untreated 100 percent vinylidene cyanide-vinylidene chloride yarn, 100 percent wool, and commercially available polyacrylonitrile yarn modified to accept acid dyes. The concentration of dye in the exhausted baths at the end of one hour at 95° C. is:

	g. dye/l.
100% vinylidene cyanide-vinyl acetate (amine-treated)	0.036
100% vinylidene cyanide-vinyl acetate (untreated)	1.25
100% vinylidene cyanide-vinylidene chloride (amine-treated)	0.010
100% vinylidene cyanide-vinylidene chloride (untreated)	1.22
100% wool (untreated)	0.145
Acid dyeable polyacrylonitrile (untreated)	0.800
Acid dyeable polyacrylonitrile (amine-treated)	0.790

It is apparent that the vinylidene cyanide interpolymers which are amine-treated exhaust the dye bath to a remarkably greater extent than the other samples of synthetic yarns.

Union dyeing tests are conducted wherein a sample of vinylidene cyanide-vinyl acetate yarn is first treated with 4.4 weight percent ethylene diamine at 100° C. for two hours. The treated yarn is then mixed with an equal amount of wool. A similar sample of commercially available acid dyeable polyacrylonitrile and wool is also prepared. The two pairs of samples are then dipped into an acid dye bath.

The vinylidene cyanide-vinyl acetate and wool pair dyes uniformly over the entire surface, both synthetic and natural. The acid dyeable polyacrylonitrile-wool pair exhibits very non-uniform dyeing with the wool dyed to a much deeper shade.

Cross sections of the dyed fibers are examined for dye penetration.

Fiber:	Percent penetration
100% vinylidene cyanide - vinyl acetate (amine-treated)	100
100% vinylidene cyanide-vinyl acetate (untreated)	0
100% wool	100
Commercially available acid dyeable polyacrylonitrile	10–20
Commercially available acid dyeable polyacrylonitrile (amine-treated)	10–20

The data of this example show that the dilute amine treatment has tremendously improved the acid dyeability of the vinylidene cyanide interpolymer fibers. The effect appears to be unique with the vinylidene cyanide based materials since similarly treated polyacrylonitrile based fibers show little or no change.

EXAMPLE 2

Similar examples using the same fibers as in Example 1 and 10.0 weight percent morpholine and 10.0 weight percent piperazine as the dilute amines, with fiber im-

mersion times of 3 hours and 6 hours at reflux temperatures respectively, give approximately equivalent dyeing results.

EXAMPLE 3

Samples of a 100 percent vinylidene cyanide-vinyl acetate fiber, prepared as shown in U.S. Patent 2,615,866, are treated for various times in 0.9, 2.1 and 4.4 weight percent aqueous ethylene diamine solutions at 100° C. and at 120° C. Periodically a sample is removed and dyed, the procedure being continued until the optimum treatment time has been determined for each concentration at each temperature level. Optimum treatment time is judged as the minimum immersion time to give dye bath exhaustion of a five percent owf. Fast Light Red 4BA Acid dye solution using five percent owf, formic acid and a 40 to 1 bath ratio in one hour at 95° C.

Optimum Immersion Time

	0.9 Wt. Percent	2.1 Wt. Percent	4.4 Wt. Percent
120° C.	70 min.	30 min.	10 min.
100° C.	8 hrs.	3 hrs.	2 hrs.

Other levels of time, temperature and concentration will be found to be optimum when alternate amines are used.

When polyacrylonitrile fiber is substituted in the procedure of this Example, the minimum treatment time required to reach dye bath exhaustion ranges from 24 hours on up, further indicating that the improvements shown by the practice of this invention on vinylidene cyanide copolymers are not obtained with polyacrylonitrile fiber.

EXAMPLE 4

100 percent vinylidene cyanide-vinyl acetate filament is twisted into regular cord. Half of the cords are dipped for 100 minutes at 100° C. in a 4.4 weight percent water solution of ethylene diamine. The dipped cords are scoured in hot water, then scoured, along with undipped control cords of the same composition and structure, in boiling ethanol to remove all finish. All cords are then conditioned at 60 percent relative humidity and 75° F. and are treated on a laboratory flex tester of the type described in U.S. Patent 2,488,761.

Cord:	Flex life, hours
Control (average of 10)	6.4
Amine-treated (average of 12)	10.0

EXAMPLE 5

A Sensitive Research Instrument Corporation electrostatic volt meter, model ESD, 0–3000 volts range, is used to compare static charge build-up on amine-treated vinylidene cyanide-vinyl acetate fabric against that built up on untreated vinylidene cyanide-vinyl acetate fabric. The fabrics are conditioned at 60 percent relative humidity and 75° F., but tested at 30 percent relative humidity because the volt meter discharges too rapidly at the higher level.

When amine-treated, dyed fabric is rubbed on stroke with wool, nylon, cotton, bright chromium or back of the hand, the volt meter registers 0–600 volts. Control fabric untreated, under the same conditions registers 1900–2700 volts. Freedom from static charge build-up is of vital concern in gaining public acceptance of a synthetic fiber.

EXAMPLE 6

Vinylidene cyanide-vinyl acetate fibers as prepared under the teaching of U.S. Patent 2,615,866 are soluble in nitromethane, dimethyl formamide and acetonitrile. Vinylidene cyanide-vinyl acetate fibers after dilute amine treatment, as in Example 1, are unexpectedly found to be insoluble when they are immersed in these solvents.

Untreated vinylidene cyanide-vinyl acetate fibers are insoluble in boiling acetone but shrink 20 percent after one minute of such abuse. The amine-treated fibers do not shrink at all under the same conditions.

EXAMPLE 7

Samples of square woven 100 percent vinylidene cyanide-vinyl acetate fabric are treated 8 hours at 100° C. in a one percent water solution of ethylene diamine, scoured first in hot water, then three times in ethanol, dried, and compared to untreated control fabric at various ironing temperatures.

Time (Seconds)	Temperature ° C. (Sole Plate of Iron)	Control	Amine-Treated
20	190	Slight glaze	No change.
7	205	Badly glazed	Do.
5	215	Severly glazed	Slightly glazed.

This increase in maximum safe ironing temperature is a most surprising and most welcome result of the dilute aqueous amine treatment. Standard "rayon" settings on electric irons will not burn the amine-treated fabrics.

EXAMPLE 8

Samples of amine-treated vinylidene cyanide-vinyl acetate are compared to similar samples of wool after immersion in 0.1 N sodium hydroxide at room temperature with periodic checks for damage, i.e. shrinkage and loss in tenacity:

Fabric	Time in 0.1 N NaOH to Cause	
	Slight Damage, hrs.	Severe Damage, hrs.
Wool	0.1	0.2
Vinylidene cyanide-vinyl acetate (treated)	25.0	32.0

EXAMPLE 9

Permanence of acid dyeability induced in vinylidene cyanide-vinyl acetate fibers by this dilute amine treatment is found to be unchanged by exposing treated, dyed fibers up to 150 hours 8 inches from a sun lamp, scouring them in boiling detergent solutions, or exposing them to dry heat in a 110° C. forced-air oven:

Time at 110° C. in Forced-Air Oven After Treatment, Before Dyeing, hrs.	Concentration of Dye—in Exhausted Dye Bath After 5% Dyeing (1.25 g/l. before dyeing), g/l.
1.0	0.036
2.0	0.038
3.5	0.057
92.25	0.055
122.5	0.063

There is no visual difference between the 2.0 hour and the 122.5 hour samples.

The foregoing examples are merely illustrative, and not limiting, of the scope of this invention. Variations and modifications of the invention will be apparent to those skilled in the art. For instance, while the examples have indicated batch operations, proper scaling of equipment could make the process a continuous one. The invention is intended to be limited only by the scope and spirit of the appended claims.

We claim:

1. A fiber product that is produced by the reaction of an initial fiber consisting of equimolar vinylidene cyanide-vinyl acetate interpolymer with a .25 weight percent to 25 weight percent aqueous solution consisting essentially of ethylene diamine for ten mintues to ninety minutes at a temperature of 100° to 120° C.

2. A fiber product that is produced by the reaction of an initial fiber consisting of equimolar vinylidene cyanide-

vinylidene chloride interpolymer fiber reacted with a .25 weight percent to 25 weight percent aqueous solution consisting essentially of ethylene diamine for ten minutes to ninety minutes at a temperature of 100° to 120° C.

3. The process for enhancing the dyeability of synthetic interpolymer fibers consisting of 50 mol percent vinylidene cyanide and one other olefinic monomer copolymerizable therewith selected from the group consisting of vinyl acetate and vinylidene chloride, which consists essentially of treating said fibers with a 0.25 weight percent to 25.0 weight percent aqueous solution consisting essentially of an amine selected from the group consisting of water-soluble primary alkyl amines containing 1 to 4 carbon atoms, water-soluble primary alkylene diamines containing 2 to 8 carbon atoms, water-soluble ethylene polyamines containing 2 to 5 ethylene (—CH_2CH_2—) groups and water-soluble secondary heterocyclic amines selected from the group consisting of piperidine, piperazine, and morpholine for a time and at a temperature sufficient for the amine to react with the cyano groups in the vinylidene cyanide interpolymer structure to an extent that is equivalent to said reaction at the cyano groups of 10 to 15 weight percent aqueous solutions consisting essentially of ethylene diamine reacted therewith for five to ninety minutes at 100° C. to 120° C.

4. The process for enhancing the dyeability of synthetic interpolymer fibers consisting of 50 mol percent vinylidene cyanide and one other olefinic monomer copolymerizable therewith selected from the group consisting of vinyl acetate and vinylidene chloride, which consists essentially of treating said fibers with a 0.25 weight percent to 25.0 weight percent aqueous solution consisting essentially of water-soluble primary alkyl amines containing 1 to 4 carbon atoms for a time and at a temperature sufficient for the amine to react with the cyano groups in the vinylidene cyanide interpolymer structure to an extent that is equivalent to said reaction at the cyano groups of 10 to 15 weight percent aqueous solutions consisting essentially of ethylene diamine reacted therewith for five to ninety minutes at 100° C. to 120° C.

5. The process for enhancing the dyeability of synthetic interpolymer fibers consisting of 50 mol percent vinylidene cyanide and one other olefinic monomer copolymerizable therewith selected from the group consisting of vinyl acetate and vinylidene chloride, which consists essentially of treating said fibers with a 0.25 weight percent to 25.0 weight percent aqueous solution consisting essentially of water-soluble primary alkylene diamines containing 2–8 carbon atoms for a time and at a temperature sufficient for the amine to react with the cyano groups in the vinylidene cyanide interpolymer structure to an extent that is equivalent to said reaction at the cyano groups of 10 to 15 weight percent aqueous solutions consisting essentially of ethylene diamine reacted therewith for five to ninety minutes at 100° C. to 120° C.

6. The process for enhancing the dyeability of synthetic interpolymer fibers consisting of 50 mol percent vinylidene cyanide and one other olefinic monomer copolymerizable therewith selected from the group consisting of vinyl acetate and vinylidene chloride, which consists essentially of treating said fibers with a 0.25 weight percent to 25.0 weight percent aqueous solution consisting essentially of water-soluble ethylene polyamines containing 2 to 5 ethylene (—CH_2CH_2—) groups for a time and at a temperature sufficient for the amine to react with the cyano groups in the vinylidene cyanide interpolymer structure to an extent that is equivalent to said reaction at the cyano groups of 10 to 15 weight percent aqueous solutions consisting essentially of ethylene diamine reacted therewith for five to ninety minutes at 100° C. to 120° C.

7. The process for enhancing the dyeability of synthetic interpolymer fibers consisting of 50 mol percent vinylidene cyanide and one other olefinic monomer copolymerizable therewith selected from the group consisting of vinyl acetate and vinylidene chloride which consists essentially of treating said fibers with a 0.25 weight percent to 25.0 weight percent aqueous solution consisting essentially of water-soluble secondary heterocyclic amines selected from the group consisting of piperidine, piperazine, and morpholine for a time and at a temperature sufficient for the amine to react with the cyano groups in the vinylidene cyanide interpolymer structure to an extent that is equivalent to said reaction at the cyano groups of 10 to 15 weight percent aqueous solutions consisting essentially of ethylene diamine reacted therewith for five to ninety minutes at 100° C. to 120° C.

8. The process for enhancing the dyeability of synthetic interpolymer fibers consisting of 50 mol percent vinylidene cyanide and one other olefinic monomer copolymerizable therewith selected from the group consisting of vinyl acetate and vinylidene chloride, which consists essentially of treating said fibers with a 0.25 weight percent to 25.0 weight percent aqueous solution consisting essentially of ethylene diamine for a time and at a temperature sufficient for the amine to react with the cyano groups in the vinylidene cyanide interpolymer structure to an extent that is equivalent to said reaction at the cyano groups of 10 to 15 weight percent aqueous solutions consisting essentially of ethylene diamine reacted therewith for five to niney minutes at 100° C. to 120° C.

9. The process for enhancing the dyeability of synthetic interpolymer fibers consisting of 50 mol percent vinylidene cyanide and one other olefinic monomer copolymerizable therewith selected from the group consisting of vinyl acetate and vinylidene chloride, which consists essentially of treating said fibers with a 0.25 weight percent to 25.0 weight percent aqueous solution consisting essentially of piperazine for a time and at a temperature sufficient for the amine to react with the cyano groups in the vinylidene cyanide interpolymer structure to an extent that is equivalent to said reaction at the cyano groups of 10 to 15 weight percent aqueous solutions consisting essentially of ethylene diamine reacted therewith for five to ninety minutes at 100° C. to 120° C.

10. The process for enhancing the dyeability of synthetic interpolymer fibers consisting of 50 mol percent vinylidene cyanide and one other olefinic monomer copolymerizable therewith selected from the group consisting of vinyl acetate and vinylidene chloride, which consists essentially of treating said fibers with a 0.25 weight percent to 25.0 weight percent aqueous solution consisting essentially of morpholine for a time and at a temperature sufficient for the amine to react with the cyano groups in the vinylidene cyanide interpolymer structure to an extent that is equivalent to said reaction at the cyano groups of 10 to 15 weight percent aqueous solutions consisting essentially of ethylene diamine reacted therewith for five to ninety minutes at 100° C. to 120° C.

11. The process for enhancing the dyeability of synthetic interpolymer fibers consisting of 50 mol percent vinylidene cyanide and 50 mol percent vinyl acetate, which consists essentially of treating said fibers with a 0.25 weight percent to 25.0 weight percent aqueous solution consisting essentially of ethylene diamine for a time and at a temperature sufficient for the amine to react with the cyano groups in the vinylidene cyanide interpolymer structure to an extent that is equivalent to said reaction at the cyano groups of 10 to 15 weight percent aqueous solutions consisting essentially of ethylene diamine reacted therewith for five to ninety minutes at 100° C. to 120° C.

12. The process for enhancing the dyeability of synthetic interpolymer fibers consisting of 50 mol percent vinylidene cyanide and 50 mol percent vinylidene chloride, which consists essentially of treating said fibers with a 0.25 weight percent to 25.0 weight percent aqueous solution consisting essentially of ethylene diamine for a time and at a temperature sufficient for the amine to react with the cyano groups in the vinylidene cyanide interpolymer structure to an extent that is equivalent to said

reaction at the cyano groups of 10 to 15 weight percent aqueous solutions consisting essentially of ethylene diamine reacted therewith for five to ninety minutes at 100° C. to 120° C.

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