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Alderson

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[54] **PROCESS AND PRODUCT**

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[52] **U.S. Cl.** ..... **264/290 N;** 8/115.5

[51] **Int. Cl.²** **B29C 17/02**

[58] **Field of Search** ..... 264/290 N, 210 F; 8/115.5, 8/115.6; 260/45.85 N

[56] **References Cited**

UNITED STATES PATENTS

2,550,650	4/1951	Arnold	8/115.5
3,102,323	9/1963	Adams	260/40 R
3,117,173	1/1964	Adams	264/210 F
3,233,019	2/1966	Adams	260/210 F
3,418,267	12/1968	Busse	260/33.8 R
3,772,067	11/1973	Alderson	117/138.8 N

OTHER PUBLICATIONS

Chem. Dictionary, 1961, page 253.

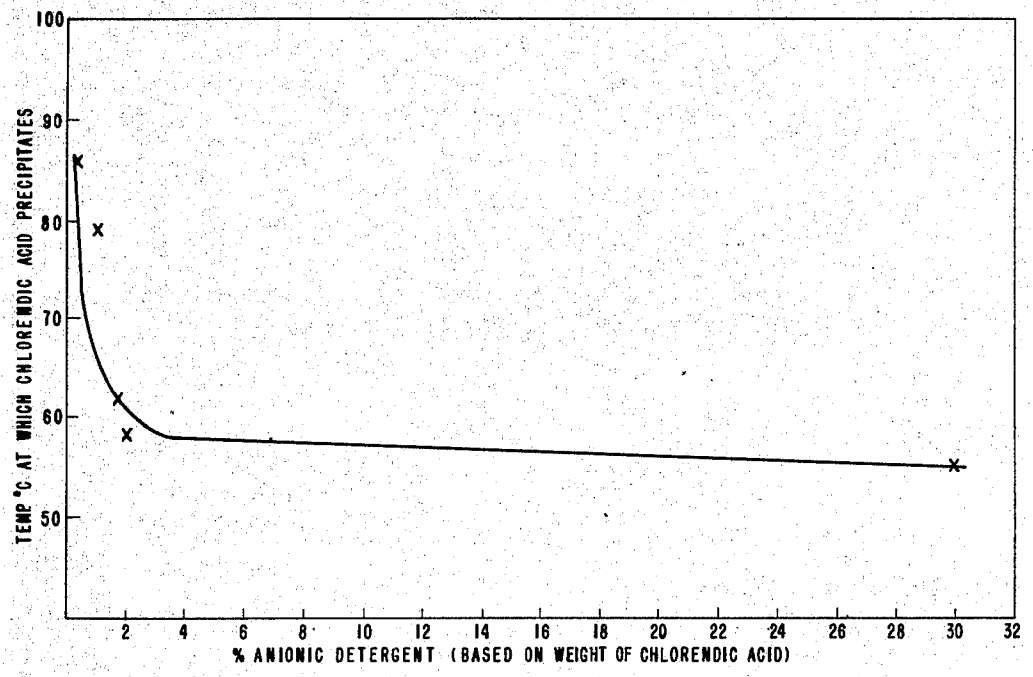
Swartz, A. M., "Surface Active Agents," p. 518, 1958.

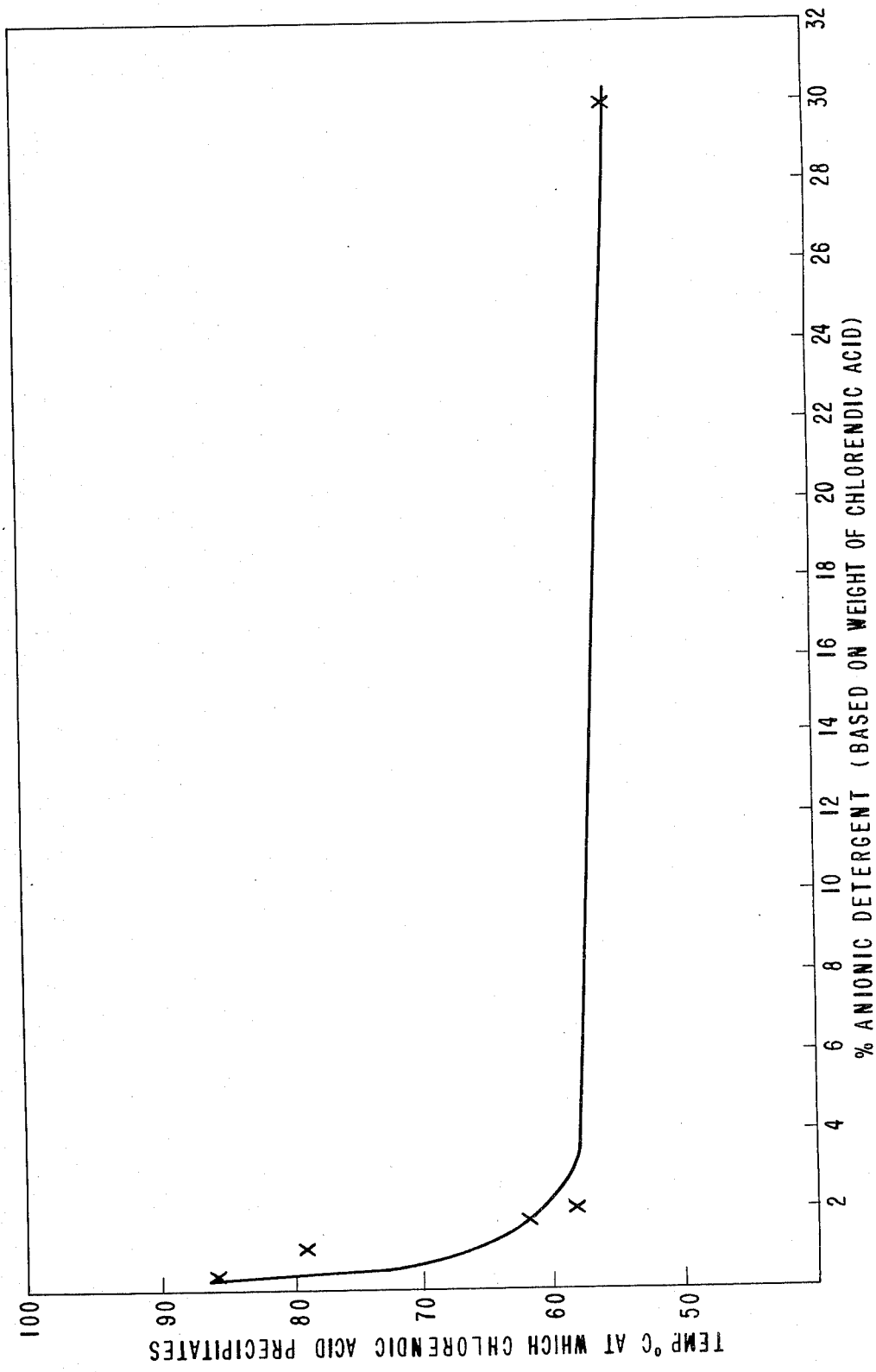
Primary Examiner—Theodore Morris

[57] **ABSTRACT**

Polyamide filaments are treated to improve flame resistance by being drawn in an aqueous bath containing chlorendic acid and an anionic detergent.

4 Claims, 4 Drawing Figures




TEMP °C AT WHICH CHLORENDIC ACID PRECIPITATES
100
90
80
70
60
50
% ANIONIC DETERGENT (BASED ON WEIGHT OF CHLORENDIC ACID)
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32

PROCESS AND PRODUCT

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for preparing flame-resistant polyamide filaments containing imbibed chlorendic acid and to the solutions used for imbibing into the filaments.

2. Description of the Prior Art

Methods for treating polyamides to improve their resistance to burning are known. For example, flame retardants may be added to molten polymer prior to shaping the polyamide, as in U.S. Pat. No. 3,418,267. Other processes apply flame retardants such as chlorendic acid to filaments after the drawing step, see U.S. Pat. No. 3,772,067. Still other processes are known for applying fire-retardant coatings to fabrics.

All of these prior art processes have disadvantages. Some flame retardants thermally decompose at polyamide melt temperatures. Other have a deleterious effect on subsequent spinning and drawing operations.

Most flame retardants are applied to the polyamide fiber after drawing, often after the fiber has been processed into fabric. This additional treatment step is time consuming and expensive. Also, during the drawing process, the polymer chains become oriented and crystallized. Penetration of the flame retardant into the oriented fiber is much more difficult and special treatment, e.g., elevated temperatures and long reaction times, may be required to increase the rate of absorption of the flame retardant and to facilitate removal of water or other solvent.

The imbibition of certain additives during the polyamide drawing process is also known. Many additives are very effectively imbibed during drawing and the imbibed additives sometimes show improved fastness properties. In addition, the imbibition takes place during the usual drawing step, thus eliminating a separate processing step. Imbibition drawing is shown in U.S. Pat. Nos. 3,590,106, 3,233,019, and Canadian Pat. No. 867,263.

DEFINITION OF THE INVENTION

This invention is a process for flame retarding polyamide fibers by imbibing chlorendic acid from an aqueous bath. The process depends on the use of an anionic dispersing agent to form a homogeneous solution of chlorendic acid in water at temperatures from 55°–100°C. Drawing of the filament in the bath gives a flame-resistant fiber.

BRIEF DESCRIPTION OF DRAWING

The figure shows the preceipitation temperature of 10% chlorendic acid in an anionic dispersing agent-water solution over the range 50° to 87°C.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The filaments produced by the present invention contain from 2 to about 18% by weight of chlorendic acid. Chlorendic acid is believed to be present in the filaments in a salt form in combination with the amine ends of the polymer molecules and dispersed throughout the polyamide matrix. The acid can substantially be entirely extracted from the filaments. For example, aqueous solutions containing from 1 to 5% by weight of a base such as ammonia, sodium carbonate, or sodium hydroxide are effective extracting agents.

The filaments of this invention show a significant reduction in burning propensity compared to untreated fibers. As is well known in the art, fabric construction greatly influences the amount of flame retardant required, i.e., lightweight fabrics require more additive than heavy constructions. A superior rating as determined by the vertical flame test is obtained when the chlorendic acid content of medium weight knitted and woven goods is at least 3% by weight. At contents greater than about 6% by weight, the filaments are rated self-extinguishing or nearly so when a combustion source is removed, and filaments containing 6 to 10% of chlorendic acid are a preferred embodiment of this invention. While amounts greater than 10% by weight may be incorporated, the resistance of the filament to burning is not increased proportionately.

The polymers useful in the practice of this invention are fiber-forming, long chain, synthetic polyamides formed from dicarboxylic acids (particularly hydrocarbon dicarboxylic acids) and diamines (particularly hydrocarbon diamines). Polyhexamethylene adipamide is a highly preferred polyamide. The polymers made from bis(4-aminocyclohexyl)methane and dodecanedioic acid and copolymers including polyhexamethylene isophthalate or terephthalate (6I or 6T) may be used.

Chlorendic acid melts in water at 70°C. but is maintained as a distinct oil phase up to 96°–97°C., at which temperature it becomes miscible with water. On cooling a solution of chlorendic acid in water, the monohydrate of chlorendic acid crystallizes starting at about 93°C. In the process of this invention, a homogenous, aqueous solution of chlorendic acid is obtained by heating a mixture of an anionic dispersing agent, water and chlorendic acid above 97°C. Anionic dispersing agents such as sodium alkylarylsulfonate or sodium laurylsulfate may be used. On cooling a mixture of Alkanol DW (trademark for a sodium alkylarylsulfonate anionic dispersing agent manufactured by E. I. du Pont de Nemours, Inc.) water and chlorendic acid, the solution remains homogeneous down to about 57°C. The precipitation temperature of 10% chlorendic acid in water in the presence of varying amounts of this sodium alkylarylsulfonate is shown in the FIGURE.

The amount of chlorendic acid in the imbibition (drawing) bath may vary from about 1 to 15%. There is little effect of chlorendic acid concentration in the bath on imbibition uptake by the yarn over the range from 7 to 15%, and this range is preferred. Chlorendic acid must be in solution to be imbibed by nylon yarn during drawing. A concentration of at least 2% dispersing agent, based on the weight of the chlorendic acid used, is required to keep the chlorendic acid in solution at the lower temperatures. The concentration of dispersing agent should be preferably between 4 and 10% by weight, based on chlorendic acid. Higher bath temperatures favor increased imbibition, and temperatures above 80°C. are preferred. Draw ratios of at least 1.5X are ordinarily employed. Slow drawing speeds also favor increased imbibition.

In the following examples illustrating the invention, all percentages are by weight. The vertical flame test is described in ASTM-D626 and is used to measure the flame resistance of filaments prepared in the examples. The Steiner tunnel test (ASTM-E-84) is described in ASTM Standards 14, 412 (1968). The chlorendic acid

content of filaments is determined by coulometric analysis of chloride using the method described in Cotlov et al., Journal of Laboratory and Clinical Medicine, 51, 461–468, 1958, and calculated as chlorendic acid. In practice, it has been noted that the weight the filaments gain from imbibition of chlorendic acid differs from the chlorendic acid content as determined by analysis by no more than 2%. Thus, a measure of weight gained can be taken as a meaningful indication of the chlorendic acid content. The significance of this approximation can be augmented by flame performance where filaments showing a weight gain of at least 6% are flame resistant, i.e., they self-extinguish frequently in a matter of seconds (e.g., less than 30 seconds).

EXAMPLE 1

This example shows the effect of temperature on chlorendic acid uptake.

A 34-filament yarn of polyhexamethylene adipamide is drawn 3X to a final yarn denier of 70 in a portable draw bath containing water, chlorendic acid and an alkylaryl-sulfonate (Alkanol DW). The concentration of ingredients was kept constant but the temperature was varied as shown in Items 1–3 of the Table. The draw bath is 30 inches long of the general type described by Mummery in U.S. Pat. No. 3,077,004. Wind-up speed in 75 yds./minute, allowing a 0.6 second residence time in the draw bath. The tabulated data (Items 1–3) show that chlorendic acid uptake is favored by high bath temperature.

EXAMPLE 2

This example shows the effect of bath concentration over the range of 7–15% on chlorendic acid uptake.

Conditions similar to Example 1 except for varying the concentration of the anionic detergent and chlorendic acid and using temperatures as indicated in the Table (Items 4–7) are employed to determine the effect of chlorendic acid concentration in the bath on imbibition uptake. The tabulated data (Items 4–7) show that chlorendic acid concentration in the bath over the range of 7–15% has little effect on chlorendic acid uptake.

EXAMPLE 3

This example shows that the chlorendic acid must be in solution for effective imbibition.

Conditions similar to Example 1 except for varying the concentration of the anionic detergent and chlorendic acid and using temperatures as indicated in the Table (Items 8–11) are employed to determine the effect of solubility of chlorendic acid on imbibition uptake. Items 8 and 9 involve draw baths in which were inhomogeneous solutions. The tabulated data (Items 8–11) show that complete solubility of chlorendic acid is necessary in order to approach the 6% range which is required for an effective fire retardancy in a woven or knitted fabric.

EXAMPLE 4

This example shows the effect of the anionic detergent concentration in the range of 4–30% on chlorendic acid uptake.

Conditions similar to Example 1 except for the temperature and concentrations are utilized to determine the effect of changing the anionic detergent concentration. The data (Items 12–15 of the Table) show that within the concentration range of 4–30% there is no marked effect on chlorendic acid uptake.

EXAMPLE 5

This example shows the flame resistance of the treated fibers.

A 25 liter draw bath of the type described in Example 1 is installed between the draw rolls of an experimental draw machine. The draw bath is held at 78°–83°C. and bath concentration averages 2.7% chlorendic acid and 25% sodium alkylarylsulfonate based on the weight of chlorendic acid. Fifteen thousand denier polyhexamethylene adipamide tow is drawn 3X at 25 yards/minute, allowing a 0.2 second residence time in the draw bath. The drawn yarn contains 4.3% chlorendic acid. It is crimped in a stuffer box, cut to 6 ½ inch staple, carded, drafted, and spun into yarn. The yarn is tufted into 28 ounce, 1 ¾ inch pile height, ⅜ inch gauge shag carpets in a nonwoven polypropylene carpet backing to which nylon staple has been needled. The carpets are beck dyed and latexed with styrene-butadiene-rubber latex filled with aluminum trihydrate. Comparable carpet made with untreated polyhexamethylene adipamide yarn was used as a control.

Flame retarded carpet made as above does not ignite in a three second ignition in the vertical flame test; control carpet burns completely. Flame retarded carpet made as above has a Steiner tunnel rating of 141, the control carpet has a Steiner tunnel rating of 188.

TABLE

Item	T,°C.	% Chlorendic Acid in Bath	% Anionic Detergent in Bath**	% Chlorendic Acid on Yarn
1	87	11	10	25
2	72	11	10	8.0
3	60	11	10	7.0
4	85	15	30	18
5	87	11	10	25
6	86	10	30	20
7	85	7	6	22
8	52	7*	30	1.7
9	55	12*	30	4.4
10	60	7	6	5.6
11	59	12	30	5.9
12	60	15	4	6.0
13	60	7	6	5.6
14	60	11	10	7.0
15	59	12	30	5.9

*Inhomogenous solutions
**On weight of chlorendic acid

What is claimed is:

1. A process for imbibing chlorendic acid in a fiber of a synthetic polyamide formed from a dicarboxylic acid and a diamine which comprises drawing said filament at least 1.5X. in an aqueous bath consisting essentially of from 1–15% by weight of chlorendic acid, and at least about 2% by weight of an anionic detergent, said bath being at a temperature of at least about 55°, to 100°C.

2. The process of claim **1** wherein the bath temperature is at least 80°C.

3. The process of claim **1** wherein the filament is polyhexamethylene adipamide.

4. The process of claim **1** wherein the anionic detergent is sodium alkylarylsulfonate.

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