Dec. 16, 1969 H. ZAHN ET AL 3,484,272
PROCESS FOR COATING A SUBSTRATE OF KERATINOUS FIBERS WITH POLYAMIDE
Filed Oct. 10, 1966 5 Sheets-Sheet 1

Fig. 1.

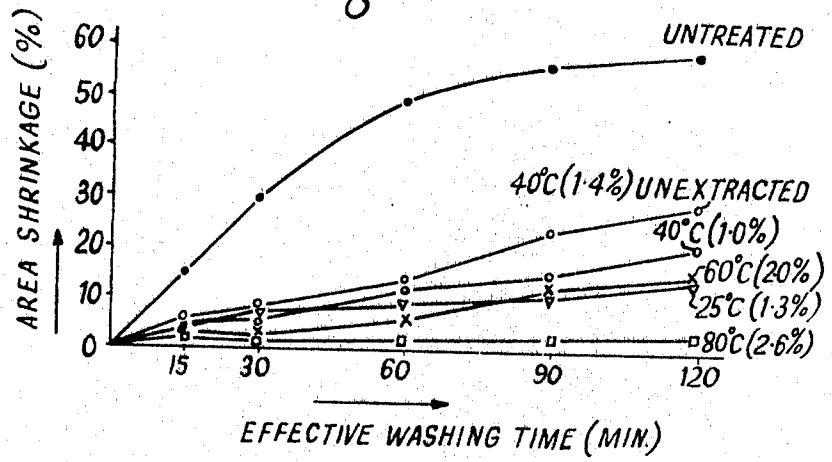


Fig. 2.

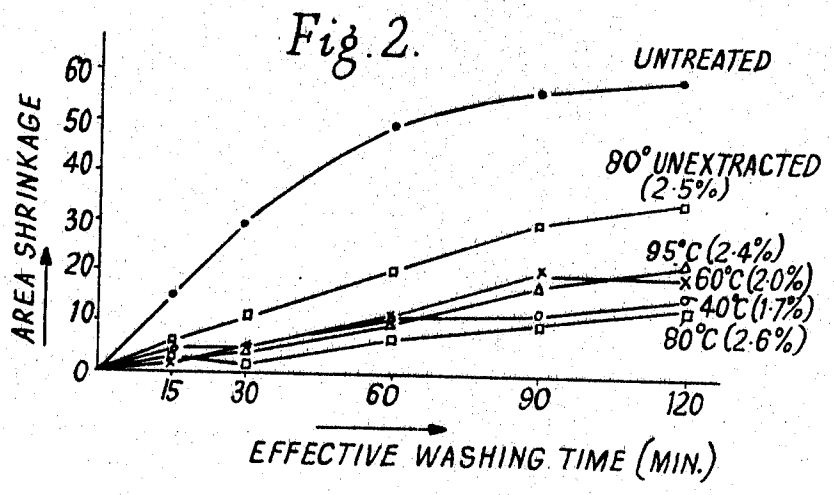


Fig. 3.

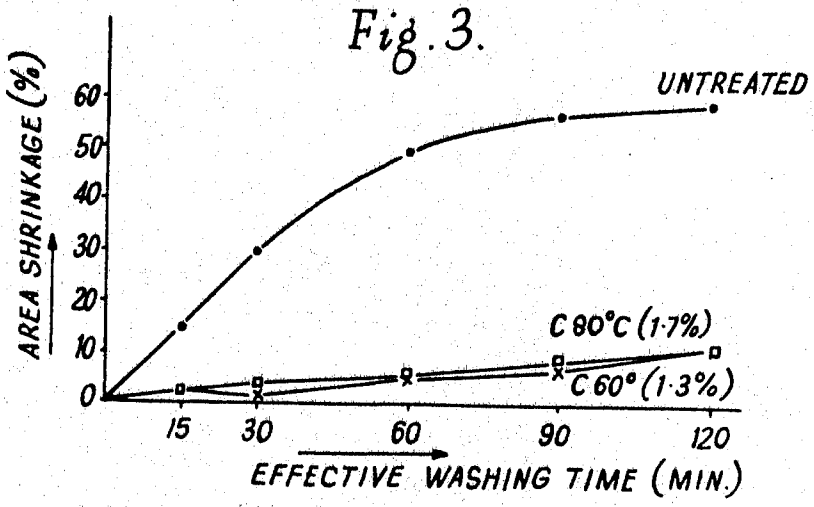

AREA SHRINKAGE (%)
0
10
20
30
40
50
60
UNTREATED
C 80°C (1·7%)
C 60° (1·3%)
15
30
60
90
120
EFFECTIVE WASHING TIME (MIN.)

Fig. 4.

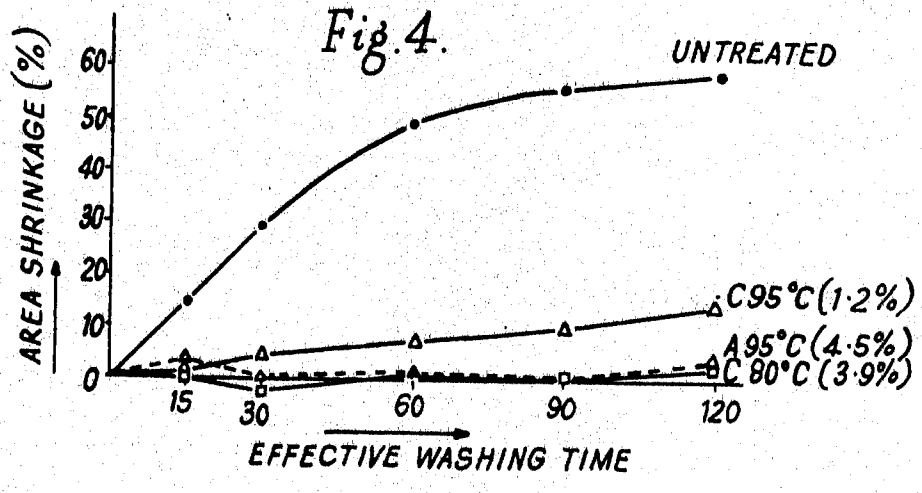

AREA SHRINKAGE (%)
0
10
20
30
40
50
60
UNTREATED
C 95°C (1·2%)
A 95°C (4·5%)
C 80°C (3·9%)
15
30
60
90
120
EFFECTIVE WASHING TIME

Fig. 5.

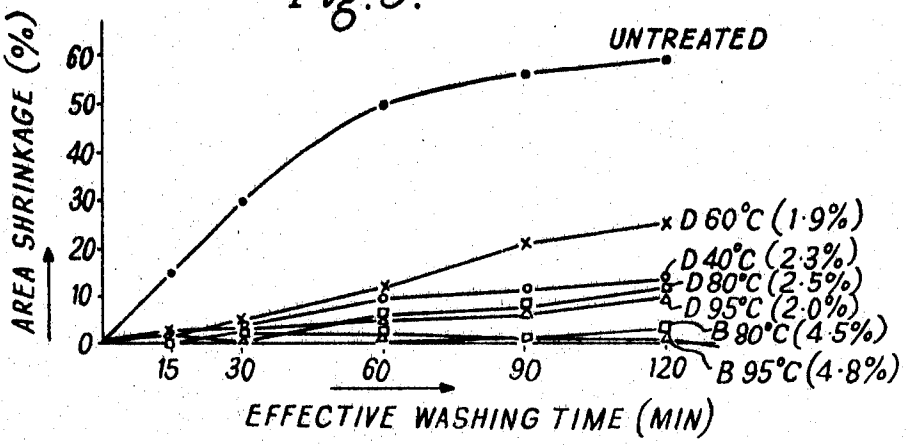

AREA SHRINKAGE (%)
60
50
40
30
20
10
0
UNTREATED
D 60°C (1·9%)
D 40°C (2·3%)
D 80°C (2·5%)
D 95°C (2·0%)
B 80°C (4·5%)
B 95°C (4·8%)
15
30
60
90
120
EFFECTIVE WASHING TIME (MIN)

Fig. 6.

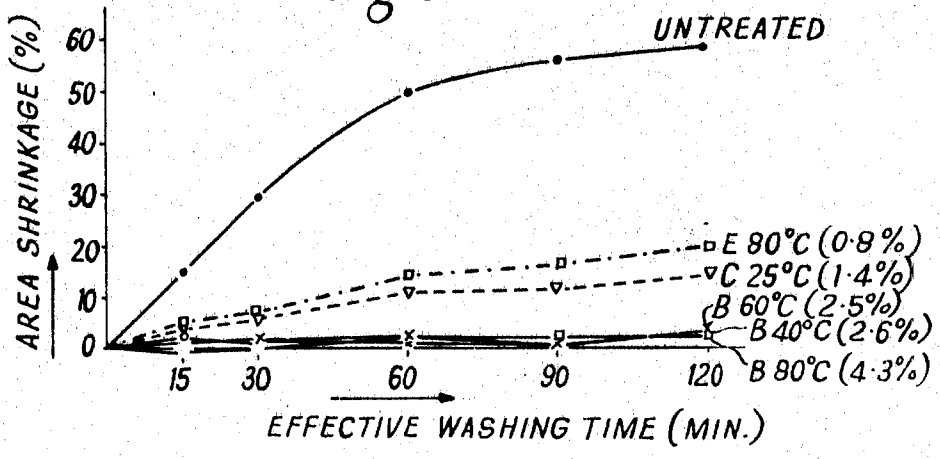

AREA SHRINKAGE (%)
60
50
40
30
20
10
0
UNTREATED
E 80°C (0·8%)
C 25°C (1·4%)
B 60°C (2·5%)
B 40°C (2·6%)
B 80°C (4·3%)
15
30
60
90
120
EFFECTIVE WASHING TIME (MIN.)

Fig. 7.

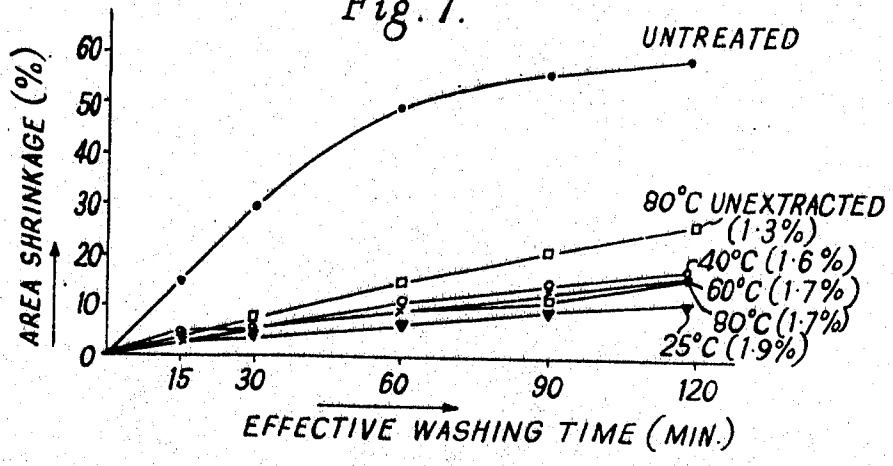

AREA SHRINKAGE (%)
0
10
20
30
40
50
60
15
30
60
90
120
EFFECTIVE WASHING TIME (MIN.)
UNTREATED
80°C UNEXTRACTED (1·3%)
40°C (1·6%)
60°C (1·7%)
80°C (1·7%)
25°C (1·9%)

Fig. 8.

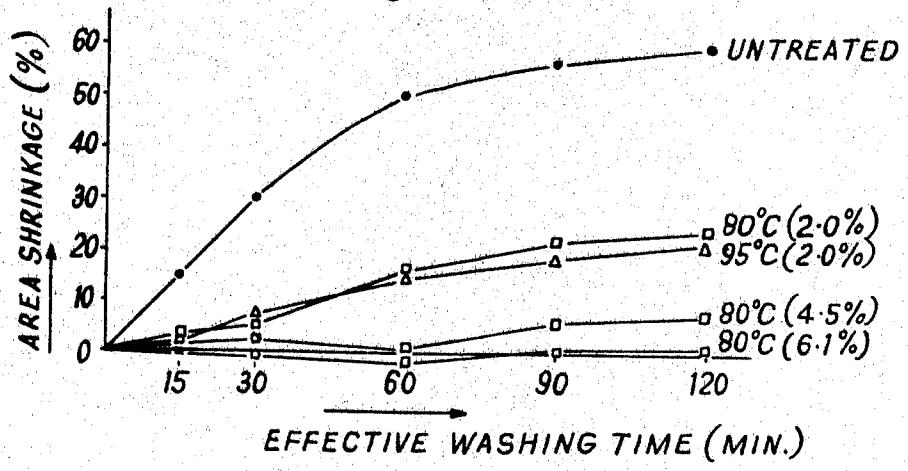
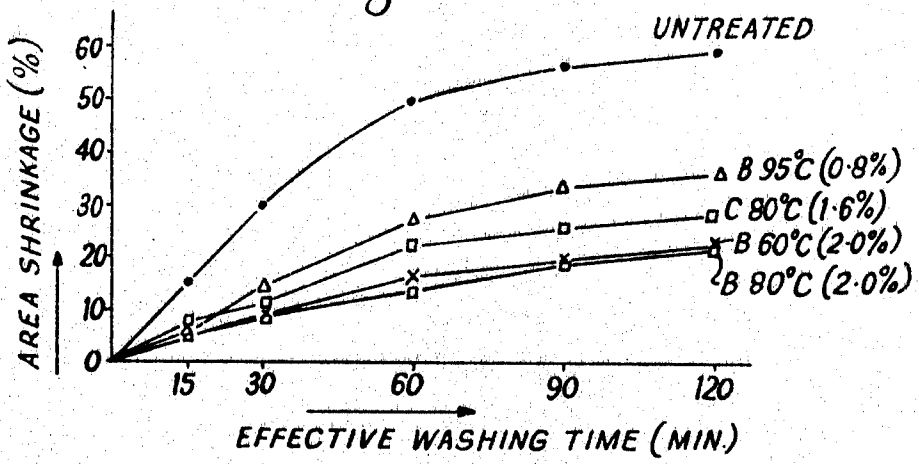

AREA SHRINKAGE (%)
0
10
20
30
40
50
60
15
30
60
90
120
EFFECTIVE WASHING TIME (MIN.)
UNTREATED
80°C (2·0%)
95°C (2·0%)
80°C (4·5%)
80°C (6·1%)

Fig. 9.


UNTREATED
B 95°C (0·8%)
C 80°C (1·6%)
B 60°C (2·0%)
B 80°C (2·0%)
AREA SHRINKAGE (%)
0
10
20
30
40
50
60
15
30
60
90
120
EFFECTIVE WASHING TIME (MIN.)

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3,484,272

PROCESS FOR COATING A SUBSTRATE OF KERATINOUS FIBERS WITH POLYAMIDE

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Int. Cl. D06m 15/60
U.S. Cl. 117—62.1 5 Claims

ABSTRACT OF THE DISCLOSURE

Fibrous or filamentary substances are coated with polyamide prepared in situ by the reaction of a diamine and a dicarboxylic acid ester in dilute solution or suspension.

The present invention relates to the coating of fibrous or filamentary, flexible substrates with a polymer. Such substrates are preferably natural fibrous substrates, such as keratinous fibers, cotton, silk etc. In relation to the present invention the term "substrates" also means products which have been manufactured from the fibrous or filamentary materials, such as slivers, yarns, combings, woven or knitted fabrics etc. Further examples of fiber-containing materials are paper, cardboard and the like. Filamentary substrates in the sense of the invention, which are not of natural origin, include for example synthetic threads or fibers.

A special object of the present invention is to coat keratinous or keratin-containing fibers, the coating being effected with a polyamide film. Keratin-containing fibers in this sense include wool fibers in particular. The expression "wool" or "wool fibers" when used in connection with the invention is to be understood as including all kinds of keratin-containing fibers, and in particular fibers which are obtained from the fleece of sheep, goats, llamas, vicunas, alpacas etc., where nothing to the contrary is said in the specification.

It is known to manufacture nylon 610 with the aid of interfacial poly-condensation (IFP process) from hexamethylene diamine and sebacyl dichloride. The hexamethylene diamine is dissolved in water and the sebacyl dichloride is dissolvde in a solvent which is not miscible with water, for example carbon tetrachloride. (E. L. Wittbecker and P. W. Morgan, J. Polymer Sci., 40, 289 (1959)); P. W. Morgan and S. L. Kwolek, J. Polymer Sci., 40, 299 (1959).)

This so-called IFP process has also been applied for nonfelting finishes on wool. In this case, wool steeped with an aqueous hexamethylene diamine solution is treated with sebacyl dichloride in an organic solvent which is not miscible with water. The polyamide film formed at the water/organic solvent phase boundary masks the surface scales of the fibers. One result of this is the lowering of the felting capacity of the wool. The best non-felting effect has been obtained with nylon 610. A nylon covering of 1–2% (R. E. Whitfield, L. A. Miller and W. L. Wasley, Textile Res. J., 31, 704 (1961)) is sufficient to produce a satisfactory non-felting effect. This known process has some disadvantages for the purposes of rendering wool felt-resistant. These are essentially the use of an organic solvent, the sensitivity as regards hydrolysis of the sebacyl dichloride and the considerable impairment of the handle of the treated wool.

The present invention arises from the problem of avoiding the obvious and known disadvantages, which result from the use of acid chlorides and organic solvents and

which arise particularly in the treatment of natural fibrous or filamentary materials such as have been mentioned above. This applies particularly to the non-felting treatment of keratinous fibers. It has been found, surprisingly, that these disadvantages can be overcome if treatment is carried out in an aqueous emulsion or solution without the use of an acid chloride.

The process for coating fibrous or filamentary substrates with a polymer, in accordance with the invention, is characterised in that a diamine and a dicarboxylic acid ester in dilute form are reacted in the presence of the substrate, in some cases using elevated temperatures.

The substrates are preferably present in cleaned or purified form, in order that the layer formed as a film on the substrate may be unitary as far as possible. As already mentioned, there are preferably used as substrates keratin-containing fibers or materials made from them, since their properties are particularly improved after treatment in accordance with the process of the present invention. The reaction is preferably carried out in an aqueous medium, and possibly in the presence of small quantities of an inert organic solvent. The concentrations used should be so chosen that a coating of the required thickness is formed on the substrate. The thickness of the coating depends, apart from the concentration of the aqueous solution or dispersion employed, on the type of substrate. Absorbent substrates, which therefore take up a certain quantity of the aqueous solution or dispersion, will therefore receive, even with low concentrations, thicknesses of coating such as can be obtained only with higher concentrations in the case of non-absorbent substrates. The person skilled in the art can easily determine the optimum conditions for each substrate by tests. In general, coatings having a weight of about 1–4%, preferably about 2–3%, referred to the dry weight of the coated substrate, are required.

Suitable starting materials within the meaning of the invention are, in particular, aliphatic diamines and esters of aliphatic dicarboxyl acids, in particular dicarboxylic acid derivatives and diamines such as are customarily used in the manufacture of polyamides (nylon). For the coating of keratinous materials, the use of hexamethylene diamine as diamine and an activated sebacic acid ester as dicarboxylic acid ester have proved particularly suitable, since a high non-felting effect is obtained.

Other examples of diamines which can be used for the purposes of the invention, are ethylene diamine and trimethylhexamethylene diamine. These compounds, as well as hexamethylene diamine are available commercially in any desired quantity. In carrying out in practice the process according to the invention, it should be considered on the basis of the available information what starting materials, that is, diamine and dicarboxylic ester, can be prepared most cheaply on the large scale. Other examples of dicarboxylic esters which can be used for the purposes of the invention include the activated esters of succinic acid, adipic acid, suberic acid and dodecandioic acid.

Under the term "activated dicarboxylic acid ester" are to be understood those in the sense of R. Schwyzer, B. Iselin and M. Feuver (Helv. chim. Acta, 38 (1955), 69). The activation is effected by electron-attracting groups, whereby the carbonyl carbon atom is made positive and is rendered more readily accessible to a nucleophilic attack by amino groups.

The steeping of the substrate with the solution or emulsion of the reaction components may be carried out in a one-bath or a two-bath operation. In the one-bath operation the substrate is preferably steeped with a mixture of an aqueous solution of hexamethylene diamine and an aqueous emulsion of a sebacic acid ester prepared at about 5° C. and the reaction components are caused

to react together on the wool by warming to room temperature or above. This process may be used in particular when the velocity of reaction between the reaction components, for example between the sebacic ester and hexamethylene diamine, is not too high. This is the case, for example, when using bis-p-thiocresyl sebacate. At very high velocities of reaction between the sebacic ester and hexamethylene diamine it is often impossible in practice to prepare and preserve the mixture of aqueous solution of hexamethylene diamine and aqueous emulsion of the ester without premature reaction occurring between the components. In these cases the aqueous solutions or emulsions of the reaction components, for example the aqueous solution of the hexamethylene diamine and the emulsion of the ester, must be applied one after the other to the substrate, for example the wool. Sebacic esters having such relatively high reaction velocities are, for example, bis-2,4,5-trichlorophenyl sebacate, bis-o-nitrophenyl sebacate and bis-p-nitrophenyl sebacate. The reaction components are then caused to react together on the substrate. The wool or wool fibers are impregnated with the aqueous solution and emulsion, preferably until a weight increase of 80–90% based on the weight of the conditioned wool has occurred. After steeping, the wool is preferably treated with steam, which brings about the formation of the polyamide. The speed of formation of the polyamide is essentially a function of the reaction temperature and time. The higher the reaction temperature the shorter the reaction time. The formation of the polyamide may, for example, be effected by warming the wool, steeped with the above-mentioned mixture of aqueous solution and aqueous emulsion prepared at 5° C., to room temperature. The reaction times are relatively long in this case and amount to many hours. With heating to 40, 60, 80° C. and above the reaction time is shortened considerably and amounts only to a few minutes. Since extended reaction times are harmful to the wool, short reaction times are desirable. On the other hand, the wet tensile strength and wet elongation under tension fall sharply at high reaction temperatures of, for example, 80° C. and 95° C. Consequently, such sebacic esters as are highly activated, that is, exhibit a high reaction velocity with hexamethylene diamine, are particularly suitable for the process according to the invention. In this connection, for example, very slight damage was obtained with bis - 2,4,5 - trichlorophenyl sebacate.

Hexamethylene diamine is preferably used in the lowest possible concentrations, for example in the form of aqueous solutions which contain about 25–35 mmol per 100 ml.

The quantity of nylon covering obtained is essentially responsible for the degree of the non-shrinking effect of wool, that is, the anti-felting effect. The area shrinkage of knitted wool is particularly low in the case of wool treated by the process according to the invention, if a nylon covering of about 1–4%, preferably about 2–3%, based on the dry weight of the wool, is formed. When using bis-2,4,5-trichlorophenyl sebacate and forming a coating of about 2.5%, the area shrinkage of knitted wool material, for example, after 2 hours of effective washing time is reduced from 60% to 3%. The uptake of moisture falls, owing to the treatment, from 0.6 to 1.4%. The reaction temperature appears to influence the extent of the non-shrinking effect only to the extent that it determines the thickness of the nylon coating. The higher the reaction temperature employed, the thicker is the nylon coating, as a rule. The size of the nylon coating is of course determined, apart from the reaction temperature employed, by the concentrations and quantities of the reaction components.

After the production of the nylon coating the treated wool is washed as soon as possible, preferably firstly with a soda solution and then with water. If the alcohol component of the sebacic ester split off in the formation of the nylon is insoluble in water and in soda solution, washing is preferably effected with a solvent by which the said alcohol component can be removed. For example, when using bis-p-thiocresyl sebacate, the p-thiocresol that is liberated may be removed by washing with alcohol.

The production of the activated sebacic esters employed in accordance with the invention may be carried out by known methods, in particular by the so-called "mixed anhydride method" (Th. Wieland and H. Bernhard, Liebigs Ann. Chem., 572, 190 (1951); R. A. Boissonais, Helv. Chim. Acta, 34 874 (1951); J. R. Vaughan, Jr. and R. L. Osato, J. Amer. Chem. Soc., 74, 676 (1952); N. F. Albertson, Organic Reactions, 12, p. 157), the "carbodi-imide" method (J. C. Sheehan and G. P. Hess, J. Amer. Chem. Soc., 77, 1067 (1955)); the "acid chloride" method or other known processes. As a rule, the best yields with a high degree of purity are obtained with the acid chloride method. In this case one may, for example, proceed as follows:

0.3 mol of any of the following compounds are dissolved in 300 ml. absolute dioxan: thiophenol, p-thiocresol, p-nitrophenol, o-nitrophenol, 2,4-dinitrophenol, p-nitrothiophenol, 2,4,5-trichlorophenol, N-hydroxysuccinimide or N-hydroxyphthalimide. After the addition of 42 ml. (0.3 mol) of triethulamine, 31.7 ml. (0.15 mol) of sebacyl dichloride in 300 ml. absolute dioxan are slowly added in drops with stirring and ice cooling. Upon warming, triethylammonium chloride separates out. The mixture is kept in a refrigerator for a few hours and is then poured into 2 litres of water, whereupon the ester precipitates. After a few hours the deposit precipitate is filtered off at the pump, washed several times with water and then recrystallised. Very pure products are obtained even after a single recrystallisation.

The properties of some sebacic esters are given in the following Table 1:

TABLE 1.—PROPERTIES OF THE SYNTHESISED SEBACIC ESTERS

Ester	Recrystallisable from—	Appearance of crystals	M.P., ° C.
Bis-thiophenyl sebacate	Ethanol	Colourless needles	58–59.5
Bis-thiocresyl sebacate	Methanol	Colourless rods	70–70.5
Bis-p-nitrophenyl sebacate	Isopropanol or benzene	Colourless crystals	
Bis-o-nitrophenyl sebacate	Ethanol	Greenish rods	
Bis-2,4-dinitrophenyl sebacate	do	Very light yellow crystals	83.5–84
Bis-p-nitrothiophenyl sebacate	Isoproponol or benzene	Bright yellow rods	96–98
Bis-2,4,5-trichlorophenyl sebacate	Ethanol	Colourless rods	70–71
Bis-N-succinimide sebacate	Methylene chloride/ether	Fine colourless crystals	162
Bis-N-phthalimide sebacate	do	Platelike colourless crystals.	134–36
Bis-cyanomethyl sebacate	Methanol	do	43–44
Dimethyl sebacate	Purified by distillation	Liquid colourless	(1)

[1] $B.P._{.10}$: 160° C.

In carrying out the process according to the invention, stable emulsions in water must be formed from these sebacic esters. Such stable emulsions are obtained by dissolving the ester in question in a solvent immiscible with water, such as benzene or methylene chloride, and adding it to an aqueous emulsifying solution whilst vibrating it. Commercially available emulsifiers are employed. The emulsifier sold under the trademark "Emulphor O"

is suitable, for example. However, the products known under the trademark "Nekanil O" (BASF) and "Stokopal T" (Stockhausen) may for example also be used.

Of the above-mentioned sebacic esters, the bis-o-nitrophenyl, bis-p-nitrophenyl, bis-2,4,5-trichlorophenyl and bis-p-thiocresyl esters are particularly suitable for the process according to the invention. The other activated esters have disadvantages when used for the process according to the invention, such as:

(1) Sensitivity of the activated ester to hydrolysis.
(2) Molecular weight of the corresponding polyamide too low.
(3) Poor emulsifying capacity.
(4) Discoloration of the treated wool.
(5) Unpleasant odour (e.g. of thiophenyl ester).

In the process according to the invention, particularly good results are obtained when using bis-2,4,5-trichlorophenyl sebacate and bis-o-nitrophenyl sebacate. Together with good non-felting effects, the damage occurring during the treatment is very slight, as a result of short reaction times and low concentrations of hexamethylene diamine. The phenols freed during the polycondensation can be readily washed out with warm water and dilute soda solution. In order to remove the p-thiocresol a subsequent extraction with alcohol is necessary. The handle of the treated wool is pleasant and better than that of wool which has been treated in accordance with the known IFP process. The dyeing capacity is improved by the treatment, and the uptake of moisture is reduced. Since very good non-felting effects can be obtained even at low temperatures, the reaction temperature should be kept as low as possible. A particular technical advantage of the process according to the invention is that it can be carried out in an aqueous emulsion which contains about 10% benzene.

So far as can be determined, the polyamide formed on the wool fibers is not chemically bound to the wool, but is deposited mechanically on the surface of the fibers in the form of a thin film. The same applies to wool treated by the IFP process.

EXAMPLES

The unbleached, combed wool yarn used for the test treatment was, in accordance with the requirement of a standard process for testing the felting property of wool yarns, knitted into a tubular article (Z. ges. Textiland, 66 (1964), 358; see also H. J. Fleuning, Melliand Textilber, 44 (1963), 189, 288). This knitted wool article was extracted for 12 hours with ethanol. Frequently the carded wool yarn was of a degree of purity such that extraction with ethanol was unnecessary. In these cases a conventional isoionic washing with water is sufficient. After this treatment the article was rinsed with water, dried and conditioned.

The sebacic ester was dissolved in water and mixed, whilst being vibrated, with 20 ml. of a 20% aqueous emulsifying solution (Emulphor O 0.20% based on the weight of ester). The emulsion was cooled to 5° C. and treated with hexamethylene diamine. Wool samples of about 35 g. were dipped into this emulsion, twice wrung out by hand and then squeezed out to about 80–90% increase in weight. The samples, rolled in filter paper, were then fixed in a vacuum steam bath. The steam pressure was controlled so that the liquid content of the wool remained constant. For the purpose of fixing at room temperature the samples were rolled in plastic and placed in a desiccator. The following subsequent treatments were then carried out:

(1) Rinsing with warm water.
(2) Treatment for ¼ hour with 2% soda solution.
(3) Rinsing with warm water.
(4) Neutralising with 1% acetic acid.
(5) Rinsing with cold water.

The samples were then centrifuged, dried and conditioned. The weight increase after alcohol extraction for six hours was determined.

The testing of the felting capacity was carried out by a washing machine test in accordance with the above-mentioned standard procedure.

The alkalinity of the wool was determined by the method of M. Harris and A. Smith in accordance with the I.W.V. specification. (Amer. Dyestuff Reptr., 25, 542 (1936), see also "Spezifikationen fur Test-Methoden"; Internationale Wollvereininung, Techn. Ausschuss, published by the Internat. Wool Secretariat, London (1960).)

The urea bisulphite solubility was determined by the method of K. Lees and F. F. Elsworth (Proc. Int. Wool Text. Res. Conf. Australia, vol. C, 363 (1955)).

The cystine was ascertained in wool hydrolysates by the procedure of T. Gerthsen. (Techn. Komitee der Intern. Wollvereinigung, Oslo, Rapport Nr. 12 (1962), see also Rapport Nr. 16, Paris (1964)).

Lanthionine was determined in wool hydrolysates by the procedure of L. M. Dowling and W. G. Crewther (Anal. Biochem., 8 (1964), 244).

The determination of the wet tensile strength and elongation was effected and derived from tensile tests made on yarn in accordance with DIN 53834 with an apparatus made in 1955 by the Otto Wolpert (Ludwigshafen).

For test dyeings, the wool was dyed with an acid dye (Supranol Cyanine G) in accordance with the manufacturer's instructions.

The determination of the nylon content of the wool was carried out as follows:

During the treatment with nylon 610 the moisture uptake is somewhat lowered. Hence the weight increase resulting from the treatment must be determined, not under normal ambient conditions (DIN 53802), but in the dry state.

(a) Calculation of the theoretical coating.—The wool samples were weighed before and after impregnation. From the increase in the weight of the wool was calculated the quantity of reaction mixture taken up and from this the theoretical nylon content.

(b) Calculation of the quantity of nylon actually taken up.—The dry weight and the conditioned weight of the wool samples was determined before and after the treatment by a parallel dry determination. The dry weight determination was carried out by cutting off pieces of about 2 g., weighing them, drying them at 105° C. for two hours and weighing after cooling for 1 hour in a desiccator. The difference between the dry weight before and after the treatment represents the nylon content.

EXAMPLE 1

Application of nylon 610 made from bis-o-nitrophenyl sebacate and hexamethylene diamine

The application was carried out with different ester or diamine concentrations at different temperatures.

The baths had the following compositions.

Bath A:

Bis-o-nitrophenyl sebacate	7.8 g. (17.5 mmol).
Benzene	12.0 ml.
Emulsifier (Emulphor O)	1.6 g.
50% hexamethylene diamine solution	16.2 g. (70 mmol).

With water made up to 100.0 ml.

Bath B:

Bis-o-nitrophenyl sebacate	1.8 g. (17.5 mmol).
Benzene	12.0 ml.
Emulsifier (Emulphor O)	1.6 g.
50% hexamethylene diamine solution	8.1 g. (35.0 mmol).

With water made up to 100.0 ml.

Bath C:
Bis-o-nitrophenyl sebacate ___ 5.5 g. (12.5 mmol).
Benzene _____ 8.0 ml.
Emulsifier (Emulphor O) ___. 1.2 g.
50% hexamethylene diamine solution _____ 11.6 g. (50 mmol).
With water made up to 100.0 ml.

EXAMPLE 2

Application of nylon 610 made from bis-p-nitrophenyl sebacate and hexamethylene diamine

Bath A:
Bis-p-nitrophenyl sebacate ___ 7.8 g. (17.5 mmol).
Benzene _____ 40.0 ml.
Emulsifier (Emulphor O) ___ 1.5 g.
50% hexamethylene diamine solution _____ 16.2 g. (70 mmol).
With water made up to 120.0 ml.

Bath B:
Bis-p-nitrophenyl sebacate ___ 7.8 g. (17.5 mmol).
Benzene _____ 40.0 ml.
Emulsifier (Emulphor O) ___ 1.5 g.
50% hexamethylene diamine solution _____ 8.1 g. (35.0 mmol).
With water made up to 120.0 ml.

Bath C:
Bis-p-nitrophenyl sebacate ___ 5.5 g. (12.5 mmol).
Benzene _____ 30.0 ml.
Emulsifier (Emulphor O) ___ 1.1 g.
50% hexamethylene diamine solution _____ 11.6 g. (50.0 mmol).
With water made up to 120.0 ml.

Bath D:
Bis-p-nitrophenyl sebacate ___ 5.5 g. (12.5 mmol).
Benzene _____ 30.0 ml.
Emulsifier (Emulphor O) ___ 1.1 g.
50% hexamethylene diamine solution _____ 5.8 g. (25.0 mmol).
With water made up to 120.0 ml.

EXAMPLE 3

Application of nylon 610 made from bis-2,4,5-trichlorophenyl sebacate and hexamethylene diamine

Bath B:
Bis-2,4,5-trichlorophenyl sebacate _____ 9.5 g. (17.5 mmol).
Benzene _____ 13.0 ml.
Emulsifier (Emulphor O) ___ 2.0 g.
50% hexamethylene diamine solution _____ 8.1 g. (35.0 mmol).
With water made up to 100.0 ml.

Bath C:
Bis-2,4,5-trichlorophenyl sebacate _____ 7.0 g. (12.5 mmol).
Benzene _____ 10.0 ml.
Emulsifier (Emulphor O) ___ 1.4 g.
50% hexamethylene diamine solution _____ 11.6 g. (50.0 mmol).
With water made up to 100.0 ml.

Bath D:
Bis-2,4,5-trichlorophenyl sebacate _____ 7.0 g. (12.5 mmol).
Benzene _____ 10.0 ml.
Emulsifier (Emulphor O) ___ 1.4 g.
50% hexamethylene diamine solution _____ 5.8 g. (25.0 mmol).
With water made up to 100.0 ml.

Bath E:
Bis-2,4,5-trichlorophenyl sebacate _____ 5.6 g. (10.0 mmol).
Benzene _____ 8.0 ml.
Emulsifier (Emulphor O) ___ 1.2 g.
50% hexamethylene diamine solution _____ 9.3 g. (40.0 mmol).
With water made up to 100.0 ml.

EXAMPLE 4

Application of nylon 610 made from bis-p-thiocresyl sebacate and hexamethylene diamine

Bath A:
Bis-2,4,5-trichlorophenyl sebacate 7.3 g. (17.5 mmol).
Benzene _____ 15.0 ml.
Emulsifier (Emulphor O) ___ 1.5 g.
50% hexamethylene diamine solution _____ 16.2 g. (70.0 mmol).
With water made up to 100.0 ml.

Bath B:
Bis-p-thiocresyl sebacate ___ 7.3 g. (17.5 mmol).
Benzene _____ 15.0 ml.
Emulsifier (Emulphor O) ___ 1.5 g.
50% hexamethylene diamine solution _____ 8.1 g. (33.0 mmol).
With water made up to 100.0 ml.

Bath C:
Bis-p-thiocresyl sebacate ____ 5.2 g. (12.5 mmol).
Benzene _____ 10.0 ml.
Emulsifier (Emulphor O) ___ 1.1 g.
50% hexamethylene diamine solution _____ 11.6 g. (50.0 mmol).
With water made up to 100.0 ml.

Bath F:
Bis-p-thiocresyl sebacate ____ 6.2 g. (15.0 mmol).
Benzene _____ 12.0 ml.
Emulsifier (Stokopal T) _____ 1.2 g.
50% hexamethylene diamine solution _____ 9.4 g. (40.5 mmol).
With water made up to 100.0 ml.

Bath G:
Bis-p-thiocresyl sebacate ____ 6.2 g. (15.0 mmol).
Benzene _____ 12.0 ml.
Emulsifier (Stokopal T) _____ 1.2 g.
50% hexamethylene diamine solution _____ 18.4 g. (79.5 mmol).
With water made up to 100.0 ml.

Bath H:
Bis-p-thiocresyl sebacate ____ 10.3 g. (25.0 mmol).
Benzene _____ 20.0 ml.
Emulsifier (Stokopal T) _____ 2.0 g.
50% hexamethylene diamine solution _____ 15.6 g. (67.5 mmol).
With water made up to 100.0 ml.

The results obtained in accordance with Examples 1 to 4 are shown in Tables 2 to 5.

Shrinkage curves of knitted samples treated in accordance with the examples are shown in FIGS. 1 to 9 of the accompanying drawings. In the drawings:

FIG. 1 shows shrinkage curves for knitted samples treated with nylon 610 made from bis-o-nitrophenyl sebacate and hexamethylene diamine (bath A) at four different temperatures;

FIG. 2 shows shrinkage curves for knitted samples treated with nylon 610 made from bis-p-nitrophenyl sebacate and hexamethylene diamine (bath B) at four different temperatures;

FIG. 3 shows shrinkage curves for knitted samples treated with nylon 610 made from bis-o-nitrophenyl sebacate and hexamethylene diamine (bath C) at two different temperatures;

FIG. 4 shows shrinkage curves for knitted samples treated with nylon 610 made from bis-p-nitrophenyl sebacate ad hexamethylene diamine (baths A and C) at two different temperatures;

FIG. 5 shows shrinkage curves for knitted samples treated with nylon 610 made from bis-p-nitrophenyl sebacate and hexamethylene diamine (baths B and D) at four different temperatures;

FIG. 6 shows shrinkage curves for knitted samples treated with nylon 610 made from bis-2,4,5-trichlorophenyl sebacate and hexamethylene diamine (baths B, C, E) at four different temperatures;

FIG. 7 shows shrinkage curves for knitted samples treated with nylon 610 made from bis-2,4,5-trichlorophenyl sebacate and hexamethylene diamine (bath D) at four different temperatures;

FIG. 8 shows shrinkage curves for knitted samples treated with nylon 610 made from bis-p-thiocresyl sebacate and hexamethylene diamine (bath A) at two different temperatures; and

FIG. 9 shows shrinkage curves for knitted samples treated with nylon 610 made from bis-p-thiocresyl sebacate and hexamethylene diamine (baths B and C) at three different temperatures.

TABLE 2.—RESULTS OF TREATMENTS CARRIED OUT UNDER VARIOUS REACTION CONDITIONS, USING BIS-o-NITROPHENYL SEBACATE AND HEXAMETHYLENE DIAMINE

Bath	Hexamethylene diamine concentration (mMol/100 ml.)	Ester concentration (mMol/100 ml.)	Polycondensation: Temperature (° C.)	Polycondensation: Time (min.)	Weight increase (percent)	Yield of nylon (percent)
Untreated						
B	35	17.5	95	5	2.3	62
	35	17.5	95	5	2.4	59
A	70	17.5	80	7	2.8	67
	70	17.5	80	7	2.6	65
	70	17.5	80	7	3.4	86
C	50	12.5	80	7	1.7	64
	50	12.5	80	7	1.7	67
B	35	17.5	80	7	2.6	68
	35	17.5	80	7	[1] 2.5	65
A	70	17.5	60	12	1.6	45
	70	17.5	60	12	2.0	50
C	50	12.5	60	15	1.5	50
	50	12.5	60	15	1.3	47
B	35	17.5	60	15	2.5	64
	35	17.5	60	15	2.0	42
A	70	17.5	40	60	1.0	23
	70	17.5	40	60	1.4	35
B	35	17.5	40	60	1.7	40
	35	17.5	40	60	1.5	38
A	70	17.5	25	[2]	1.2	31
	70	17.5	25	[2]	1.3	34

Bath	Moisture uptake of wool (percent)	Area shrinkage after 120 min. effective washing time (percent)	Wet tensile strength (g.)	Wet elongation (percent)	Alkali solubility (percent)	Urea-bisulphate solubility (percent)	Cystine content (percent)	Lanthionine content (percent)
Untreated	12.6	60	335	45.7	12.3	16.2	10.3	0.65
B	12.0		230	44.2	8.4			
		22.0						
A	11.9		220	42.6	8.0			
		3.5						
		7.0						
C	12.1		207	43.1	7.3			
		11.0						
B	11.2	14.0	318	46.6	9.9			
		[1] 35						
A	12.2		320	45.6	9.4	6.1	9.4	0.78
		15.0						
C	12.3		286	43.8	9.0			
		12.0						
B	11.4		308	45.6	9.5			
		20						
A	12.25	21	321	46.1	9.9			
		[1] 29						
B		16						
	11.85		346	45.1	9.2	8.1	9.7	
A	12.2		303	47	8.1			
		14						

[1] Material not extracted with alcohol.
[2] 24 hours.

TABLE 3.—RESULTS OF TREATMENTS CARRIED OUT UNDER VARIOUS REACTION CONDITIONS, USING BIS-p-NITROPHENYL SEBACATE AND HEXAMETHYLENE DIAMINE

Bath	Hexamethylene diamine concentration (mMol/100 ml.)	Ester concentration (mMol/100 ml.)	Polycondensation Temperature (° C.)	Polycondensation Time (min.)	Weight increase (percent)	Yield of nylon (percent)
Untreated						
A	70	17.5	95	15	4.5	143
	70	17.5	95	15	4.5	124
C	50	12.5	95	15	1.2	59
B	35	17.5	95	15	4.2	108
	35	17.5	95	15	4.8	145
D	25	12.5	95	15	2.0	106
	25	12.5	95	15	2.7	140
C	50	12.5	80	15	4.2	188
	50	12.5	80	15	3.9	176
B	35	17.5	80	15	4.5	114
	35	17.5	90	15	2.5	56
D	25	12.5	80	15	2.5	121
	25	12.5	80	15	2.5	121
D	25	12.5	60	30	1.9	82
	25	12.5	60	30	1.6	67
D	25	12.5	40	120	2.3	100
	25	12.5	40	60	1.0	43

Bath	Moisture uptake of wool (percent)	Area shrinkage after 120 min. effective washing time (percent)	Wet tensile strength (g.)	Wet elongation (percent)	Alkali solubility (percent)	Urea-bisulphate solubility (percent)	Cystine content (percent)	Lanthionine content (percent)
Untreated	12.6	60	335	45.7	12.3	16.2	10.3	0.65
A		3						
	12.2		87	34.9	9.0			
C	12.3	14	90	37.1	8.7			
B	11.0		210	42.6	9.2			
		0.5						
D		10						
	12.2		196	42.8	8.2			
C	12.4		226	43.4	8.1			
		2						
B		3						
	12.1		256	43.7	8.2			
D		12						
	12.3		283	46.3	8.6			
D		22						
	11.4		305	46.1	8.3	3.5		
D		13						
	12.4		313	45.6	8.9	6.2	9.7	0.72

TABLE 4.—RESULTS OF TREATMENTS CARRIED OUT UNDER VARIOUS REACTION CONDITIONS, USING BIS-2,4,5-TRICHLOROPHENYL SEBACATE AND HEXAMETHY-LENE DIAMINE

Bath	Hexamethylene diamine concentration (mMol/100 ml.)	Ester concentration (mMol/100 ml.)	Polycondensation Temperature (°C).	Polycondensation Time (min.)	Weight Increase Percent	Yield of Nylon Percent
Untreated						
E	40	10	80	10	0.8	37
	40	10	80	10	0.8	38
B	35	17.5	80	10	4.1	100
	35	17.5	80	10	4.3	104
	35	17.5	80	10	4.7	107
D	25	12.5	80	10	1.3	44
	25	12.5	80	10	1.7	58
	25	12.5	80	10	0.8	28
E	35	17.5	60	15	2.5	62
	35	17.5	60	15	2.7	66
	35	17.5	60	15	2.5	61
D	25	12.5	60	15	+1.7	60
	25	12.5	60	15	1.7	64
B	35	17.5	40	60	2.2	56
	35	17.5	40	60	2.6	63
D	25	12.5	40	60	1.6	60
	25	12.5	40	60	1.6	68
D	25	12.5	25	(1)	1.9	69
	25	12.5	25	(1)	1.7	62
C	50	12.5	25	(1)	1.3	48
	50	12.5	25	(1)	1.4	57

Bath	Moisture uptake of wool (Percent)	Area shrinkage after 120 min. effective washing time (Percent)	Wet tensile strength strength (g.)	Wet elongability (Percent)	Alkali solubility (Percent)	Urea-bisulphate solubility (Percent)	Cystine content (Percent)	Lanthionine content (Percent)
Untreated	12.6	60.0	335	45.7	12.3	16.2	10.3	0.65
E	11.6		241	42.2	8.1			
		20.0						
B		7.0						
		3.0						
	11.7		318	46.4	9.4	8.2	9.7	
D		[2] 27.0						
		16.0						
	12.0		274	44.6	8.5			
B		3.0						
		4.0						
	11.2		322	48.4	9.9			
D	11.2		340	46.6	8.6			
		16.0						
B	11.2		339	46.4	8.9	7.0		
		3.0						
D	11.2	18.0						
			340	49.4	8.4			
D		11.0						
	11.2		342	46.6	8.5	8.5	9.9	0.71
C	11.2		320	47.4	7.4			
		14.0						

[2] Material not extracted with alcohol.

TABLE 5.—RESULTS OF TREATMENTS CARRIED OUT UNDER VARIOUS REACTION CONDITIONS, USING BIS-P-THIOCRESYL SEBACATE AND HEXAMETHYLENE DIAMINE

Bath	Hexamethylene diamine concentration (mMol/100 ml.)	Polycondensation: Ester concentration (mMol/100 ml.)	Polycondensation: Temperature (° C.)	Polycondensation: Time (min.)	Weight increase (percent)	Yield of nylon (percent)
Untreated						
A	70	17.5	95	15	1.0	31
	70	17.5	95	15	0.7	21
B	35	17.5	95	15	0.8	25
	35	17.5	95	15	0.9	21
A	70	17.5	80	30	6.1	145
	70	17.5	80	30	4.5	115
	70	17.5	80	30	3.0	75
A	70	17.5	80	30	1.2	44
	70	17.5	80	30	2.0	60
B	35	17.5	80	30	1.3	40
	35	17.5	80	30	1.0	27
C	50	12.5	80	30	1.6	75
B	35	17.5	60	60		
	35	17.5	60	60		
F	40.5	15.0	80	45	2.0	58
	40.5	15.0	80	45	1.6	43
G	79.5	15.0	80	45	1.8	38
	79.5	15.0	80	45	2.4	56
H	67.5	25.0	80	45	3.2	60

Bath	Moisture uptake of wool (percent)	Area shrinkage after 120 min. effective washing time (percent)	Wet tensile strength (percent)	Wet elongation (percent)	Alkali solubility (percent)	Urea-bisulphate solubility (percent)	Cystin content (percent)	Lanthionine content (percent)
Untreated	12.6	60	335	45.7	12.3	16.2	10.3	0.65
A		21						
	12.6		34	31.7	8.3			
B		36						
	11.4		146	39.1	7.5			
A		0.7						
		7.0						
	12.3		116	38.9	7.4			
A	12.45				7.4			
		24						
B		22						
	12.2		240	43.9	7.0			
C	11.7	29	200	42.8	6.2			
B		22						
	11.8		272	45.2	7.6	1.9	8.0	1.74
F	11.8	7.5						
		4.0						
G	11.8	5.5						
		3.0						
H	11.8	7.5						

What is claimed is:

1. A process for coating a substrate of keratinous fibers with polyamide which comprises reacting a solution or suspension of hexamethylene diamine and an activated ester of sebacic acid in the presence of the substrate at a temperature between about 25–95° C.

2. A process according to claim 1 wherein the substrate is previously impregnated with the solution or suspension at a temperature of about 5° C.

3. A process according to claim 1 wherein the reaction is effected in an aqueous medium.

4. A process according to claim 3 wherein the substrate is impregnated with a solution or emulsion of the diamine or the ester and then with an emulsion or solution of the ester or the diamine, respectively.

5. A process according to claim 3 wherein the medium contains a small portion of an inert organic solvent.

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