

(CONVENTION. By one or more persons and/or a Company.)

636372

3
Form 4.

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

(1) Here
insert (in
full) Name
or Names of
Applicant or
Applicants,
followed by
Address(es).

~~My~~⁽¹⁾ We PRECISION PROCESSES (TEXTILES) LIMITED

of Dylan Laboratories, Ambergate, Derby DE5 2EY, England

(2) Here
insert Title
of Invention.

hereby apply for the grant of a Patent for an invention entitled:⁽²⁾
NEW POLYMERS AND PREPOLYMERS AND THEIR USE IN A METHOD FOR THE TREATMENT
OF WOOL

(3) Here insert
number(s)
of basic
application(s).

which is described in the accompanying complete specification. This applications is a Covention
application and is based on the application numbered:⁽³⁾

8916906.4

(4) Here insert
Name of basic
Country or
Countries, and
basic date or
dates.

for a patent or similar protection made in:⁽⁴⁾ United Kingdom
on 24th July 1989

~~My~~
Our

address for service is WATERMARK PATENT & TRADEMARK ATTORNEYS
290 Burwood Road, Hawthorn, Victoria, Australia.

DATED this 24th day of July 1990

REPRINT OF RECEIPT

MO19727 24/07/90

(5) Signa-
ture(s) of
Applicant(s)
or
Seal of
Company and
Signatures of
its Officers as
prescribed by
its Articles of
Association.

(5) PRECISION PROCESSES (TEXTILES) LIMITED

by

D. B. Mischlewski

Registered Patent Attorney

To: THE COMMISSIONER OF PATENTS.

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

DECLARATION IN SUPPORT OF A CONVENTION
APPLICATION FOR A PATENT OR PATENT OF ADDITION(1) Here
insert (in
full) Name of
Company.

In support of the Convention Application made by⁽¹⁾ Precision
Processes (Textiles) Limited, of Dylan Laboratories,
Ambergate, Derby DE5 2EY, England.

(2) Here
insert title
of invention.

(hereinafter referred to as the applicant) for a Patent
for an invention entitled:⁽²⁾ New Polymers and
Prepolymers and their use in a Method for the
Treatment of Wool.

(3) Here
insert full Name
and Address,
of Company
official
authorized
to make
declaration.

I,⁽³⁾ David Longley Connell
of Precision Processes (Textiles) Limited, of Dylan
Laboratories, Ambergate, Derby DE5 2EY, England.

do solemnly and sincerely declare as follows:

(4) Here
insert basic
Country or
Countries
followed by
date or dates
and basic
Applicant or
Applicants.

1. I am authorised by the applicant for the patent
to make this declaration on its behalf.
2. The basic application as defined by Section 141 of the Act was
made in⁽⁴⁾ Great Britain
on the 24th day of July 1989, by Precision
Processes (Textiles) Limited.
on the day of 19, by

(5) Here
insert (in
full) Name
and Address
of Actual
Inventor or
Inventors.

3.⁽⁵⁾ David Longley Connell, of Ithersey, Burland
Green Lane, Western Underwood, Derbyshire DE6 4PF,
and Anthony Szpala, of 9 Dovedale Close, Marehay,
Ripley, Derbyshire DE5 8HS.

is/are the actual inventor of the invention and the facts upon which the applicant
is entitled to make the application are as follow:

The applicant is the assignee of the two above-named inventors
by virtue of an Assignment dated 10th August 1989.

4. The basic application referred to in paragraph 2 of this Declaration
was the first application made in a Convention country in
respect of the invention the subject of the application.

DECLARED at Ambergate, Derby
this 23 day of July 1990
Precision Processes (Textiles) Limited

(6) Signature.

(6)

To: THE COMMISSIONER OF PATENTS.

DAVID LONGLEY CONNELL
TECHNICAL DIRECTOR



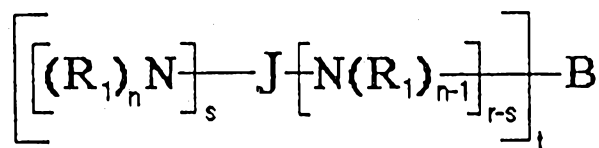
AU9059795

(12) PATENT ABRIDGMENT (11) Document No. AU-B-59795/90
 (19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 636372

- (54) Title
 NEW POLYMERS AND PREPOLYMERS AND THEIR USE IN A METHOD FOR THE TREATMENT OF WOOL
- (51)⁵ International Patent Classification(s)
 C08G 065/32 C08G 081/00 D06M 015/61
- (21) Application No. : 59795/90 (22) Application Date : 24.07.90
- (30) Priority Data
- (31) Number (32) Date (33) Country
 8916906 24.07.89 GB UNITED KINGDOM
- (43) Publication Date : 24.01.91
- (44) Publication Date of Accepted Application : 29.04.93
- (71) Applicant(s)
 PRECISION PROCESSES (TEXTILES) LIMITED
- (72) Inventor(s)
 DAVID LONGLEY CONNELL; ANTHONY SZPALA
- (74) Attorney or Agent
 WATERMARK PATENT & TRADEMARK ATTORNEYS, Locked Bag 5, HAWTHORN VIC 3122
- (57) Claim

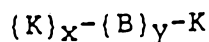
1. A polymer or prepolymer having one of the following structural formulae:

i)



or

ii)



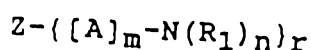
wherein

J represents a residue derived from a polyfunctional polyether;

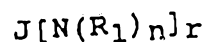
K represents the monofunctional or polyfunctional residue derived from partial reaction of a prepolymer of the formula:

(11) AU-B-59795/90
(10) 636372

-2-



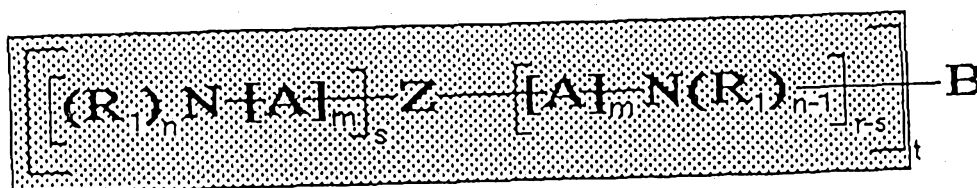
or



(I)

(II)

that is, it represents the shaded area in the following formula:



B is the residue created by bi- or polyfunctional reaction between any polyfunctional reactive group and the parent amine of the title compound (formula (I) where R_1 is hydrogen in all cases) or is the residue of a reactive amino-acrylic polymer or a reactive polyamide polymer;

Z represents a residue of a polyol;

A represents a polyalkylene oxide residue;

R_1 represents a fibre reactive grouping such as the residue derived from monofunctional reaction of an epihalohydrin, an alkyl or alkyl aryl polyhalide or a methylol grouping derived from monofunctional reaction of formaldehyde, or is alkyl, hydroxyalkyl or hydrogen, with the proviso that at least one group R_1 per polyoxyalkyleneamine residue, and preferably at least one for each nitrogen, retains residual fibre reactivity;

m is between 4 and 50;

(11) AU-B-59795/90
(10) 636372

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n is 2 or 3, with the proviso that, where n is 3, the nitrogen atom involved also bears a formal positive charge;

p is 1 or 2, with the proviso that, where p is 2, the nitrogen atom involved also bears a formal positive charge;

r equals the functionality of group Z;

t is a number representing the functionality of reaction of the residue B;

s is a number between 1 and r-1;

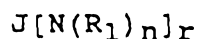
x is between 2 and 30; and

y is from $\frac{x}{t-1}$ to x,

with the general proviso that, in any given instance, the significance of a particular group Z, A, B, R, J or K in any given structure shall not be dictated by the significance of any other such group in the same formula, and further, wherever a formal positive charge is present in the structure, then an appropriate counter anion is taken to be present.

5. A method for the treatment of wool so as to impart shrink resistance which comprises treating the wool with an aqueous solution of a polymer so as to cause the polymer to be applied to the wool fibres, characterised in that the polymer is a polymer or prepolymer having one of the following structural formulae:

i)

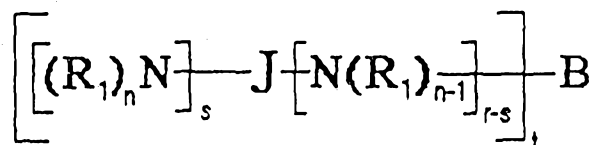


(11) AU-B-59795/90
(10) 636372

-4-

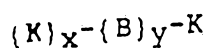
or

ii)



or

iii)



wherein

J represents a residue derived from a polyfunctional polyether;

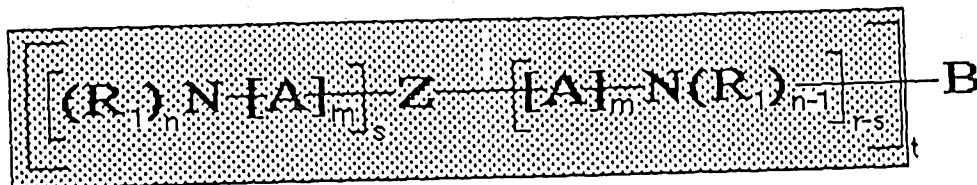
K represents the monofunctional or polyfunctional residue derived from partial reaction of a prepolymer of the formula:



(I)

(II)

that is, it represents the shaded area in the following formula:



B is the residue created by bi- or polyfunctional reaction between any polyfunctional reactive group and the parent amine of the title compound (formula (I) where R_1 is hydrogen in all cases) or is the residue of a reactive amino-acrylic polymer or a reactive polyamide polymer;

(11) AU-B-59795/90
(10) 636372

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Z represents a residue of a polyol;

A represents a polyalkylene oxide residue;

R₁ represents a fibre reactive grouping such as the residue derived from monofunctional reaction of an epihalohydrin, an alkyl or alkyl aryl polyhalide or a methylol grouping derived from monofunctional reaction of formaldehyde, or is alkyl, hydroxyalkyl or hydrogen, with the proviso that at least one group R₁ per polyoxyalkyleneamine residue, and preferably at least one for each nitrogen, retains residual fibre reactivity;

m is between 4 and 50;

n is 2 or 3, with the proviso that, where n is 3, the nitrogen atom involved also bears a formal positive charge;

p is 1 or 2, with the proviso that, where p is 2, the nitrogen atom involved also bears a formal positive charge;

r equals the functionality of group Z;

t is a number representing the functionality of reaction of the residue B;

s is a number between 1 and r-1;

x is between 2 and 30; and

y is from $\frac{x}{t-1}$ to x,

with the general proviso that, in any given instance, the significance of a particular group Z, A, B, R, J or K in any given structure shall not be dictated by

(11) AU-B-59795/90

-6-

(10) 636372

the significance of any other such group in the same formula, and further, wherever a formal positive charge is present in the structure, then an appropriate counter anion is taken to be present.

636372

Form 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

Class

Int. Class

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority :

Related Art :

Name of Applicant : PRECISION PROCESSES (TEXTILES) LIMITED

Address of Applicant : Dylan Laboratories, Ambergate, Derby DE5 2EY, England

Actual Inventor : DAVID LONGLEY CONNELL and ANTHONY SZPALA

Address for Service : **WATERMARK PATENT & TRADEMARK ATTORNEYS.**
 LOCKED BAG NO. 5, HAWTHORN, VICTORIA 3122, AUSTRALIA

Complete Specification for the invention entitled:

NEW POLYMERS AND PREPOLYMERS AND THEIR USE IN A METHOD FOR THE TREATMENT
OF WOOL

The following statement is a full description of this invention, including the best method of performing it known to us

NEW POLYMERS AND PREPOLYMERS AND THEIR USE
IN A METHOD FOR THE TREATMENT OF WOOL

This invention relates to new polymers and prepolymers derived from polyoxyalkyleneamines. The
5 polymers and prepolymers may be used in a process for the treatment of wool so as to impart shrink resistance. The polyoxyalkyleneamines of interest are a family of polyamines which have as their backbone repeated oxyalkylene units. Such
10 materials have been available commercially for a number of years, for example, under the trade name of Jeffamines (Jeffamine is a registered trade mark). Belgian Patent No. 634,741 describes the preparation of polyoxyalkyleneamines by the reductive amination of
15 polypropylene glycol ether with ammonia in the presence of Raney nickel catalyst and hydrogen. U.S. Patent Nos. 3,236,895 and 3,462,393 teach the synthesis of polyoxyalkyleneamines by the amination of polypropylene glycol via a sulphonic acid ester. In
20 U.S. Patent No. 3,654,370 polyoxyalkyleneamines are produced by treating the corresponding polyol with ammonia and hydrogen over a nickel/copper/chromium catalyst.

The polyoxyalkyleneamines have found a variety
25 of uses. They are particularly effective as epoxy curing agents and have been used in epoxy adhesives, protective or decorative coatings and reinforced composites. Other applications include use in anti-static agents, surfactants, agricultural chemicals, cosmetics, oil recovery chemicals and textile treating
30 agents.

With regard to the latter application, that of textile treating agent, polyoxyalkyleneamines have been applied to a variety of fibres and textiles for various purposes. For example, German OS 2,645,954 describes the improvement of crease, abrasion and pilling resistance of wool textiles by the use of crosslinking agent amines (such as Jeffamine D-400) during the shrinkproofing of such textiles. However, the polyoxyalkyleneamine is used as a catalyst for the crosslinking of epoxy groups, following the application of resins from perchloroethylene, and its association with shrinkproofing treatment itself is merely incidental. British Patent No. 942,875 refers to the formation of water-soluble anti-static coatings for fibres by reacting polyoxyalkylenediamines with aldehydes. US Patent No. 3,175,987 discloses the reaction of polyethylene glycol diamine with an epoxide for the purpose of treating nylon cloth so as to resist soiling. German OS 2,058,317 refers to the reaction of a triethylene glycol diamine with urea to form a permanent press fabric treatment.

Japanese Patent No. 71/33,152 describes the treatment of a nylon textile with an E-caprolactam-polyethylene glycol diamine-adipic acid copolymer to give improved washfast stain resistance, while Japanese Patent No. 71/37,675 relates to the melt-blending of a polyester fibre with a hexamethylenediammonium terephthalate-E-caprolactamdiamino-polyethylene glycol-adipic acid copolymer for the purpose of improving dyeability. US Patent No. 3,738,864 discloses that the treatment of fibres with the reaction product of a polyoxypropylenediamine (Jeffamine D-1000) and a polyepoxide results in material with durable anti-

static properties. US Patent No. 4,255,311 describes a composition useful for treatment of textiles so as to prevent creasing and which was prepared from a water-soluble epoxide resin, an acrylic copolymer and a polyoxyalkylene polyamine. US-A-3,676,287 teaches that adhesion in glass fibre-reinforced elastomers can be improved by coating the fibres with a mixture which includes a lubricant prepared by condensing Jeffamine D-2000 with oleic acid.

Japanese Patent No. 84/89325 describes high rigidity resin compositions formed from a mixture of poly(phenyleneterephthalamide)-epichlorohydrin reaction product, Jeffamine D-230 and Jeffamine AC-398. US Patent No. 4,382,852 relates to demulsifiers for breaking bituminous oil-in-water emulsions and which are prepared by the condensation of certain polyoxyalkylenediamines (i.e. Jeffamines ED-2001, ED-600, ED-900, M-1000, D-230 and M-360) with epichlorohydrin. J. Med. Chem., 26(1), 7-11 refers to the preparation of compounds by the reaction of aryl glycidyl ethers with various Jeffamines and the evaluation of their affinity for β -adrenergic receptors of rat heart and lung. US Patent No. 4,323,709 discloses the reaction of epichlorohydrin with Jeffamine M-600 to give polymers useful as hydrocarbon oil additives. US Patent No. 4,239,497 describes fuel oil stabilising agents which inhibit sedimentation and discolouration during storage and are manufactured by the reaction of epichlorohydrin with amine-terminated polyoxypropylenes such as Jeffamine M-600. There is no suggestion in the prior art that any of these products could be used as shrink-resist polymers in processes for imparting a degree of shrink resistance to wool.

Many ways of rendering wool shrink resistant are known. Typically, these involve subjecting the wool to an oxidative treatment, either alone or followed by a polymer treatment. The latter type of two-step treatment has become very popular and is now the major process used throughout the world.

Various two-step shrink-proofing processes in which wool is treated first with an oxidative chlorinating agent and subsequently with a pre-formed synthetic polymer have been developed. A wide variety of polymers can be used in aqueous solution or dispersion, including polyamide-epichlorohydrin resins and polyacrylates. A review of work in this field by J. Lewis appears in Wool Science Review, May 1978, pages 23-42. British Patent Nos. 1,074,731 and 1,340,859 and U.S. Patent Nos. 2,926,154 and 2,961,347 describe two-step shrink-proofing processes and resins or polymers suitable for use therein. These polymers are typically reactive polyamides. The polyamides can be derived from a polyalkylene polyamine and a dicarboxylic acid, e.g. diethylenetriamine and adipic acid, and are prepared by reaction with epichlorohydrin.

These conventional two-step processes confer good levels of shrink resistance but, despite achieving considerable commercial success, they do have significant disadvantages. It will be appreciated that the polymer is added to the oxidised wool to supplement the shrink resistance imparted by the oxidative pretreat, which may in some cases thus not be as severe as would be needed if this were the only treatment used to achieve the shrink resistance. The application of polymers, however, usually results in wool which has an undesirably harsh handle. To

overcome this problem a softening agent is customarily employed during subsequent processing of the wool. Further, if the wool which has been treated with polymer is then dyed, the resulting rub fastness is generally inferior. This is particularly evident with certain dyestuffs commonly used in the wool industry. In general, it is found that the softening agents which are used to improve the handle of the wool will either exacerbate the poor rub fastness or are removed during the dyeing operation.

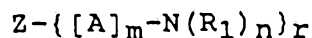
The present invention provides new polymers and prepolymers which can be used in a method for the shrinkproofing of wool. This method not only confers a good level of shrink resistance, but also gives improved dyeing properties and a soft handle even without the use of additional softening agents.

The polymers and prepolymers of this invention essentially result from the reaction of one or more polyoxyalkyleneamines, either as a simple mixture or joined by a polyfunctional bridging group in a prior reaction, with an epihalohydrin or other reactive species, such as formaldehyde, so as to generate a grouping on the molecule capable of reacting with protein fibre surfaces. The reactants are used in such proportions that preferably, though not necessarily, all of the amino groups are reacted.

The present invention relates to polymers and prepolymers which may be represented by any one of the following formulae:-

30

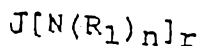
i)



(I)

35

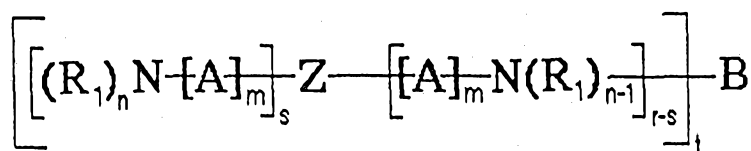
which may be expressed more simply as:



(II)

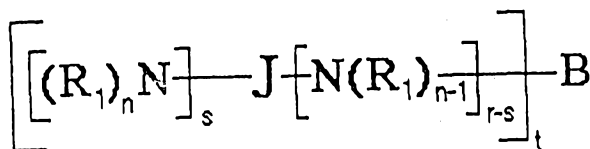
or

ii) structure involving crosslinking or bridging of the above groups (I) or (II):



(III)

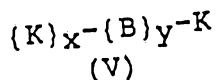
which may be expressed more simply as:



(IV)

or

iii) a low molecular weight polymeric structure formed from the above groups (I) or (II):



(V)

wherein

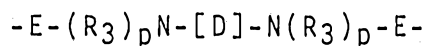
Z represents a residue of a polyol, preferably a di- or trivalent polyol;

A represents a polyalkylene oxide residue, that is a polyether chain produced by polymerisation of, for example, ethylene, propylene or butylene oxides or tetrahydrofuran;

B is the residue created by bi- or

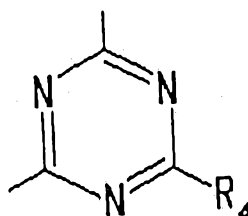
polyfunctional reaction between any polyfunctional reactive group and the parent amine of the title compounds (formula (I) where R_1 is hydrogen in all cases), or is the residue of a reactive amino-acrylic polymer (e.g. of the type described in EP-A-0129322) or a reactive polyamide polymer (e.g. of the type described in EP-A-0260017A or a Hercosett polymer), and may be taken, for example, to represent

a group



(VI)

a group

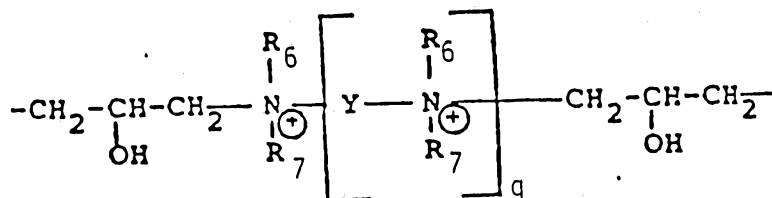


(VII)

a group resulting from the reaction of a bi- or polyfunctional species capable of reacting with amino groups, for example: epihalohydrins, alkyl di- and polyhalides, di- or polycarboxylic acids or their acyl halides and anhydrides, dicyandiamide, urea and formaldehyde,

a group derived from low molecular weight reactive resins such as the Bisphenol A type,

or a group derived from reaction of a cationic polymeric reactive species such as



where R₆ and R₇ are selected from C₁-C₅ alkyl and C₂-C₅ hydroxyalkyl radicals.

Y is selected from C₂-C₆alkylene radicals,
2-hydroxy-1,3-propylene radicals, and the radicals:

-CH₂CH₂NHCONHCH₂CH₂- and

-CH₂CH₂CH₂NHCONHCH₂CH₂CH₂-

and q is an integer of from 0 to 20, provided that when q is greater than 2, each of the symbols Y need not necessarily have the same significance;

D represents a straight or branched chain hydrocarbon, polysiloxane or polyalkylene oxide residue, and which may also either bear functional groups or may contain functional groups, such as amino groups, which may in turn either bear one or more groups R₁ or, where B is polyfunctional rather than bifunctional, may represent a further functional reaction point of the group B with the rest of the molecular structure;

E represents a group resulting from the reaction of a bi- or polyfunctional species capable of reacting with amino groups, for example: epihalohydrins, alkyl di- and polyhalides, dicarboxylic acids or their acyl halides and anhydrides, dicyandiamide, urea and formaldehyde;

J represents a residue derived from a polyfunctional polyether;

K represents the monofunctional or polyfunctional residue derived from partial reaction of the basic prepolymers in formulae (I) or (II), i.e. it represents the shaded area in formula (III) as follows:

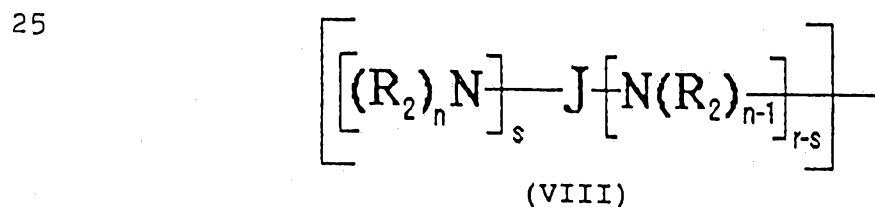


5 R₁ represents a fibre reactive grouping such as the residue derived from monofunctional reaction of an epihalohydrin, an alkyl or alkyl aryl polyhalide or a methylol grouping derived from monofunctional reaction of formaldehyde, or is alkyl, hydroxyalkyl or hydrogen, with the proviso that at least one group R₁ per polyoxyalkyleneamine residue, and preferably at least one for each nitrogen, retains residual fibre reactivity;

15 R₂ represents a fibre reactive grouping such as the residue derived from monofunctional reaction of an epihalohydrin, an alkyl or alkyl aryl polyhalide or is a methylol grouping derived from monofunctional reaction of formaldehyde, or alkyl, hydroxyalkyl or hydrogen;

20 R₃ represents hydrogen or C₁-C₄ alkyl or hydroxyalkyl;

 R₄ represents halogen or a group



30 or one of alkylamino, hydroxyalkylamino, alkoxy, alkylarylamino or a group $-(\text{R}_3)_p \text{N} - [\text{D}] - \text{R}_5$

35 or a functional reaction point of the group B with the rest of the molecular structure, where B is polyfunctional rather than bifunctional;

R₅ represents hydrogen or
a group -N(R₂)_n or -N(R₃)_n;

m is between 4 and 50;

5

n is 2 or 3, with the proviso that, where n is
3, the nitrogen atom involved also bears a formal
positive charge;

10

p is 1 or 2, with the proviso that, where p is
2, the nitrogen atom involved also bears a formal
positive charge;

15

r equals the functionality of group Z;

t is a number representing the functionality of
reaction of the residue B;

20

s is a number between 1 and r-1;

x is between 2 and 30; and

y is from $\frac{x}{t-1}$ to x,

25

with the general proviso that, in any given instance,
the significance of a particular group Z, A, B, R, J
or K in any given structure shall not be dictated by
the significance of any other such group in the same
formula, and further, wherever a formal positive
charge is present in the structure, then an
appropriate counter anion is taken to be present, for
example chloride ion.

30

35

The term "fibre reactive grouping" as used
herein is to be understood as meaning a group having

residual chemical reactivity such that it will be capable of causing a molecule to be bound to the surface of a fibre in such a way as not to be readily removable therefrom. Examples include the fibre reactive dyes in which a variety of reactive halogen groupings are sited on the molecule and which, during dyeing, react with hydroxy or amino functionalities on the fibre surface to produce a chemical bond. It will be understood that electrical bonding forces, rather than chemical forces, could be involved and that a "reaction" as such need not occur. The terminology further includes species which will be attracted to a fibre surface and bind themselves thereto by means of cross-linking mechanisms.

The term "polyfunctional reactive group" as used herein is to be understood as meaning a group which is capable of reacting with the amino functionality of compounds of formula I or II. The reactivity of group B needs to be complimentary to that of group R₁ in those compounds.

It will be understood that the polymers and prepolymers may be derived from mixtures of one or more polyoxyalkyleneamines and that these may be joined by bridging groups. The bridging groups serve to link the polyoxyalkyleneamines and some examples of suitable groups were mentioned above. The bridging groups themselves could, of course, bear reactive species capable of reacting with protein fibres. It will also be appreciated that the bridging group B could be incorporated into the molecular structure, whilst the prepolymer is being applied to the fibre, as a separate reactive crosslinking agent.

The chemistry and reactions of the epihalohydrins, the alkyl polyhalides and formaldehyde, etc. are well known and it is not

necessary to describe in detail the conditions required for their reaction with the polyoxyalkyleneamines according to this invention.

5 The proportions used, however, are preferably such as to ensure that substantially all of the amino groups in the polyoxyalkyleneamine residues are reacted. The reaction is best performed at elevated temperature, typically within the range of from 40 to 150°C.

10 The polymers and prepolymers of this invention are suitable for use in a method for imparting shrink resistance to wool and which comprises treating the wool with an aqueous solution of the polymer to be applied to the wool fibres. The application of the polymer alone can produce an acceptable level of
15 shrink resistance in the wool. It is, however, well known that the treatment of wool fibres with various reagents, such as oxidative agents or reducing agents, can improve the effectiveness of a polymer treatment. The polymer treatment may be carried out prior to, in
20 conjunction with or subsequent to any such further treatment of the wool. Most preferably, the polymer is applied subsequent to an oxidative pretreatment of the wool.

25 As previously mentioned, oxidative pretreatments are a conventional procedure in the shrink-proofing of wool and a number of suitable treatments are well known. For example, the wool could be treated with permonosulphuric acid. Alternatively, a chlorinating oxidative pretreatment
30 may be employed and this would typically involve the use of chlorine gas. Chlorinating agents such as hypochlorite or sodium dichloroisocyanurate may also be employed, (optionally together with potassium permanganate or permonosulphate), typically at levels
35 of 0.25-2.0% active chlorine by weight on the weight

of the dry wool (o.w.w.), most preferably 0.5-1.2%.
The optimum level of chlorine employed is generally
dependent upon the level of polymer used in the next
stage of the process. The pretreatment will, by
itself, produce a small degree of shrink-resistance in
the wool.

The wool is subjected to antichlorination
treatment with sulphite and rinsed and is then ready
for the polymer application stage.

The polymer or prepolymer may be applied to
the wool in a conventional manner from a bath. The
total amount of polymer solids applied to the wool
fibre in the method of this invention is generally
from 0.005 to 10% by weight, most preferably from
0.05% to 2.0%. The polymer or prepolymer can be used
in either a batch or a continuous process for the
treatment of wool.

Following the polymer treatment, the wool is
dried and may then be further processed in the usual
manner.

It has surprisingly been found that treatment
of wool with the polymers or prepolymers of this
invention results in a good level of shrink
resistance. The treated wool also has a soft handle
and there will usually be no need to use an additional
softening agent. It has been found that the polymers
are generally more effective than the polyamide types
(e.g. Hercosett polymers) currently in commercial use,
and result in an acceptable shrink resist with much
lower polymer solids being deposited on the wool.
This advantage, coupled with the lower cationicity of
the polymers, further results in better dyeing
characteristics. Rate of strike is lower and so the
risk of unlevel dyeing is greatly reduced. Further,
on repeated washing in a mixed wash load, there is

less dye pickup from the laundry liquor and thus the garments will appear to soil less readily. In addition, having regard to the concern expressed about the amount of chlorinated materials being released
5 into the environment, the present process has the desirable advantages of using polymers that can be applied to the wool at lower levels and which do not necessarily contain chlorine reactive species.

It is believed that the polymers and
10 prepolymers of this invention could also be used for other applications such as, for example, emulsion breakers, anti-static agents, anti-crease agents and to impart stain resistance.

The polymers, prepolymers and method of this
15 invention will now be illustrated by the following Examples.

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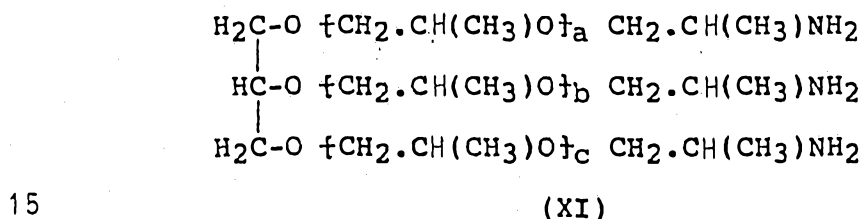
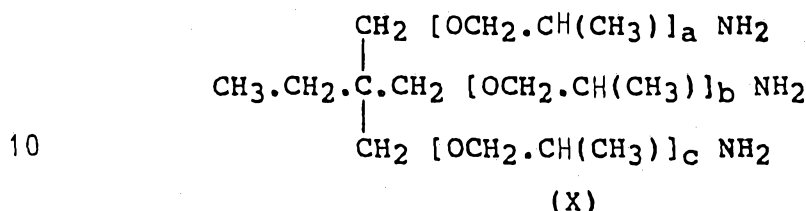
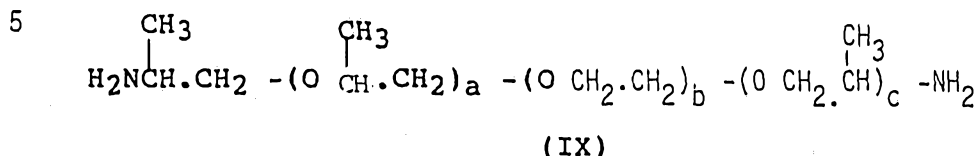
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Raw Materials Used for Synthetic Work

In the following examples, various amino containing prepolymers have been used. Their structures may be defined by one of the following structures.



Although in most cases the manufacturer quotes exact structures, additional technical data has been provided in the examples.

In the following examples a distinction is made between the preparations based on the ratio of epichlorohydrin to amino nitrogen. For example a 1:1 molar ratio uses 1 mole of epichlorohydrin for each nitrogen atom in 1 mole of the amino containing prepolymer.

Example 1

(1.1) Preparation of prepolymer (1:1) adduct

25 A solution was prepared containing 3000g (approx. 1 mole) of a compound of formula XI (where $a + b + c = 50$, molecular weight approximately 3000, total amine 6.45 Mequivalents/g) in 6726.4 g of a mixture of 70 parts by weight isopropyl alcohol and 30 parts by weight water. To this solution was added 273.6 g (2.96 mole) epichlorohydrin with efficient stirring at room temperature in a reaction flask fitted with a water cooled reflux condenser. The mixture was then heated until the isopropanol began to boil, and then maintained at reflux for approximately 4 hours or until when 5 ml of the reaction mixture was diluted with 30 ml water a clear solution resulted. The flask was then allowed to cool and the reaction mixture tested as in 1.4 below.

(1.2) Preparation of prepolymer (2:1) adduct

The procedure described in 1.1 above was followed with the following changes: 6452.5 g of 70% weight/weight isopropyl alcohol in water were used for the solution and 547.5 g (5.92 mole) of epichlorohydrin added.

(1.3) Preparation of prepolymer (3.1) adduct

The procedure described in 1.1 above was followed except that 6178.9 g of 70% weight/weight isopropyl alcohol in water were used for the solution and 821.1 g (8.88 mole) epichlorohydrin added.

(1.4) Performance Evaluation

The three adducts prepared in 1.1-1.3 above were tested for their ability to stabilise wool against shrinkage by applying them to wool swatches which had been pretreated with an oxidative shrink resist pretreatment as follows.

A quantity of 23.5 micron quality wool top was treated with a mixture of 2% o.w.w. dichloroisocyanuric acid sodium salt and 1% o.w.w. potassium permonosulphate according to the Dylan XC2 process (Precision Processes (Textiles) Ltd) to produce a moderate degree of shrink resistance. This top was then spun to 2 x 24s worsted count and knitted into swatches with a cover factor of 1.29DT.

Each swatch was then scoured for 15 min in 1% o.w.w. commercial nonionic detergent (Millsour XBN, Precision Processes (Textiles) and 3% o.w.w. of sodium bicarbonate at 45°C with a 30:1 liquor ratio, then rinsed once in warm water and once in cold. The swatches were treated as follows.

The wet goods were entered into a fresh bath at a liquor ratio of 30:1. A 1% weight/weight solution of the product from examples 1.1-1.3 above which was to be tested was prepared in cold water. A sufficient quantity of this solution was then drip fed into the treatment bath over 15 minutes, whilst agitating the test swatch, such that an amount of prepolymer solids equivalent to 1% by weight of the dry weight of the swatch was added to the bath. The temperature of the bath was then raised to 40°C and held at this temperature for approximately 20 minutes, whilst agitating the swatch, until the bath was shown to have exhausted by taking 10 ml of bath liquor and treating this with 2 ml of a 1% solids solution of sodium dodecylbenzene sulphonate in water, the absence of cloudiness or precipitate indicating exhaustion.

The treated swatches were then hydroextracted and tumble dried, then tested in a Wascator FOM7 washing machine according to the Test Method TM31 of the International Wool Secretariat. Shrinkage figures were then calculated, giving the following results:

<u>Preparation Example</u>	<u>% area shrinkage after 1 x 7A followed by 5 x 5A washes</u>
1.1	14.3
1.2	0.8
1.3	2.0
Untreated Swatch (XC2 only)	53.9

Example 2

Various adducts of various polyamine prepolymers were prepared according to the general procedure described in 1.1 above with the variations shown overpage in Table I.

Example 3

The various adducts from Example 2 were tested for their ability to stabilise wool against shrinkage during washing using the procedure given in Example 1.4, with the following results:

<u>Preparation from Example</u>	<u>% area felting Shrinkage 5 x 5A</u>	
	<u>2 x 5A</u>	<u>5 x 5A</u>
2.1	0.6	11.1
2.2	-0.4	-1.3
2.3	2.2	7.7
2.4	3.8	18.2
2.5	-1.1	-3.1
2.6	0.2	7.5
2.7	-5.2	0.1
2.8	15.6	-
2.9	11.5	-
2.10	10.3	-
2.11	10.3	-

Note: negative figures in the above table indicate that the swatch extended rather than shrinking.

Example 2 - Table I

Example No.	Structure formula of amine	Value of a,b,c	Solvent mixture	Weight of Solvent g	Amine Content mEq/g	Weight of amine g	Weight of epichlorohydrin g
2.1	XI	a+b+c = 85	70% isopropanol in water	13720	0.46	5000	440
2.2	XI	a+b+c = 85	70% isopropanol in water	13207	0.46	5000	660
2.3	X	a+b+c = 5.3	water	2930	6.45	440	584.3
2.4	X	a+b+c = 5.3	water	3072	6.45	440	876.5
2.5	IX	a+c = 33 b = 0	50% isopropanol in water	5743	0.96	2000	461.2
2.6	IX	a+c = 33 b = 0	50% isopropanol in water	6088	0.96	2000	609.2
2.7	IX	a+c = 68 b = 0	75% isopropanol in water	10618	0.45	4000	550.4
2.8	IX	a+c = 2.5 b = 40.5	water	5584	0.88	2000	393.2
2.9	IX	a+c = 2.5 b = 40.5	water	6043	0.88	2000	589.8
2.10	IX	a+c = 2.5 b = 86	water	10115	0.45	4000	335.2
2.11	IX	a+c = 2.5 b = 86	water	10507	0.45	4000	503.2

Example 4

The dyeing properties of the material produced in Example 1.3 were examined by dyeing treated swatches with various dyestuffs. Samples of the dyebath liquor were extracted at various
5 temperatures as the dyeing progressed, and the amount of dye present in the dyebath evaluated spectrophotometrically. All dyeings followed the same temperature pattern. Goods were entered cold in a wet state and the temperature increased to the boil at 1°C per minute to the boil and held at the boil for 1
10 hour. The goods were then rinsed and dried before testing for shrinkage and colour fastness. In all cases 2% o.w.w. of dyestuff was used, with 1.5% o.w.w. Albegal B (Ciba Geigy) and 2.0% ammonium acetate, the dyebath being held at pH5.5.

Dye fastness results were comparable with those obtained from
15 dyeings on a commercially available polyamide type resin (Polymer PKS, Precision Processes (Textiles) Ltd) dyed according to the same procedure.

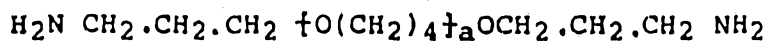
Figures 1 and 2:

The attached graphs show the degree of strike of the dyestuff
20 onto the fibre with increasing temperature when compared with swatches treated with commercially available polyamide resin and swatches which had only been given the pretreatment outlined in Example 1.4 above. The rate of strike of the dyestuff is reduced against that of the polyamide based polymer. Shrinkage
25 testing gave the following for 3 x 5A on the IWS TM31 test:

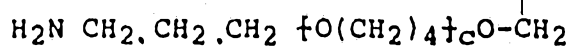
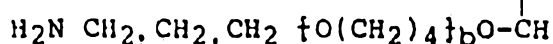
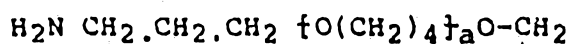
Acidol Yellow M5GL	8.1%
Sandolan Milling Red NFBL	13.7%

Example 5

The general procedure of example 1, using in all cases a 70% isopropanol in water solvent, was followed to prepare a number of further adducts of polyether amines either having the general structures



(XII)



(XIII)

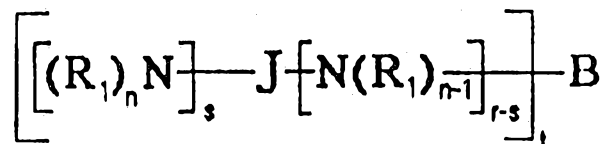


(XIV)

The details of the preparations are outlined in Table II. The products were tested as described above (Example 1.4) and found useful as shrink resist agents.

Example 6

Various bridged adducts were prepared according to the general formula



The following general preparative techniques were used:

A: Condensation reactions with acids:

A known quantity of the amino polyether was placed in a flask equipped with stirrer, distillation condenser, nitrogen bleed and dropping funnel. A known quantity of the bridging compound was added, and the mixture heated to 180-190°C with stirring until water was evolved. This was allowed to distill off until the theoretical quantity of water was evolved, or no further water could be removed. The flask was allowed to cool, and a suitable quantity of a specified isopropanol (IPA): water mixture was added to dissolve the product. A specified amount of epichlorohydrin was added and allowed to react at reflux temperature until amine titration indicated the reaction to be complete.

B: Reaction with other bifunctional compounds:

A known quantity of aminopolyether was placed in a flask with a specified quantity of isopropanol (IPA): water mixture. A specified quantity of bridging compound was added and the mixture heated at reflux with stirring for 3 hours. When amine titration indicated the reaction to be complete, a specified quantity of epichlorohydrin was added to the mixture and this was further heated for 4 hours or until an amine titration indicated the reaction to be complete.

Details of the various preparations are given in Table III. The products were found to be useful as shrink resist agents.

Notes to Table III

Note 1 The compound described in example 2.1 of British Patent 1,213,745, as a 50% solution in water.

Note 2 The compound described in example 2.2. of British Patent 1,213,745, as a 50% solution in water.

Example 7

To illustrate the in-situ crosslinking effect of reactive polymers, the following polymers were prepared:

- 7.1) A reactive polyamide polymer prepared according to the procedure described in Example 3 of European Patent Application No. 0260017.
- 7.2) A reactive water soluble polyacrylate polymer was prepared as follows: into a suitable resin flask equipped with stirrer and reflux condenser were loaded 164g of isopropanol. The flask was heated to reflux for 1 hour to degas the solvent, then a mixture of 71.5g methyl methacrylate, 35.8g of dimethylaminoethyl methacrylate and 0.965g of azobisisobutyronitrile was dripped into the boiling solvent over 1 hour. The mixture was refluxed for 6 hours. The flask was cooled to 25°C and 64.5g of 3.53M hydrochloric acid and 97.4g of water added. Then 23.6g of epichlorohydrin was added and the mixture stirred for 24 hours at 25°C.
- 7.3) The preparation described in 7.2 was repeated using 2.412g of azobisisobutyronitrile. Before adding the epichlorohydrin, 26.9g of an alpha, omega-glycidyl organofunctional polydimethyl siloxane (Tego OF3010, Goldschmidt) followed by 21.24g of epichlorohydrin, and the reaction completed as before.
- 7.4) The preparation described in 7.3 was repeated except that 14.59g of a polyether diepoxy resin of molecular weight 640 (DER 732, Dow Chemicals) was added in place of the organofunctional polydimethylsiloxane.

The polymers were then applied to wool as follows:

- 7.5) The procedure described in 1.4 above was followed except that varying quantities of selected products from the Examples 7.1-7.4 above were applied together with a polymer selected from Examples 1.1-1.3 5 or 6.
- 7.6) The procedure of 7.5 was repeated using untreated swatches knitted from 23.5 micron quality top spun to 2 x 21s worsted count. The swatches were then scoured as described in 1.4 and treated with 6% on weight of wool of commercial potassium permonosulphate (Dylanize Salt, PPT), at pH4.0 which was then neutralised with 5% o.w.w. sodium sulphite. Thereupon the procedure from line 28 in example 1.4 was followed.

Table IV shows the quantities and identity of the polymers used and the results obtained.

Example 8

A specified quantity of aminopolyether was weighed into a flask equipped with stirrer, reflux condenser and dropping funnel 200ml of a isopropanol: water mixture was added to dissolve the resin and a specified quantity of formaldehyde solution (37% w/w in water) was added. The mixture was heated at reflux for 4 hours.

Table V gives details of the preparation of such methylol-terminated resins. The products were useful as shrink resist agents when tested as described in Example 1.4.

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Example 9

Into a suitable resin flask equipped with a stirrer was placed 50g of water, 300g of methylethyl ketone and 187.5g of cyanuric chloride. The contents of the flask were maintained at 0°C whilst 4200g of a diamino polyether of structure XII (where $a=26$) was slowly dripped in at such a rate that the temperature did not exceed 2°C. The flask was stirred at below 2°C for two hours, then slowly allowed to warm to room temperature, then heated slowly to 40°C until the titrated amine value remained constant. To this mixture was slowly added 185g of epichlorohydrin, then the flask fitted with a reflux condenser and the contents raised to reflux temperature until the titrated amine value remained constant. Evaluated as above, the product was found useful as a shrink resist agent.

Table II

Example	Structure formula of amine	Values of a,b,c	Weight of solvent g	Weight of amine g	Weight of epichlorohydrin g
5.1	XIV	a=26	277	100	18.76
5.2	XII	a=28	2418	881	155.3
5.3	XIII	a+b+c=18	320	100	36.7

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Table III

Example	Bridging compound	Preparation procedure	Structure formula of amine	Value of a,b,c	Solvent Mixture	Weight of solvent g	Weight of amine g	Weight of Bridging compound g	Weight of epichlorohydrin g
6.1	$\text{H}_2\text{C}-\underset{\text{O}}{\underset{\text{O}}{\text{CH}}}(\text{OCH}_2\text{CH}_2)_n-\underset{\text{O}}{\underset{\text{O}}{\text{CH}}}-\text{CH}_2$ n=13,2	B	XI	a+b+c ~5.3	70 IPA 30 water	200	40	14.4	16.6
6.2	as 6.1 n=13,2	B	XI	a+b+c ~5.3	70 IPA 30 water	200	40	21.6	12.5
6.3	as 6.1 n=13,2	B	XII	a=-27	70 IPA 30 water	200	40	2.11	2.41
6.4	as 6.1 n=13,2	B	XII	a=-27	70 IPA 30 water	200	40	1.60	2.77
6.5	$\text{CH}_2-\underset{\text{O}}{\underset{\text{O}}{\text{CH}}}\text{CH}_2\text{O}(\text{CH}_2)_3\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{Si}-\text{O} \\ \\ \text{CH}_3 \end{array}\right]_n\text{Si}(\text{CH}_3)_3-\text{OCH}_2-\underset{\text{O}}{\underset{\text{O}}{\text{CH}}}-\text{CH}_2$ n=12	B	XII	a=-7	50 IPA 50 water	200	80	63.13	9.9
6.6	$\text{HOOC}-\text{C}_6\text{H}_4-\text{COOH}$	A	XII	a=9	70 IPA 30 water	200	80	2.92	16.5
6.7	as 6.6	A	XII	a=-27	70 IPA 30 water	200	80	3.32	3.7
6.8	$\text{HOOC}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COOH}$	A	XII	a=-9	50 IPA 50 water	200	80	6.47	12.97
6.9	as 6.8	A	XII	a=-9	50 IPA 50 water	200	80	12.94	9.99
6.10	$\text{HOOC}[\text{CH}_2]_6\text{COOH}$	A	XII	a=-7	50 IPA 50 water	200	305.6	29.2	37.0
6.11	as 6.10	A	IX	a+c=2.5 b=8.5	50 IPA 50 water	200	320	36.52	46.3
6.12	Note 1	B	XI	a+b+c=85	IPA	200	100	22.1	12.3
6.13	Note 2	B	IX	a+c=2.5 b=40.5	water	200	100	20.1	12.3
6.14	1,3-dibromopropane	B	XII	a=-7	50 IPA 50 water	200	40	5.05	4.9
6.15	1,6-dichlorohexane	B	XII	a=-7	50 IPA 50 water	200	40	3.88	4.9
6.16	1,10-dibromodecane	B	XII	a=-7	50 IPA 50 water	200	40	7.5	4.9
6.17	1,4-di(chloromethyl)benzene	B	XII	a=-7	50 IPA 50 water	200	40	4.38	4.9

Table IV

Example	Prepolymer from Example	% solids applied o.w.w.	Reactive polymer of example	% solids applied o.w.w.	Shrinkage test results			Application procedure
					2 x 5A	3 x 5A	5 x 5A	
7.7	1.3	0.75	7.1	0.25	-2.2	-	-1.0	7.5
7.8	5.2	0.25	7.2	0.25	-	-0.5	2.6	7.5
7.9	5.2	0.375	7.2	0.125	-	2.6	4.3	7.5
8.0	5.2	1.36	7.1	0.14	6.2	13.1	-	7.6
8.1	5.2	1.46	7.1	0.04	6.5	7.3	-	7.6
8.2	5.2	1.36	7.3	0.14	4.2	8.4	-	7.6
8.3	5.2	1.36	7.4	0.14	3.1	8.8	-	7.6

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Table V

Example	Structure formula of amine	values of a, b, c	weight of resin g	weight of CH ₂ O* g	solvent mix IPA:water
8.1	XI	a+b+c=50	100	15.99	70:30
8.2	IX	a+c=2.5 b=15.5	40	2.6	50:50
8.3	IX	a+c=2.5 b=15.5	40	5.2	50:50
8.4	IX	a+c=33 b=0	40	1.2	50:50
8.5	IX	a+c=33 b=0	40	2.3	50:50
8.6	XII	a= 27	80	2.28	70:30
8.7	XII	a= 27	80	4.56	70:30

* expressed as CH₂O not formalin solution

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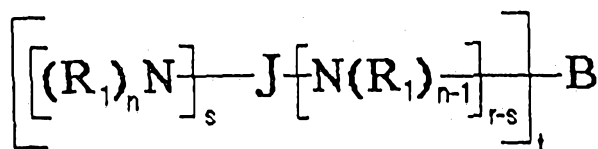
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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

CLAIMS

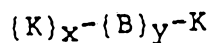
1. A polymer or prepolymer having one of the following structural formulae:

i)



or

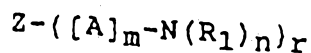
ii)



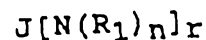
wherein

J represents a residue derived from a polyfunctional polyether;

K represents the monofunctional or polyfunctional residue derived from partial reaction of a prepolymer of the formula:



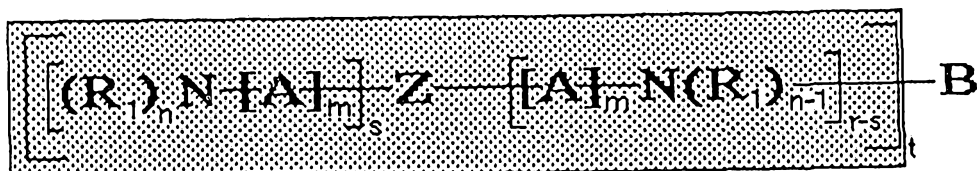
or



(I)

(II)

that is, it represents the shaded area in the following formula:



B is the residue created by bi- or polyfunctional reaction between any polyfunctional reactive group and the parent amine of the title compound (formula (I) where R_1 is hydrogen in all cases) or is the residue of a reactive amino-acrylic polymer or a reactive polyamide polymer;

Z represents a residue of a polyol;

A represents a polyalkylene oxide residue;

R_1 represents a fibre reactive grouping such as the residue derived from monofunctional reaction of an epihalohydrin, an alkyl or alkyl aryl polyhalide or a methylol grouping derived from monofunctional reaction of formaldehyde, or is alkyl, hydroxyalkyl or hydrogen, with the proviso that at least one group R_1 per polyoxyalkyleneamine residue, and preferably at least one for each nitrogen, retains residual fibre reactivity;

m is between 4 and 50;

n is 2 or 3, with the proviso that, where n is 3, the nitrogen atom involved also bears a formal positive charge;

p is 1 or 2, with the proviso that, where p is 2, the nitrogen atom involved also bears a formal positive charge;

r equals the functionality of group Z;

t is a number representing the functionality of reaction of the residue B;

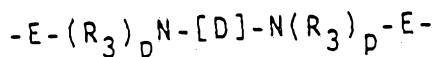
s is a number between 1 and r-1;

x is between 2 and 30; and

y is from $\frac{x}{t-1}$ to x,

with the general proviso that, in any given instance, the significance of a particular group Z, A, B, R, J or K in any given structure shall not be dictated by the significance of any other such group in the same formula, and further, wherever a formal positive charge is present in the structure, then an appropriate counter anion is taken to be present.

2. A polymer or prepolymer as claimed in claim 1, wherein B is the group:



where

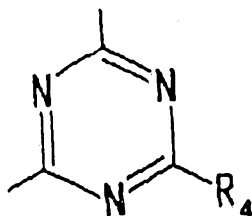
E represents a group resulting from the reaction of a bi- or polyfunctional species capable of reacting with amino groups;

D represents a straight or branched chain hydrocarbon, polysiloxane or polyalkylene oxide residue, and which may also either bear functional groups or may contain functional groups, such as amino groups, which may in turn either bear one or more groups R₁ or, where B is polyfunctional rather than bifunctional, may represent a further functional reaction point of the group B with the rest of the molecular structure;

R₃ represents hydrogen or C₁-C₄ alkyl or hydroxyalkyl;

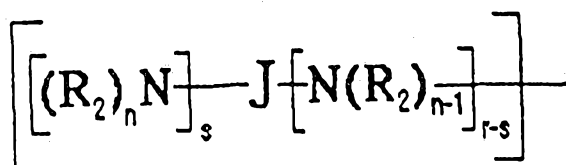
and p is as defined above.

3. A polymer or prepolymer as claimed in claim 1, wherein B is the group:



where

R₄ represents halogen or a group



or one of alkylamino, hydroxyalkylamino, alkoxy, alkylarylamino or a group $-(R_3)_pN-[D]-R_5$

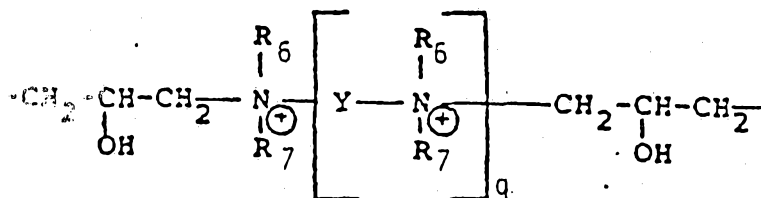
or a functional reaction point of the group B with the rest of the molecular structure, where B is polyfunctional rather than bifunctional;

R₅ represents hydrogen or a group $-N(R_2)_n$ or $-N(R_3)_n$;

R₂ represents a fibre reactive grouping such as the residue derived from monofunctional reaction of an epihalohydrin, an alkyl or alkyl aryl polyhalide or is a methylol grouping derived from monofunctional reaction of formaldehyde, or alkyl, hydroxyalkyl or hydrogen;

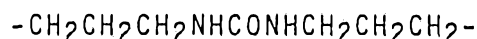
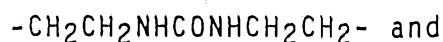
and J, R₃, n, p, r and s are as defined above.

4. A polymer or prepolymer as claimed in claim 1, wherein B is a group derived from reaction of a cationic polymeric reactive species of the formula:



where R₆ and R₇ are selected from C₁-C₅ alkyl and C₂-C₅ hydroxyalkyl radicals,

Y is selected from C₂-C₆alkylene radicals, 2-hydroxy-1,3-propylene radicals, and the radicals:

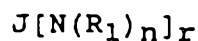


and q is an integer of from 0 to 20, provided that when q is greater than 2, each of the symbols Y need not necessarily have the same significance.

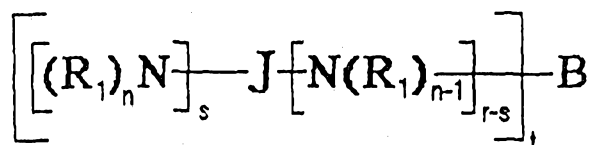
5. A method for the treatment of wool so as to impart shrink resistance which comprises treating the wool with an aqueous solution of a polymer so as to cause the polymer to be applied to the wool fibres,

characterised in that the polymer is a polymer or prepolymer having one of the following structural formulae:

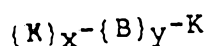
i)



or
ii)



or
iii)



wherein

J represents a residue derived from a polyfunctional polyether;

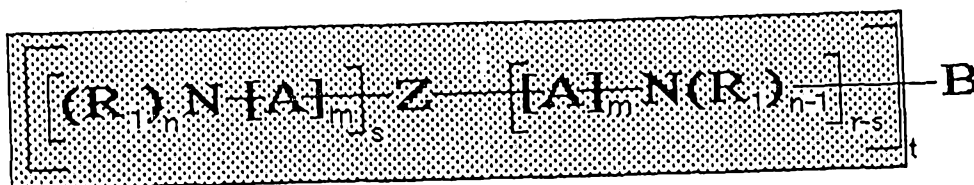
K represents the monofunctional or polyfunctional residue derived from partial reaction of a prepolymer of the formula:



(I)

(II)

that is, it represents the shaded area in the following formula:



B is the residue created by bi- or polyfunctional reaction between any polyfunctional reactive group and the parent amine of the title compound (formula (I) where R_1 is hydrogen in all cases) or is the residue of a reactive amino-acrylic polymer or a reactive polyamide polymer;

Z represents a residue of a polyol;

A represents a polyalkylene oxide residue;

R₁ represents a fibre reactive grouping such as the residue derived from monofunctional reaction of an epihalohydrin, an alkyl or alkyl aryl polyhalide or a methylol grouping derived from monofunctional reaction of formaldehyde, or is alkyl, hydroxyalkyl or hydrogen, with the proviso that at least one group R₁ per polyoxyalkyleneamine residue, and preferably at least one for each nitrogen, retains residual fibre reactivity;

m is between 4 and 50;

n is 2 or 3, with the proviso that, where n is 3, the nitrogen atom involved also bears a formal positive charge;

p is 1 or 2, with the proviso that, where p is 2, the nitrogen atom involved also bears a formal positive charge;

r equals the functionality of group Z;

t is a number representing the functionality of reaction of the residue B;

s is a number between 1 and r-1;

x is between 2 and 30; and

y is from $\frac{x}{t-1}$ to x,

with the general proviso that, in any given instance, the significance of a particular group Z, A, B, R, J or K in any given structure shall not be dictated by the significance of any other such group in the same formula, and further, wherever a formal positive charge is present in the structure, then an appropriate counter anion is taken to be present.

6. A method for the treatment of wool as claimed in claim 5, wherein the treatment with the polymer is carried out prior to, in conjunction with or subsequent to an oxidative treatment of the wool.

7. A method for the treatment of wool as claimed in claim 6, wherein the oxidative treatment involves the use of a chlorinating agent.

8. A method for the treatment of wool as claimed in claim 6, wherein the oxidative treatment involves the use of permonosulphuric acid.

9. A method for the treatment of wool as claimed in any of claims 5 to 8, wherein the total polymer solids applied to the wool fibre is from 0.05% to 2.0% by weight.

10. A method for the treatment of wool as claimed in any of claims 5 to 9, which is in the form of a batch process.

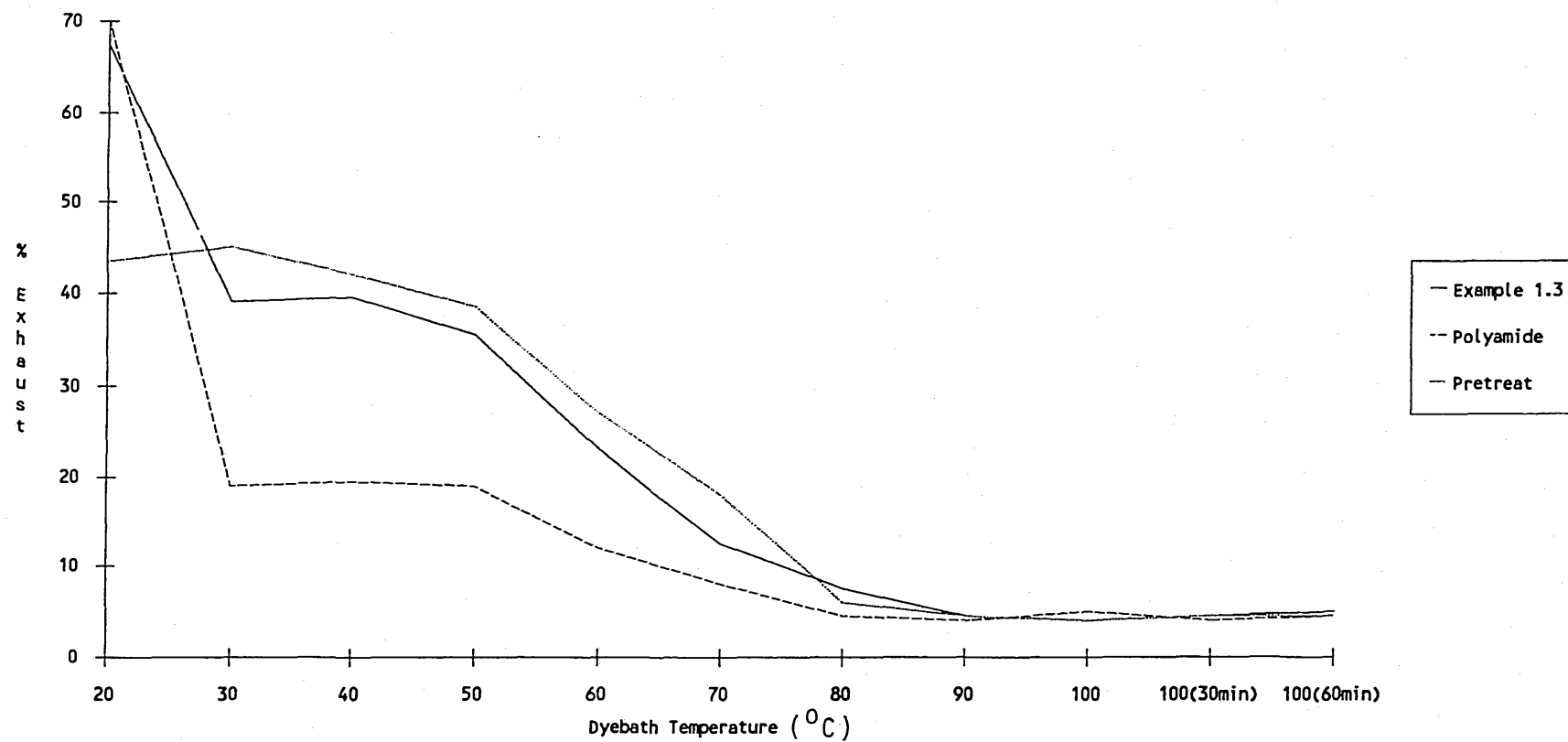
11. A method for the treatment of wool as claimed in any of claims 5 to 9, which is in the form of a continuous process.

DATED this 24th day of July 1990.
PRECISION PROCESSES (TEXTILES) LIMITED

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"THE ATRIUM"
290 BURWOOD ROAD
HAWTHORN. VIC. 3122.

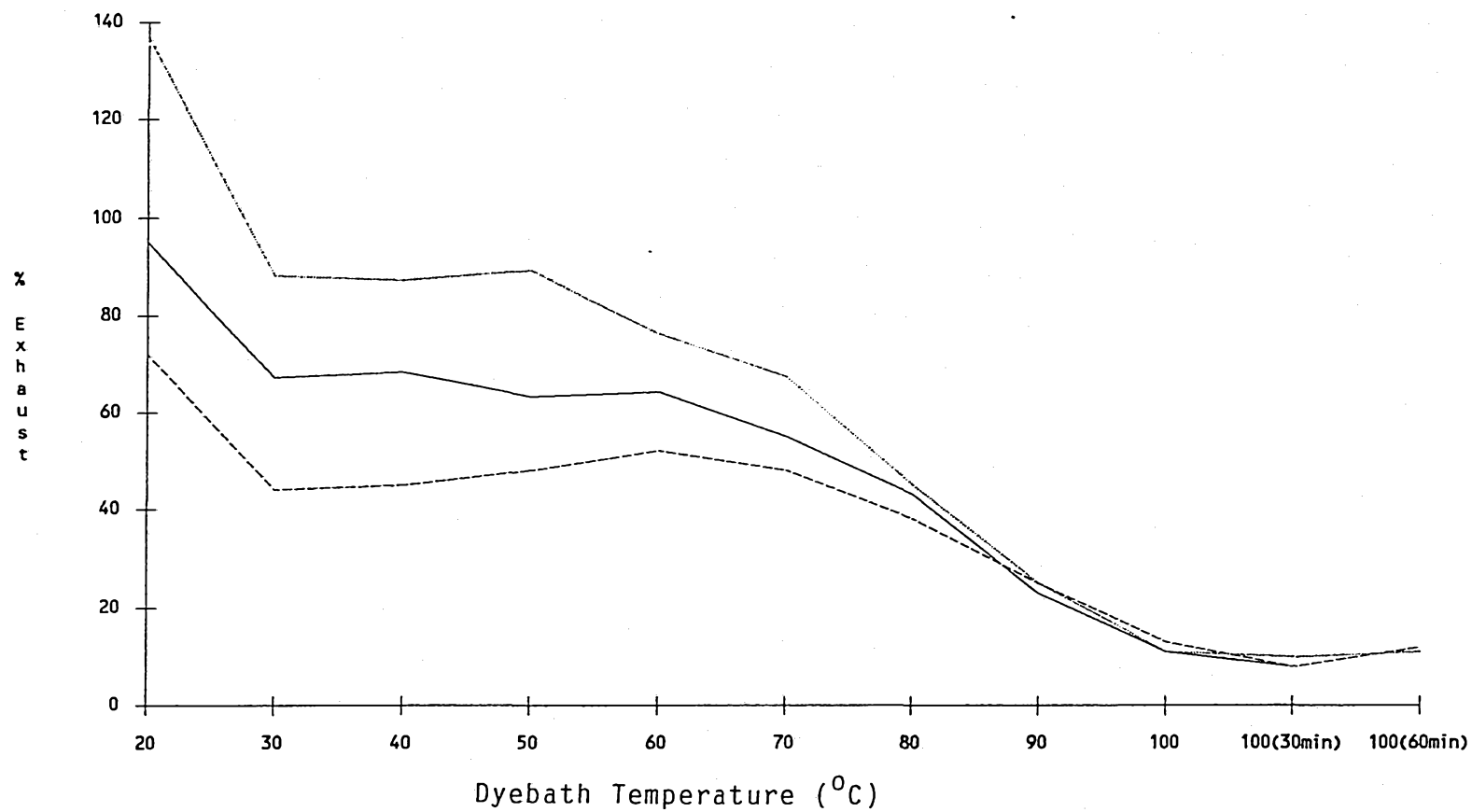
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FIGURE 1 - Sandolan Milling Red NFBL



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FIGURE 2 - Acidol Yellow M5GL



2/9