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## SHRINKPROOFED WOOL AND METHOD OF PRODUCING SAME

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This invention relates to shrinkproofing of wool and more particularly to a new process for preventing or decreasing the tendency of wool to shrink, and to wool impregnated with a shrinkproofing material.

Woolen textiles are characterized by their tendency to felt when subjected to mechanical working. This felting tendency causes woolen goods to shrink under ordinary wearing conditions and especially during laundering and it is, therefore, a serious disadvantage in many wool applications. A number of methods have been proposed for reducing the tendency of wool to shrink, such as treatment with chlorine, sulfuryl chloride, hypohalites, and similar substances. These treatments are not free from disadvantages in that they may produce harshness and discoloration, and that they involve objectionably acidic materials which degrade wool upon prolonged exposure. Alkaline treatments, for example with alcoholic potassium hydroxide, have also been proposed but they require accurate control and are only moderately suitable for application to dyed woolens. More recently, shrinkproofing of wool by impregnation with certain polymeric materials of a resinous nature has come under investigation. In general, such treatments have the advantage that the polymeric materials are comparatively easy to apply, have no serious effect on dyes and do not degrade the wool, although they often alter appreciably the handle and softness of the woolen yarn or fabric.

Certain amino polymers have previously been used to treat wool, for example to increase its dye receptivity, or as emulsifying agents in the coating of wool with water insoluble materials such as waxes. However, such treatments did not produce shrinkproofing, nor could they be expected to do so. For example, impregnating wool with a wax dispersed in an aqueous solution of an amino polymer gives a stiff coating removable by dry cleaning solvents, whereas a satisfactory shrinkproofing treatment must result in a soft fabric with permanent shrinkage resistance.

It is an object of this invention to provide a new process for preventing or decreasing the tendency of wool to shrink. A further object is to provide a shrinkproof wool. A still further object is to provide a shrinkproofing treatment for wool resulting in a soft fabric with substantially permanent shrinkage resistance. Other objects will appear hereinafter.

These objects are achieved by using a special type of polymeric material having basic amino groups and a special treatment for shrinkproofing

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the wool. It has now been discovered that wool can be made resistant to shrinking by treatment with a solution of a synthetic high molecular weight basic amino polymer and with formaldehyde, said polymer having hydrogen on the amino nitrogen and containing at least three and not more than fifty chain carbon atoms for each amino group and maintaining the impregnated wool at a temperature between 20° C. and 200° C. until the amino polymer has become insoluble in water and organic solvents.

The formaldehyde treatment, which serves to insolubilize the amino resin within the fabric, may be carried out either simultaneously with or after the treatment with the amino polymer. For example, the wool fabric may be impregnated with the solution of amino polymer and then treated, with or without previous evaporation of the solvent, with aqueous formaldehyde or with formaldehyde vapor. It is generally more convenient, however, to prepare a single treating solution containing both the amino polymer and the formaldehyde, particularly when an aqueous acid is used as the solvent. Such solutions are quite stable. In particular, dilute acidic solutions of reduction aminated ethylene/carbon monoxide polymer and formaldehyde may be stored for many months without deteriorating. It is only necessary to use as much formaldehyde as is needed to react with the amino groups of the polymer. In practice, however, it is desirable to use an excess of formaldehyde since this does no harm and insures complete insolubilization. Preferably, there is used between 2% and 200% of formaldehyde based on the weight of the amino polymer.

Impregnation of the wool is carried out so that, after drying, the wool contains between 4 and 10%, and preferably between 7 and 10% of amino polymer based on the original weight of the wool. There are no advantages to having more than 10% of amino polymer present in the wool, and over-impregnation in general leads to poor handle of the fabric.

The process is completed by a curing treatment which promotes the reaction between the amino polymer and the formaldehyde and insolubilizes the shrinkproofing composition. This is done by maintaining the treated, dry fabric at a temperature above 20° C. until the impregnating composition has become insoluble in organic solvents and in water or dilute acidic solutions. The curing may be done at low temperature, for example, 20 to 25° C., but in this case it requires several days for completion. Preferably, the

treated wool is heated at temperatures between 80° and 150° C., the preferred range being 90° to 125° C. Insolubilization of the amino resin is thus achieved in a short time, a period of between 5 and 30 minutes heating being generally sufficient. Temperatures above 200° C. should be avoided to prevent degradation of the wool.

The polymeric materials suitable for use in the process of this invention are linear, or substantially linear, polyamines of high molecular weight, i. e., at least 1,000 and in which the amino groups are primary or secondary, and which are soluble either in organic solvents or in water or in dilute aqueous acids. The upper limit of molecular weight is dictated only by the solubility of the resin. In general, it is undesirable to use resins having molecular weight in excess of about 5,000, although even such materials are satisfactory if they are soluble. It has been found that satisfactory results are obtained with polyamines which are not too rich in amino nitrogen. The chemical structure of the suitable polymers should be such that there are at least three carbon atoms in the linear polymer chain for each primary or secondary amino group present. The desired structure may result from the fact that the polymer is inherently incapable of having less than three chain carbons per amino nitrogen or from the fact that a polymer capable of having less than three chain carbons per nitrogen is only partially aminated (e. g., partially reduced-aminated methylvinyl ketone polymers) or from a combination of both factors. On the other hand, sufficient amino groups must be at hand to react with formaldehyde to form an insoluble structure within the fabric. For this reason, the polyamine should preferably have not more than 50 linear chain carbon atoms for each primary or secondary amino group. Within the above limitations, any synthetic amino polymer is suitable for use.

In the preferred mode of operation of this invention, the polymeric material is a polyamine obtained by reductive amination of an ethylene/carbon monoxide copolymer. These polyamines, and processes for preparing them are described in detail in application Serial Number 4,932, filed on January 28, 1948, by H. H. Hoehn, now Patent No. 2,495,255, issued January 24, 1950. They are the reaction products of the reductive-amination of a monoolefin/carbon monoxide polymer in which the polymeric polyamine has a main carbon chain and primary or secondary amino-nitrogen groups as lateral substituents with the nitrogen thereof directly attached to a carbon atom which is an integral part of the main carbon chain. The ethylene/carbon monoxide copolymers themselves are disclosed and claimed in application Serial Number 552,374, filed by M. M. Brubaker on September 1, 1944, now abandoned, of which Patent No. 2,495,286, issued January 24, 1950, is a continuation-in-part. The polyamine, preferably one obtained from a polymer having an ethylene/carbon monoxide ratio from 4:1 to 11:1 under conditions producing the highest possible degree of amination, that is having at least 70% of the carbonyl groups replaced by amino groups, is dissolved in dilute acetic acid. To the solution is added sufficient formaldehyde and water to make a solution containing about 5% polyamine, 5% acetic acid and 3% formaldehyde. This solution is applied to wool flannel which is then squeezed, dried at ordinary temperature and cured by heating at about 100° C. for about 15 minutes. The wool

retains about 7-10% of its weight of the impregnating materials, which is now insoluble in water and organic solvents. The fabric is substantially shrinkproof.

In the experiments described below, shrinkage was determined by a hand-milling test which is very similar to that described by Chamberlain and Menkart in *Journal Soc. Dyers and Colourists*, 61, 286 (1945). In operating this test, a 7" x 7" square of the wool fabric is squeezed intermittently by hand for 15 minutes in a 0.25% soap solution containing 0.1% sodium carbonate, the solution being at 40-45° C. The test sample is given about one squeeze per second, using moderate hand pressure and revolving the test piece so that it does not tend to pack tightly during the milling operation. At the end of the milling the sample is rinsed well in distilled water and spread on a paper towel to dry. When nearly dry it is pressed gently with a hot flat iron, using only vertical pressure. The area before and after the milling treatment is determined and the loss in area expressed in percentage of area shrinkage.

In addition to the milling shrinkage just referred to, it should be noted that wool fabrics also show some shrinkage when merely wet with water and dried. This type of shrinkage, designated as relaxation shrinkage, is due to a release of the stretched condition of wool fiber resulting from the fabric manufacture. It usually amounts to 3 to 12% of the area and is thus much less important than the milling shrinkage.

The invention is illustrated in detail in the following examples in which proportions are expressed in parts by weight unless otherwise stated:

#### Example I

The polymer used in this example was prepared by hydrogenating in dioxane solution with 5 parts of Raney nickel catalyst 50 parts of an ethylene/carbon monoxide polymer containing ethylene and carbon monoxide in the mole ratio of 4.1:1, and 25 parts of anhydrous ammonia. The reaction temperature was 120° C. and the total pressure 167 atmospheres. After 5 hours, the product of the reductive-amination was a viscous straw-colored resin containing 76.41% C, 11.48% H, 2.82% total nitrogen (Dumas) and 1.02% amino nitrogen (Van Slyke). From these data it may be calculated that 17% of the carbonyl groups of the ethylene/carbon monoxide polymer were converted to amino groups and that 36% of the nitrogen present was in the form of primary amino nitrogen.

The above-described polyamine was dissolved in benzene to give a solution of 10% polymer concentration. Wool flannel fabric of plain weave, weighing about 5 ounces per square yard, was immersed and worked in this solution until thoroughly wet. After pressing to remove excess solution, the fabric retained about 100% by weight of solution. The impregnated fabric was dried in air, the air-dried fabric retaining about 10% by weight of polyamine, then dipped into a 10% aqueous formaldehyde solution, dried and heated at 125° C. for 15 minutes. After rinsing in soapy water and air-drying again it showed no appreciable discoloration and had an excellent soft hand substantially identical to that of the untreated fabric. The water rinse caused a relaxation shrinkage of about 5%. A hand-milling test as described above resulted in a shrinkage of only about 3%. In comparison, an untreated sample of the same fabric immersed in soapy water,

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rinsed and dried showing about 10% relaxation shrinkage and over 40% milling shrinkage when subjected to the same hand-milling test. A second hand-milling test applied to the same treated fabric produced no additional shrinkage but when applied to the untreated control caused an additional shrinkage of about 16%.

#### Example II

A polyamine was prepared by hydrogenating 50 parts of an ethylene/carbon monoxide copolymer containing ethylene and carbon monoxide in a mole ratio of 5.79:1 in the presence of 100 parts of anhydrous ammonia with 5 parts of Raney nickel catalyst and no solvent. The hydrogen pressure was 600 atmospheres and the temperature 150° C. After 15 hours, the reaction product was a straw-colored, soft, tacky resin containing 80.46% C, 13.18% H, 5.23% total nitrogen (Dumas) and 4.13% primary amino nitrogen (Van Slyke). From these data it may be calculated that 87% of the carbonyl groups were converted to amino groups and that 79% of the total nitrogen was present as primary amino nitrogen.

The above-described polyamine was dissolved in warm, dilute aqueous acetic acid and to the solution was added aqueous formaldehyde and sufficient water to give a solution containing 5% polyamine, 5% acetic acid and about 3% formaldehyde. This solution was applied to the wool flannel of Example I, as described in that example, the air-dried fabric retaining 8% by weight of polyamine. After heating at 120° C. for 15 minutes the fabric showed about 3.5% relaxation shrinkage and no additional shrinkage after 15 minutes hand-milling test. When the curing procedure was carried out by heating the treated fabric at 100° C. for 15 minutes, the fabric showed about 3% relaxation shrinkage and 4% felting shrinkage in the standard hand-milling test. The same grade of untreated (control) wool flannel under the same test procedure showed about 10% relaxation shrinkage and over 40% felting shrinkage.

When the formaldehyde was omitted from the formulation given above, the test fabric showed about 7% relaxation shrinkage and 26% additional felting shrinkage using the same test procedure.

#### Example III

A polyamine was prepared by hydrogenating a mixture of 50 parts of an ethylene/carbon monoxide copolymer containing ethylene and carbon monoxide in the mole ratio of 8.2:1 and 100 parts of anhydrous ammonia with 5 parts of a ruthenium-on-alumina catalyst containing 5% ruthenium by weight. The hydrogen pressure was 450 atmospheres and the temperature 250° C. After 15 hours, the reaction product was a hard, nontacky, colorless wax containing 82.49% C, 13.90% H, 2.85% total nitrogen (Dumas) and 1.92% primary amino nitrogen (Van Slyke). From these data it may be calculated that 70% of the carbonyl groups were converted to amino groups and that 67% of the total nitrogen was present as primary amino nitrogen.

The above described polyamine was dissolved in 8% aqueous acetic acid by warming to 90° C. The solution was cooled to about 60° C. and 37% aqueous formaldehyde was added with sufficient water to give a solution containing 5% polyamine, 5% acetic acid and about 3.5% formaldehyde. The solution was cloudy but did not precipitate on standing. Wool flannel of the grade used

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in Example I was immersed in the solution and worked until thoroughly wet, then squeezed to remove excess liquid, the fabric retaining about 150% by weight of solution. After air-drying, the treated fabric, which retained about 7.5% by weight of polymer, was cured by heating at 100° C. for 15 minutes. After rinsing with soapy water the fabric had an excellent soft hand. After extraction with tri-chloroethylene, the treated fabric showed a relaxation shrinkage of about 5%. After two consecutive hand-milling tests of 15 minutes each, it showed no appreciable change from the original area, whereas an untreated (control) fabric of identical grade showed a relaxation shrinkage of about 12% and additional felting shrinkages of 35% and 50%, respectively, after one and two hand-milling treatments.

#### Example IV

A polyamide containing secondary amino groups was prepared by heating a mixture of 60.7 parts sebacic acid, 31.0 parts diethylenetriamine and 40 parts methanol with stirring under nitrogen atmosphere, allowing the temperature to increase gradually as the methanol distilled through a short fractionation column. The temperature of the reaction melt increased gradually to 175° C. and was held at this point with continuous stirring for two hours, during which water was evolved and distilled from the reaction vessel. The fractionating column was removed to facilitate separation of the water and the temperature of the melt was increased slowly during an additional period of 2 hours to a final temperature of 208° C. The viscous reaction mass was cooled with slow stirring to about 100° C. and treated slowly with stirring with 200 parts of 10% aqueous acetic acid. The polyamine dissolved slowly to form a solution containing about 22% solids and having a pH of 5.6. To this solution was added sufficient aqueous formaldehyde and water to make up a solution containing 5% polymer and 3.5% formaldehyde. This solution was applied to wool fabric as in the preceding example. The treated fabric, containing 8-10% by weight of amino resin, was cured by heating at 120° C. for 15 minutes or at 100° C. for 30 minutes. It showed no noticeable discoloration, and exhibited about 7% relaxation shrinkage and about 7% felting shrinkage when subjected to the hand-milling test.

#### Example V

A polyamine was prepared by heating di(p-amino-cyclohexyl)methane with Raney nickel catalyst. At 170° C., rather vigorous evolution of ammonia began and continued with decreasing activity as the temperature of the reaction mixture was increased over a period of 2 hours to a final temperature of 315° C. The mixture solidified on cooling to a brittle, wax-like product.

The above described polyamine was dissolved in dilute acetic acid and the solution filtered to remove the catalyst, then treated with sufficient formaldehyde and water to make a solution containing 5% polyamine, 5% acetic acid and 3% formaldehyde. This solution was applied to wool flannel as described in the preceding examples, giving about 8% polymer retention in the fabric. The treated fabric after air-drying and curing at 120° C. for 20 minutes showed practically no discoloration, and a relaxation shrinkage of about 5%. After being subjected to a hand-milling test, the fabric showed an additional shrinkage of only 2%.

In addition to the polymers of the examples, there may be mentioned the partially aminated products obtained by catalytically hydrogenating resins having ketone groups in the presence of ammonia or amines (U. S. Patent 2,063,158); the reaction products of vinyl ketone polymers with ammonia or primary amine (U. S. Patent 2,122,707); the partial esterification products of polyacrylic or polymethacrylic acids with amino alcohols having hydrogen on the amino nitrogen; the polyamides or polyesters having intralinear secondary amino groups; the linear polyamines resulting from the condensation of diamines with evolution of ammonia; the products obtained by reacting ethylene/carbon monoxide copolymers with hydrazine; and the like.

Of the various amino resins suitable for use in this invention, those which give the best results as regards degree of shrinkproofing, absence of harshness and good color are the resins obtained by catalytically hydrogenating copolymers of carbon monoxide with aliphatic olefins such as ethylene, propylene, the butylenes, butadiene, and the like, or mixtures of these olefins, in the presence of ammonia or primary monoamines, for example, methylamine, propylamine, butylamine, aniline, cyclohexylamine, and the like. Of this class, the most satisfactory ones are the resins obtained from ethylene/carbon monoxide polymers, and in particular those in which the ethylene/carbon monoxide mole ratio is between 4:1 and 11:1, and having at least 70% of the carbonyl groups replaced by amino groups. The most economical, and therefore preferred, species in this group is that obtained by catalytically hydrogenating an ethylene/carbon monoxide polymer in the presence of ammonia and thus having two hydrogen atoms connected to the amino-nitrogen groups.

The amino polymer is applied to the wool as a solution, which may be either in an organic solvent, or in water if the polymer is soluble in water, or in a dilute acid. Any organic solvent substantially unreactive with the amino polymer and formaldehyde and non-injurious to the wool may be used, including methanol, ethanol, benzene, toluene, cyclohexane, trichloroethylene, and the like. Organic solvents have certain obvious disadvantages and it is therefore preferred to use an aqueous solution, if the polymer is soluble in water, or a dilute acid solution. Since strong acids, even when dilute, are corrosive and may damage the wool, the preferred acids are those having a dissociation constant below about  $5 \times 10^{-2}$ , such as formic, acetic, propionic, glycolic, oxalic, phosphoric, boric acids and the like, although stronger acids may be used with proper precautions. The preferred acid is acetic acid. The aqueous acidic solution need contain only as much acid as is necessary to dissolve the amino polymer which is generally between 0.2 and 10% acid depending upon the type of polymer used. The polymer itself is desirably present in sufficient concentration to impregnate the wool to the extent of 4 to 10% of its dry weight. A convenient range of polymer concentration in the impregnating solution is between 2 and 20% by weight, although more concentrated solutions can be used if desired.

The impregnating solutions should be free from insoluble materials (e. g., materials emulsified in aqueous acidic solutions) since these interfere with the shrink-proofing process and furthermore are partly or wholly removable by sub-

sequent mechanical treatments or solvent treatments.

Wool may be subjected to the shrinkproofing process of this invention in any desired form such as yarn, fabric or manufactured garments. The treatment results in wool which is substantially shrinkproof and remains so permanently. The shrinkproofing treatment described herein may also be applied in conjunction with and supplementary to other shrinkproofing treatment, e. g., with chlorine, sulfonyl chloride and the like.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A method of shrinkproofing wool which comprises contacting wool with (a) a solution of a synthetic basic amino polymer of molecular weight of at least 1000 having a main polymer chain and containing a plurality of amino groups in which hydrogen is attached to the amino nitrogen, said main polymer chain having at least 3 and not more than 50 carbon atoms to each amino group and said amino polymer being selected from the class consisting of amino polymers in which the amino nitrogen is an integral part of said main polymer chain, amino polymers in which the amino nitrogen is directly attached by a single bond to a carbon atom of said main polymer chain and amino polymers in which the amino nitrogen is linked directly by one aliphatic carbon atom to a carbon atom of said main polymer chain, and with (b) from 2% to 200% of formaldehyde, based upon the weight of said amino polymer, until said wool is impregnated with at least 4% of said amino polymer, based upon the original weight of the wool, removing any excess solution until said wool contains from 4% to 10% of said amino polymer, based upon the original weight of the wool, drying and maintaining the impregnated wool at a temperature between 20° to 200° C. until said amino polymer becomes insolubilized therein.

2. A method of shrinkproofing wool which comprises contacting wool with (a) a solution of a synthetic basic amino polymer of molecular weight of at least 1000 consisting of the reaction product of the reductive-amination of a polymer of a monoolefin containing from 2 to 4 carbon atoms with carbon monoxide, which amino polymer has a main carbon chain having amino nitrogen groups as lateral substituents with the nitrogen thereof directly attached to a least one hydrogen atom and to a carbon atom which is an integral part of said main carbon chain, and with (b) from 2% to 200% of formaldehyde, based upon the weight of said amino polymer, until said wool is impregnated with at least 4% of said amino polymer, based upon the original weight of the wool, removing any excess solution until said wool contains from 4% to 10% of said amino polymer, based upon the original weight of the wool, drying and maintaining the impregnated wool at a temperature between 20° and 200° C. until said amino polymer becomes insolubilized therein.

3. A method of shrinkproofing wool which comprises contacting wool with (a) a solution of a synthetic basic amino polymer\* of molecular weight of at least 1000 consisting of the reaction product of the reductive-amination of a polymer

of ethylene with carbon monoxide, which amino polymer has a main carbon chain having amino nitrogen groups as lateral substituents with the nitrogen thereof directly attached to at least one hydrogen atom and to a carbon atom which is an integral part of said main carbon chain, and with (b) from 2% to 200% of formaldehyde, based upon the weight of said amino polymer, until said wool is impregnated with at least 4% of said amino polymer, based upon the original weight of the wool, removing any excess solution until said wool contains from 4% to 10% of said amino polymer, based upon the original weight of the wool, drying and maintaining the impregnated wool at a temperature between 20° and 200° C. until said amino polymer becomes insolubilized therein.

4. A method of shrinkproofing wool which comprises contacting wool with (a) a solution of a synthetic basic amino polymer of molecular weight of at least 1000 consisting of the reaction product of the reductive-amination of a polymer of ethylene with carbon monoxide in which the mole ratio of ethylene to carbon monoxide is from 4:1 to 11:1, which amino polymer has a main carbon chain having at least 70% of the carbonyl oxygen replaced by amino nitrogen groups as lateral substituents with the nitrogen thereof directly attached to at least one hydrogen atom and to a carbon atom which is an integral part of said main carbon chain, and with (b) from 2% to 200% of formaldehyde, based upon the weight of said amino polymer, until said wool is impregnated with at least 7% of said amino polymer, based upon the original weight of the wool, removing any excess solution until said wool contains from 7% to 10% of said amino polymer, based upon the original weight of the wool, drying and maintaining the impregnated wool at a temperature between 80° and 150° C. until said amino polymer becomes insolubilized therein.

5. A shrinkproofed wool impregnated with the insolubilized reaction product of (a) from 4 to 10%, based upon the original weight of the wool, of a synthetic basic amino polymer of molecular weight of at least 1000 having a main polymer chain and containing a plurality of amino groups in which hydrogen is attached to the amino nitrogen, said main polymer chain having at least 3 and not more than 50 carbon atoms to each amino group and said amino polymer being selected from the class consisting of amino polymers in which the amino nitrogen is an integral part of said main polymer chain, amino polymers in which the amino nitrogen is directly attached by a single bond to a carbon atom of said main polymer chain and amino polymers in which the amino nitrogen is linked directly by one aliphatic carbon atom to a carbon atom of said main polymer chain, and of (b) from 2% to 200% of formaldehyde, based upon the weight of said amino polymer.

6. A shrinkproofed wool impregnated with the insolubilized reaction product of (a) from 4 to 10%, based upon the original weight of the wool, of a synthetic basic amino polymer of molecular weight of at least 1000 consisting of the reaction product of the reductive-amination of a polymer of a monoolefin containing from 2 to 4 carbon atoms with carbon monoxide, which amino polymer has a main carbon chain having amino nitrogen groups as lateral substituents with the nitrogen thereof directly attached to at least one hydrogen atom and to a carbon atom which is an integral part of said main carbon chain, and of (b) from 2% to 200% of formaldehyde, based upon the weight of said amino polymer.

7. A shrinkproofed wool impregnated with the insolubilized reaction product of (a) from 4 to 10%, based upon the original weight of the wool, of a synthetic basic amino polymer of molecular weight of at least 1000 consisting of the reaction product of the reductive-amination of a polymer of ethylene with carbon monoxide, which amino polymer has a main carbon chain having amino nitrogen groups as lateral substituents with the nitrogen thereof directly attached to at least one hydrogen atom and to a carbon atom which is an integral part of said main carbon chain, and of (b) from 2% to 200% of formaldehyde, based upon the weight of said amino polymer.

8. A shrinkproofed wool impregnated with the insolubilized reaction product of (a) from 7 to 10%, based upon the original weight of the wool, of a synthetic basic amino polymer of molecular weight of at least 1000 consisting of the reaction product of the reductive-amination of a polymer of ethylene with carbon monoxide in which the mole ratio of ethylene to carbon monoxide is from 4:1 to 11:1, which amino polymer has a main carbon chain having at least 70% of the carbonyl oxygen replaced by amino nitrogen groups as lateral substituents with the nitrogen thereof directly attached to at least one hydrogen atom and to a carbon atom which is an integral part of said main carbon chain, and of (b) from 2% to 200% of formaldehyde, based upon the weight of said amino polymer.

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