

Dec. 24, 1957

C. E. PARDO, JR.  
SHRINKPROOFING OF WOOL WITH EPOXY  
RESINS AND POLYALKYLENEIMINES  
Filed Sept. 18, 1956

2,817,602

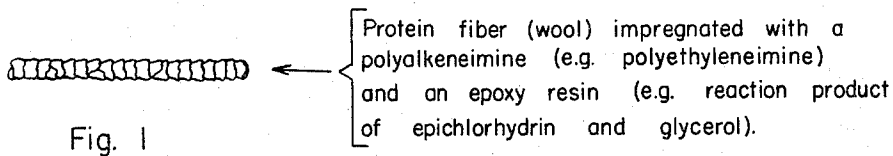
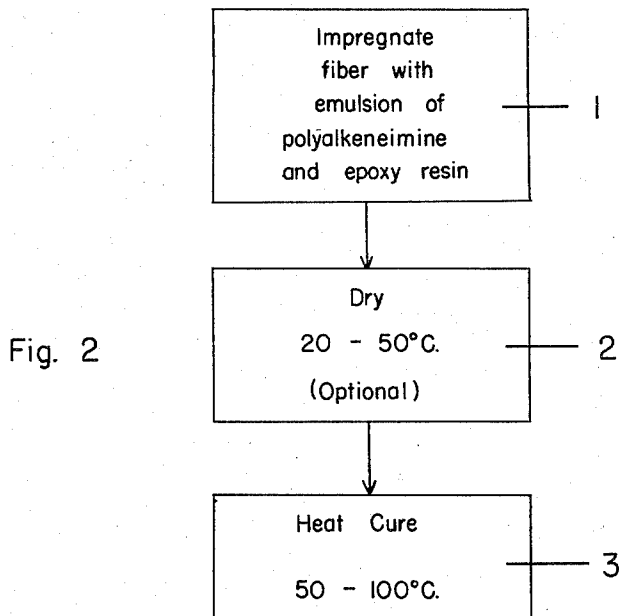


Fig. 1



Clay E. Pardo, Jr.  
INVENTOR.

BY *24 August*

1

2,817,602

## SHRINKPROOFING OF WOOL WITH EPOXY RESINS AND POLYALKYLENEIMINES

Clay E. Pardo, Jr., Albany, Calif., assignor to the United States of America as represented by the Secretary of Agriculture

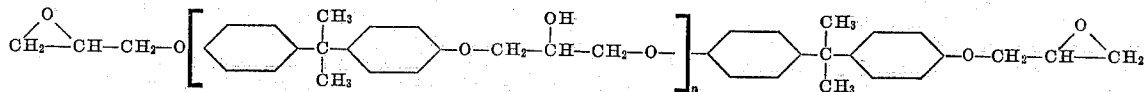
Application September 18, 1956, Serial No. 610,691

6 Claims. (Cl. 117-141)

(Granted under Title 35, U. S. Code (1952), sec. 266)

A non-exclusive, irrevocable, royalty-free license in the invention herein described, for all governmental purposes, throughout the world, with the power to grant sublicenses for such purposes is hereby granted to the Government of the United States of America.

This invention relates to processes for shrinkproofing and feltproofing proteinous fibers, especially wool. In particular, the invention is concerned with procedures



wherein the fiber is treated with an epoxy resin and a polyalkyleneimine and then cured with the application of heat whereby to produce a fiber which exhibits a marked resistance to shrinkage as compared with the original fiber. Further objects and advantages of the invention will be obvious from the description herein.

In the accompanying drawing,

Fig. 1 illustrates the protein fiber, and

Fig. 2 is a diagram of the process involved.

It is well known that laundering causes severe shrinkage of woolen textiles. This technical disadvantage seriously restricts the application of wool in the textile industry and much research has been undertaken in order to modify the natural fiber to improve its shrinkage properties. In general, known methods of treating wool to improve its shrinkage characteristics have the disadvantage that the hand of the fabric is impaired, or, if the amount of agent applied is limited to avoid impairment of the hand, the degree of shrinkage protection is relatively low.

It has now been found that if the wool is treated with an epoxy resin and a polyalkyleneimine the shrinkage characteristics of the fiber are drastically improved. The treated wool is almost completely shrinkproof under normal laundering procedures. The reason for the effectiveness of the process of this invention cannot be explained on a scientific basis. However, it is believed that the agents applied to the wool actually react therewith forming part of the protein molecule. This view is substantiated by the fact that the agents cannot be removed from the wool by washing with hot water or by laundering. Additional advantages of the process are that the treated wool is not impaired for its intended purposes. Thus its tensile strength and hand are not adversely affected.

In applying the process of this invention the wool is impregnated with an emulsion containing the epoxy resin and the polyalkyleneimine. The treatment is advantageously performed by immersing the wool in an excess of the emulsion or by applying the emulsion by spraying, brushing or other conventional application techniques. To assist in wetting the wool with the solution, the wool may be run through padding rolls or the like.

Although polyethyleneimine is preferred, one can use any other polyalkyleneimine. Typical examples are the polymers of: propylene imine; 1,2-butylene imine; 2,3-butylene imine; 2,2-dimethyl-ethylene imine; 2,2,3-tri-

2

methyl-ethylene imine; 2,2-dimethyl-3-propyl-ethylene imine; cyclohexylethylene imine; phenyl ethylene imine; etc. These compounds as well known in the art can be prepared, for example, by polymerizing the alkylene imine in the presence of a catalyst such as sodium bisulphite, hydrochloric acid, sulphuric acid, acetic acid, hydrogen peroxide, and so forth. Generally, it is preferred to use the polyalkylene imines which are at least partially soluble in water.

Regarding the epoxy resin constituent of the treating bath, one can use any of the known resins which contain epoxy radicals. As well known in the art, these resins may be prepared by condensing epichlorhydrin with a polyhydric alcohol or phenol, for example, ethylene glycol, diethylene glycol, glycerol, diglycerol, catechol, resorcinol, a trihydroxybenzene, a di(hydroxyphenyl) methane, a di(hydroxyphenyl) ethane, a di(hydroxyphenyl) propane, etc. A preferred type of epoxy resin is that prepared by condensing epichlorhydrin with 2,2-bis(parahydroxyphenyl) propane, often referred to in the industry as bisphenol-A. The structure of these resins is illustrated by the formula—

wherein  $n$  varies between zero and about 10, corresponding to a molecular weight about from 400 to 8,000.

The emulsion applied to the protein fibers in accordance with this invention contains as its principal ingredients the epoxy resin and the polyalkyleneimine. The total concentration of these agents is not critical and may be varied, for example from as low as about 0.1% to as high as about 10%. It is obvious that when the concentration of the agents is increased, more of these materials will be deposited on fiber and generally a greater degree of shrinkage protection will be afforded, assuming that in each case the fiber takes up the same amount of the liquid preparation. The relative proportions of polyalkyleneimine and epoxy resin has an important effect on the degree of shrinkproofing attained. In most cases a ratio of about 0.5 part to 5 parts of polyalkyleneimine per part of epoxy resin is preferred as yielding maximum shrinkproofing effect, maximum fastness of the treatment to washing, and maximum retention of whiteness. Where the proportion of polyalkyleneimine is substantially above 5 parts per part of epoxy resin, higher curing temperatures are required, the treated wool tends to develop a yellow color, and the deposited material has a lesser degree of fastness to washing. Where the proportion of polyalkyleneimine is below 0.5 part per part of epoxy resin, the degree of shrinkproofing is reduced.

In making up the treatment emulsion, the polyalkyleneimine is usually first dissolved in water and the epoxy resin is added and agitation applied to emulsify the epoxy resin in the solution. To prevent settling out of the epoxy resins, one may add a small proportion of a conventional emulsifying agent. For such purpose one may use agents such as the long chain alkyl sodium sulphates or sulphonates, long chain alkyl benzene sodium sulphonates, esters of sulposuccinic acid, etc., typical examples being sodium lauryl sulphate, sodium dodecane sulphonate, sodium alkyl ( $C_{10}$ - $C_{20}$ ) benzene sulphonate, sodium dioctylsulphosuccinate, etc. Preferably, agents of the non-ionic type are used, for example, the reaction products of ethylene oxide with fatty acids, polyhydric alcohols, alkyl phenols, and so forth. Typical examples of such agents are a polyoxyethylene stearate containing 20 oxyethylene groups per mol, a polyoxyethylene ether of sorbitan monolaurate containing 16 oxyethylene groups per mol, a polyoxyethylene ether of sorbitan monostearate con-

taining 20 oxyethylene groups per mol, a distearate of polyoxyethylene ether of sorbitol containing 40 oxyethylene groups per mol, iso-octyl phenyl ether of polyethylene glycol, and so forth. Cationic agents may also be used, for example long chain alkyl trimethyl ammonium chlorides, bromides, or methosulphates.

Although water is usually used as the sole solvent or diluent in the treating bath, one can use diluents containing water and organic water-soluble solvents such as methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, any of the isomeric butyl alcohols, etc.

After the fiber has been impregnated with the emulsion of epoxy resin and polyalkyleneimine as illustrated in Fig. 2, step 1, it is subjected to a heat curing treatment. This treatment as illustrated in Fig. 2, step 3, involves subjecting the impregnated material to a temperature of about 50 to about 100° C. to promote reaction between the epoxy resin and the imine and between these agents and the fiber thus to provide a permanent modification of the fiber. The time of cure will vary depending on such factors as the temperature selected, the chemical nature of the fiber being treated, the reactivity of the epoxy resin and imine selected and so forth. In general a cure time of about 15 to 120 minutes may be used. A preferred curing operation involves first drying the treated fiber at a temperature of about 20 to 50° C. as illustrated in Fig. 2, step 2, and then heating the fiber at 75 to 100° C. for 15 to 120 minutes to effect the cure.

After the textile material has been cured, it may be washed with water or laundered to remove excess agents which have not been bonded to the protein molecule. The textile material is then dried in the usual manner and is ready for use.

The proportion of epoxy resin and polyalkyleneimine bonded to the protein fiber may be varied widely by varying the concentration of these agents in the treatment liquid and the amount of this liquid taken up by the fiber. Usually these conditions are so chosen that the fiber takes up about from 0.1% to 10% of the weight of the epoxy resin and polyalkyleneimine. In general the greater the proportion of the agents taken up by the fiber, the greater will be the shrinkage protection afforded. It is also obvious that the degree of shrinkproofing obtained will vary depending on such factors as the original characteristics of the fiber, the type of epoxy resin and polyalkyleneimine chosen and so forth. In any particular situation the fiber may be subjected to pilot trials, applying different proportions of the chosen epoxy resin and polyalkyleneimine and selecting the conditions which give the desired degree of shrinkproofing.

It is to be noted that by the use of a combination of epoxy resin and polyalkyleneimine results are obtained which cannot be achieved by either of the agents alone. For example, if wool is treated solely with a polyalkyleneimine and then heat-cured a certain degree of shrinkproofing is obtained. However, treatment with both imine and epoxy resin gives better results as explained below: When wool is treated with the imine alone, the imine is not totally fast; about 30% of the imine is lost when the treated wool is subjected to washing in running hot water (55° C.) for one hour. However, when wool is treated with both imine and epoxy resin, these agents become firmly bonded to the fiber so that there is no loss of the agents by the same washing treatment. When the wool is treated with the imine alone a high curing temperature of about 120° C. is needed; this high temperature tends to cause yellowing of the wool. In the case of treatment with both epoxy resin and imine, a lower curing temperature is effective and a lesser time of cure is needed whereby discoloration of the wool does not occur. Another point is that the combination of epoxy resin and imine produces a higher degree of shrinkproofing than treatment with the imine alone. A further item is that when the wool is treated with the combination of epoxy

resin and imine, it can be subjected to conventional dyeing factors which involve extended immersion in a boiling dye bath. Under such conditions the dye bath does not extract any appreciable amount of the epoxy resin and imine from the fiber. Under the same conditions, however, wool treated with the imine alone will lose a great deal of its imine content and its shrinkage resistance will be impaired. It is further to be emphasized that treatment of wool with the epoxy resin alone yields no shrinkage improvement. For example, a sample of woolen cloth was impregnated with an aqueous emulsion containing 5% of an epoxy resin (produced by condensing epichlorhydrin with glycerol), then cured at 50° C. for 20 min. and 75° C. for 10 minutes. The wool showed an uptake of epoxy resin of 6%. On subjecting the treated cloth to a standard washing procedure it exhibited an area shrinkage of 36.1%, whereas a sample of untreated (control) wool under the same washing treatment gave an area shrinkage of 36%.

The process of this invention is particularly adapted for the treatment of wool but may also be applied to other proteinous fibers such as mohair, fibers from fleece-bearing animals other than sheep and goats, animal hair, silk, fibers made from proteins such as zein, casein, peanut protein, soybean protein, keratins, etc. The proteinous fiber may be in the form of actual fibers or may be in the form of threads, yarns, woven or knitted materials, garments, etc.

The invention is further demonstrated by the following examples which are given only by way of illustration but not limitation.

#### Example I

A. Forty grams of a 50% aqueous solution of polyethyleneimine (molecular weight about 20,000 to 30,000) was diluted to a volume of 350 ml. by addition of water. To this solution was added 10 grams of a commercial epoxy resin which is a reaction product of epichlorhydrin and glycerol. The resin is a liquid at ordinary temperature and has an epoxide equivalent of 140-165.

Enough water was added to bring the total volume to 500 ml. and the mixture was homogenized to produce an emulsion. This liquid, designated A, thus contained 4% of polyethyleneimine and 2% of epoxy resin. A portion of liquid A was diluted with an equal volume of water to produce a second liquid designated B, containing 2% polyethyleneimine and 1% of epoxy resin. Another portion of A was diluted with three times its volume of water to produce a third liquid, designated C, containing 1% polyethyleneimine and 0.5% epoxy resin.

The above liquids were padded onto swatches of woolen cloth under conditions that the cloth took up about 100% of its weight of liquid. The impregnated swatches were dried by heating for 20 minutes at 50° C., then cured by heating for 10 minutes at 75° C.

The uptake of treatment agents in the swatches treated with the respective emulsions were as follows:

| Sample. | Content of epoxy resin and imine, Percent (dry basis) |
|---------|-------------------------------------------------------|
| A.....  | 4.14                                                  |
| B.....  | 2.5                                                   |
| C.....  | 1.17                                                  |

Samples of the treated cloth were subjected to washing in running hot water (55° C.) for one hour. There was no measurable decrease in the resin-imine content of the samples.

B. The treated cloth samples and a sample of untreated cloth (control) were subjected to tests to measure their shrinkage characteristics. In these tests, the cloth samples were subjected to a laundering operation in which the cloth was violently agitated in a 0.5% solution of sodium

5

oleate at 40° C. with a cloth to solution ratio of 1 to 50, the area of the cloth being measured before and after laundering. This test was repeated three times. The results obtained are set forth below:

| Sample       | Content of epoxy resin and imine, Percent | First washing, area shrinkage, Percent | Second washing, area shrinkage, Percent | Third washing, area shrinkage, Percent |
|--------------|-------------------------------------------|----------------------------------------|-----------------------------------------|----------------------------------------|
| A.....       | 4.14                                      | 1                                      | 1                                       | 2                                      |
| B.....       | 2.5                                       | zero                                   | zero                                    | 1                                      |
| C.....       | 1.17                                      | 5.9                                    | 18.5                                    | 28.7                                   |
| Control..... | zero                                      | 38                                     | 65                                      | 70                                     |

#### Example II

Samples of woolen cloth treated as described in Example I, part A, were subjected to dyeing tests as follows:

A series of dye baths were prepared, each containing:

0.1 gram National Fast Wool Red GL, 150%

1 gram Glauber's salt

1 gram sodium bisulphate

500 ml. water

Samples of the treated wool (A, B, and C) and a sample of untreated wool (control) were dyed in these baths using the following technique in each case: A 10-gram sample of wool was placed in 500 ml. of the dye bath which was brought to a boil in 20 minutes and held at the boil for 70 minutes. The cloth sample was then removed from the dye bath, rinsed in water and conditioned for 30 minutes in a 1% solution of sodium acetate to neutralize the acidity of the dye bath.

It was observed that the treated samples (A, B, and C) were dyed a slightly deeper shade of red than the control (untreated) sample.

The dyed samples were then each subjected to a single laundering to ascertain their shrinkage characteristics, using the procedure set forth in Example I, part B. The following results were obtained:

| Sample       | Area shrinkage, Percent |
|--------------|-------------------------|
| A.....       | 1.7                     |
| B.....       | 1.8                     |
| C.....       | 27.0                    |
| Control..... | 39.4                    |

#### Example III

A series of aqueous emulsions were prepared containing varying amounts of polyethyleneimine (molecular weight about 20,000-30,000) and a commercial epoxy resin which is a reaction product of epichlorhydrin and 2,2-bis(parahydroxyphenyl) propane. This resin is a liquid at ordinary temperatures, has a viscosity of 50 to 150 poises at 25° C. and an epoxide equivalent of 175-210. To assist in forming the emulsion there was added 10% (based on the weight of epoxy resin) of the iso-octyl phenyl ether of polyethylene glycol ("Triton X-100").

The compositions of the different emulsions are set forth below:

| Emulsion | Total concentration of polyethyleneimine and epoxy resin, Percent | Ratio of polyethyleneimine to epoxy resin |
|----------|-------------------------------------------------------------------|-------------------------------------------|
| A.....   | 5.0                                                               | 5:1                                       |
| B.....   | 2.5                                                               | 5:1                                       |
| C.....   | 5.0                                                               | 2:1                                       |
| D.....   | 2.5                                                               | 2:1                                       |
| E.....   | 5.0                                                               | 0.5:1                                     |
| F.....   | 2.5                                                               | 0.5:1                                     |
| G.....   | 5.0                                                               | 0.2:1                                     |
| H.....   | 2.5                                                               | 0.2:1                                     |

6

The above emulsions were padded onto swatches of woolen cloth under conditions that the cloth took up about 100% of its weight of the emulsion. The impregnated swatches were dried by heating for 20 minutes at 50° C. then cured by heating 60 minutes at 100° C.

The cured wool samples were then subjected to laundering under the conditions described in Example I, part B, and the area of the samples determined before and after laundering. The results obtained are set forth below:

| Sample           | Uptake of polyethyleneimine and epoxy resin, Percent | Ratio of polyethyleneimine to epoxy resin | Area shrinkage, Percent |
|------------------|------------------------------------------------------|-------------------------------------------|-------------------------|
| A.....           | 5.2                                                  | 5:1                                       | zero                    |
| B.....           | 2.3                                                  | 5:1                                       | zero                    |
| C.....           | 5.3                                                  | 2:1                                       | zero                    |
| D.....           | 2.7                                                  | 2:1                                       | zero                    |
| E.....           | 9.4                                                  | 0.5:1                                     | 1.0                     |
| F.....           | 5.9                                                  | 0.5:1                                     | 0.2                     |
| G.....           | 10.1                                                 | 0.2:1                                     | 16.9                    |
| H.....           | 5.7                                                  | 0.2:1                                     | 14.5                    |
| I (control)..... | none                                                 | none                                      | 40.0                    |

#### Example IV

A series of aqueous emulsions were prepared containing varying amounts of polyethyleneimine (molecular weight about 20,000-30,000) and a commercial epoxy resin which is a reaction product of epichlorhydrin and glycerol. This resin is a liquid at ordinary temperatures and has an epoxide equivalent of 140-165.

The compositions of the different emulsions are set forth below:

| Emulsion | Total concentration of polyethyleneimine and epoxy resin, percent | Ratio of polyethyleneimine to epoxy resin |
|----------|-------------------------------------------------------------------|-------------------------------------------|
| J.....   | 5.0                                                               | 5:1                                       |
| K.....   | 2.5                                                               | 5:1                                       |
| L.....   | 5.0                                                               | 2:1                                       |
| M.....   | 2.5                                                               | 2:1                                       |
| N.....   | 5.0                                                               | 0.5:1                                     |
| O.....   | 2.5                                                               | 0.5:1                                     |
| P.....   | 5.0                                                               | 0.2:1                                     |
| Q.....   | 2.5                                                               | 0.2:1                                     |

The above emulsions were padded onto swatches of woolen cloth under conditions that the cloth took up about 100% of its weight of the emulsion. The impregnated swatches were then dried by heating for 20 minutes at 50° C., followed by curing at 100° C. for 60 minutes.

The cured wool samples were then subjected to laundering under the conditions described in Example I, part B, and the area of the samples determined before and after laundering. The results are tabulated below:

| Sample           | Uptake of polyethyleneimine and epoxy resin, percent | Ratio of polyethyleneimine to epoxy resin | Area shrinkage, percent |
|------------------|------------------------------------------------------|-------------------------------------------|-------------------------|
| J.....           |                                                      | 5:1                                       | 0.6                     |
| K.....           | 1.                                                   | 5:1                                       | 4.3                     |
| L.....           |                                                      | 2:1                                       | zero                    |
| M.....           | 1.2                                                  | 2:1                                       | 2.5                     |
| N.....           | 4.2                                                  | 0.5:1                                     | zero                    |
| O.....           | 1.6                                                  | 0.5:1                                     | 7.0                     |
| P.....           | 3.3                                                  | 0.2:1                                     | 6.4                     |
| Q.....           | 2.0                                                  | 0.2:1                                     | 18.0                    |
| R (control)..... | none                                                 | none                                      | 40.0                    |

Having thus described the invention, what is claimed is:

1. A process for shrinkproofing protein fibers which comprises impregnating the fibers with an emulsion containing a polyalkyleneimine and an epoxy resin and

thereafter curing the impregnated fiber at a temperature from about 50 to about 100° C.

2. A process for shrinkproofing wool which comprises impregnating wool with an emulsion containing polyethyleneimine and an epoxy resin and thereafter curing the impregnated fiber at a temperature from about 50 to about 100° C.

3. A process for shrinkproofing wool which comprises impregnating wool with an emulsion containing polyethyleneimine and an epoxy resin, the latter being a reaction product of epichlorhydrin and a 2,2-di(hydroxyphenyl) propane, thereafter curing the impregnated wool at a temperature of about 50° to about 100° C.

4. A process of shrinkproofing wool which comprises impregnating wool with an emulsion containing polyethyleneimine and an epoxy resin, the latter being a reaction product of epichlorhydrin and glycerol, thereafter curing the impregnated wool at a temperature of about 50 to about 100° C.

5. A protein fiber impregnated with a polyalkyleneimine and an epoxy resin.

6. Heat-cured polyalkyleneimine and epoxy resin-impregnated wool, wherein the content of polyalkyleneimine and epoxy resin is essentially non-extractable by hot water and laundering media, and which exhibits on laundering a shrinkage substantially less than that of the original wool.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

|           |                   |               |
|-----------|-------------------|---------------|
| 2,512,996 | Bixler            | June 27, 1950 |
| 2,553,696 | Wilson            | May 22, 1951  |
| 2,682,515 | Naps              | June 29, 1954 |
| 2,723,924 | Mackinney         | Nov. 15, 1955 |
| 2,790,736 | McLaughlin et al. | Apr. 30, 1957 |

##### OTHER REFERENCES

"Application of Some Epoxide Resins in the Plastic Industry," Narracott, British Plastics, October 1951.

"Curing Agents for Epoxy Resins," Rouse et al., Official Digest, November 1953.