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3,490,938

## ELECTROCONDUCTIVE FLOCK

Merwin Frederick Hoover, Bethel Park, and Robert O. Carothers, Coraopolis, Pa., assignors, by mesne assignments, to Calgon Corporation, a corporation of Delaware

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U.S. Cl. 117—100

6 Claims

### ABSTRACT OF THE DISCLOSURE

New electroconductive flocking fibers are disclosed, employing polymers of diallyl quaternary ammonium compounds to form an electroconductive coating.

### BACKGROUND OF THE INVENTION

This invention relates to flocked fabrics and methods of making them; in particular it relates to rendering textile flocking materials more suited for electrostatic flocking by increasing their surface conductivity through the use of certain polymers.

Plush fabrics or similar materials are made by passing an adhesive-coated backing through an electrostatic field into which is introduced a quantity of short fibers, known as "flock," having an electrostatic charge. Under the influence of the electrostatic field, the flock (i.e. fibers on the order of  $\frac{1}{16}$ – $\frac{1}{4}$  inch) are directed onto the adhesive in an orientation perpendicular to the backing. Under proper control, this process can produce a uniform coating of perfectly aligned, closely set fibers even on rounded contours. See the reference to this process in Chemical Engineering, Jan. 17, 1966, page 87. See also U.S. Patents 3,203,821 and 2,715,585 and "Flocking," Special Edition No. 2 of Bayer Farben Review, a publication of the Dye-stuffs Sales Division of Farbenfabriken Bayer AG, Leverkusen, Germany.

The ability of the flock to achieve maximum polarity is critical to its alignment with the lines of force of the field, and therefore to its orientation with respect to the backing. At maximum polarity, the charges at the ends of the fibers are as strong as possible and as far apart as possible under the circumstances. A fiber having a charge of given strength may respond to the electrostatic field by aligning itself in the field with varying resolution depending on the distribution of the charge throughout its length. The distribution of the charge or the polarity, i.e. the relative concentrations of the charge at the ends of a given flock unit, is strongly influenced by the conductivity of the flock, particularly on its surface. The surface of the flock should be uniform with respect to conductivity; otherwise there will be minor poles of relatively positive and negative areas at points other than on the ends of the flock. The minor poles and consequently irregular field around the individual flock are likely to cause a poor response or misalignment of the fiber with respect to the flocking field.

In addition to polarization or alignment, conductivity is also important to the acceptance of a charge. When the flock is initially introduced to the field, it must be able to accept a full charge immediately, and a relatively high conductivity is beneficial in this respect. This is an important factor because the introduction of large quantities of flock fibers to the field is a difficult process to control, and the maximum charge must be accepted by the fibers under even relatively adverse conditions.

It also may be observed that there are great variations in conductivities, and hence the various responses outlined above, from one kind of fiber to another and even from lot to lot of a given type of fiber. The response of the

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flock also fluctuates with the relative humidity of the atmosphere in which the flocking operation is performed. Variable responses due to humidity are caused by the relative difficulty of placing a charge on the flock and the dissipation of it from the flock into the atmosphere under more humid conditions.

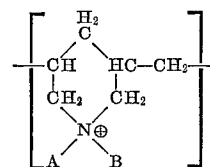
It is also a known disadvantage of fibers having relatively poor conductivity that the charge is only slowly dissipated after impingement into the adhesive-coated substrate. As a result, fibers approaching the newly impinged fibers are repelled or deflected so that they have a tendency to strike the adhesive at an angle depending on the intensity of the repelling force. Fibers of high conductivity are immediately drained of their charge and, other factors being optimum, will form a very even, upright, parallel product.

There are some important fibers which are limited in their use because of their lack of any significant conductive properties. Perhaps most notable of these is polypropylene, a fiber which otherwise has many properties desirable for flocking, such as strength and ready availability. Attempts have been made to coat such fibers with various salts to render them conductive. However, due partly to the fact that inorganic salts generally tend to particulate and separate into crystals upon drying, a continuous conductor is not formed on the surface by such materials.

### SUMMARY OF THE INVENTION

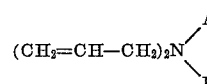
We have found that certain polymeric materials, to be described further herein, are capable of forming a continuous electroconductive surface on flocking fibers, overcoming all of the problems due to insufficient or uneven conductivity described above, and providing many benefits. The use of flock of our invention in conventional electrostatic flocking processes and machines results in a uniform, well-aligned product. Our invention is useful for any kind of fiber on which a film may be formed, including polypropylene and glass as well as the more conventional textile fibers.

The polymers we employ in our invention are of the general type disclosed by Butler in U.S. Patent 3,288,770, although several of the specific polymers we may employ are not contemplated in that disclosure. The polymers we employ have repeating units of the general formula:



where A is lower alkyl (up to 4 carbon atoms) and B is selected from the group consisting of lower alkyl,  $\beta$ -propionamido, carboxymethyl, and fatty alkyl groups of up to 18 carbon atoms. Where fatty alkyl groups are used, those having 8–18 carbon atoms are preferred.

For convenience, the polymers of Butler will be referred to herein as the diallyl quaternary ammonium polymers. They are made in accordance with the methods described by Butler in the above U.S. patent, from diallyl quaternary ammonium monomers of the formula

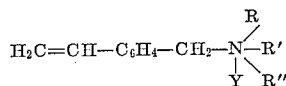


by a suitable polymerization method such as with a redox system or thermal peroxide initiators. The anion associated with the diallyl monomers used to prepare the polymers of our invention is chloride.

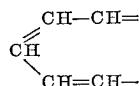
We do not intend to be limited to homopolymers however. Copolymers of diallyl quaternary ammonium salts can be made with each other and with copolymerizable monomers, especially monoethylenically unsaturated monomers, such as acrylamide and other acrylic monomers, for example. See Schuller & Thomas U.S. Patent 2,923,701. The diallyl quaternary moiety of the copolymers should constitute at least 90% of the copolymer by weight for best results. Other copolymerizable monomers which are useful in addition to acrylamide fall into several groups, (a) through (c):

(a) Monomers such as N-substituted acryl amides disclosed in British Patent 788,079 as being useful in making antistatic agents for synthetic fibers. Examples are N-( $\beta$ -diethylamino - ethyl) - methacrylamide, N-( $\gamma$ -dimethylamino - propyl) - methacrylamide, N-( $\gamma$ -diethylamino - propyl) - methacrylamide, N-( $\beta$ -piperidinoethyl) - methacrylamide, N-( $\beta$ -dimethylamino - ethyl) - acrylamide, N-( $\beta$ -diethylamino - ethyl) - acrylamide, and N-( $\gamma$ -dimethylamino - propyl) - acrylamide, N-( $\beta$ -dimethylamino - ethyl) - methacrylamide, N-( $\beta$ -morpholinethyl) - methacrylamide, N-( $\gamma$ -piperidino-propyl)-methacrylamide and N-( $\gamma$ -hexamethylene-amino-propyl)-methacrylamide;

(b) Vinyl benzyl monomers of the general formula

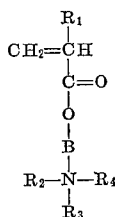


wherein R, R' and R'' each represents individually a monovalent radical selected from the group consisting of  $\text{CH}_2\text{OHCH}_2-$ ;  $\text{CH}_3\text{CHOHCH}_2-$ ;  $\text{CH}_2\text{OHCHOHCH}_2-$ ; and alkyl, aryl, cycloalkyl, and arylalkyl hydrocarbon radicals, and R, R' and R'' collectively represent the trivalent radical of the formula:



wherein, the three valences are attached to the nitrogen atom, the said R groups containing a total of not more than 12 carbon atoms in the sum of the constituent radicals, such as are discussed in Silvernail & Zembal U.S. Patent 3,011,918.

(c) Monomers such as are disclosed and discussed in Hayek U.S. Patent 2,741,568, of the general formula



where R is a member of the class consisting of hydrogen, methyl and ethyl radicals, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are alkyl radicals of from 1 to 4 carbon atoms, and B is a saturated bivalent hydrocarbon radical of from 1 to 4 carbon atoms.

Any polymerizable (monoethylenically unsaturated) quaternary ammonium compounds, such as trialkyl ammonium salts of amino ethyl acrylates and methacrylates, N-(trialkyl amino alkyl) acrylamides, polyvinyl pyridine quaternaries, etc., are also useful as monomers in our invention. See, for example, the disclosure of U.S. Patent 3,264,137.

The preferred polymer is a homopolymer of dimethyl diallyl ammonium chloride, which is linear and water soluble. It may be cross linked if a permanently insoluble conductive surface is desired, by incorporating a cross-linkable comonomers such as acrylamide, N-methylol-acrylamide, diacetoneacrylamide, etc. into the copolymer polymerization mixture in amounts up to about 10% or less by weight. Very small amounts of N,N'-methylene

bisacrylamide may be used in the monomer mix to create a branched or cross-linked product.

A film of any of the above polymers may be deposited on the fiber by spraying, dipping, or any other method of depositing from a solution to be followed preferably by drying. A very thin film of the polymer is sufficient to achieve significant improvements in the various factors affected by conductivity. The treatment may take place in the tow or after the flock is cut.

A preferred method of placing the film on the flock is to pass the tow through a solution of the polymer, dry the tow, and cut or chop the tow into small segments.

A two percent solution of the homopolymer of dimethyl diallyl ammonium chloride has a viscosity which is handy to work with if dipping is to be the method of application. Generally the thickness of the applied film is immaterial, and great variations in thickness are tolerable. Concentrations greater than 10% will be operable but inconvenient to use.

Our polymers are compatible with commercial conductive treatments such as Catanac SN and Leomine KP, and other so-called antistatic additives. Catanac SN, a product of American Cyanamid Co. is stearamidopropyl-dimethyl  $\beta$ -hydroxyethyl ammonium nitrate.

We have tested the conductivity of our treated fiber under standardized conditions as follows: The fiber tow sample is washed or scrubbed to remove any extraneous sizing or like materials, dried and weighed. It is then dipped in the subject polymer solution, wrung, and dried by hanging in a room under ambient conditions. The tow is then cut into approximate flock size ( $\frac{1}{16}$  inch- $\frac{1}{4}$  inch) and left to stand for conditioning in a constant known humidity. Still under the same humidity and temperature conditions, a weighed quantity, usually one gram, is placed in a pressure cylinder equipped with electrodes similar to the Textometer described in FIG. 18 of the publication "Flocking" previously referred to. Resistivity readings are taken of the treated flock compressed between the electrodes at a pressure of 200 pounds.

Tables I and II show the results of such tests on nylon (27 denier) and polypropylene fibers. In each test, after treatment with the respective concentration of a homopolymer of dimethyl diallyl ammonium chloride and drying as outlined above, the flock was conditioned at the noted relative humidity and 75° F. before being compressed at 200 pounds per square inch and measured for conductivity.

TABLE I.—NYLON FIBERS

|                         | Grams polymer per cm. <sup>2</sup> nylon | Resistance at 56% rel. hum. in ohms |
|-------------------------|------------------------------------------|-------------------------------------|
| Polymer conc., percent: |                                          |                                     |
| 0.....                  | .....                                    | 2.8×10                              |
| 0.5.....                | 1.90×10 <sup>-6</sup>                    | 1.5×10 <sup>8</sup>                 |
| 1.5.....                | 5.86×10 <sup>-6</sup>                    | 3.7×10 <sup>8</sup>                 |
| 3.0.....                | 2.49×10 <sup>-5</sup>                    | 1.5×10 <sup>9</sup>                 |
| 5.0.....                | 5.01×10 <sup>-5</sup>                    | 4.0×10 <sup>9</sup>                 |

TABLE II.—POLYPROPYLENE FIBERS

|                         | Grams polymer per gram fiber | Resistance 15 51% rel. hum. in ohms |
|-------------------------|------------------------------|-------------------------------------|
| Polymer conc., percent: |                              |                                     |
| 0.....                  | .....                        | 6.5×10 <sup>8</sup>                 |
| 0.5.....                | 9.13×10 <sup>-3</sup>        | 3.7×10 <sup>7</sup>                 |
| 1.0.....                | 1.55×10 <sup>-2</sup>        | 4.4×10 <sup>7</sup>                 |
| 1.5.....                | 2.16×10 <sup>-2</sup>        | 7.2×10 <sup>7</sup>                 |
| 3.0.....                | 5.10×10 <sup>-2</sup>        | 1.2×10 <sup>8</sup>                 |
| 5.0.....                | 1.24×10 <sup>-1</sup>        | 3.2×10 <sup>8</sup>                 |

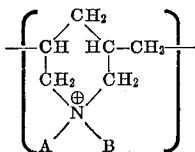
We do not intend to be limited to the above specific examples and illustrations.

We claim:

1. A synthetic flocking fiber having a coating comprising an electroconductive polymer of 3,5 methylene N,N dimethyl piperidinium units.

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2. A synthetic flocking fiber comprising a fiber having thereon a film of electroconductive polymer comprising at least 90% by weight repeating units of the formula



where A is an alkyl group of up to 4 carbon atoms and B is A, carboxymethyl,  $\beta$ -propionamido, or a fatty alkyl group of up to 18 carbon atoms.

3. Flocking fiber of claim 2 in which up to 10% by weight of the electroconductive polymer comprises repeating units derived from acrylamide, N-substituted acrylamides, and monoethylenically unsaturated quaternary ammonium monomers.

4. Fiber of claim 2 in which the fiber is polypropylene.

5. Fiber of claim 2 in which the fiber is nylon.

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6. Flocking fiber of claim 2 in which the polymer is substantially a homopolymer of dimethyl diallyl ammonium chloride.

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WILLIAM D. MARTIN, Primary Examiner

U.S. Cl. X.R.

117—4, 17, 138.8, 139.5

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,490,938

January 20, 1970

Merwin Frederick Hoover et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, Table I, last column, line 1 thereof, " $2.8 \times 10$ " should read --  $2.8 \times 10^9$  --; same column 4, Table II in the heading "Resistance 51% rel. hum. in ohms" cancel "15" and insert -- at --.

Signed and sealed this 23rd day of February 1971.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, J

Commissioner of Paten