Patented June 22, 1948 2,443,782

UNITED STATES PATENT OFFICE

2,443,782

TEXTILE MATERIAL OF COMPARATIVELY LOW ELECTRIC RESISTANCE AND METHOD OF PRODUCING THE SAME

Kenneth H. Barnard, Short Hills, N. J., Jayson C. Balsbaugh, Newton, Mass., and Melville J. Blackwood, Maplewood, N. J., assignors to Pacific Mills, Boston, Mass., a corporation of Massachusetts

No Drawing. Application April 7, 1944, Serial No. 530,050

10 Claims. (Cl. 117—160A)

1

Our invention relates to fibrous textile material, such as cloth, yarns or raw stock, permanently loaded with a finely divided electrically conductive substance, preferably a ground carbonaceous substance such as carbon black or graphite, and to the method of producing the same. Our treated material has a resistance in ohms $\frac{1}{10,000}$ to $\frac{1}{1,000,000}$ of the resistance of the same material in a dry untreated state and a correspondingly increased conductance.

The object of the invention is to provide such an electrically conductive fibrous material, which has many uses.

Such material, in sheet form, may be used to prevent or inhibit the generation and/or the accumulation of static electricity in articles from which the discharge of sparks might cause serious explosions, as for example, transmission belts and shoes in industrial plants which manufacture explosives, shoes in hospital operating rooms where there are explosive anaesthetic fumes, and in the form of sheets or yarns in tires on trucks carrying gasoline or other explosives, in hose carrying gasoline and in many like situations.

A preferred method of producing such electrically conductive material is as follows:

Fibrous material is first substantially freed of all impurities, as by boiling, bleaching and thoroughly washing, although this is not necessary in all cases.

The fibrous material is impregnated with a cationic agent of positive electrical charge. The cationic material may be, for example, an amine compound, an ammonium compound, or a sulfonium compound or a phosphonium compound or the like. We have obtained very good results with tetra alkyl quaternary ammonium halides and particularly with cetyl dimethyl benzyl ammonium chloride. By this impregnation, the fibers are given a positive electric charge whereby they have an affinity for the conductive substance, which is electro-negatively charged and with which the textile material is to be loaded.

The maximum amount of cetyl dimethyl benzyl ammonium chloride on a dry basis adsorbed by cellulose fabric is about 0.75%, that is, 3% of a water dispersion of 25% concentration. We have found that the adsorption of the cationic agent on cellulose is practically constant and that the amount reacted does not depend upon the concentration, providing sufficient is available. The concentration only affects the rate of reaction, so for practical operating speeds we use 2% of the original water dispersion of cetyl dimethyl benzyl ammonium chloride based on the total weight of the impregnating bath.

2

After such impregnation, the material is squeezed to about 100% absorption of solution and dried.

The fibrous material is then impregnated with a stabilized aqueous dispersion of an electrically conductive substance of negative charge. We prefer finely-divided carbonaceous substances, such as colloidal carbon black or graphite, as such conductive substances.

We prefer, as the stabilizing agent, a polymerized sodium salt of alkyl naphthalene sulfonic acid (in which the alkyl groups are limited to short chain groups). We use 4% to 15% of stabilizing agent according to the particle size of the carbon black. For example, if the black is comparatively fine, the diameter of its particles averaging 0.015 to 0.0175 micron, we have found that 10% to 15% of the polymerized sodium salt of alkyl naphthalene sulfonic acid, based on the weight of the black, should be dissolved in the water in which the black is to be dispersed, and if the black is coarser, its particle diameter averaging about 0.028 micron, we use 4% to 6%. We have found that the carbon black in the mixture is largely in clusters of which the diameters vary from the ultimate particle size of the black to a maximum of 30 microns.

The mixture of stabilizing agent, carbon black and water is ground in a pebble or colloid mill until the clusters of carbon black are broken up so that the diameter of substantially all of them is less than 12 microns. The stabilizing agent increases the negative electric charge normally found on carbon black or graphite in a water dispersion so that this charge will keep the black particles from undue coalescing after they have once been dispersed by mechanical action of the pebble or colloid mill.

We have found that when the fabric is impregnated with this mixture the clusters of black, being less than 12 microns in diameter, penetrate between the fibers, which are spaced apart from 3 to 12 microns, and become permanently imbedded in the fabric by the agglomerating action of the positively charged cationic agent, which increases the size of the clusters so that they are larger than the interfiber spaces and are thus imprisoned in the fabric.

The fabric is given several washes in warm water whereby the excess carbon black covering the outer surfaces of the fabric and the not truly adsorbed particles of black are washed off.

The impregnated fabric is squeezed and then

dried. This drying operation further fixes the adsorbed black so that it is effectively and permanently fixed on and between the fibers. By "permanently fixed" we mean that the adsorbed black is not removed by water or solvent washes.

According to our research the operation is as follows: The fibers of the material, normally negative in electric charge, are made positive by the cationic agent. The carbonaceous substance and the stabilizing agent, in aqueous dispersion, are ground in water until substantially all of the clusters of the substance are reduced to less than 12 microns in diameter. The stabilizing agent increases the negative charge of the particles of the carbonaceous substance so that they are mutually repellent and thereby assists in inhibiting the coalescence of the particles and clusters. When the material is soaked in the dispersion, the clusters penetrate between its fibers. The cationic agent reduces the negative charge, or neutralizes it, on some of the carbonaceous particles so that the particles, not being so completely of the same charge, attract one another and agglomerate into clusters which are so large that they are imbedded in between the fibers of the fabric and are not dislodged in normal use. The material thereby becomes permanently loaded with the carbonaceous substance to an amount, if desired, up to 10% of the weight of the dry untreated fabric according to the amount of the carbonaceous substance in the impregnating dispersion and the degree of discharge of the particles.

The impregnated fibrous material may be starched, dried and calendered if certain finishes or hand are desired.

The following examples are illustrative of preferred methods according to our invention.

Example 1.—A cotton cloth (38½" 64 x 60—5.35 yards per pound) thoroughly cleaned by boiling, bleaching and washing is treated with a hot solution of 1% acetic acid to insure that the cloth is not alkaline. It is soaked in a 2% aqueous solution of cetyl dimethyl benzyl ammonium chloride for five minutes at 100° F., with constant agitation. The cloth is squeezed to contain about its own weight of solution and dried until dry to the touch.

We prepare an aqueous dispersion of carbon black by grinding in a ball mill a mixture in water of carbon black, of an average particle diameter of about .016 micron, and of 10% of a polymerized sodium salt of alkyl naphthalene sulfonic acid to the weight of the black until the diameters of substantially all of the clusters of carbon black are less than 12 microns.

The cloth, which has been treated with cetyl dimethyl benzyl ammonium chloride, is immersed with agitation in a 5% aqueous dispersion of this mixture at about 100° F. for five minutes, thereby thoroughly soaking the cloth with the dispersion. It is washed in warm water to remove loose carbon black, squeezed and dried.

We prefer carbon black of small particle size of an average diameter of .015 to .0175 micron because the electrical conductivity of carbon black in general increases as the particle size diminishes.

Example 2.—A light weight rayon cloth is cleaned of spinning oils and extraneous materials by washing in hot soap and soda and rinsing in water to remove all impurities by well known methods. The cloth is treated with 1% acetic acid to acidify it. It is then treated with a 1% solution of cetyl dimethyl benzyl ammonium chloride for 15 to 20 minutes in a long bath where the ratio of liquor to goods is kept at about 30 to 1. The cloth is squeezed to remove excess liquor and dried. The cloth is run in a bath of the same dispersion of carbon black as in Example 1, in which there are 30 parts of liquor to 1 part of cloth, for 5 minutes to completely wet the cloth and cause it to adsorb the particles of black. The cloth is washed in four warm water washes to remove excess black, then squeezed and dried.

Example 3.—A light weight cotton cloth is boiled and washed in the usual manner to thoroughly clean it. It is treated with 2% acetic acid in a padder by dipping and squeezing in the usual manner. It is padded with 5% cetyl dimethyl benzyl ammonium chloride by dipping, squeezed, and dried at high speed as in the usual method for finishing cotton cloth. The cloth is then run back and forth for 10 minutes through a jig containing a bath of 10% graphite, in place of carbon black, dispersed with polymerized sodium salt of alkyl naphthalene sulfonic acid, as described in Example 1. The cloth is washed with several washes, squeezed and dried in a continuous manner as in cotton finishing.

Example 4.—A skein of 22's cotton yarn of normal twist, about twenty turns to the inch, is immersed in a 2% solution of cetyl dimethyl benzyl ammonium chloride at 100° F. in which the weight ratio of liquor to yarn is approximately 200 to 1. The skein is turned and moved continuously to agitate the liquor for 15 minutes. The skein is removed from the liquor and centrifuged to remove excess solution and then dried at 220° F. until dry to the touch. It is then immersed in a bath at 100° F. of a 5% dispersion of carbon black, made according to the method set forth in Example 1, in which the ratio of liquor to skein weight is approximately 200 to 1. The skein is moved continuously in the bath for 15 minutes. It is then washed in four rinse waters at room temperature, centrifuged and dried at 220° F. until dry to the touch.

The loaded blacked fabric may be impregnated and/or coated with starch, resin or other materials and calendered or not depending upon the final use to be made of the treated fabric. Or the blacked fabric may be left without further finishing as the final use demands.

Any kind of fibrous textile may be treated by our method, above described, including cotton, wool and synthetic fibers such as rayon or the like.

The preferred negatively charged conducting substances with which the fibrous material is impregnated are finely divided, or ground, carbon black and graphite, but other conducting substances having similar properties, such as finely divided metal particles, may be used in combination with the carbon black or graphite, or alone, provided they are semi-colloidally dispersed and of clusters less than 12 microns in diameter.

The conductive fibrous material in appropriate form made by this process may be used as the outside or inside of an article or portion thereof, for example, the outer layer of a transmission belt or the inner sole of a conductive shoe. Or, the conductive fibrous material may be imbedded in another article, as for example, conductive tire cords in the tread or the wall structure of tires. Our conductive material in the latter case is most effective when the material of the article, in which it is imbedded, is also conductive, such for example, as electro-conductive rubber.

This application is a continuation-in-part of our application, Serial Number 432,904, filed February 28, 1942, now abandoned.

We claim:

1. A treated fibrous textile material having permanently reduced electrical resistance less than 1/10,000 of its electrical resistance in its dry untreated state, containing a reaction product of an acidified fibrous cellulosic textile material and cetyl dimethyl benzyl ammonium chloride, and clusters exceeding 12 microns in diameter of carbon particles permanently embedded in said material, said textile material being substantially free of unfixed carbon particles removable by washing.

2. In the art of loading fibrous textile material with carbon particles to decrease the electrical resistance of the textile material, the method of improving fixation of the carbon particles in the fibrous material and thereby imparting permanence to the reduced electrical resistance thereof, comprising grinding agglomerated clusters of carbon particles in aqueous dispersion in the presence of 4% to 15% of a salt of a polymerized short-chain-alkyl naphthalene sulfonic acid by weight of the carbon particles, until substantially all of said clusters are reduced to less than 12 microns in diameter and then immersing in said dispersion a fibrous textile material, the fibers of which bear an impregnation of about 2% by weight of said fibers of cetyl dimethyl benzyl ammonium chloride, thereby causing the dispersed clusters of negatively charged carbon particles to penetrate between the fibers of the textile material and there be agglomerated into clusters having diameters exceeding 12 microns, washing unfixed carbon particles from said textile material and drying said material.

3. In the art of loading fibrous textile material with carbon particles to decrease the electrical resistance of the textile material, the method of improving fixation of the carbon particles in to the fibrous material and thereby imparting permanence to the reduced electrical resistance thereof, which comprises grinding agglomerated clusters of negatively charged carbon black particles in aqueous dispersion in the presence of 4% to 15% of a salt of a polymerized short-chain-alkyl naphthalene sulfonic acid by weight of the carbon particles until substantially all of said clusters are reduced to less than 12 microns in diameter, preparing a cellulosic fabric by acidifying the cellulosic material thereof and then impregnating it with cetyl dimethyl benzyl ammonium chloride, immersing the prepared fabric in said dispersion thereby causing the dispersed clusters of negatively charged carbon particles to penetrate between the fibers of the textile material and there be agglomerated into clusters having diameters exceeding 12 microns, washing out unfixed carbon particles, and drying said material.

4. In the art of loading fibrous cellulosic material with carbon black to decrease the electrical resistance of the fibrous cellulosic material, the method of improving adherence of the carbon black to the fibrous material and thereby imparting permanence to the reduced electrical resistance thereof which comprises grinding agglomerated clusters of negatively charged carbon black particles in aqueous dispersion in the presence of a salt of a polymerized short-chain-alkyl naphthalene sulfonic acid to inhibit the agglomeration of said clusters, until substantially all of said clusters are reduced to less than 12 microns in diameter, preparing a fibrous cellulosic fabric by acidifying the cellulosic material and then reacting cetyl dimethyl benzyl ammonium chloride therewith, immersing the prepared fabric in said dispersion thereby causing the dispersed clusters of negatively charged carbon black particles to penetrate between the fibers of the fibrous material and there be agglomerated into clusters having diameters exceeding 12 microns, washing and drying said material.

5. A treated fabric having an electrical resistance less than 1/10,000 of the electrical resistance of the fabric when dry and untreated, comprising a fibrous textile material and up to 10% of the weight of the dry untreated fabric of clusters greater than 12 microns in diameter of carbon particles, averaging not more than 0.028 micron in diameter, permanently fixed between the fibers of said fabric, said fabric being substantially free of unfixed carbon particles removable by washing.

6. The fabric specified in claim 5 having a coating of starch thereon.

7. The fabric specified in claim 5 having a coating of resin thereon.

8. A treated fibrous textile material having an electrical resistance less than 1/10,000 of the electrical resistance of the fibrous textile material when dry and untreated, comprising a fibrous textile material of which fibers are spaced not more than 12 microns apart and carbon particles averaging not more than 0.028 micron in diameter and being in clusters permanently fixed between the fibers of said fibrous textile material and of sizes greater than the spaces between the fibers, said fibrous textile material being substantially free of unfixed carbon particles removable by washing.

9. In the art of loading fibrous textile material with carbon particles to decrease the electrical resistance of the fibrous textile material, the method of improving fixation of the carbon particles in the fibrous material and thereby imparting permanence to the reduced electrical resistance thereof which comprises grinding agglomerated clusters of negatively charged carbon particles in aqueous dispersion in the presence of a salt of a polymerized short-chain-alkyl naphthalene sulfonic acid to inhibit the agglomeration of said clusters, until substantially all of said clusters are reduced to less than 12 microns in diameter, preparing a fibrous textile fabric by acidifying the cellulosic material thereof and then reacting cetyl dimethyl benzyl ammonium chloride therewith, immersing the prepared fabric in said dispersion thereby causing the dispersed clusters of negatively charged carbon particles to penetrate between the fibers of the fibrous material and there be agglomerated into clusters having diameters exceeding 12 microns, washing unfixed carbon particles from the textile material and drying said material.

10. A treated fibrous textile material having an electrical resistance less than 1/10,000 of the electrical resistance of the fibrous textile material when dry and untreated, comprising a fibrous textile material substantially free of unfixed carbon particles removable by washing and containing up to 10% of the weight of the dry untreated fibrous textile material of carbon particles averaging not more than 0.028 micron in diameter, said particles being in clusters comprising sizes greater than the interfiber spaces of said fibrous textile material and thereby being

permanently fixed between the fibers of said fibrous textile material.

KENNETH H. BARNARD.
JAYSON C. BALSBAUGH.
MELVILLE J. BLACKWOOD.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,327,904	Carter	Jan. 13, 1920
1,686,063	Benbow	Oct. 2, 1928
2,338,480	Auxier	Jan. 4, 1944

FOREIGN PATENTS

Number	Country	Date
483,496	Great Britain	Oct. 22, 1938

OTHER REFERENCES

Harold, The Rubber Age, London, Oct. 1939, pages 250–254.