

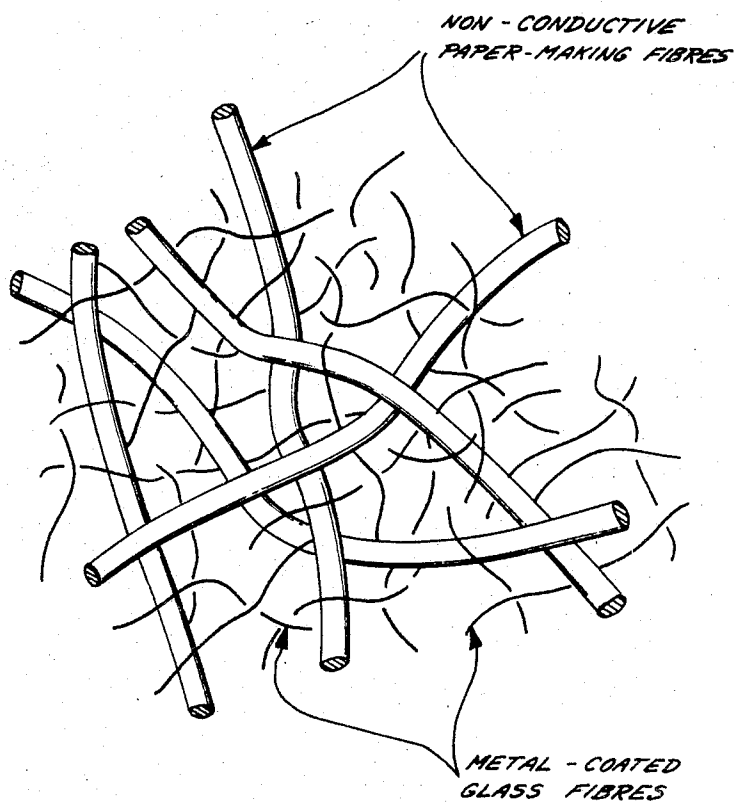
Sept. 8, 1964

W. A. SELKE ET AL

3,148,107

ELECTRICALLY CONDUCTIVE PAPER AND METHOD OF MAKING IT

Filed Feb. 1, 1962



INVENTORS:  
WILLIAM A. SELKE and  
JOHN H. MATHEWS

BY

*Frederick Breitenfeld*  
Attorney

1

3,148,107

## ELECTRICALLY CONDUCTIVE PAPER AND METHOD OF MAKING IT

William A. Selke, Stockbridge, and John H. Mathews, Lee, Mass., assignors to Kimberly-Clark Corporation, Neenah, Wis., a corporation of Delaware  
Filed Feb. 1, 1962, Ser. No. 170,395  
10 Claims. (Cl. 162-132)

This invention relates generally to the manufacture of paper, and has particular reference to paper having electric conductivity.

This application for patent is a continuation-in-part of the application filed August 18, 1959, Serial No. 834,396, now abandoned.

It is a general object of the invention to provide a practical procedure whereby standard paper-making machines and conventional paper-making techniques may be employed to produce, on a commercial scale, paper having predetermined special conductive qualities.

Conductive paper has a wide range of uses in industry. For example, it is employed in the field of electrostatic printing and for related purposes. It is also of utility in the manufacture of transformer bushings, cable insulations, and analogous products in which, for safety purposes, electrical stresses are to be distributed to avoid potentially dangerous concentrations. Also, many types of heating panels and luminescent panels and similar products can employ conductive paper advantageously.

Prior methods of imparting conductivity to paper have generally involved incorporating in the paper either particulate conductive materials such as carbon black, graphite, powdered metals, etc., or ionic materials such as salts dissolved in glycerol, quaternary ammonium compounds, and the like. Both of these methods have serious drawbacks. The inclusion of particulate conductive material tends to degrade the mechanical properties of the paper, and the dark color of such papers limits their suitability for use in certain applications. Paper made electroconductive by the inclusion of ionic materials varies greatly in conductivity with changes in moisture content. Such papers can become substantially non-conductive during periods of low relative humidity.

One object of this invention is to provide electroconductive papers which do not vary in conductivity when exposed to vary relative humidity. Another object is to provide electroconductive papers which are white, or nearly white, in color. A further object is to provide electrical conductivity in paper without detracting from the mechanical properties of the paper. A still further object is to provide electrical conductivity in transparent papers without seriously impairing their transparency. Still another object of the invention is to provide electrical conductors in sheet form which are porous and permeable to water vapor.

The successful accomplishment of the desired objectives is predicated upon a novel and improved manner of incorporating in the paper, in reliably controllable uniform fashion, fibrous elements having the required electrically conductive properties and also the necessary capability of bonding with paper fibers during usual paper-forming procedures.

In accordance with the invention a separate preliminary procedure creates metal-coated fibers having the ability compatibly to mingle with and become adequately interengaged with the primary fibers of which the paper is made. Glass fibers are the preferred carriers for the metal coating; silver is the preferred metal which is deposited upon them.

2

One of the more particular objects of the invention is to afford satisfactory commercially-practical solutions to the problems involved in the silvering of fine fibers. These include the determination and attainment of the treatment-bath proportions best suited for adequate adherence of the silver to the carrier fibers, the diameters required of the carrier fibers, the concentrations to be employed in the silver depositing solution, the optimum thickness of silver upon the carrier fibers, and the most effective percentages of silvered fibers to be incorporated in the final paper.

It has been found that carrier fibers having a very small diameter and a high ratio of length to diameter, when coated with silver or equivalent metal and incorporated in a paper, are admirably adapted in relatively small weight concentrations to provide large numbers of conductive paths through the paper. A multiplicity of continuous conductive paths imparts to the paper an electrical conductivity which is "fine grained" and uniform. These properties are required in most cases of industrial use of such papers. To achieve this result the carrier fibers should have a diameter in the range from 0.05 micron to 5.5 microns, preferably from 0.2 to 1.5 microns.

While other fibers can be used, glass fibers are particularly suitable for the purpose, since glass is chemically inert and the fiber surface is smooth and hydrophilic. Inasmuch as adequate conductivity can be obtained with extremely thin metal films (less than one-millionth of an inch), only small amounts of silver are needed to achieve the objectives of the invention.

The accompanying figure is an enlarged schematic representation of the intermingled fibers of a paper sheet formed in accordance with this invention.

The silver films may be applied to the fibers by chemical reduction in aqueous media, by methods analogous to those used in the manufacture of glass mirrors, the Brashear process being an example. However, the deposition of silver on the surface of fine diameter glass fibers is best effected by special techniques and by the control of process variables within well defined limits in order to obtain products which are useful for the present purpose. Specifically, it has been found that the following conditions should be observed:

(1) The ratio of fiber surface area to solution volume during the reduction of the silver complex should be at least about 1 square centimeter of fiber surface per cubic centimeter of solution volume, and is preferably at least about 100 square centimeters per cubic centimeter.

(2) The concentration of silver in the silvering solution must be at least about .0005 mol of silver per liter of solution, and is preferably at least about .007 mol per liter.

(3) The weight of coating deposited must be at least about  $5 \times 10^{-6}$  grams of metal per  $\text{cm}^2$  of fiber surface, and preferably at least about  $10^{-5}$  grams per  $\text{cm}^2$ . The preferred range of coating weight is from  $10^{-5}$  to  $5 \times 10^{-5}$  grams per  $\text{cm}^2$ . Coatings heavier than  $5 \times 10^{-5}$  grams per  $\text{cm}^2$  may be applied but economic considerations dictate that the weight of silver be at the minimum required by the end use intended.

The following example illustrates the silvering of glass fibers in accordance with this invention.

### EXAMPLE 1

One part by weight of glass fibers with an average diameter in the range of 0.2 to 0.5 micron was washed successively with a strong detergent solution and deionized water. The fibers were then immersed in a 5%

stannous chloride solution at a temperature of about 65° C. and held for about 10 minutes. The fibers were drained and thoroughly washed with deionized water. The sensitized fibers were then added to 250 parts of water and violently agitated until the fibers were shortened sufficiently to form a uniform dispersion. This dispersion was added to 750 parts of an ammoniacal silver solution containing .004 mol of silver, and dextrose was added to reduce the silver to metallic form. Gentle agitation of the mixture was continued during deposition of the silver coating. The silvered fibers produced were electrically conductive, very dark gray in color, and were found to be coated with an amount of silver equal to about  $8 \times 10^{-6}$  grams per  $\text{cm}^2$  of fiber surface.

Fibers silvered in accordance with this process are not bright and metallic in appearance but vary in color from a dull, almost black, to very light gray or buff with a soft satin sheen, depending upon the thickness of the coating and the conditions of application. Light colored fibers prepared by this process can be incorporated in white papers with very little effect on the appearance of the sheet. Table I illustrates the effect, on the color of the silver deposit, of variation in surface-to-volume ratio, concentration of metal in the silver solution, and weight of coating deposited.

Table I

| Approximate Surface to Volume Ratio | Silver Conc. (mols/liter) | Approximate Coating Weight (gms. of metal per $\text{cm}^2$ ) | Brightness <sup>1</sup> | Color            |
|-------------------------------------|---------------------------|---------------------------------------------------------------|-------------------------|------------------|
| 1.....                              | .0005                     | $1.5 \times 10^{-5}$                                          | 14                      | Very dark gray.  |
| 10.....                             | .0008                     | $8 \times 10^{-6}$                                            | 14                      | Do.              |
| 25.....                             | .007                      | $3 \times 10^{-5}$                                            | 17                      | Dark Gray.       |
| 50.....                             | .018                      | $3 \times 10^{-5}$                                            | 26                      | Medium gray.     |
| 67.....                             | .023                      | $3 \times 10^{-5}$                                            | 46                      | Very light gray. |
| 100.....                            | .035                      | $3 \times 10^{-5}$                                            | 53                      | Do.              |
| 200.....                            | .01                       | $6 \times 10^{-6}$                                            | -----                   | Black.           |

<sup>1</sup> Percent light reflectance in comparison with a standard magnesite disc, measured with a Bausch & Lomb opacity meter.

Silvered glass fibers prepared in accordance with this process can be incorporated in various types of papers. The primary fibers of the paper may be natural cellulosic fibers, synthetic fibers, or mixtures. Generally, in order to insure continuity of conductive paths along the main plane of the sheet, about 1% by weight, or more, of the conductive fibers are required in the sheet. However, for certain uses of the paper, conductivity along the plane of the sheet may not be necessary, or may be of secondary importance; that is, conductivity only in the direction transverse to the main plane of the sheet may be the primary consideration. In that case, as little as 0.3% by weight of conductive fibers is usually sufficient.

The following examples show the results of incorporating the conductive fibers into various types of paper:

## EXAMPLE 2

Glass fibers having an average diameter in the range of 0.2 to 0.5 micron were coated with silver by the process described, the weight of coating being equal to about  $1.5 \times 10^{-5}$  grams per  $\text{cm}^2$  of fiber surface. Five parts by weight of these conductive fibers were mixed with 195 parts of well-beaten kraft wood pulp in an otherwise conventional paper-making slurry and formed into paper by conventional paper-making procedures. The finished product weighed 30 lbs. per 3000 square feet, contained about 2% by weight of the silvered fibers in uniform dispersion, and had a resistance along the main plane of the sheet of  $5 \times 10^5$  ohms per square.

## EXAMPLE 3

Glass fibers having an average diameter in the range of 0.2 to 0.5 micron were coated with silver by the

process described, the weight of silver deposited being equal to about  $5 \times 10^{-5}$  grams per  $\text{cm}^2$  of fiber surface. One part by weight of these fibers was mixed with 20 parts by weight of well-beaten kraft wood pulp and formed into paper by conventional paper-making procedures. The finished product weighed 30 lbs. per 3000 square feet, contained about 4% by weight of the silvered fibers in uniform dispersion, and had an electrical resistance along the main plane of the sheet of 250 ohms per square.

## EXAMPLE 4

Glass fibers having an average diameter in the range of 0.2 to 0.5 micron were coated with silver by the process described, the weight of coating being equal to about  $3 \times 10^{-5}$  grams per  $\text{cm}^2$  of fiber surface. Four parts by weight of these fibers were mixed with 200 parts of well-beaten bleached kraft wood pulp and 20 parts of titanium dioxide, and two parts of a commercial cationic wet strength resin were added. This mixture was formed into paper by conventional paper-making procedures. The finished product weighed 30 lbs. per 3000 square feet, contained about 1½% by weight of the silvered fibers in uniform dispersion, and had a resistance along the main plane of the sheet of  $2 \times 10^8$  ohms per square. This paper was nearly white in color and entirely conventional in texture and appearance.

## EXAMPLE 5

Glass fibers having an average diameter in the range of 0.2 to 0.5 micron were coated with silver by the process described, the weight of silver deposited being equal to about  $4 \times 10^{-5}$  grams per  $\text{cm}^2$  of fiber surface. Three parts by weight of these fibers were mixed with 40 parts of an acrylic fiber (Orlon, one denier per filament, ¼ inch cut). The fibers were formed into a sheet on the wire of a paper machine, bonded with 20 parts of an acrylic resin, and dried. The final product was a very open, transparent paper weighing 9 lbs. per 3000 square feet. This paper contained about 5% by weight of the silvered fibers in uniform dispersion, and had a resistance along the main plane of the sheet of 10 ohms per square.

## EXAMPLE 6

Glass fibers having an average diameter in the range of 0.2 to 0.5 micron were coated with silver by the process described, the weight of silver deposited being equal to about  $5 \times 10^{-5}$  grams of silver per  $\text{cm}^2$  of fiber surface. Three parts of these fibers were mixed with 50 parts of well-beaten wood pulp and formed into a sheet. The wet conductive sheet was couched from the forming wire of the paper machine to a strong wood pulp paper weighing 22 lbs. per 3000 square feet and the laminated sheet was dried. The conductive sheet weighed 7½ lbs. per 3000 square feet, contained about 5% by weight of the silvered fibers in uniform dispersion, and the conductive side of the laminated product had a lateral resistance of 20 ohms per square.

This example is illustrative of the economical procedure that can be followed where transverse conductivity through the sheet is not required. Since silver is an expensive metal it is desirable to maintain the basis weight of the conductive paper as low as possible, thus minimizing the cost per unit area. Since very light weight papers can be made which are completely satisfactory from the standpoint of electrical conductivity, but inadequate in mechanical strength, they can be laminated or paper-bonded to a heavier and stronger non-conductive paper as described in this Example. With papers made from natural cellulosic fibers the lamination can be accomplished by simply pressing the wet conductive layer onto the supporting paper, adhesion being provided by the inherent bonding ability of natural cellulose.

## EXAMPLE 7

Glass fibers having an average diameter in the range of 0.2 to 0.5 micron were coated with silver by the process described, the weight of silver deposited being equal to about  $10^{-5}$  grams of silver per  $\text{cm}^2$  of fiber surface. These fibers were mixed with well-beaten wood pulp and formed into paper by conventional paper-making procedures, the proportions of metal-coated glass fibers and wood pulp, and the paper-making process, being so controlled as to give a final product that weighed 15 lbs. per 2000 square feet, contained about 1% by weight of the metal coated fibers, and had electrical resistance along the main plane of the sheet of about  $2 \times 10^6$  ohms per square.

## EXAMPLE 8

Glass fibers having an average diameter in the range of 0.2 to 0.5 micron were coated with silver by the process described, the weight of silver deposited being equal to about  $10^{-5}$  grams of silver per  $\text{cm}^2$  of fiber surface. These fibers were mixed with well-beaten wood pulp and formed into paper by conventional paper-making procedures, the proportions of metal-coated glass fibers and wood pulp, and the paper-making process, being so controlled as to give a final product that weighed 5 lbs. per 2000 square feet, and contained about 0.3% by weight of the metal-coated glass fibers. This paper had a resistance of  $2 \times 10^6$  ohms in a direction perpendicular to the main plane of the sheet when placed between electrodes 6 cm. in diameter with an electrode pressure of 71 grams per  $\text{cm}^2$ .

## EXAMPLE 9

Glass fibers having an average diameter in the range of 0.05 to 0.1 micron were coated with silver by the process described, the weight of silver deposited being equal to about  $6 \times 10^{-6}$  grams of metal per  $\text{cm}^2$  of fiber surface. These fibers were mixed with an aqueous slurry of well-beaten kraft wood pulp and formed into paper by conventional paper-making procedures, the proportions of metal-coated glass fibers and wood pulp, and the paper-making process, being so controlled as to give a final product containing about 6% by weight of uniformly distributed metal-coated fibers and weighing 9 lbs. per 2000 square feet. This paper was found to have electrical resistance along the main plane of the sheet of about 30 ohms per square.

## EXAMPLE 10

Glass fibers having an average diameter in the range of 4.5 to 5.5 microns were coated with silver by the process described, the weight of silver deposited being equal to about  $2 \times 10^{-5}$  grams of metal per  $\text{cm}^2$  of fiber surface. These fibers were mixed with an aqueous slurry of well-beaten kraft wood pulp and formed into paper by conventional paper-making procedures, the proportions of metal-coated glass fibers and wood pulp, and the paper-making process, being so controlled as to give a final product containing about 16% by weight of uniformly distributed metal-coated fibers and weighing 12 lbs. per 2000 square feet. This paper was found to have electrical resistance along the main plane of the sheet of about 28000 ohms per square.

## EXAMPLE 11

Glass fibers having an average diameter in the range of 0.75 to 1.6 microns were coated with silver by the process described, the weight of silver deposited being equal to about  $10^{-5}$  grams of metal per  $\text{cm}^2$  of fiber surface. These fibers were mixed with an aqueous slurry of well-beaten kraft wood pulp and formed into paper by conventional paper-making procedures, the proportions of metal-coated glass fibers and wood pulp, and the paper-making process, being so controlled as to give a final product containing about 8% by weight of uniformly distributed metal-coated fibers and weighing 10 lbs. per 2000 square feet. This paper was found to have electrical resist-

ance along the main plane of the sheet of about 200 ohms per square.

Conductive paper formed in accordance with the techniques of this invention has many advantages. For example, it is just as porous and permeable as conventional papers, hence it can be utilized to advantage in the manufacture of cable coverings, transformer bushings, etc., where its permeability facilitates the drying procedure preparatory to impregnation with dielectric oils or resins. Also, it can be made nearly white in color, which gives excellent printing contrast when it is used in electrostatic printing processes. Moreover, its conductivity is unaffected by changes in atmospheric humidity. Another advantage stems from the fine diameter of the conductive fibers, and their high ratio of length to diameter, since it is possible to provide a "fine grain" pattern of continuous conductive paths and still maintain the fibers sufficiently spaced to achieve a high degree of transparency. Accordingly, the paper can be used as the conductive layer adjacent to the phosphor in luminescent lighting panels, where optical transparency is required. Other useful applications of the improved paper are numerous, as will be readily recognized.

In many respects, of course, the details herein described may be modified by those skilled in the art without necessarily departing from the spirit and scope of the invention as expressed in the appended claims.

What is claimed is:

1. An electrically conductive paper formed of a major proportion of uncoated non-conductive fibers and a minor proportion of electrically conductive metal-coated fibers composed of chemically inert material having a smooth hydrophilic surface and having diameters in the range from 0.05 to 5.5 microns, the amount of metal deposited upon said coated fibers being at least  $5 \times 10^{-6}$  grams per square centimeter of fiber surface, said coated fibers being uniformly distributed throughout the sheet in an amount equal to at least 0.3% by weight of said sheet.

2. An electrically conductive paper as defined in claim 1, the coated fibers being glass and the metal being silver.

3. An electrically conductive paper as defined in claim 1, said coated fibers having diameters, before coating, in the range from 0.2 to 1.5 microns.

4. An electrically conductive paper as defined in claim 1, the amount of metal deposited upon said coated fibers being in the range from  $10^{-5}$  to  $5 \times 10^{-5}$  grams per square centimeter of fiber surface.

5. An electrically conductive paper comprising paper-bonded layers of which at least one is an electrically conductive sheet as defined in claim 1, the other layer or layers being nonconductive.

6. A method of making an electrically conductive paper which consists in providing a main mass of non-conductive paper-making fibers, separately providing other fibers composed of a chemically inert material having a smooth hydrophilic surface and having diameters in the range from 0.05 to 5.5 microns, coating said other fibers with a metal having electric conductivity so as to make the fibers electrically conductive, said metal being deposited on the fibers to the extent of at least  $5 \times 10^{-6}$  grams thereof per square centimeter of fiber surface, forming an aqueous slurry containing a mixture of said main mass of fibers and said coated fibers, and converting said slurry into a paper sheet in which the coated fibers are uniformly distributed, the coated fibers being employed in an amount sufficient to provide at least 0.3% by weight of said coated fibers in said sheet.

7. The procedure defined in claim 6, in which said metal is silver and the fibers coated with it are glass, the silver being deposited on the fibers by reduction of a silver complex in a solution in which the fibers are immersed, the concentration of silver in the solution being at least 0.0005 mol per liter.

8. The procedure defined in claim 7, in which the ratio

of fiber surface to solution volume is at least 1 square centimeter per cubic centimeter.

9. The procedure defined in claim 6, in which said metal is silver and the fibers coated with it are glass, the silver being deposited on the fibers by reduction of a silver complex in a solution in which the fibers are immersed, the concentration of silver in the solution being at least 0.007 mol per liter and the ratio of fiber surface to solution volume being at least 100 square centimeters per cubic centimeter.

10. A method of making an electrically conductive

paper which consists in forming an electrically conductive sheet in accordance with the procedure set forth in claim 6, and paper-bonding said sheet to at least one other paper layer having no conductivity.

# References Cited in the file of this patent

## UNITED STATES PATENTS

|           |            |               |
|-----------|------------|---------------|
| 2,721,139 | Arledter   | Oct. 18, 1955 |
| 2,900,274 | Whitehurst | Aug. 18, 1959 |
| 3,022,213 | Pattilloch | Feb. 20, 1962 |