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CONDUCTIVE CELLULOSIC PAPER CONTAINING ASBESTOS AND ACID SALT OF A POLYVALENT METAL

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This invention relates to conductive paper and more particularly to such paper which is useful for high speed printing, electrostatic printing in duplicating machines and for other purposes where the accumulation of static charges on the surface of paper is a problem.

This problem has long occupied the attention of the art. The problem is especially acute in the printing industry where static electricity is generated each time a sheet or web to be printed passes over a roller. In letter press, offset and gravure printing processes, the problem is particularly serious because of the high heat which is used to dry the printing ink. The heat also dissipates the surface moisture which under ordinary circumstances would aid in conducting the charge from the paper. In bindery operations, static interferes with jogging and sheeting and with the operation of the folding machines.

Many specialty papers usually known as conductive or antistatic papers have been developed in efforts to cope with this problem. The most successful papers so far developed have been papers with a surface coating of a humectant such as a glycol which aids in retaining surface moisture. Often the humectant will contain an inorganic salt such as sodium chloride which decreases the resistivity of the paper by providing ions in the water normally absorbed on the surface of the paper. The ions aid in dissipating the static charge. These papers have not been completely satisfactory. In areas of low relative humidity or under conditions of high heat, the humectants employed do not retain sufficient moisture to be effective. The papers coated with inorganic salts also fail under conditions of low humidity where little or no ionization takes place. Moreover, the salts may corrode metal equipment.

There is as yet no universally accepted definition for conductive or antistatic papers. One definition which has been suggested for conductive paper is paper with a surface resistivity in the semiconductor range of 10^8 to 10^{10} ohms over 85 to 25% relative humidity. The surface resistivity of antistatic paper is higher than that of conductive paper. The surface resistivity of ordinary paper is of the order of 10^{11} ohms or higher at a relative humidity of about 50%. In order to be useful for high speed letter press printing and similar operations, the resistivity of the paper used should be lower than 10^{11} ohms under the conditions of use.

The term "conductive paper" as used herein is specifically intended to include both conductive and antistatic papers.

Ordinary untreated paper although unsuitable at low relative humidity, may have a resistivity lower than 10^{11} ohms under conditions of high relative humidity, i.e. 60% or higher and, therefore, might possibly be used for some purposes where static electricity is a problem. However, it is rarely feasible and often impossible to maintain the relative humidity in the area of operations at a high enough level to permit the use of ordinary paper. For example, simultaneous maintenance of a high temperature to dry printing inks and a high relative humidity to retain surface conductivity is practically impossible. Further, it would generally not be considered practical to hold the relative humidity of an office at a high level simply to

permit the use of ordinary paper in a duplicating machine. The problem then is to provide a paper with a resistivity below 10^{11} ohms at low relative humidity. Papers prepare in accordance with this invention exhibit low resistivity even at low relative humidities.

The conductive and antistatic papers of this invention are fibrous webs in which the fibers are more or less randomly oriented and are predominantly cellulosic in nature. The webs contain hydrated asbestos and may also contain at least one water soluble acid salt of a polyvalent metal. The webs are manufactured in accordance with the usual paper-making techniques modified so that hydrated asbestos and possibly a salt is dispersed throughout the web. They have a resistivity of less than 10^{11} ohms at a relative humidity of 50%.

A most convenient method of dispersing the asbestos is to add it to the fiber slurry in the head box before the web is formed. The asbestos which is retained in the web is preferably randomly distributed throughout the web.

Asbestos is a well-known fibrous mineral silicate naturally available in various physical forms in many areas throughout the world. In its natural state, it generally contains up to about 13% by weight of water of crystallization. For many commercial purposes the asbestos is usually heat treated to drive out the water of crystallization. For the pruposes of this invention, it is not essential to dehydrate the asbestos. It may be used in its hydrated form. The preferred form of hydrated asbestos for use in this invention is chrysotile which is a short fibered form. Other forms such as, for example, tremolite, anthophyllite, amosite and crocidolite may also be employed.

Conductive papers of this invention containing hydrated asbestos with no added salt preferably contain at least 5% asbestos by weight. The web may contain as much as 25% by weight of asbestos but it is generally not desirable to use much more than this since there is some loss of tensile strength as the proportion of asbestos is increased. The surface resistivity of one paper prepared in accordance with this invention containing 12.6% by weight of asbestos when measured by the procedure of Hayek as described in Tappi, February 1960, vol. 43, No. 2, page 105, was 10^{10} ohms at a relative humidity of 33%. The surface resistivity of a similar paper containing 17.2% by weight of hydrated asbestos was 10^9 ohms at a relative humidity of 30%.

As aforesaid, the resistivity of the papers of this invention can be improved by the addition of a salt. The preferred salts are halides, especially chlorides of divalent and trivalent metals. Of these, aluminum chloride and ferric chloride are preferred for their property of lowering surface resistivity. If the whiteness of the conductive paper is important, aluminum chloride is the preferred salt since it does not tend to discolor the paper.

The fibrous webs of this invention will impart an acid pH to a cold water extract prepared and tested in accordance with the Tappi Standard Method T 435 *m* 52 titled Hydrogen Ion Concentration of Paper Extracts. In this procedure a defined quantity of paper is extracted with a defined quantity of distilled water at a specified temperature for a specific period of time. The pH of the water extract is customarily measured with a conventional pH meter. Two extraction procedures, one at low temperature and the other at high temperature are accepted as standard. The cold water extracts obtained from the preferred fibrous webs or papers of this invention will have a pH of from about 4 to about 5, before being subjected to any further treatment such as coating.

Papers which impart an acid pH to a cold water extract as defined above will generally contain from about 0.1 to about 0.4% of the selected salt and from about 3 to about 25% hydrated asbestos by weight.

Conductive cellulosic paper containing asbestos and acid salt of a polyvalent metal (US Patent 3,337,392, 1967) Published by AsbestosClaims.Law
ACL Doc 22136 · Page 1 of 2 asbestosclaims.law/library/22136/1

Papers may be prepared in accordance with this invention with resistivities as low as 10^7 ohms.

While other procedures may be employed, the preferred method of incorporating the salt into the web is by adding it at the head box while maintaining a careful control of the pH. For example, if the method of manufacture is a batch process and aluminum chloride is the salt, sufficient salt should be added to the slurry in the head box to maintain an acid pH preferably between 4 and 5. In the continuous process of paper manufacture, the aluminum chloride solution in the head box can be recirculated from the Fourdrinier wire to a reservoir where more aluminum chloride is added and the resulting solution metered into the head box so as to maintain the desired pH.

At a relative humidity of 25%, the surface resistivity of a paper containing 10% hydrated asbestos by weight and prepared from a slurry in which the aqueous phase was an aluminum chloride solution with a pH of 4.3 was less than 10^{10} ohms as determined by the Hayek procedure. A similar paper prepared from an aluminum chloride solution at a pH of 5.5 had a surface resistivity under 10^{11} ohms at a relative humidity of 30%. The resistivity of another similar paper prepared from an aluminum chloride solution at a pH of 4.2 was only $10^{8.5}$ ohms at 40% relative humidity.

The papers of this invention are used in exactly the same manner as other papers which have heretofore been utilized for their conductive or antistatic properties, no special techniques being required. They may, for example, be coated with various known starch-clay mixtures to enhance desirable printing characteristics such as opacity, ink receptivity and brightness. They may be used to prepare photographic papers by coating them with gelatin emulsions containing photosensitive agents. They may be used to prepare electrostatic printing papers such as are used in various well known duplicating machines by coating with polymeric suspensions containing photoconductive agents such as zinc oxide. They may also be used to prepare electrosensitive papers for use in various well known facsimile devices. The papers are especially useful for the manufacture of specialized operating room apparel such as shoes which are utilized to minimize the danger of explosions due to the generation of electrical sparks in an atmosphere which may contain a high concentration of a volatile anesthetic.

Although particular embodiments of this invention are herein disclosed for purposes of explanation, various modifications thereof after study of the specification will be apparent to those skilled in the art to which the invention pertains. Reference should accordingly be had to the appended claims in determining the scope of this invention.

What is claimed and desired to be secured by Letters Patent is:

1. A conductive paper comprising a cellulosic web having from about 3% to about 25% by weight of asbestos and from about 0.1 to about 0.4% by weight of an acid salt of a polyvalent metal dispersed therethrough, said paper having a surface resistivity of less than 10^{11} ohms at a relative humidity of 50% and imparting an acid pH to a cold water extract.

2. A conductive paper comprising a cellulosic web having from about 3% to about 25% by weight of asbestos and from about 0.1 to about 0.4% by weight of aluminum chloride dispersed therethrough, said paper having a surface resistivity of less than 10^{11} ohms at a relative humidity of 50% and imparting an acid pH to a cold water extract.

3. A conductive paper comprising a cellulosic web having from about 3% to about 25% by weight of asbestos and from about 0.1 to about 0.4% by weight of ferric chloride dispersed therethrough, said paper having a surface resistivity of less than 10^{11} ohms at a relative humidity of 50% and imparting an acid pH to a cold water extract.

4. A conductive paper as in claim **1** wherein the polyvalent metal salt is a halide of a divalent or a trivalent metal.

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