

United States Patent

[11] 3,607,377

[72] Inventors **Robert A. Cross**
Waltham;
John F. Hegarty, Somerville, both of Mass.
 [21] Appl. No. **788,087**
 [22] Filed **Dec. 30, 1968**
 [45] Patented **Sept. 21, 1971**
 [73] Assignee **Amicon Corporation**
Lexington, Mass.

1,558,495	10/1925	Overbury	162/129
1,577,074	3/1926	Perry et al.	162/129 X
3,264,137	8/1966	Gess	117/201
3,335,100	8/1967	Geyer	117/201 X
3,337,392	8/1967	Carlson et al.	162/138
3,461,191	8/1969	Dale	162/153 X
3,480,847	11/1969	Sewell et al.	162/138 X

Primary Examiner—Ralph S. Kendall
Attorney—R. W. Furlong

[54] **ELECTROCONDUCTIVE PAPER**
10 Claims, No Drawings

[52] U.S. Cl. **117/201,**
 96/1.8, 96/85, 117/154, 162/129, 252/518, 260/37
 [51] Int. Cl. **B44d 1/18**
 [50] Field of Search..... 117/201,
 218, 217, 152, 154, 155; 162/138, 129; 96/85, 1.8,
 1.5; 260/37, 41; 252/500, 518

[56] **References Cited**

UNITED STATES PATENTS

1,532,083 3/1925 Shaw 162/129

ABSTRACT: A cellulosic paper sheet, suitable for use as a substrate for receiving a coating of a light-sensitive electroconductive material such as zinc oxide, which paper sheet comprises a coating thereon of from 0.5 to 5 lbs. per ream of colloidal chrysolite asbestos and a quantity of lithium chloride therein to impart a surface resistivity of less than 10^{10} ohms at a relative humidity of 15 percent, while maintaining a volume resistivity of greater than 10^{10} ohms under the same environmental conditions.

ELECTROCONDUCTIVE PAPER

BACKGROUND OF THE INVENTION

It has long been a problem in the art to provide conductive papers which, when coated with such light-sensitive electroconductive materials as zinc oxide, provide papers suitable for use in electrostatic printing operations. By "conductive paper" is meant a paper with a surface resistivity of from 10^8 to 10^{10} ohms in an environment of from 90 to 12 percent relative humidity. The importance of maintaining the desired conductivity over a wide range of humidity is particularly important. Treating a paper with glycerine-based humectants has not been completely satisfactory because in places having low relative humidity, or under high-temperature storage conditions, there is a tendency for such papers to drift from the desired range of resistivity. Moreover, at high relative humidities, such papers become rather limp and have inferior handling qualities.

The prior art has recognized the value of using a colloidal chrysolite asbestos to impart conductivity to cellulosic paper. More particularly, Willard E. Carlson's U.S. Pat. No. 3,337,392 discloses the use of such an asbestos and polyvalent metal salts in the formation of a conductive paper matrix. However, it has now been discovered that the optimum advantage in utilizing colloidal chrysolite asbestos is to be obtained in avoiding the dispersal of the material throughout the paper web, i.e. in restricting the presence of the asbestos to the surface of the paper. A distribution of the conductivity-imparting material in the substrate stock is undesirable for a number of reasons. For example, this mode of employing the conductivity-imparting material increases the likelihood of "strike-through" of the material which interferes with image formation on the underlying sheets in a pad of sheets. Also, confining a given quantity of conductivity-imparting material to the surface of a sheet of substrate paper to yield high surface conductivity results in better image formation than when the same quantity of material is dispersed through the bulk of the sheet which dispersal, while elevating the bulk conductivity, reduces the surface conductivity.

Moreover, such paper as disclosed by Carlson leaves much to be desired at low relative humidities, i.e. those in the 12 to 20 percent range.

Other approaches used in the prior art are those utilizing polymers bearing quaternary ammonium groups. These materials are particularly good, probably because they are readily retained on the paper surface. Still, such polymers are expensive and, are also under some conditions, undesirably odorous.

SUMMARY OF THE INVENTION

Therefore, it is an object of the invention to provide means for achieving a coating composition comprising colloidal chrysolite asbestos which coating can be retained on the surface of a paper, thereby contributing to avoiding the aforementioned problem, and to obtaining of a highly satisfactory surface-conductive paper for use as a substrate for papers used in electrostatic-printing processes over a wide range of humidity levels.

Another object of the invention is to provide novel compositions for forming such coatings.

A further object of the invention is to provide a paper suitable for storage and use at relative humidities as low as from about 12 percent.

Other objects of the invention will be obvious to those skilled in the art on reading the instant specification.

The above-listed objects have been substantially accomplished by coating a suitable paper substrate with a composition comprising defibrillated colloidal asbestos in such a concentration that it forms a gel structure within the coating composition thereby (1) entrapping any other leachable components of the composition, and (2) providing a coating that will have excellent "holdout," i.e. a substrate coating that offers a substantial resistance to the penetration of solvent used

in the copy-making process. Among the more important optional ingredients of the coating that will be retained are the hygroscopic salts such as calcium chloride, lithium chloride, etc. Indeed a particular advantage of the invention is that it provides an excellent means for retaining the monovalent lithium chloride on the surface of the paper to be treated and thereby means for providing an excellent low-humidity paper. Operable coating compositions according to the invention can be achieved with salt: asbestos ratios of up to 1:1. The coating compositions are normally applied while suspended at from 1 part to 10 parts solids per 100 parts of water. The coating process is carried out so that an ultimate coating of from 0.5 to 5 lbs. of asbestos per ream of paper is achieved.

The colloidal chrysolite asbestos preferred for use in the invention is that known as Coalinga asbestos.

Asbestos is a widely available and relatively inexpensive material having certain desirable physical properties which make it very useful as a filler in various chemical compositions. However, in order to achieve maximum effectiveness of the asbestos in improving properties of chemical compositions, it is necessary to reduce it to the form of primary fibrils.

A particular chrysolite asbestos material preferred in the present invention is obtained from a deposit located near Coalinga, California. This is a newly found deposit believed to be the largest single asbestos deposit in the world. Asbestos mined at this location is short-fibered chrysolite asbestos and would be classified between grade 5 and grade 7 according to the Canadian Standards Classification. Coalinga asbestos, however, has a much more uniform distribution of individual fiber lengths and diameters than do comparable grades of Canadian chrysolite asbestos. In addition, the surface area of Coalinga asbestos is substantially greater than that of the Canadian type of asbestos. Refined asbestos obtained from the Coalinga deposit has properties which are substantially different from any prior art asbestos. While not wishing to be limited to the geographic deposit at Coalinga, California, the type of asbestos recovered from ore such as found there is preferred in the present invention.

It is surprising that a coating of Coalinga asbestos provides really good electrostatic-printing paper over a rather wide range of humidities without the addition of salt. However, to achieve the broader advantages of the invention, some salt and/or polyelectrolyte complex resin is advantageously included in the coating formulation.

The most advantageous salt used in the composition of the invention is the monovalent lithium chloride not only because it provides excellent low-humidity moisture retention properties, but also because it is retained in the asbestos-gel coating to a surprising extent. Other hygroscopic salts may also be included in the composition of the invention. Among some such salts are calcium chloride, sodium bromide, potassium nitrate, aluminum chloride and the like.

The polyelectrolyte complex resins useful in the process of the invention include those such as described in an article entitled "Polyelectrolyte Complexes" by Alan S. Michaels in the Oct. 1965 issue of Industrial and Engineering Chemistry, a publication of the American Chemical Society. The polyelectrolyte complex resin formed by the ionic association of a sulfonate polyanion such as poly(sodium styrene sulfonate) and a quaternary ammonium-type polycation such as poly(vinylbenzyltrimethyl ammonium chloride).

It has been found that such resins when incorporated into compositions according to the invention, provide a relatively high increase in film-forming properties with a relatively low drop in conductivity. Quantities of up to 0.5 part of polyelectrolyte complex resin per part of asbestos are suitable for use in the coating compositions of the invention.

Adjuvants such as pigments, thickening aids, inert fillers and other such materials known to the art may be added to these formulations insofar as they do not upset the balance of electroconductive properties which it is the purpose of this invention to achieve. However, the conductivity-imparting portion of the composition can consist essentially of the asbestos,

salt and/or polyelectrolyte complex resin as described hereinabove.

Water will, of course, usually be the convenient vehicle for use in the coating operation whether asbestos alone, asbestos and salt, and/or a polyelectrolyte complex resin are used in the process of the invention.

ILLUSTRATIVE EXAMPLE OF THE INVENTION

Example 1

A chrysolite asbestos of the Coalinga type sold by Union Carbide Corporation was dispersed in water to form a slurry containing 5 percent of the asbestos. The pH of the slurry was lowered to about 4.3 with a small quantity of acetic acid. Thereupon the pH of the slurry was raised to 5.5 by adding a small quantity of barium hydroxide thereto. Then a single drop of a 31 percent aqueous solution of poly(vinylbenzyltrimethyl ammonium chloride) was added to the slurry.

Separately, a dispersion of 325-mesh anionic polyelectrolyte complex resin of the type sold under the trade designation Ioplex by Amicon Corporation was also dispersed to form a 5 percent solids suspension in water.

These two dispersions, i.e. the asbestos and resin dispersions, were mixed in quantities so that the resultant dispersion contained five parts asbestos and one part polyelectrolyte complex resin. Thereupon enough lithium chloride was dissolved in the slurry so that the resin-to-salt ratio was 1 to 1.

The slurry was drawn down onto a sheet of Crocker Videograph paper using a No. 18 wire-wound casting rod of the type well known in the paper-coating art. The resulting coating weight, on a dry basis, was about 1.7 lbs per ream of paper. This coated paper was dried for 5 minutes in a circulating air oven at 80° C. A smooth, colorless, coating was observed on the dried sheet.

Conductivity of the paper was tested by placing the sheet in a dry box having a relative humidity of 16 percent. After conditioning the paper for about 16 hours in this dry environment, its surface and volume resistivity were tested with a 6105 Resistivity Adapter sold by Keithley Instruments Co. and a Keithley 621 Electrometer using a Sorenson High Voltage Power Supply, respectively. Surface resistivity was 2×10^9 ohm/sq. and volume resistivity was 10^{11} ohm-cm.

These values indicated that there was little or no strike-through of the coating composition below the surface of the paper.

Example 2

The procedure of example 1 was repeated excepting that the polyelectrolyte complex resin was omitted from the paper-coating composition.

The surface resistivity of the resulting paper was 5×10^9 ohms/sq.

Example 3

The procedure of example 1 was again repeated excepting that (1) both the polyelectrolyte complex resin and the lithium chloride salt were omitted from the formulation; (2) the coating contained 2.3 lbs per ream of asbestos; and (3) the testing was carried out at 45 percent relative humidity.

Surface resistivity was 1×10^9 .

What is claimed is:

1. A conductive cellulosic paper sheet comprising a paper substrate and a coating thereon, said coating comprising a colloidal chrysolite asbestos in the quantity of from 0.5 to 5 lbs. per ream of paper sheet, said resultant sheet having a surface resistivity of less than 10^{10} ohms at a relative humidity of 15 percent and a volume resistivity of more than about 10^{10} ohm-cm. at 15 percent relative humidity.
2. A conductive sheet as described in claim 1 which comprises a hygroscopic salt as a component of said coating in a quantity such that a salt-to-asbestos ratio of up to about 1 to 1 is achieved.
3. A conductive sheet as described in claim 2 wherein said hygroscopic salt is lithium chloride.
4. A conductive sheet as described in claim 1 wherein said coating comprises a polyelectrolyte complex resin in a quantity such that a resin-to-asbestos ratio of up to about 0.5 to 1 is achieved.
5. A conductive sheet as defined in claim 4 wherein said polyelectrolyte complex resin is of the type formed by the ionic cross linking of a sulfonate-type polyanion and a quaternary ammonium-type polycation.
6. A process for imparting electroconductivity to a sheet of paper at humidities as low as 12 percent comprising the steps of:
 1. forming an aqueous coating composition including at least 1 part colloidal chrysolite asbestos per 100 parts of water,
 2. coating said composition on said paper sheet to deposit, on the surface thereof, a gel network comprising from 0.5 to 5 lbs. of asbestos per ream of paper, and
 3. drying said paper sheet, thereby forming a paper of the desired electroconductive character.
7. A process as defined in claim 6 wherein a polyelectrolyte complex resin is included in said coating composition.
8. A process as defined in claim 7 wherein a hygroscopic salt is included in said coating composition.
9. A coating composition, suitable for use in imparting conductivity to paper at low humidity levels, said composition consisting essentially of:
 1. 10 parts of colloidal chrysolite asbestos,
 2. 2 to 10 parts of lithium chloride,
 3. 0 to 5 parts of a polyelectrolyte complex resin, and
 4. a quantity of water in which to disperse the foregoing ingredients.
10. The coating composition of claim 9 including at least 2 parts of a polyelectrolyte complex resin.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,607,377 Dated September 21, 1971

Inventor(s) Robert A. Cross and John F. Hegarty

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

Column 1, line 21, "chrysolite" should be spelled
--chrysotile--;

Column 1, line 26, "chrysolite" should be spelled
--chrysotile--;

Column 1, line 55, "chrysolite" should be spelled
--chrysotile--;

Column 2, line 14, "chrysolite" should be spelled
--chrysotile--;

Column 2, line 23, "chrysolite" should be spelled
--chrysotile--;

Column 2, line 27, "chrysolite" should be spelled
--chrysotile--;

Column 2, line 32, "chrysolite" should be spelled
--chrysotile--;

Column 3, line 11, "chrysolite" should be spelled
--chrysotile--;

Column 4, claim 1, line 11, "chrysolite" should be
spelled --chrysotile--;

Column 4, claim 2, line 18, "asbestos" is misspelled;

Column 4, claim 6, line 34, "chrysolite" should be
spelled --chrysotile--;

Column 4, claim 9, line 48, "chrysolite" should be
spelled --chrysotile--.

Signed and sealed this 21st day of March 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents