

[54] **ELECTROCONDUCTIVE RECORDING
MEDIUM AND PROCESS OF MAKING THE
SAME**

[75] Inventor: **Floyd T. Gould**, Sudbury, Mass.

[73] Assignee: **Honeywell Information Systems Inc.**,
Waltham, Mass.

[22] Filed: **Oct. 13, 1972**

[21] Appl. No.: **297,562**

Related U.S. Application Data

[63] Continuation of Ser. No. 103,325, Dec. 1, 1970,
abandoned.

[52] **U.S. Cl.**..... **117/215**, 117/1.7, 117/201,
117/223, 117/154, 346/135

[51] **Int. Cl.**..... **B44d 1/18**

[58] **Field of Search** 117/1.7, 215, 201, 223,
117/154, 104 R; 254/518; 346/135

[56] **References Cited**

UNITED STATES PATENTS

2,637,657 5/1953 Ogols 117/157

3,075,859	1/1963	Relph et al.	117/201
3,152,903	1/1964	Shepard et al.	117/34
3,429,706	2/1969	Shepard et al.	117/34
3,513,021	5/1970	Sweeney et al.	117/201
3,620,831	11/1971	Gould	117/201

Primary Examiner—Cameron K. Weiffenbach
Attorney, Agent, or Firm—William F. White; Ronald
T. Reiling

[57]

ABSTRACT

A novel electroconductivity additive, potassium formate, is suspended in an aqueous solution and applied to paper during the papermaking process. The resulting impregnated paper is in one embodiment coated with a dielectric during the papermaking process thereby producing a low cost electrographic paper.

20 Claims, No Drawings

ELECTROCONDUCTIVE RECORDING MEDIUM AND PROCESS OF MAKING THE SAME

CROSS REFERENCE TO A RELATED APPLICATION

This is a continuation of application Ser. No. 103,325, filed Dec. 1, 1970, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to an improved recording medium which has been treated with an electroconductive and moisture absorbant chemical agent to increase the conductivity of the medium at low relative humidities. This invention further relates to a process for introducing the subject agent into paper during the papermaking process to thus produce an electrically conductive paper.

There are numerous applications of electrically conductive paper in the field of recording. One example is an electrically conductive paper that has been coated on one side with a thermally sensitive chemical. When current is passed through the paper in a path between two electrical contacts, a thermal-chemical change takes place in the coating which in turn produces a visible image of the described path. Perhaps the largest use of electrically conductive paper is in the field of electrostatic printing where it constitutes a major part of an electrographic medium.

An electrographic medium is a charge retentive medium on which information is recorded by impressing varying voltages over the medium in a pattern corresponding to the information to be recorded. This voltage pattern creates a charged surface on the medium which may be described as a "latent charge image." This "latent charge image" is permanently fixed and made visible by first applying a toner to the surface of the medium (which adheres to the various charged portions) and thereafter permanently fixing the toner to the medium by fusing with heat.

Electrographic paper itself consists of a dielectric layer capable of accepting and retaining a localized static electric charge, and an electroconductive paper substrate which conducts directly underneath the dielectric layer. In order for the dielectric layer to accept a localized charge, it is necessary that essentially all of any locally impressed voltage be applied across the dielectric layer. This requires a relatively good conductive substrate. Ordinary paper which is dry, is several orders of magnitude less electrically conductive than is required for effectively conducting an electrostatic charge. When ordinary paper is allowed to absorb water from air which is maintained at 65 percent relative humidity or above, the paper becomes a much better conductor of electricity. It becomes a good enough conductor to be an effective conducting substrate for some forms of electrographic printing. However this conductivity only prevails in the higher relative humidities and rapidly falls off at the lower relative humidities.

The addition of a conductivity and moisture absorbant agent to ordinary paper increases the range of relative humidity over which the paper will remain sufficiently conductive. Various electrically conductive additives have been previously introduced into paper in order to achieve an acceptable conductivity for electrographic recording in the low relative humidity

ranges. Most of these will only extend the conductivity capability of the paper down to 30 percent relative humidity. They are furthermore costly and subject to not being easily or economically introducible into the paper. This is especially true when expensive organic solvents are used to suspend the additives, which leads to further expense in retrieving the solvents. Another costly approach is to first completely form the finished paper and thereafter, by separate process, coat the paper with the conductivity additive.

In the case of electrographic paper, an additional problem arises of insuring the structural integrity of the dielectric layer when the same is exposed to the electroconductivity agent. This problem is realized when the dielectric is soluble in the electroconductivity agent. This problem is even further complicated when it is attempted to simultaneously impregnate the paper with an electroconductivity agent and coat the paper with a suitable dielectric material.

It is therefore an object of this invention to provide an electroconductivity additive which may be easily and economically introduced into paper.

It is another object of this invention to provide an electroconductivity additive which may be introduced into an electrographic paper without deleteriously affecting the dielectric coating.

It is still another object of this invention to provide a recording medium that is electrically conductive at low relative humidities.

These and other objects and advantages of the invention will be apparent from the following description of the embodiments of the invention.

SUMMARY OF THE INVENTION

The present invention provides a low-cost electrically conductive paper that possesses a good conductivity at low relative humidities (i.e. down to and including 20 percent relative humidity). The invention achieves these desirable characteristics by impregnating a paper substrate with the soluble salt, potassium formate. This is done during the papermaking process itself and results in a thorough dispersal of the conductivity agent throughout the paper at an appreciably low cost. In addition, the conductivity agent is specifically compatible with most of the dielectric layers used in electrographic recording media.

DESCRIPTION OF THE PREFERRED EMBODIMENT

According to the present invention, potassium formate, KOOCH, is dispersed in an aqueous solution which is thereafter suitably applied to the paper. A preferred and economically advantageous time for applying this aqueous solution occurs during the paper making process itself. It is to be noted however that this aqueous solution can be applied to paper at any time such as for example in a separate process following a completed manufacture of the paper itself. In addition to potassium formate being introduced during the papermaking process, the dielectric coatings of Example A of Applicant's commonly assigned U.S. application, Ser. No. 788,063 are also introduced. This latter addition of a dielectric coating within close proximity to the introduction of potassium formate is permissible due to the insolubility of most dielectrics in potassium formate. In other words, due to the lack of solubility of most dielectrics in potassium formate, there is no deg-

radiation of the dielectric coating structure, and, more specifically, the thickness of the dielectric. This is important when it is realized that the dielectric coating should be continuous and of uniform thickness in order to insure unvarying charge retention capability. Furthermore, the particular ease with which both a solution of potassium formate and a solution of one of the dielectrics from Example A of Applicant's commonly assigned U.S. application Ser. No. 788,063, now U.S. Pat. No. 3,620,831, is introduced results in a particularly low cost, highly conductive electrographic paper.

Specific examples follow of treating a paper so as to produce either a highly conductive paper or a highly conductive electrographic paper. It should be pointed out at this time that this invention does not depend on any particular paper substrate and in fact is applicable to many other substrates such as cloth, porous or fibrous ceramics, or wood.

EXAMPLE A

In the usual papermaking process, a wet mat of paper is produced that is successively partially dried, sized, completely dried, and then calendered. In practicing the present invention, the paper is processed in a similar manner except that when the mat is partially dried (i.e. the mat is soft, semi-dried with approximately 10 percent moisture left) it is fed through a bath containing an aqueous solution of potassium formate. The point at which this naturally occurs within the papermaking process is at the size press stage which immediately follows the first drying stage. It is to be noted that the aforementioned 10 percent moisture factor merely indicates the general state that the paper is in at the size press stage, namely, wet enough to be receptive to the potassium formate solution for easy penetration into it.

The aqueous solution of potassium formate is prepared by first forming a saturated solution of potassium formate and thereafter further diluting the saturated solution with even more water. The saturated solution of potassium formate is prepared at room temperature by dissolving 331 grams of potassium formate per 100 grams of water, or creating a 77 percent by weight solution of potassium formate. This saturated solution is further combined with water in a ratio of 1 part by weight of it to 9 parts by weight of water. Hence the percent by weight of potassium formate in the final aqueous solution will amount to approximately 7.7 percent. It is to be noted that this percentage by weight can vary down to as little as 3 percent and still provide enough potassium formate for sufficient impregnation of the paper.

The aqueous solution of potassium formate is next heated to approximately 140° F which merely reflects the paper temperature at the size press stage. The paper passes this process point at a speed of approximately 3,000 feet per minute and is impregnated with the potassium formate by a number of different methods. One method is to spray the speeding paper with the potassium formate solution as it passes by the process point. Another method is to position a bath in the path of the paper so as to immerse the paper as it passes through.

The paper is thereafter suitably dried and calendered. A normal ream of paper will, after drying, contain an approximate percentage by weight of potassium

formate of 2 to 3 percent. Thus for a 30 pound ream of paper measuring 3,000 square feet, the total amount of potassium formate will be approximately 0.6 to 0.9 pounds. This percentage weight of potassium formate is extremely small for the increase in paper conductivity that is obtained, as will be explained hereinafter.

EXAMPLE B

The electroconductive paper of Example A is herein coated with a dielectric so as to form an electrographic paper. This coating is made possible primarily because of the insolubility of most dielectrics when exposed to a solution or wetted area containing potassium formate. The dielectric coatings of Example A of Applicant's commonly assigned U.S. application Ser. No. 788,063 are specifically described herein because of their particular adaptability to the environment of the papermaking process itself. It should be noted however that these and other dielectrics may be easily deposited at any time on a paper substrate that has either been or subsequently will be impregnated with potassium formate. For example, the dielectrics of the other examples in the aforementioned application are also chemically compatible with a potassium formate impregnated substrate.

The aforementioned dielectric coatings of Example A of Applicant's commonly assigned U.S. application Ser. No. 788,063 are seen to comprise the metallic salts of organic fatty acids wherein the salt has a metal iron selected from the group consisting of zinc, nickel, copper, and cobalt. The fatty acid radicals examined in the application included the octanoates, laurates, stearates, palmitates, oleates, linoleates, cholates and abietates. These metallic soaps are disclosed as being suspended in a water-ammonia solution and introducible as a coating on the paper during the papermaking process.

A solution containing one of the aforementioned metallic salts is prepared by mixing together, at room temperature, five parts by weight of zinc stearate, one part by weight of ammonia and ninety four parts by weight of water. It is to be noted that the 1 percent by weight of ammonia is minimal and additional amounts can be added without creating objectionable results. It is also to be noted that the zinc stearate can be present in as small of an amount as 3 percent by weight and can be increased to as much as 12 percent by weight. The mixture is next slowly heated to boiling to dissolve the zinc stearate as evidenced by a white-translucent solution.

The water-ammonia solution affords a water solution of the subject metallic salts which is particularly desirable for use on-line in the aqueous environment of papermaking. This solution can be applied to the paper in conjunction with the solution of potassium formate of Example A by a number of different methods. A first method is to combine the major ingredients into one solution and either spray, or coat one surface of the paper with the combination solution. A single solution containing all of the major ingredients is prepared by adding a saturated solution of potassium formate (approximately 77 percent by weight) to the previously formed water-ammonia suspension of one of the metallic salts. The major ingredients are readily combinable because: (1) the water-ammonia is quite compatible with the potassium formate and (2) the metallic salts are not dissolved by the potassium formate. A second method is to apply the two solutions separately by first

coating, dipping, immersing or spraying the potassium formate on the wet mat of paper and thereafter coating or spraying a single surface of the paper with the water ammonia solution of one of the metallic salts. It is important to note here that the potassium formate solution must penetrate the paper and hence should be preferably applied to both surfaces in order to gain a maximum surface wetting of the paper. This is not true of the water-ammonia solution of one of the metallic salts which must coat (and not penetrate) only one surface of the paper. It is to be furthermore noted that the paper can also be first coated on one surface with the water-ammonia solution of one of the metallic salts and thereafter sprayed or coated on the opposite surface with the aqueous solution of potassium formate. Thus the two solutions may be separately applied in any order. This is due mainly to the complete compatibility of the two solutions with each other, and with the aqueous environment of the papermaking process. The application of the two solutions either in combination or separately is to preferably occur at the papermaking process step identifiable as the size press stage with the paper traveling at 3,000 feet per minute. Further drying of the paper with subsequent calendaring next takes place within the papermaking process.

The resulting electrographic paper from the aforementioned process consists of a discrete dielectric coating of 90 to 150 micro inches on a paper substrate that has been substantially impregnated with the potassium formate. The dielectric coating comprises approximately 3 percent by weight of the original paper whereas the potassium formate is approximately 2 to 3 percent of the original paper weight.

It is therefore to be seen that the electroconductive agent, potassium formate is both usable as an additive alone or in combination with a dielectric to either form an electrically conductive paper or an electrographic paper. In the latter case, the electroconductive additive can be introduced either alone or in combination with suitable dielectrics that are also easily introduced into the paper during the papermaking process.

A series of tests have been run on paper impregnated with potassium formate both with and without the dielectric coatings. The results of these tests show that the addition by weight of 2 to 5 percent of the original paper weight of potassium formate results in a conductivity of ordinary bond (30 to 40 pounds) of approximately 5×10^6 ohms per square at only 18 percent relative humidity. This amount of conductivity below the 20 percent relative humidity point is highly desirable.

It was previously mentioned that paper becomes a good conductor of electricity when placed in a humid environment (i.e. 65 percent relative humidity). Potassium formate, in addition to being a good conductivity additive, also attracts and tends to hold water in the paper, and thus further increases the paper conductivity. An indication of the water holding ability of potassium formate is indicated by its solubility in water. At room temperature, 1.4 molecules of water dissolve one molecule of potassium formate or 3.31 grams of potassium formate per 1.00 grams of water. Compared to calcium chloride, which is considered a very soluble salt, potassium formate is almost six times as soluble on a molecule for molecule basis.

In addition to being a very effective moisture absorbant and conductivity additive for paper, potassium

formate meets the following requirements for a product which is to be handled by people. It is non-poisonous, nonflammable, noncorrosive, nonallergic, and does not promote the growth of fungus. It is also colorless, odorless, chemically neutral in water, inexpensive and readily available. These desirable properties make this conductivity additive even more attractive for the massive uses of a paper recording medium that contains it.

Having described the invention, what is claimed as new and secured by letters Patent is:

1. A paper impregnated with a moisture absorbent, electrically conductive agent, said moisture absorbent, electrically conductive agent comprising potassium formate in the amount of at least 2 percent by weight of said paper, said potassium formate attracting and holding water so as to thereby increase the paper conductivity.

2. An electrographic recording medium for receiving a latent charge image by application of a voltage thereacross comprising:

a conductive substrate comprising a paper impregnated with a moisture absorbent, electrically conductive agent, said moisture absorbent, electrically conductive agent comprising potassium formate, said potassium formate attracting and holding water so as to thereby increase the electrical conductivity of the paper; and,

a thin dielectric coating deposited on said conductive substrate.

3. The electrographic recording medium of claim 2 wherein the medium percentage by weight of potassium formate is 2 percent of the original paper weight.

4. An electrographic recording medium for receiving a latent charge image by application of a voltage thereacross comprising:

a conductive substrate comprising a paper impregnated with a moisture absorbent, electrically conductive agent, said moisture absorbent, electrically conductive agent comprising potassium formate; and

a thin dielectric coating deposited on said conductive substrate, said thin dielectric coating consisting essentially of a metallic salt of an organic fatty acid, wherein said salt has a metal ion selected from the group of metals consisting of zinc, nickel, copper, and cobalt.

5. The electrographic recording medium of claim 4 wherein the thickness of the dielectric coating is in the range of 90 to 150 micro inches.

6. The electrographic recording medium of claim 5 wherein the minimum percentage by weight of potassium formate is 2 percent of the original paper weight.

7. The electrographic recording medium of claim 4 wherein the dielectric coating consists essentially of zinc stearate.

8. The electrographic medium of claim 7 wherein the thickness of the dielectric coating is in the range of 90 to 150 micro inches.

9. The electrographic recording medium of claim 8 wherein the minimum percentage by weight of potassium formate is 2 percent of the original paper weight.

10. A method of increasing the electrical conductivity of paper, measured in ohms per square, comprising

the step of impregnating said paper with potassium formate.

11. A process of manufacturing an electrographic medium having a conductive paper substrate and a continuous dielectric surface layer, said process comprising the steps of:

- a. dissolving a first solute consisting essentially of a metallic salt of an organic fatty acid, in an ammonia and water solvent, so as to create a water-ammonia solution suspending the metallic salt, wherein said salt has a metal ion selected from the group of metals consisting of zinc, nickel, copper, and cobalt;
- b. dissolving a second solute consisting essentially of a saturated solution of potassium formate in the water-ammonia solution;
- c. spraying the resulting water-ammonia suspension of potassium formate and the selected metallic salt thereby impregnating the paper with the potassium formate and coating the paper with the metallic salt; and
- d. drying the resulting coated and impregnated paper so as to form a hardened electrographic medium that is usable over a broad range of relative humidities.

12. A process of manufacturing an electrically conductive recording medium having a paper substrate comprising the successive steps of:

- a. dissolving a solute, consisting essentially of potassium formate in water thereby forming an aqueous solution of potassium formate;
- b. impregnating the paper substrate with the aqueous solution of potassium formate, and
- c. drying the paper substrate so as to form a hardened paper that is electrically conductive at low relative humidities.

13. The process of claim 12 in which said paper is a wet, partially dried paper mat and wherein said step of impregnating the paper includes immersing the partially dried paper mat in the aqueous solution of potassium formate.

14. The process of claim 12 in which said paper is a wet, partially dried paper mat and wherein said step of impregnating the paper includes spraying the partially dried paper mat with the aqueous solution of potassium formate.

15. A process of manufacturing an electrographic medium having a conductive paper substrate and a continuous discrete dielectric surface layer, said process comprising the steps of:

- a. dissolving a first solute consisting essentially of a metallic salt of an organic fatty acid, in an ammonia and water solvent, so as to create a water-ammonia solution suspending the metallic salt, wherein said salt has a metal ion selected from the group of metals consisting of zinc, nickel, copper,

and cobalt;

- b. dissolving a second solute consisting essentially of potassium formate in water to thereby create an aqueous solution of potassium formate;
- c. impregnating the paper substrate with the aqueous solution of potassium formate;
- d. coating the impregnated paper substrate with the ammonia-water solution of metallic salt; and
- e. drying the resulting coated and impregnated paper so as to form a hardened electrographic medium that is usable over a broad range of relative humidities.

16. The process of claim 15 in which said paper is a wet, partially dried paper mat and wherein said step of impregnating the paper includes immersing the partially dried paper mat in the aqueous solution of potassium formate.

17. The process of claim 15 in which said paper is a wet, partially dried paper mat and wherein said step of impregnating the paper includes spraying the partially dried paper mat with the aqueous solution of potassium formate.

18. A process of manufacturing an electrographic medium having a paper substrate and a continuous discrete dielectric surface layer, said process comprising the steps of:

- a. dissolving a first solute consisting essentially of a metallic salt of an organic fatty acid, in an ammonia and water solvent, so as to create a water-ammonia solution suspending the metallic salt, wherein said salt has a metal ion selected from the group of metals consisting of zinc, nickel, copper, and cobalt;
- b. dissolving a second solute consisting essentially of potassium formate in water to thereby create an aqueous solution of potassium formate;
- c. coating the impregnated paper substrate with the ammonia-water solution of metallic salt;
- d. impregnating the paper substrate with the aqueous solution of potassium formate; and
- e. drying the resulting coated and impregnated paper so as to form a hardened electrographic medium that is usable over a broad range of relative humidities.

19. The process of claim 18 in which said paper is a wet, partially dried paper mat and wherein said step of impregnating the paper includes immersing the partially dried paper mat in the aqueous solution of potassium formate.

20. The process of claim 18 in which said paper is a wet, partially dried paper mat and wherein said step of impregnating the paper includes spraying the partially dried paper mat with the aqueous solution of potassium formate.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,811,935 Dated May 21, 1974

Inventor(s) Floyd T. Gould

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

IN THE CLAIMS

Claim 3, Line 32, delete "medium" and insert --minimum--.

Signed and sealed this 17th day of September 1974.

(SEAL)

Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,811,935 Dated May 21, 1974

Inventor(s) Floyd T. Gould

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

IN THE CLAIMS

Claim 3, Line 32, delete "medium" and insert --minimum--.

Signed and sealed this 17th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents