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[54] **ELECTROGRAPHIC RECORDING MEDIUM**
12 Claims, No Drawings

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[52] U.S. Cl..... **117/201,**
117/154, 117/167
[51] Int. Cl..... **B44d 1/18**
[50] Field of Search..... **117/201,**
167, 154

[56] **References Cited**
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ABSTRACT: Zinc stearate, other hydrophobic metal salts of organic fatty acids, and, in some instances, the acids themselves, are coated on a substrate such as paper to provide electrographic media of unusually low cost and resistance to high humidity. The coating materials can be selected for application in powder or extruded form, from a water-compatible solvent, or from an organic solvent.

ELECTROGRAPHIC RECORDING MEDIUM

BACKGROUND OF THE INVENTION

This invention concerns a low-cost electrographic medium that displays good reproduction qualities over a wide humidity range. More particularly, the invention relates to such a medium having a substrate, preferably paper, with a dielectric coating of either an organic fatty acid or a hydrophobic metallic salt of an organic fatty acid (commonly referred to as a metallic soap).

An electrographic medium is a sheet on which information, both alphanumeric and graphic, can be recorded by electronic means and hence without impacting the sheet, as with type or other markers. The medium generally has a supporting substrate, typically of paper, coated with a dielectric layer.

In brief, information is recorded on an electrographic medium by impressing, suitably with an electrode structure, a voltage across the medium in a pattern corresponding to the information. The substrate conducts the charge so that essentially all the applied voltage is across the dielectric layer. This voltage pattern across the dielectric layer contains all the information to be recorded and is referred to herein as a "latent charge image," or simply "latent image."

After the medium is exposed or imaged in this manner, the latent image is fixed, i.e., made permanent and usually visible, by applying a toner to the medium. The toner, generally in liquid suspension or powder form, is designed according to known techniques to adhere only to either the latent image on the medium or to the nonimage surfaces of the medium. In either case, the toner is fixed to the medium, typically by fusing with heat, to complete the recording operation.

The latent image preferably has a large potential gradient across the dielectric layer to facilitate the desired pickup of toner. For this reason, the dielectric layer preferably is very thin, and hence it requires a substrate for mechanical support. However, the gradient should not exceed the breakdown gradient of air, for otherwise the air at the surface of the dielectric layer will electrically break down and disperse the charge image.

It is also known that the structure of the dielectric layer and of the substrate should not disperse or dislocalize the applied voltage pattern. This has an effect similar to writing with pen on a blotter; the information pattern becomes blurred.

Also, inasmuch as most documents are frequently written on, electrographic media should accept writing; whether applied by pencil, pen, crayon or like markers.

In addition to retaining the latent charge image impressed on it during "exposure" to the information to be recorded, the dielectric layer must maintain the charge localized in the same pattern with which it was impressed. Further, the dielectric must maintain the charge localized for a sufficient time so that a toner can be applied to the medium, and processed to render the latent image permanent and visible. Should the localized charge disperse, there is a degradation of the finished copy. The electrographic medium of the present invention maintains an applied charge localized for such a period.

Presently, various electrographic papers exist, most of which have a dielectric layer of resin such as polystyrene, polyacrilate or acetate compounds. These materials are usually applied to the substrate in solution with a nonaqueous solvent such as acetone. It is apparent that application of the dielectric coating using an aqueous vehicle is desirable from a cost standpoint and from the standpoint of alleviating fire hazards and avoiding poisonous fumes. However, resin materials, being insoluble in water, are incompatible with a water environment. Further, the resin materials and the necessary organic solvents are expensive, and the fact that the dielectric cannot be applied as, essentially, an integral part of the process further increases the cost of electrographic paper produced in this manner. Due to the aforementioned considerations, therefore, a preferred process for producing the electrographic paper of this invention is discussed with

reference to the papermaking process. It is to be understood, however, that this electrographic medium can likewise be produced in an environment of other solvents such as kerosene. The other prior art dielectric materials that are applied in a water environment involve chemicals that are relatively expensive and in most circumstances difficult to prepare.

Therefore, it would be advantageous to apply the dielectric layer during the formation of the paper substrate in conventional papermaking equipment, with chemicals having low cost, and preferably with a process involving few steps.

In papermaking processes, there are substances added to the paper pulp to increase its wear strength, to provide a particular texture, or for waterproofing purposes. In the past, insoluble soaps of a fatty acid have been mixed directly with the paper stock to produce a water-resistant paper. The paper produced in this manner, however, is not capable of use as an electrographic medium nor was it contemplated that it should be used as such. This is due primarily to the absence of a discrete dielectric layer.

U.S. Pat. Nos. 1,370,650; 3,075,859; and 3,110,621 describe some of this prior art.

It has now been found, however, that a good electrographic medium results from coating the substrate, instead of impregnating it, with a line layer of a metallic soap. As most of the metallic soaps are insoluble in water, it had not been previously taught to provide an electrographic paper having a dielectric layer of an insoluble metallic soap.

OBJECTS OF THE INVENTION incompatible

In accordance with the foregoing statements, it is an object of this invention to provide a low-cost method of fabricating electrographic paper wherein the dielectric coating is hydrophobic.

It is a further object of the invention to provide an electrographic paper having a dielectric coating that exhibits excellent electrographic properties over a wide variation of relative humidities.

It is still a further object of the invention to provide a dielectric coating for electrographic media and which is relatively inexpensive.

Another object of the invention is to provide a dielectric coating for electrographic media which has the foregoing features and can be applied to the substrate from an aqueous composition.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

GENERAL DESCRIPTION

The present invention provides an electrographic medium of low cost and yet having good electrographic properties, especially at elevated humidities. In the past, attainment of such performance required a relatively high-cost electrographic medium. In its broad aspect, the invention achieves these desirable characteristics by the use of a hydrophobic metallic salt of an organic fatty acid as the dielectric layer of an electrographic medium. The layer is supported on a substrate, of which paper is a preferred form.

The metallic soap must be sufficiently hydrophobic that it remains nonconductive in a high-humidity environment. This enables the electrographic medium to be useful in humid environments.

Although numerous hydrophobic metallic salts of organic fatty acids (i.e. the insoluble metallic soaps) have electrographic properties, many have properties usually considered undesirable for an electrographic medium. Notwithstanding these properties, however, it is contemplated that all hydrophobic metallic salts of organic fatty acids fall within the broad spirit and scope of the present invention. Some of these undesirable properties are discussed hereinafter.

Thus, the barium and lead salts of organic fatty acids, including barium laurate, barium cholate and lead stearate, are poisonous. In addition, at least some salts of alkaline metals are not sufficiently solid for normal document use. Also, the aluminum salts of organic fatty acids are sticky, and hence probably undesirable for most applications. In other words, the material should have a melting point in excess of the highest operating temperature likely, otherwise it will be soft.

Other properties considered are smell and color. The metallic oleates and linoleates, for example, provide satisfactory dielectric layers for electrographic media, but are generally considered unsuitable because they have a noxious odor. The copper soaps result in a greenish coating on the medium, while the iron soaps result in a reddish coating. The zinc soaps, on the other hand, not only provide a good dielectric layer but are essentially colorless.

Further, different soaps are best adapted for use in different processes. Thus, where it is desired to apply the dielectric layer in an organic solvent, metallic soaps such as those of magnesium and calcium would be used. However, this use of organic solvents is generally costly due to the costs of fresh solvent and of recovering spent solvent.

Another method of applying a dielectric layer in accordance with the present invention is to use a metallic soap having a relatively long hydrocarbon chain and hence available in a powder form that can be dusted on the substrate; zinc cholate is such a substance. The subsequent application of heat to fuse the powder results in the desired dielectric layer. Alternatively, the soap can be extruded on the substrate. These processes can be practiced on line in the manufacture of a paper substrate by applying the powdered or extruded soap either prior to or subsequent to calendering of the paper.

The process considered most desirable, in that it is water compatible, provides for applying certain of the metallic soaps in a water-ammonia solution. The ammonia forms water-soluble complexes with many metallic soaps that alone are essentially water insoluble. More particularly, this application of the dielectric layer is accomplished by first partially drying the newly formed paper to remove the major quantity of moisture. A mixture of zinc stearate, for example, ammonia and water, is then deposited on the substrate and allowed to adhere thereto. After the solution is applied and the water and ammonia dried off, the highly hydrophobic metallic soap remains. The zinc soaps are considered most desirable for this process as they are nonpoisonous, colorless, water compatible and have a sufficiently high melting point. Further, because of the low cost of this approach and because the zinc soaps provide, in addition, a good writing surface, they are considered most desirable for practicing the invention. Other soaps, however, including those of silver, gold, copper, cadmium, cobalt, and nickel can also be applied in such a water-ammonia solution.

The various organic fatty acid radicals that were examined include the octanoates, laurates, stearates, palmitates, oleates, linoleates, cholates, and abietates.

The humidity conditions present during the use of electrographic paper are important to consider. In this respect, two conflicting requirements usually exist. The dielectric properties, especially ability to retain a charge, of the dielectric layer are best exhibited in an atmosphere of low humidity where resistivity is relatively high. However, the necessary conductive properties of the substrate, relative to that of the dielectric layer, usually require high humidity. Presently available electrographic paper forms a latent image, i.e., the charge image, satisfactorily in an atmosphere up to approximately 65 percent relative humidity. At high humidities, the charge retention properties are poor because the dielectric coating tends to break down.

The paper of the present invention, however, can be employed effectively at humidities considerably higher than this 65 percent value. In particular, it was discovered that since most metallic soaps are extremely hydrophobic, once deposited and allowed to dry, sufficient dielectric properties

are retained, up to a value in the vicinity of 95 percent relative humidity.

It should also be pointed out that the process of the invention is not dependent on the use of any particular paper substrate and in fact the invention is applicable to many other substrates such as cloth, ceramic tile, wood, etc.

Specific examples follow of some compounds examined in producing electrographic paper with the present invention.

EXAMPLE A

In the usual papermaking process, a wet mat of cellulosic material is produced that is, successively, partially dried, sized, completely dried, and then calendered. In practicing the present invention, the paper substrate is processed in a similar manner except that when the mat is partially dried, prior to calendering, it is subjected to a dielectric bath prepared according to the invention.

One solution is prepared by mixing together, at room temperature, five parts by weight of zinc stearate, one part by weight of ammonia 94 parts by weight of water. The mixture is then slowly heated to boiling to dissolve the zinc stearate. Additional ammonia can be added without creating objectionable results. The heated solution is observed to have a white translucent appearance.

The partially dried paper is coated with this solution, illustratively being applied by spray or roller. Further drying, and calendering as normal for the paper substrate, then causes the dielectric layer to harden to a hydrophobic coating which displays excellent electrographic properties.

In addition to zinc stearate, other metallic soaps that can be applied in a water-ammonia solution include the soaps of copper, nickel, and cobalt. For example, a coating solution, prepared by mixing seven parts by weight of cuprous stearate, two parts by weight of ammonia and 91 parts by weight of water, and applied to a paper substrate produced an electrographic medium that was highly satisfactory, even at elevated humidities. In addition, it appears that the fatty acids themselves in a water-ammonia solution provide a good electrographic paper.

EXAMPLE B

As previously mentioned, the dielectric layer of this invention can be applied in solution with an organic solvent, such as kerosene. One such coating solution was prepared by mixing, with heating where necessary, 10 parts by weight of aluminum stearate with 90 parts by weight of kerosene. The solution was then applied to a dried and calendered paper substrate. After drying, the resultant product functioned perfectly as an electrographic paper.

Other metallic soaps that can be applied in an organic solvent solution of the foregoing type include lithium, mercury, tin, lead, manganese, aluminum, iron, and bismuth. The metals of this group can be solubilized in an organic solvent using 5 to 10 percent by weight or more of the metallic soap. An example of another organic solvent used is methy ethyl ketone; however, the particular organic solvent is not considered critical to the practice of the invention.

EXAMPLE C

One method of practicing the present invention has been disclosed as a fusing method of powder-applying certain metallic soaps. This method can be practiced in the following manner. A metallic soap that is in powdered form at room temperature, such as zinc cholate, is evenly applied to cover the substrate. The powder is then fused to form a continuous coating by the application of heat and/or pressure.

Other metallic soaps, such as those of lithium, calcium and magnesium, with a long carbon chain to be available in powder form can be applied in this manner; notable example are lithium cholate and magnesium abietate.

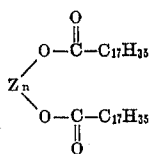
In applying the foregoing discussion, particularly the description of illustrative example, other properties of the

fatty acid compounds, particularly odor and toxicity, and color where of concern, should be considered as discussed above.

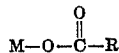
A further criterion associated with the electrographic paper of the present invention is that the soap layer not wet the paper or other substrate. The reason is to ensure that the dielectric material is in a substantially discrete layer separate from the substrate. This requirement that the soap not wet the substrate should be met regardless of how the soap is applied.

Common to all the foregoing examples is the low cost of at least many of the dielectric materials used therein, particularly when compared to the cost of prior art dielectrics used for electrographic media. Hence, it is considered that the present invention will provide electrographic media at a substantial cost saving over the prior art.

It is the inventor's judgement that the reason for attaining desirable electrographic media with the foregoing materials in the dielectric layer are attributable, at least to a limited extent, to the common organic structure associated with the hereinbefore-mentioned compounds in the dielectric layer. Zinc stearate, for example, has the formula



Nickel stearate has a similar formula in which the zinc ion is replaced by a nickel ion. Zinc palmitate likewise has a similar formula wherein the hydrogen-carbon chain is $\text{C}_{15}\text{H}_{31}$. From this it can be seen that the common structure is the



where M is a metal, or hydrogen as discussed above, and it is felt that this is a significant factor in providing the electrographic properties.

In sum, the invention teaches that the metallic salts or organic fatty acids, and in some instances the acids themselves, have sufficient hydrophobic properties, and the requisite physical properties, to function as successful and economically-useful dielectric coatings in electrographic media. Moreover, the materials are of low cost, which is of importance to facilitate wide usage of electrographic recording.

Further, these materials can be selected for any one of several application techniques. However, the realization that certain of these compounds are rendered water soluble when complexed with ammonia, and hence particularly desirable for use on line in the aqueous environment of paper making, is considered a further feature of the invention.

The invention also teaches that the zinc soaps, and particularly zinc stearate, are highly preferred for the dielectric layer of an electrographic medium. This is because the zinc salts of organic fatty acids are soluble in an ammonia-water solution, are essentially colorless and odorless, and provide a nontoxic product. Further, the product has a surface that can be written on readily, and in general, it is easy to handle.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained; and, since certain changes may be made in carrying out the above process and in the electrographic media set forth without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of

the invention, which, as a matter of language, might be said to fall therebetween.

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

1. An electrographic medium for receiving a latent charge image by application of a voltage thereacross comprising a thin dielectric surface coating deposited in a discrete continuous layer on a supporting paper substrate, said medium maintaining electrographic properties in a relatively high-humidity environment and being characterized in that said discrete dielectric coating is hydrophobic and consists essentially of a metallic salt of an organic fatty acid wherein said metal ion is said salt is selected from the group of metals consisting of zinc, nickel, copper, cobalt, aluminum, lithium, mercury, tin, lead, manganese, iron, and bismuth, and wherein said organic fatty acid radical is selected from the group consisting of stearates, palmitates, oleates, laurates, and linoleates.

2. An electrographic medium as defined in claim 1 in which said metallic salt is insoluble in water is soluble in ammonia and water.

3. An electrographic medium as defined in claim 1 in which said metallic salt is relatively insoluble in water and is soluble in organic solvents.

4. An electrographic medium as defined in claim 1 in which said metallic salt is soluble in other than a water solvent and is solid at room temperature.

5. An electrographic medium as defined in claim 1 in which said metallic salt is further characterized in that it provides a writing surface at room temperature and in said high-humidity environment.

6. An electrographic medium as defined in claim 1 wherein at least a major portion of said dielectric coating is zinc stearate.

7. An electrographic medium as defined in claim 1 wherein said coating is a solid at room temperature.

8. A process of manufacturing an electrographic medium having a paper substrate coated with a continuous discrete dielectric surface layer, said process comprising the successive steps of

a. dissolving a solute, consisting essentially of a metallic salt of an organic fatty acid, in an ammonia and water solvent, and providing sufficient solute in the solution to coat only a surface with said solute when covered with the solution, wherein said salt has a metal ion selected from the group metals consisting of zinc, nickel, copper, and cobalt and wherein said organic fatty acid radical is selected from the group consisting of stearates, palmitates, oleates, laurates, and linoleates;

b. coating said substrate with said solution; and

c. drying said coating on said substrate to harden said salt to a hydrophobic coating.

9. A process as defined in claim 8 in which said solution is coated on a wet, uncalendered paper mat, and comprising the further step of calendering said substrate subsequent to said coating step.

10. A process for manufacturing an electrographic medium comprising the steps of providing a paper substrate, applying to the surface of the substrate a continuous, thin, hydrophobic dielectric coating consisting essentially of a hydrophobic and stable metal salt of an organic fatty acid, wherein said metal ion in said salt is selected from the group of metals consisting of zinc, nickel, copper, cobalt, aluminum, lithium, mercury, tin, lead, manganese, iron, and bismuth, and wherein said organic fatty acid radical is selected from the group consisting of stearates, palmitates, oleates, laurates, and linoleates, and maintaining said substrate substantially free of said salt.

11. A process as defined in claim 10 in which said salt is soluble in ammonia and water.

12. A process as defined in claim 10 in which said salt is soluble in organic solvents.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,620,831

Dated November 16, 1971

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:

Column 1, line 71, after "the" insert -- paper-making -- .
Column 2, line 26, change "line" to -- thin -- ; line 33,
cancel "incompatible". Column 4, line 66, change "from" to
-- form -- . Column 5, line 11, change "sued" to -- used -- ;
line 46, change "themataterials" to -- the materials -- .
Column 6, line 12, change "is" to -- in -- ; line 16, change
"form" to -- from -- ; line 19, change "is", second occurrence,
to -- and -- ; line 44, change "slat" to -- salt -- .

Signed and sealed this 24th day of October 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents