

[54] **ELECTROSTATIC PRINTING PROCESS**

3,075,859 1/1963 Relph et al..... 117/201 UX
3,694,202 9/1972 Sawyer et al. 96/1.5

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[62] Division of Ser. No. 527,065, Feb. 14, 1966, abandoned, which is a division of Ser. No. 166,948, Jan. 17, 1962, abandoned.

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[51] Int. Cl. **D21h 3/66; G03g 7/00**

[58] Field of Search..... 117/201, 17.5, 212; 96/1.5, 1.4, 1.8

[56] **References Cited**

UNITED STATES PATENTS

2,297,691 10/1942 Carlson 117/201 UX

FOREIGN PATENTS OR APPLICATIONS

1,092,600 11/1967 United Kingdom..... 96/1.5
449,713 5/1969 Japan..... 96/1.5

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[57] **ABSTRACT**

The use of crystalline zeolitic molecular sieves in electrically conductive backing paper provides improved results in a conventional electrostatic printing process. The molecular sieves are employed in the backing paper in an amount sufficient to impart an electrical resistivity of less than 1×10^{12} ohm-cm over the range of relative humidity of from 5 to 90%.

2 Claims, No Drawings

ELECTROSTATIC PRINTING PROCESS

RELATED APPLICATIONS

This application is a division of application Ser. No. 527,065 filed Feb. 14, 1966, now abandoned, which in turn is a division of application Ser. No. 166,948, filed Jan. 17, 1962, now abandoned.

This invention relates to an electrostatic printing process which utilizes a zeolite-containing electrically conductive paper.

There presently exists a need for a paper which is electrically conductive over a wide range of humidity conditions. Such papers are especially needed in electrostatic printing processes, computers, and the like where it is not unusual to operate at relative humidities of less than 20%. Normally, paper has a specific resistance of 1×10^{12} ohm-cm or greater, whereas, a paper having a resistivity of 1×10^7 to 1×10^8 ohm-cm is desired in electrostatic printing processes for example.

Heretofore, the commercially available conductive papers have been extremely sensitive to change of humidity. Under conditions of high humidity, the paper will conduct electricity but as the humidity is decreased the paper loses its conductivity. As a result, in printing processes, for example, there is created the problem of maintaining good definition of images to be reproduced under low humidity conditions.

Accordingly, it is the main object of this invention to provide an electrostatic printing process using an electrically conductive paper which will retain its electrical characteristics regardless of the humidity conditions.

The invention provides an electrostatic printing process utilizing an electrically conductive paper which will maintain its electrical conductivity over the range of humidity of from about 5% to about 90%.

Whenever the electrical resistivity of a particular specimen is given, it is to be understood that the conductivity of such specimen would be the reciprocal of the resistivity.

The above objects are accomplished in general by a paper provided with a zeolite material, either natural or synthetic, sufficient to impart an electrical resistivity of less than 1×10^{12} ohm-cm over the range of relative humidity of from about 5 to 90%.

The process for making such an electrically conductive paper may comprise either incorporating the zeolite in the paper or coating the paper with a zeolite to impart to such paper an electrical resistivity of less than 1×10^{12} ohm-cm over the range of relative humidity of from about 5% to about 90%.

For purposes of this disclosure, "impregnating" means actually adding the zeolite material into the raw materials to be formed into the paper so that such zeolite is a basic constituent of the paper.

By "coating" is meant adding the zeolite to a surface of a product paper.

While the invention well described in further detail hereinbelow with reference to the greatly preferred crystalline zeolite materials such as zeolites A and X it is to be understood that the amorphous or jell type metal alumino-silicates made synthetically for water softeners and which have been called zeolites in the prior art are intended to be encompassed within the metes and bounds of this invention.

The crystalline zeolites as well as the amorphous metal-alumino-silicates suitable for use in this invention are characterized by oxygen tetrahedra containing a silicon

or aluminum ion. The aluminum ion with one less positive charge than silicon can only satisfy three negative charges of the four oxygens which surround it. To produce a stable structure it must have help from another positively charged ion. This is the function of the exchangeable ions such as sodium and calcium. Further, zeolites suitable for practicing the present invention have a framework of silicon-oxygen and aluminum-oxygen tetrahedra containing passageways therein extending in three directions.

The impregnating of zeolites into the paper to render it electrically conductive according to the invention can be effected at any point in the paper making operation or in a later separate operation. Thus, the zeolite may be added, for example, to the water slurries containing the fibrous materials to be formed into paper or the zeolite can be added at a subsequent point in the processing of the slurry, such as the beating or refining step. The zeolite can also be coated or sprayed onto a product paper. The coating of zeolites onto a paper can be accomplished by any of the methods presently employed for applying inorganic paper coatings. One such method is known as "conversion coating" and involves the application of a coating to paper already in roll form. Another method known as "on-machine coating," involves the application of a coating to one or both sides of paper as it is being made, dried and passed through the paper-making machine. The latter practice is exemplified by such methods as roll-coating, intaglio-offset coating, centrifugal-spray coating, and doctor-bar coating. Depending on the type of coating apparatus used, the coating may be applied to wet paper or dry paper as well as to paper of intermediate moisture content.

The amount of crystalline zeolite necessary to render a paper electrically conductive, according to the invention, depends on several parameters such as paper making techniques, type of paper, particle size of zeolite, etc. It has been found that when crystalline zeolite material having a particle size of 1-2 microns is coated on a paper such coating may comprise as low as 1% by weight of the paper stock. However, about 5% by weight is preferred. It is postulated that the lower limit is dependent on obtaining good point to point contact between crystalline particles which is possible with particles of the size described.

When the crystalline zeolite is actually made a constituent of the paper such point to point contact is not obtained and more zeolite is required. In this case the recommended amount of zeolite is from 5% to about 30% by weight of the paper stock. The maximum amount that can be utilized in either case (coating or impregnating) is limited by the fact that too much zeolite might affect paper strength or crease properties. It has been found that 50% by weight is the practical upper limit.

In the following discussion, the values given are for the purpose of indicating the general order of magnitude of resistivity that can be achieved by practicing the teachings of the invention, and not for the purpose of defining the ultimate values or composition attainable by such invention. Further the discussion in most part will be directed to an electrically conductive paper for use in reproduction processes and in particular to those based upon an electrostatic principle. An exemplary electrostatic printing process is described in U.S. Pat. No. 2,297,691, issued Oct. 6, 1942, to C. F. Carl-

son, the disclosure of which is incorporated herein to the extent pertinent. In this process a plane conductive backing is coated with a uniform layer of photoconductive insulating material. A strong electrostatic charge is developed on the surface of the insulating material which is then exposed to light. As a result the illuminated areas become conductive and drain off a substantial portion of the charge to the conductive backing leaving a latent electrostatic image on the insulating material surface. This latent image is then developed by contacting a dust with the surface to form an electrostatic dust image on the area of the surface which remains electrically charged, and then transferring the dust image to a sheet of paper.

In its broad aspects the invention is predicated on the discovery that when a paper is impregnated, incorporated, or coated with a crystalline zeolite, such paper will exhibit electrical characteristics, particularly electrical conductivity, which can be maintained substantially unchanged over varied relative humidity conditions.

A complete discussion of the naturally occurring crystalline zeolite materials such as chabazite, mordenite, erionite, analcite, faujasite is not believed to be necessary as there is adequate discussion of such zeolites in the literature.

Among the synthetic crystalline three-dimensional zeolites admirably suited for use in the invention are crystalline zeolites A and X which are described respectively in U.S. Pat. No. 2,882,243 and U.S. Pat. No. 2,882,244 issued Apr. 14, 1959, to R. M. Milton. Other suitable crystalline zeolites include those described as follows:

Zeolite F in U.S. Pat. No. 2,996,358

Zeolite Q in U.S. Pat. No. 2,991,151

Zeolite E in U.S. Pat. No. 2,962,355

Zeolite T in U.S. Pat. No. 2,958,952

The term "zeolite," in general, refers to a group of naturally occurring and synthetic hydrated metal aluminosilicates, many of which are crystalline in structure. There are, however, significant differences between the various synthetic and natural materials in chemical composition, physical properties and crystal structure, the latter as evidenced by X-ray powder diffraction patterns.

The structure of crystalline zeolitic molecular sieves may be described as an open three-dimensional framework of SiO_4 and AlO_4 tetrahedra. The tetrahedra are cross-linked by the sharing of oxygen atoms, so that the ratio of oxygen atoms to the total of the aluminum and silicon atoms is equal to two, or $\text{O}/(\text{Al} + \text{Si}) = 2$. The negative electrovalence of tetrahedra containing aluminum is balanced by the inclusion within the crystal of cations, for example, alkali metal and alkaline earth metal ions such as sodium, potassium, calcium and magnesium ions. One cation may be exchanged for another by ion-exchange techniques.

The crystalline zeolites may be activated by driving off at least a portion of the water of hydration. The space remaining in the crystals after activation is available for adsorption or adsorbate molecules having a size, shape and energy which permits entry of the adsorbate into the pores of the molecular sieves.

The crystalline zeolites occur as agglomerates of fine crystals or are synthesized as fine powders and are preferably tableted or pelletized for large scale adsorption uses. Pelletizing methods are known which are very sat-

isfactory because the sorptive character of the zeolite, both with regard to selectivity and capacity, remains essentially unchanged.

Crystalline zeolites in a hydrated state are uniquely suited for this invention, since these materials are electrical conductors and furthermore retain electrical conductivity over a wide range of temperatures and humidity. It is to be noticed that the invention is not predicated on the adsorbing properties of the zeolites but rather on the electrical properties.

In the first experiments which led to the invention two electrodes about one-eighth inch in diameter were inserted about 1 cm. apart into sodium zeolite A (4A) powder and the electrical resistance measured. The resistance value was found to be approximately 1×10^6 for zeolite Type 4A. Several other materials were tested in the same way including certain materials commonly used as paper coatings or fillers or pigments. These were kaolin clay, a natural calcium silicate known as wollastonite, a natural magnesium silicate known as talc, a natural amorphous silica known as diatomite, and a finely divided crystalline silica in the form of a silica flour. None of these materials exhibited any measurable electrical conductivity under the conditions described above.

After the above tests, a piece of paper was coated with zeolite 4A powder. A water slurry of zeolite 4A powder was prepared and applied to a 3 inch circle of filter paper by a filtration technique. The filter paper used was essentially a pure cellulose paper. After drying at approximately 110°C ., the ability of the coated paper to dissipate an electrostatic charge was tested. An electrostatic charge was applied to a gold leaf electroscope. The electroscope was obtained with the coated paper and the charge on the scope was dissipated as rapidly as when contacted with a metal conductor. In contrast, an uncoated paper exhibited no electrical conducting effect.

In subsequent tests, experimental papers were made by incorporating or coating paper with the following materials:

Solid	Particle Size, Microns
Sodium Zeolite A	1-5
Sodium Zeolite X	2-5
Natural Chabazite	<100
"Zeolex" (an amorphous aluminosilicate)	<100
Sodium Chloride	<100
Calcium Hydroxide	<100
Kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	2

The three crystalline zeolites were compared with the amorphous sodium aluminosilicate "Zeolex" to determine the effect of crystallinity.

The crystalline zeolites were compared with other crystalline ionic materials such as sodium chloride and calcium hydroxide, and with kaolin.

Two methods were employed in the preparation of the experimental paper specimens: (a) the materials listed above were applied in the form of a coating on a surface of a paper; (b) the paper was reconstituted with the material incorporated within its fibers. The paper chosen for this work, was ashless filter paper. This paper was chosen for the following reasons: (1) the paper contains no original contaminating filler or sizing, and (2) because it consists of loosely packed cel-

lulose fibers that could be fairly easily reconstituted. Any paper could be so treated by suitable processes known in the papermaking art.

The coated papers were prepared by dispersing the insoluble powders (crystalline zeolites, kaolin, and the like) in distilled water. The dispersion was then applied to a circular piece of filter paper, 9 cm. in diameter. The water-soluble sodium chloride and partially soluble calcium hydroxide were dissolved to form a saturated water solution. Then a calculated amount of the water soluble material was added to the solution and the mixture filtered through the paper specimen. By supporting the paper specimen on the glass frit mounted in a pressure filter a smooth uniform coating was obtained. Each paper specimen prepared in this manner contained about 17 wt-% of the solids. The coated paper specimens were all dried in the air at 95°C.

In order to prepare paper specimens containing the incorporated filler, the following procedure was used. About 1.53 grams of the filter paper was dispersed in distilled water in the form of a pulp slurry by agitation in 200 cc. of water in a mixer. The insoluble powders (zeolite or clays) were then added to the pulp slurry, thoroughly mixed in a blender and then filtered rapidly onto a matt in a pressure filter of 1-liter capacity under 60 psig. pressure of gaseous nitrogen. The slurry was later separated from the matt as a paper. The filtering procedure provided dense paper compacts with a reasonably uniform thickness and density. The soluble materials [NaCl and Ca(OH)₂] were prepared in the form of a concentrated solution prior to addition to the water-pulp slurry followed by filtration. The quantity of salt contained in the saturated solution adsorbed by the paper was considered in computing the composition of the final paper compact. Two series of reconstituted paper compacts were prepared containing, respectively, 17 wt-% and 70 wt-% of the materials described above. In another series, paper specimens containing varying amounts of zeolite Type 4A powder were prepared using the procedure above described.

After preparation, the paper specimen was cut into a strip 2½ by 1 inches. Each end of the strip was fitted to an electrode consisting of two rectangular copper plates under spring tension, each measuring 1.0 × 0.25 inches. On this basis, the conducting length of each specimen of paper was 2 inches and the thickness of all of the coated papers was assumed to be constant at 0.01 inches. The reconstituted paper compacts containing the incorporating solids varied considerably in thickness and, therefore, the thickness had to be measured separately for each sample with a micrometer. From the resistance, *r*, in ohms and the conducting length, *L*, in cms, and cross-sectional area, *A*, in cm², of each specimen, the specific resistance, *R*, was computed for each measurement. $R = r \times A/L$.

The resistivity of all the specimens containing 17 wt-% of the filler was measured at 27°C. in a dry nitrogen atmosphere, and in air, at 65% relative humidity. The instrument used in measuring the resistance of each paper specimen was the Type H DC bridge, distributed by the Instrument Division of Federal Telephone and Radio Company of Clifton, N.J. This instrument has a measuring range of 1×10^6 to 5×10^{14} ohms and is capable of applying a voltage varying from 0 to 1,000 volts to the specimen to be measured. The resistances of all coated papers and reconstituted paper specimens containing 17 wt-% of the filler were measured under an applied voltage of 100 volts. The resis-

tance of all of the other specimens were measured under an applied voltage of 500 volts. The time for each measurement was held constant at 3 minutes so that any possible capacity effect might be kept constant. Resistivity data for these conditions is tabulated in Table I. From the data in Table I, it is evident that for these samples, a concentration of 17 wt-% of the crystalline zeolite reduces the electrical resistivity significantly at high humidities. It is to be understood that this figure is not the lower limit but merely indicative of the results that can be obtained by incorporating or coating crystalline zeolites on paper.

The resistivity of the paper containing the above-mentioned materials incorporated to the extent of 70 wt-% was measured in air at 5%, 25% and 65% relative humidity, at 27°C. Prior to equilibration in the humidity chamber, these specimens were dried at 95°C. in air. Resistivity data is given in Table II.

The resistivity of the series of paper specimens containing incorporated crystalline zeolite Type 4A in a range of varying concentrations was measured in air at 25% and 65% relative humidity at 27°C. These data are shown in Table III.

At a relative humidity of 5% at 27°C., it is found that the paper specimens containing 70 wt-% of the crystalline zeolite 13X in particular, reduced the resistivity of the paper by at least at factor of 1×10^4 to 1×10^5 , whereas the amorphous material Zeolex was much less effective and sodium chloride exhibited no effect at all. The observed resistance of both the paper control specimen and the paper containing sodium chloride was greater than 1×10^{13} ohm-cm. It is apparent that the resistivity of the paper specimen is dependent upon relative humidity to varying degrees depending upon the added pigment or material present. The resistivity of the paper with no additives is most dependent upon relative humidity, since it experiences a resistivity change of about 1×10^5 . The paper specimens containing the zeolite materials are the least dependent upon humidity and exhibit a change in resistivity of about 10. Under the same conditions, the paper specimens containing sodium chloride exhibited a change in resistivity of about 1×10^3 .

From the above discussed data, it will be apparent that the crystalline zeolite materials can be used to achieve an electrically conductive paper at almost all conditions of humidity. The specific quantity of a crystalline zeolite which must be impregnated in or coated on a paper to impart the electrical properties will depend upon the method of producing the paper, the type paper and use of such paper. A considerable reduction in the quantity of crystalline zeolite needed to render the paper electrically conductive can possibly be obtained with more refined paper making techniques which will be obvious to the artisan in the papermaking art.

While the present invention has been described in reference to two specific techniques for preparing a paper containing a crystalline zeolite material so as to render such paper conductive, improvements in these techniques and other techniques will suggest themselves to those skilled in the paper-making art. For example, it is possible to add the reactant materials for making a synthetic zeolite into the slurry and then permitting the crystals to grow as the raw materials are formed into a paper.

For example, the particle size of the molecular sieve and the ability to disperse the agglomerate particles

during application either on the paper in the form of a coating or within the fibers of the paper if so incorporated, are all important in the practice of this invention. The examples and experimental results discussed above are for the purposes of illustration only and show that the electrical conductivity of paper can be drastically improved by the application of a molecular sieve material of the crystalline zeolite type.

What is claimed is:

1. In an electrostatic printing process the improvement which comprises applying a uniform layer of photoconductive insulating material to an electrically conductive paper backing provided with a sufficient amount of crystalline zeolite material to impart to such paper an electrical resistivity of less than 1×10^{12} ohm-cm over the range of relative humidity of from 5 to

TABLE I

THE RESISTIVITY OF PAPER CONTAINING 17.2 WT-% FILLER		
Filler Material	Specific Resistance (ohm-cm)	
	Dry N ₂ Atmosphere 27°C.	65% Relative Humidity, 27°C.
Coated		
Na ₂ A Zeolite	3.8×10^{11}	6.1×10^7
Na ₂ X Zeolite	*	3.8×10^7
Chabazite	2.5×10^{11}	2.0×10^7
"Zeolex"	*	2.3×10^7
NaCl	6.4×10^{11}	8.9×10^8
Ca(OH) ₂	*	5.1×10^8
Kaolin	*	5.8×10^8
Uncoated Paper	*	1.3×10^9
Incorporated		
Na ₂ A Zeolite	*	1.4×10^8
Na ₂ X Zeolite	*	2.0×10^8
Chabazite	*	1.1×10^8
"Zeolex"	*	
NaCl	1.1×10^{12}	1.1×10^4
Ca(OH) ₂	*	2.7×10^9
Kaolin	*	3.0×10^8

* greater than 1×10^{13} ohm-cm.

TABLE II

THE RESISTIVITY OF PAPER CONTAINING 70 WT-% FILLER INCORPORATED

Filler Material	Specific Resistance (ohm-cm)		
	5% Relative Humidity, 27°C.	25% Relative Humidity, 27°C.	65% Relative Humidity, 27°C.
Blank	*	*	1.3×10^9
Na ₂ A Zeolite	3.4×10^8	4.3×10^7	3.9×10^6
Na ₂ X Zeolite	1.3×10^7	1.8×10^6	6.5×10^5
Chabazite	5.8×10^9	1.8×10^7	2.7×10^6
"Zeolex"	3.9×10^9	1.2×10^7	1.2×10^6
Ca(OH) ₂	3.9×10^9	6.7×10^{10}	1.1×10^8
Kaolin	—	1.2×10^{11}	3.5×10^8
NaCl	*	7.0×10^8	2.2×10^5

*Greater than 10^{13} ohm-cm.

TABLE III

THE EFFECT OF CONCENTRATION OF TYPE 4A POWDER ON RESISTIVITY OF PAPER

Concentration of 4A Zeolite, wt-%	Specific Resistance (ohm-cm)	
	25% Relative Humidity, 27°C.	65% Relative Humidity, 27°C.
Blank	∞*	1.3×10^9
10	9.4×10^{12}	2.6×10^8
20	4.0×10^{12}	2.5×10^8
30	2.8×10^{12}	1.5×10^8
35	1.8×10^{12}	1.6×10^8
40	2.9×10^{11}	3.5×10^8
45	2.4×10^{10}	5.1×10^7
50	1.9×10^{10}	3.8×10^7
55	1.2×10^8	1.7×10^7
60	7.6×10^7	6.4×10^6
70	4.3×10^7	3.9×10^6
80	1.5×10^7	1.9×10^5

90%; developing a strong electrostatic charge on the surface of said layer; exposing the charged layer to light source to render the illuminated areas thereof sufficiently conductive to drain off a substantial portion of said charge to said electrically conductive paper backing; then contacting a fine dust with the surface whereby to form an electrostatic dust deposit on the areas of said surface remaining charged after exposure and removing excess dust not electrostatically held on said surface.

2. A process according to claim 1 wherein the electrically conductive paper is provided with from about 1% by weight to about 50% by weight of the paper base stock of crystalline zeolite material.

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