NON-WOVEN CONDUCTIVE PAPER MAT

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FIG. 1

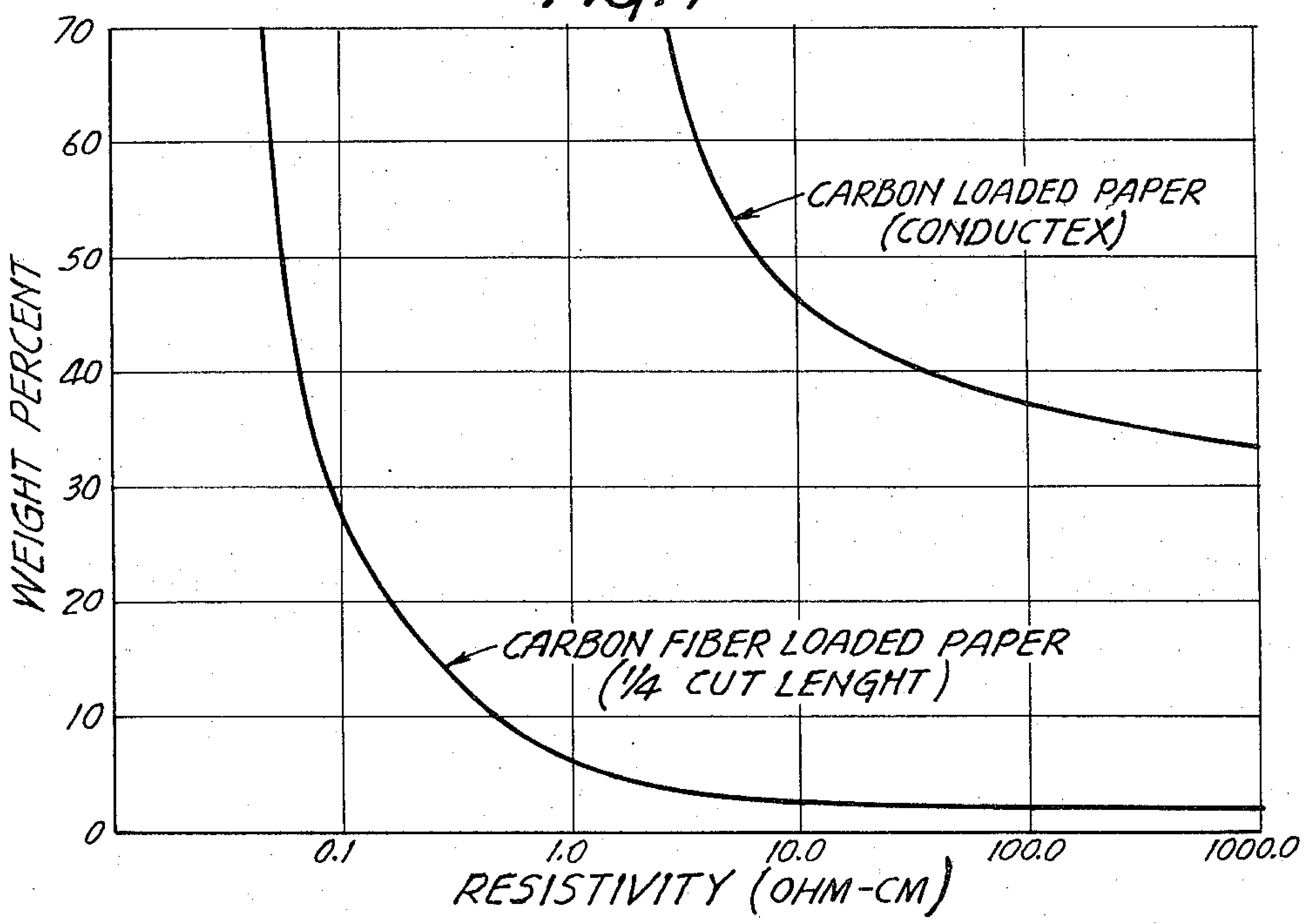
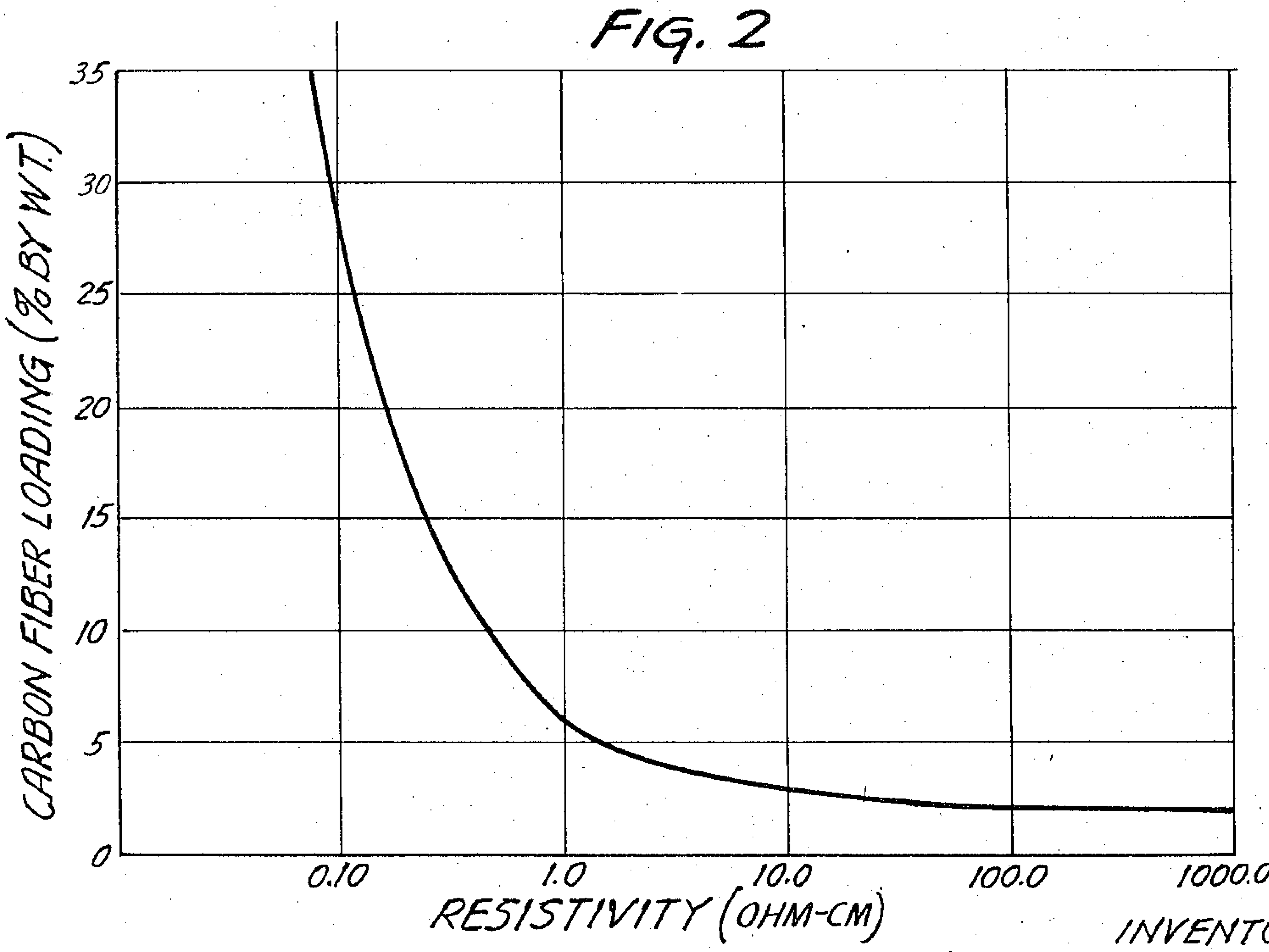


FIG. 2



INVENTORS
MANUEL FILREIS
VICTOR R. FRANER
BY Carpenter, Abbott, Coulter & Kinney
ATTORNEYS

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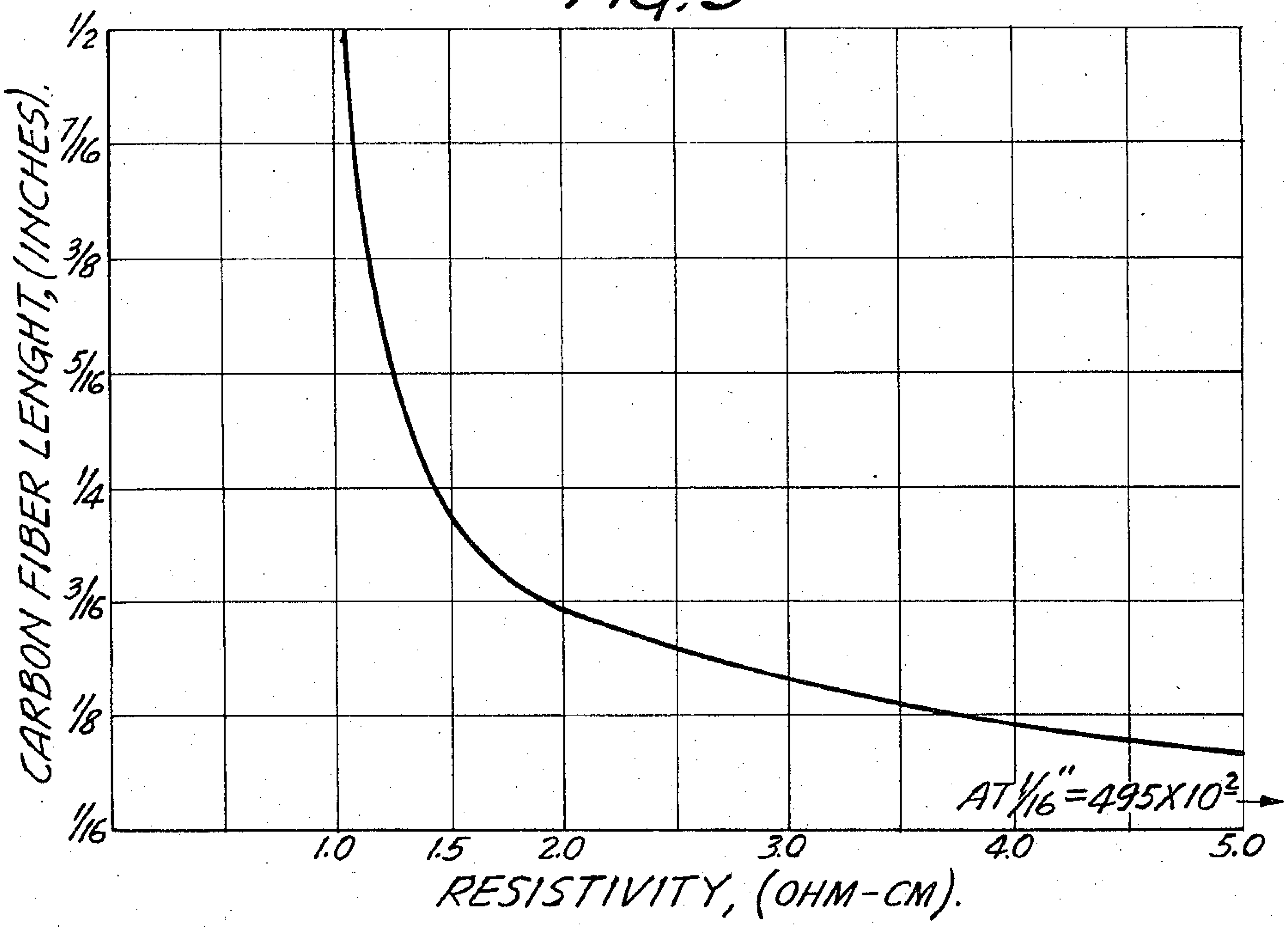
FIG. 3



INVENTORS
MANUEL FILREIS
VICTOR R. FRANER
BY
Carpenter, Abbott, Coulter & Kinney
ATTORNEYS

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3,367,851
NON-WOVEN CONDUCTIVE PAPER MAT

Manuel Filreis, Minneapolis, and Victor R. Franer, St. Paul, Minn., assignors to Minnesota Mining & Manufacturing Company, St. Paul, Minn., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

A substantially infusible porous, non-woven, electrically conducting web having 1% to 35% by weight of essentially uniformly distributed, electrically conductive carbonaceous fibers, said carbonaceous fibers having a carbon content of at least 80% by weight, an average fiber length from about 1/16 to about 7/16 inch and an average denier of from 0.25 to 5, and at least 50% of insulative, infusible fibers, said electrically conducting web having a specific resistivity from about 0.036 to about 60 ohm-cm.

This invention relates to new products and to methods for their production. In one aspect this invention relates to electrically conducting fibrous webs. In still another aspect this invention relates to substantially infusible electrically conductive papers incorporating highly carbonaceous filaments therein and to heater elements constructed therefrom.

Although various types of electrical heating elements have been developed, many problems arise in the preparation of a sheet or web which is capable of uniform heat generation over a large area, avoiding hot spots due to erratic resistance variation and localized heating. Impregnated chemicals and embedded wires and powders have not provided a satisfactory solution to these problems. Inexpensive heating panels having uniform electrical properties as well as good physical properties, such as flexibility, color, physical strength, have been the object of extensive investigation.

Electrically conductive webs and papers have also been extensively used in facsimile reproduction, wherein a conductive paper, coated with various suitable materials, is imaged by the passage of electrical current from a scanning stylus. Perhaps the most common conductive paper comprises a base web of cellulosic fibers impregnated or filled with carbon particles and coated with electrosensitive material. Such carbon powder loaded papers and their manufacture are illustratively described in U.S. Patent Nos. 3,012,928 and 3,022,213. The incorporation of carbon particles into webs to impart electrical conductivity has many disadvantages. One of the major disadvantages has been the extremely high loading of carbon powder required to obtain sheet resistivities below 60 ohm-centimeter. Moreover, at such high loading levels the sheet color is necessarily black, the handling properties (e.g. flexibility, tendency to smudge, etc.) are usually poor, the sheet density is high, and the sheet porosity is low. Although it is possible to achieve higher electrical conductivity with lower loading of finely divided conductive particles, the composition of the web or matrix into which the conductive particles are incorporated is critical, e.g. from 5% to 100% of a synthetic polymer binder, as described in U.S. Patent No. 2,993,816.

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It is an object of this invention to provide a porous, electrically conductive fibrous web which does not require electrically conductive granules.

Another object of this invention is to provide a substantially infusible electrically conductive paper which has good physical or mechanical properties and which is not necessarily dark in color.

Still another object of this invention is to provide an electrically conductive web which does not vary significantly in electrical conductivity with differing relative humidity conditions or with repeated web flexure.

Yet another object of this invention is to provide an electrically conductive web of high porosity and low density.

It is also an object of this invention to provide a novel electrical heating element.

A further object of this invention is to provide a simple and economical procedure for preparing the aforementioned electrically conductive webs.

Accordingly, it has been found that a substantially infusible non-woven, porous, fibrous web having at least 50 weight percent of infusible fibers and from 1% to 35% by weight of essentially uniformly distributed, electrically conductive, highly carbonaceous filaments will provide the above and other advantages, provided the carbonaceous filaments have an average fiber length of 1/16 to 7/16 inch and an average denier from 0.25 to 5 (preferably about 0.4 to 1), the filament length being at least ten times the filament diameter. It has also been found that such electrically conductive webs can be made on a conventional paper making machine and that the specific electrical resistivity can be maintained at values between about 0.036 and about 60 ohm-cm. The ready dispersibility of the highly carbonaceous fibers in aqueous slurries, particularly wood or other cellulosic pulp slurries, is exceptional, since the density difference between such conductive fibers and wood fiber is small and fiber segregation is minimized.

The major fibrous components, constituting at least 50 weight percent of the non-woven web, are substantially infusible and may be either of synthetic or natural origin. For manufacture on a paper machine using conventional procedures the non-woven web may be prepared from an aqueous suspension of infusible organic or inorganic fibers having paper making properties, including cellulose, cellulose derivatives, asbestos, asbestos-glass mixtures, asbestos-cellulose mixtures, cellulose-glass mixtures, etc. Various other infusible staple fibers and fillers, e.g. metal filaments and flakes, mica flakes, thermoset resins, titanium dioxide, zinc oxide, may also be used. Minor amounts of heat fusible material, e.g. fibrids, not altering the basic infusibility of the construction, may also be included. Although it is generally preferred to incorporate the conductive carbonaceous filaments into an insulative non-woven matrix, the electrical properties of the sheet may be modified for certain uses by including other conductive materials therein, usually in a minor amount compared to the amount of conductive carbonaceous filaments. The use of cellulosic paper making pulp as the major component of these conductive webs is particularly preferred.

Electrically conductive highly carbonaceous (i.e. over 80% carbon, preferably over 90% carbon) filaments are well known. In one method for their preparation fibers high in cellulosic content are heated in the absence of oxygen and moisture within the temperature range of about 300° F. to about 1500° F. until substantially complete carbonization has been effected, and subjecting the material further to a temperature above about 1500° F. for a sufficient time to render it electrically conductive. This method is described in U.S. Patent No. 3,011,981. Another procedure, described in U.S. Patent No. 3,107,-152, involves heating a cellulosic material at a rate of about 10° C. temperature rise per hour to about 50° C. temperature rise per hour from an initial temperature of about 100° C. to about 400° C., followed by a heating rate of up to 100° C. per hour to a final temperature of about 900° C., followed by a further heating until substantial graphitization has occurred. Other carbonization procedures are described in U.S. Patent No. 3,071,637. The highly carbonaceous tow, roving, fibers, filaments, or fabrics produced in the above manner and with a denier from 0.5 to 5 are beaten or chopped to provide an average fiber length from 1/16 to 7/16 inch, preferably from 1/8 to 3/8 inch. When the average fiber length falls below this lower limit, the resistivity of the web at constant loading increases markedly, whereas average fiber lengths above the maximum becomes difficult to handle and blend with the other fibers and can also tend to produce sheets with erratic resistivities from lot to lot. Within the range of useful deniers, some increase in conductivity may be attained with the smaller deniers at the same loading levels.

Although the electrically conductive, highly carbonaceous filaments are relatively friable, they have sufficient flexibility to withstand normal flexing of the porous web or paper into which they have been incorporated and do not otherwise necessarily significantly affect other desirable physical properties of the final sheet within the above-mentioned loading levels. However, if less than about 1% or more than about 35% of the carbonaceous filaments are used, control of resistivity becomes extremely difficult.

FIGURE 1 illustrates the lower resistivity achieved in a wood pulp paper with 1/4 inch carbonaceous filaments (about 90 weight percent carbon) as compared to similar levels of carbon powder loading. It is seen that a paper with 60% carbon powder (Conductex) loading corresponded in resistivity to a paper containing about 4% carbonaceous filaments, the latter having the additional advantage of higher porosity, lighter color, and better handling properties. In general, conventional carbon powder loaded paper requires from about 50% to over 100% carbon loading to achieve values at specific resistivity comparable to the conductive webs of this invention, and such sheets readily smudge and lose carbon at the higher loading values. Similarly the incorporation of metal flakes into a paper sheet requires over about 50% loading before a significant change in the specific resistivity is achieved, and both metal flakes and metal filaments tend to increase the sheet density and decrease sheet porosity. Due to the oxidation of certain metals, such as aluminum and copper, papers relying on metal flakes or filaments can vary considerably in specific resistivity over an extended period of time. Moreover, metal filaments have been found to be difficult to disperse in a pulp slurry and to impart some undesirable properties to the sheet, e.g. stiffness, etc.

FIGURE 2 shows the variation in specific resistivity with loading achieved with 1/4 inch carbonaceous fibers (90 weight percent carbon). Control of resistivity with these carbon fibers is attained with from 3% to 35% by weight of the carbonaceous fibers, the range of 4% to 30% being preferred.

FIGURE 3 illustrates the relationship of fiber length to specific resistivity in a paper having a 5% loading of carbonaceous filaments (about 90 weight percent carbon). Adequate control of resistance requires an average fiber length from 1/16 to 7/16 inch, preferably from 1/8 inch to 3/8 inch.

From the above it will be seen that, within the specified limits, the resistivity of the final sheet, as well as sheet color and physical properties, can be carefully controlled. By varying the basis weight (10 to 100 pounds per 3000 square feet ream) and freeness or porosity of the sheet (30 to 70 degrees Schopper-Riegler freeness), as well as the physical properties of the other fibers and fillers used, even further regulation can be achieved. The following illustrates typical procedures for preparing conductive webs or papers in accordance with this invention.

Example 1

Highly carbonaceous, electrically conductive cloth, prepared by graphitizing procedures described earlier, was cut into 2 inch squares and dispersed with water in a slusher, the treatment being continued until the cloth was reduced to fibers having an average length of about 1/8 inch. These carbonaceous fibers (about 90 weight percent carbon) were then uniformly dispersed in an aqueous paper pulp slurry in a stock chest to provide a 9% loading of the conductive fibers, the balance being wood pulp. This slurry was added to the headbox of a 9 inch paper machine for the paper making run, the paper machine having an 80 mesh wire screen, the caliper being maintained at between 5 and 6 units during the run. The specific resistivity of the resulting paper was 0.540 ohm-cm. as measured with a Wheatstone bridge.

Example 2

Highly carbonaceous electrically conductive fibers (1/4 inch length, 0.4 denier, 99.9% carbon) were dispersed in an aqueous slurry containing as solids 60.6 weight percent asbestos fiber (paper making grade), 12 weight percent glass microfibers (1/4 inch length) and 24 weight percent of powdered, fusible phenol-formaldehyde type resin, the carbonaceous fibers constituting 3.4 weight percent of the total solids. Using a 10 inch by 12 inch Williams hand sheet former with an 80 mesh wire a sheet was formed and dried. The resulting paper had a thickness of 6.5 mils and a resistivity of 0.975 ohm-cm. When electrical contacts are bridged with this sheet and the voltage is regulated to provide sufficient heating to effect fusion of the phenolic powder, the resistivity dropped to a value of about 0.8125 ohm-cm., which value remained constant thereafter.

Following the procedures of Example 2 further hand sheets were prepared as shown in Table I, the average length of the carbonaceous fibers being about 1/4 inch.

TABLE I

Ex.	Solids	Thickness mil	Resistivity (ohm-cm.) Before Fusion	Resistivity (ohm-cm.) After Fusion
3	6% carbonaceous fibers (99.9% carbon). 12% glass microfibers (1/4 inch length). 58% asbestos, paper making grade. 24% fusible powdered phenolic resin.	0.007	0.322	0.287
4	13% carbonaceous fiber (99.9% carbon). 12% glass microfiber (1/4 inch length). 24% fusible powdered phenolic resin. 51% asbestos, paper making grade.	0.007	0.098	0.084
5	3.4% carbonaceous fibers (99.9% carbon). 12% glass microfibers (1/4 inch length). 24% fusible powdered phenolic resin. 60.6% asbestos, paper making grade.	0.0065	0.975	0.813
6	1.25% carbonaceous fibers (99.9% carbon). 12% glass microfibers (1/4 inch length).	0.006	3.60	2.94

TABLE I—Continued

Ex.	Solids	Thickness mil	Resistivity (ohm-cm.)	
			Before Fusion	After Fusion
	24% fusible powder phenolic resin. 62.75% asbestos, paper making grade.			
7	11% carbonaceous fibers (90% carbon). 88% synthetic mica. 1% alum and polyethylene imine coagulants.	0.0045	2.79	---------
8	20% carbonaceous fibers (90% carbon). 10% glass microfibers. 69% synthetic mica. 1% alum and polyethylene imine coagulants.	0.011	0.313	---------
9	9% carbonaceous fibers (90% carbon). 16% glass microfibers. 75% asbestos, paper making grades.	0.007	1.806	---------
10	8% carbonaceous fibers (90% carbon). 92% asbestos, paper making grade.	0.0085	1.641	---------
11	16% carbonaceous fibers (90% carbon). 24% mica flakes. 59% glass microfibers. 1% alum coagulant.	0.011	13.2	---------
12	11% carbonaceous fibers (90% carbon). 19% wood pulp. 70% asbestos, paper making grade.	0.0055	0.798	---------
13	36% carbonaceous fibers ($\frac{1}{2}$ inch length, 90% carbon). 65% wood pulp.	0.0115	0.132	---------
14	9% carbonaceous fibers (90% carbon). 25% zinc oxide. 65% wood pulp. 1% alum coagulant.	0.008	2.21	---------
15	9% carbonaceous fibers (90% carbon). 25% titanium dioxide. 65% wood pulp. 1% alum.	0.012	2.02	---------
16	14% carbonaceous fibers ($\frac{3}{4}$ inch length, 90% carbon). 86% wood pulp.	0.010	0.170	---------
17	21% carbonaceous fibers (1 inch length, 90% carbon). 79% wood pulp.	0.010	0.195	---------
18	9% carbonaceous fibers (99.9% carbon). 90.9% wood pulp. 0.1% wetting agent.	0.006	0.540	---------

Example 19

A 9 inch wide roll of conductive paper containing carbonaceous fibers and wood pulp (50 degrees Schopper-Riegler freeness) was coated with a lead thiosulfate coating (0.0015 inch thickness) prepared as shown in U.S. Patent No. 2,251,742. The coated paper was air dried and cut into a size that would fit the Western Union Desk-Fax facsimile receiver. A test pattern was transmitted to the receiver and successfully imaged on the coated paper using standard procedures.

Example 20

A food warming tray was constructed using a carbonaceous fiber containing paper of this invention as the heating element. The back side of a 10 inch by 20 inch metal plate was covered with a thin electrically insulating coating capable of withstanding the elevated temperatures reached by the heating element. For operation at 120 volts with a 300 watt heating requirement, the resistance of the heating element is 48 ohms. With metal electrodes making contact at both ends of the heating element along the 10 inch dimension, the specific resistance of the heating element should be 24 ohms per square. A conductive paper having carbonaceous fibers and wood pulp meeting these requirements was cut to size and fitted with both electrodes and was then bonded to the insulating coating of the metal plate. A thermally insulating film was then used to cover the heating element, providing an

integral warming unit. When 120 volts were applied across the heating element, heat was uniformly generated by the element and transferred to the metal plate, providing a low loss, very evenly distributed heat over the tray surface. Among the advantages of this tray were immediate transfer of heat because of intimate contact, large area of heat transfer, lower element temperatures and absence of hot spots due to localized heating.

Having described our invention, we claim:

1. A substantially infusible porous, non-woven, electrically conducting web having from 1% to 35% by weight of essentially uniformly distributed, electrically conductive carbonaceous fibers, said carbonaceous fibers having a carbon content of at least 80% by weight, an average fiber length from about $\frac{1}{16}$ to about $\frac{7}{16}$ inch and an average denier of from 0.25 to 5, and at least 50% of insulative, infusible fibers, said electrically conducting web having a specific resistivity from about 0.036 to about 60 ohms-cm.

2. A porous electrically conductive paper having from 1% to 35% by weight of essentially uniformly distributed, electrically conductive, highly carbonaceous fibers having a carbon content of at least 80% by weight, an average fiber length from about $\frac{1}{16}$ to about $\frac{7}{16}$ inch and an average denier of from 0.25 to 5, and at least 50% of infusible cellulosic fibers, said electrically conductive paper having a specific resistivity from about 0.036 to about 60 ohms-cm.

3. A porous, electrically conductive paper comprising at least 50 weight percent cellulosic fiber and from 1% to 35% by weight of essentially uniformly distributed, electrically conductive, highly carbonaceous fibers having a carbon content of at least 80% by weight, an average fiber length from about $\frac{1}{16}$ to about $\frac{7}{16}$ inch and an average denier of from 0.25 to 5, said electrically conductive paper having a specific resistivity from about 0.036 to about 60 ohms-cm.

4. A substantially infusible, porous, non-woven, electrically conducting web comprising at least 50% by weight of insulative infusible fibers and from 1% to 35% by weight of essentially uniformly distributed, electrically conductive carbonaceous fibers having a carbon content of at least 80% by weight and having an average fiber length from about $\frac{1}{16}$ to about $\frac{7}{16}$ inch and an average denier of from 0.25 to 5, said electrically conductive web having a resistivity from about 0.036 to about 60 ohm-cm.

5. The electrically conductive web of claim 4 in which said carbonaceous fibers have a carbon content between about 90% and about 99.9% by weight.

6. The electrically conductive web of claim 4 in which said carbonaceous fibers have a carbon content above about 95% by weight.

7. An aqueous slurry comprising, based on total solids content, at least 50 weight percent of cellulosic fiber suitable for use on a paper machine and from 3% to 35% by weight of electrically conductive, highly carbonaceous fibers having a carbon content of at least 80% by weight, an average fiber length from about $\frac{1}{16}$ to about $\frac{7}{16}$ inch and an average denier from 0.5 to 5.

8. An electrical heating element which comprises electrical contacts bridged with a substantially infusible, porous, non-woven, electrically conductive paper comprising at least 50 weight percent of cellulosic fiber and from 3% to 35% by weight of essentially uniformly distributed, electrically conductive, highly carbonaceous fibers having a carbon content of at least 80% by weight, an average fiber length from about $\frac{1}{16}$ to about $\frac{7}{16}$ inch and an average denier from 0.5 to 5, said electrically conductive paper having a specific resistivity of from 0.036 to about 60 ohms-cm.

9. A recording sheet capable of being used in facsimile image reproduction which comprises an electro-sensitive coating on a conductive substrate, said conductive substrate being a substantially infusible, porous, non-woven, electrically conductive web having at least 50% by weight

of insulative, infusible fibers and from 1% to 35% by weight of essentially uniformly and randomly distributed, electrically conductive carbonaceous fibers with a carbon content of at least 80% by weight, an average fiber length from about 1/16 to about 7/16 inch and an average denier of from 0.25 to 5, said electrically conductive web having a specific resistivity from about 0.036 to about 60 ohms-cm.

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HOWARD S. WILLIAMS, *Primary Examiner.*

JOHN H. MACK, *Examiner.*

W. VAN SISE, *Assistant Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,367,851 February 6, 1968

Manuel Filreis et al.

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

Column 5, line 20, "grades" should read -- grade --; line 30, "36%" should read -- 35% --.

Signed and sealed this 21st day of October 1969.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents