

Dec. 31, 1963

J. J. UBER ET AL
COATED PAPER SHEET ADAPTED FOR ELECTROPHOTOGRAPHIC
REPRODUCTION
Filed Aug. 18, 1958

3,116,147

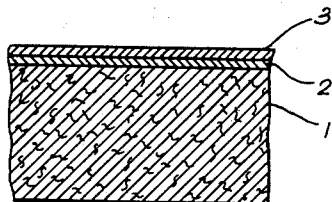


Fig. 1.

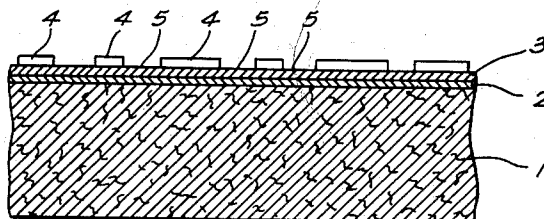


Fig. 2.

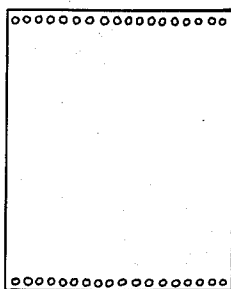


Fig. 3.

INVENTORS.
JAY J. UBER,
MORGAN E. GAGER

BY

Cleveland B. Hollenbaugh
ATTORNEY.

1

2

3,116,147

COATED PAPER SHEET ADAPTED FOR ELECTROPHOTOGRAPHIC REPRODUCTION

Jay J. Uber, South Hadley, and Morgan E. Gager, South Hadley Falls, Mass., assignors to The Plastic Coating Corporation

Filed Aug. 13, 1958, Ser. No. 755,787

8 Claims. (Cl. 96—1)

This invention relates to a paper sheet which is adapted for the electrophotographic reproduction of images, to a paper sheet carrying a coating which is adapted for the production of permanent images which can then be used as a printing plate for the reproduction of images by lithographic printing methods, and to such a lithographic printing plate.

Coated paper has heretofore been developed which is adapted for the electrophotographic reproduction of images. It is used for making a positive or a negative print by a four-step procedure. The paper is first made sensitive to light by giving it a blanket, negative, electrostatic charge on the coated side of the paper in the dark. A convenient way of doing this is by ion transfer from a corona discharge. The sheet, while carrying the electrostatic charge is exposed by any of the conventional photographic procedures, such as, by either contact or projection. The electrostatic charge is lost or reduced in the exposed areas and retained in the masked areas, to form a latent electrostatic image on the surface of the paper. The latent image on the paper is then developed by applying to the exposed surface a resin powder, hereinafter referred to as a "toner," carrying an electrostatic charge. The powder image is fixed by melting the resin powder so that it fuses to the paper surface to produce a durable image, having a light-fastness determined by the pigmentation of the toner.

The toners used for the direct production of copies must have color. This color may be furnished by natural pigmentation of the resin used or by a pigment carried thereby. The toner is retained by the image areas to form a direct image or by the background areas to form a reversed image depending upon its polarity with respect to the surface areas to be developed. When the toner is charged positively with respect to the image area to be developed, a direct image is obtained. When the toner is charged negatively with respect to the image area, a reversal image is obtained.

During the sensitization of the coating on the paper by the application of a blanket, negative electrostatic charge to its exposed surface, its reverse surface must be electrically grounded. It is grounded by placing the sheet of paper on a grounded electrical conductor. For this reason it is necessary for the paper-base sheet to be an electrical conductor to ground the lower surface of its coating to the electrically grounded conductor on which it rests. In the case of a sheet having a minimal electrical conductivity, it is necessary for the sheet to be in close and uniform contact with the electrically conductive surface on which it rests to secure a uniform dissipation of electricity from all parts of the paper base sheet. In the case of a sheet having good electrical conductivity, such close contact is unnecessary, although the sheet must be electrically grounded at one or more points.

Papers of this type carrying a developed image are suitable for use as lithographic printing plates for making multiple copies. Such printing plates are prepared by the use of a toner which, after fusion, produces a surface which is wetted by lithographic ink. Resins such as copal, sandarac, "Vinsol," and rosin, as well as hard waxes, can be used as the toner for this purpose need not carry pigment, although pigment may be included to facilitate the inspection of the image during its develop-

ment. In lithographic printing, the sheet is treated with water to make the background areas hydrophilic and the ink adheres to the hydrophobic letters or image on the sheet, but not to the background areas. This ink is then transferred to another sheet of paper by the use of a lithographic printing press. For this reason the final step in the production of a printing plate of this type is to render the background areas of the plate hydrophilic, so that they are not wetted by a lithographic ink when treated with water. Such lithographic printing plates can be prepared in a very short period of time and are satisfactory for the reproduction of a limited number of copies. They may be prepared for either direct or off-set lithographic printing.

Paper base lithographic printing plates of this type have offered several major advantages over the conventional metal based dichromate-casein printing plates, despite their limitation to relatively short runs in which a relatively small number of copies are made. They are much less expensive to produce. They can be produced in their sensitizable form and stored indefinitely. Therefore, they can be marketed in their sensitizable form, ready for immediate development, thereby avoiding the serious difficulty presented by the short useful life of a sensitized dichromate-casein metal plate. Further, when operation of a lithographic printing press on which these paper base plates are being used is interrupted, the background hydrophilic areas of the plate do not require immediate protection from atmospheric oxidation as in the case of a metal base plate of the casein-dichromate type. The requirement for protecting the background areas of the metal base dichromate-casein plates from atmospheric oxidation upon each interruption of the operation of a lithographic printing press even for a few minutes, by the application of a protective coating to the plate and then its removal prior to the resumption of the printing operation, is a major expense factor in lithographic printing.

In the foregoing, and elsewhere in this specification, the term "dichromate-casein printing plates" is used for the purposes of brevity to mean an aluminum or zinc plate which is sensitized by the application of a film of casein, egg albumin or gelatine which is made light-sensitive by ammonium dichromate.

It will be understood that, where the term "electrophotographic master" is used herein, the term is used to mean a sheet which is adapted to receive an image by electrophotographic reproduction, but which does not carry such an image and which is adapted by form and dimensions for attachment to the roll of a lithographic printing press or of a lithographic office duplicating machine.

The term "lithographic printing plate" is used in the commonly accepted sense to mean a printing plate having hydrophobic image areas which are receptive to lithographic ink and hydrophilic background areas which when wet with water, will not accept a lithographic ink. This term is used to designate plates which carry images adapted either for off-set lithography or direct lithographic printing.

As noted hereinbefore, it is necessary for the paper base of a sheet adapted for the electrophotographic reproduction of images to be an electrical conductor at the time the electrostatic charge is imposed on the sheet. This requirement is a source of major difficulty in securing uniformly satisfactory performance with electrophotographic reproduction papers under different climatic conditions. It is also a source of difficulty in the use of the sheets with different types of machines in which the papers are more or less automatically processed, under conditions in which they are exposed to somewhat elevated temperatures in a dry atmosphere before and during

the formation of the electrostatic image. Thus, when the paper base of an electrophotographic sheet becomes bone dry, it will not accept a latent electrostatic image and to perform properly must contain at least 3.5%, by weight, of moisture, i.e., be at equilibrium with an atmosphere having a relative humidity of at least about 40%.

Many theories as to the mechanism by which cellulose fibers conduct electricity have been advanced but there is no generally accepted theory. It is, however, known that the electrical conductivity of the fiber is dependent on its moisture content and upon the distribution of the moisture through the fiber structure, and that the conductivity is extremely sensitive to changes in the moisture content of the fiber.

The moisture content of a cellulosic fiber and, hence, its electrical conductivity is determined by the relative humidity of its environment. Thus, it has been shown that the resistance of cotton fibers decreases from about 10^{14} ohms at 5% relative humidity to about 10^7 ohms at 95% relative humidity. Further, there is a pronounced hysteresis in the change in the conductivity, with changes in the relative humidity, due to difference in the equilibrium moisture content of cellulose on absorption and desorption.

The effect of the relative humidity and of changes in the relative humidity on the conductivity of a paper sheet is even more pronounced than in the case, for example, a cotton fiber which has not been subjected to the paper making process. This is believed to be due to the hydration of the cellulosic fiber in the paper making process and to the presence of the sizing material which is usually present in the paper sheet. Since the degree of hydration and of sizing of two different paper sheets which are intended to be identical often differ materially even under careful control in the paper-making process, the conductivity characteristics of the two sheets will also often differ materially.

As can be appreciated from the foregoing, the control of the conductivity of the paper-base of an electrophotographic sheet and, hence, the control of its performance in the electrophotographic process is a complex problem. A sheet which gives good performance when in equilibrium, for example, with a relative humidity of 70% may be entirely useless in an atmosphere having a relative humidity of 10%.

Now it is an object of this invention to provide a paper-base sheet which is adapted for the reception of an image by electrophotographic processing, the performance of which in its processing, is largely independent of the relative humidity of its environment, which requires no special moisture-conditioning or pre-moisturing treatments to give uniformly satisfactory performance and which gives satisfactory performance under widely varying relative humidities.

Other objects of this invention and its various advantageous features will become apparent as this description proceeds.

This invention is the result of our research which has demonstrated that the presence of a hygroscopic inorganic salt within the paper-base of a sheet adapted for electrophotographic processing causes the paper-base to have the electrical conductivity required for uniformly satisfactory electrophotographic processing under all ordinary conditions of atmospheric relative humidity, without any special pre-moistening or moisture conditioning prior to the use of the sheet for the formation of an electrostatic image, and without otherwise adversely affecting other properties of the sheet. It is our belief that the action of the hygroscopic, inorganic salt in the paper-base is to increase its electrical conductivity under conditions of low relative humidity both by increasing its moisture content above that which it would normally have in the absence of such a salt and by its action as an electrolyte to further increase the electrical conductivity of the base

sheet. The action of the hygroscopic salt as an electrolyte decreases the minimal amount of moisture which the sheet must carry. This research has demonstrated that the minimum quantity of a hygroscopic, inorganic salt in the base sheet which will cause the sheet to perform satisfactorily under conditions of low humidity, does not adversely affect the performance of the sheet under conditions of high relative humidity.

The sheet adapted for the reproduction of images by electrophotographic processing, in accordance with this invention, comprises a sheet of paper which has a hygroscopic, inorganic salt throughout its body structure, which has an outer surface layer an electrophotographic coating consisting of a photoconductive, finely-divided, inorganic pigment in a matrix of a film-forming and insulating material which bonds the photoconductive pigment onto the surface of the sheet. The sheet may carry one or more intermediate coatings of an organic film-forming material between the surface of the paper base and its outer, electrophotographic coating and will preferably carry one such intermediate coating to improve its planarity.

The hygroscopic, inorganic salt which is dispersed throughout the paper-base of this electrophotographic sheet may be any one of the wide variety of such salts. In general, we prefer to use one of the more highly hygroscopic salts which is relatively non-corrosive in nature, which is non-poisonous to human beings and which does not have other objectionable features.

The various inorganic salts may be classified as to their relative hygroscopicity in terms of the percent humidity which they will maintain in a gas phase in a closed vessel containing a saturated aqueous solution of the salt together with an excess of the salt in the form of an undissolved, solid phase. In general, we prefer to use a salt which has a hygroscopicity such that it will, under these conditions, maintain less than 45% humidity in the gas phase. Table I presents a list of such salts which are suitable for our purpose, together with the percent humidity which they are capable of maintaining.

TABLE I
Hygroscopic Inorganic Salts

Solid phase:	Percent humidity
$\text{ZnCl}_2 \cdot \frac{1}{2} \text{H}_2\text{O}$	10
$\text{LiCl} \cdot \text{H}_2\text{O}$	15
$\text{K}_2\text{C}_2\text{H}_3\text{O}_2$	20
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	32.3
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	42
$\text{K}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$	43

The paper-base of the electrophotographic sheet in accordance with this invention need contain only a relatively minor percentage by weight of a hygroscopic salt, and should not contain an amount which is large enough to cause the paper-base to become noticeably moist as evidenced either by its appearance or by limpness under conditions of relatively high relative humidity. We prefer to utilize a percentage, by weight, of the hygroscopic salt which will maintain a moisture content of at least 1.3%, by weight, when in equilibrium with an atmosphere having a relative humidity of 20% and not more than 10%, by weight, when in equilibrium with an atmosphere having a relative humidity of 70%.

The range of percentages, by weight, of the inorganic salt which we may include in the base sheet, depends upon the strength of the hygroscopicity of the salt. Thus, with the strongly hygroscopic lithium chloride, we may include an amount within the range of about 0.2%, by weight, to about 1.30%, by weight, in the paper-base sheet, while with the less hygroscopic calcium chloride, we may include an amount within the range of about 0.5%, by weight, to about 2.5%, by weight.

The hygroscopic inorganic salt may be introduced into the paper-base sheet in the course of its manufacture.

5

Thus, the paper in the partially or completely dried state, after its formation on a Fourdrinier machine, may be sprayed with an aqueous solution of the hygroscopic, organic salt, or it may be impregnated with an aqueous solution of the salt by a tub-sizing operation. This operation may be carried out prior to any coating operation to which the paper may be subjected in the course of its manufacture. Alternatively, the hygroscopic salt may be included in the coating composition which is applied to the paper, in which case it is carried in part into the base sheet by the solvent of the coating composition.

We prefer not to apply an aqueous solution of the inorganic salt to a completed base paper, since such application tends to cause the paper to cockle and otherwise to become deformed. However, we may apply the inorganic salt to the paper base sheet after it is completed, in the form of a solution in a suitable organic solvent. Thus, we may apply lithium chloride or calcium chloride to a finished paper-base in the form of a solution in ethyl alcohol.

The paper sheet which forms the base of the electrophotographic film in accordance with this invention may be a coated paper identical with that heretofore used in the production of the prior art papers of this type, except that it contains a hygroscopic salt dispersed throughout the paper itself. The coated paper which has heretofore been used has been one of the conventional coated papers, i.e. one which is coated with a clay-casein coating or a similar coating. Such papers are well known to the paper industry and are commercially available under many different brand names. When using, as a base sheet, a coated paper identical with that heretofore used for the production of the prior art, electrophotographic sheets, the product in accordance with this invention is distinguished from the prior art sheets by the presence of the hygroscopic salt within the paper itself. As already noted, this intermediate film may be either a clear film of an organic, film-forming material, or such a film carrying a pigment.

Alternatively, the paper sheet which forms the base of our electrophotographic sheet may be an uncoated, cellulosic sheet containing a hygroscopic salt. The use of such a sheet offers both an economic advantage over the use of a coated sheet, such as that used in the production of the prior art papers, due to its lower cost and a technical advantage in that the use of an uncoated cellulosic base sheet results in a more translucent final sheet, than when a coated paper is used as a base sheet.

In a specific embodiment of this invention, the electrophotographic sheet is in the form of a master which is adapted by its form and dimensions for attachment to the cylinder of a lithographic printing press of either the office duplicating machine type or of the commercial printing type. Such a master may be either square or rectangular and its opposite edges by which it is attached to the press cylinder may be punched, slotted, or straight-edged to adapt it for attachment to the particular press roll on which it is to be used after its development into a lithographic printing plate. This master will preferably comprise the sheet carrying an intermediate coating of an organic film-forming material as described hereinbefore.

Another specific embodiment of this invention is a lithographic printing plate prepared by the electrophotographic development of an image on the master in accordance with this invention. This printing plate has the same form and dimensions as the master from which it is produced, as described in the foregoing. It differs from the master from which it is prepared in that the outer coating of the master comprising a film or layer of photoconductive pigment and a film-forming, insulating matrix, in turn, carries on predetermined areas of its outer surface a thin film of a hydrophobic substance, such as, for example, a resin or a wax, which is receptive to lithographic ink. The location, shape and size of the areas

6

covered by this hydrophobic material are predetermined in the production of the lithographic printing plate by the electrophotographic reproduction of an image, which may be either the positive or the negative of that which is reproduced in the process. The areas of the film or layer of the photoconductive pigment and the film-forming, insulating matrix not covered by the hydrophobic film are hydrophilic and readily wettable with water.

The products in accordance with this invention are diagrammatically illustrated in the accompanying drawing in which like reference characters are used to designate like parts wherever they may occur.

In the drawing:

FIGURE 1 is a broken cross-section of a preferred form of the electrophotographic sheet or of the electrophotographic master in accordance with this invention,

FIGURE 2 is a broken cross-section of the copy produced by the electrophotographic sheet illustrated by FIGURE 1, and of one embodiment of the lithographic printing plate in accordance with this invention, and

FIGURE 3 is a plan view of an electrophotographic master and of a lithographic printing plate in accordance with this invention.

Referring specifically to FIGURES 1 and 2, the numeral 1 designates a cellulosic sheet having within its body structure a uniformly dispersed hygroscopic salt, and carrying on its surface a thin film 2, comprising an organic film-forming solid, which may or may not be pigmented. It may, for example, be a film of a conventional paper coating material such as, for example, a casein-clay film. The paper sheet 1, may be any grade of paper made from wood pulp, from cotton rags or from mixtures of wood pulp and rags. The film 2 carries on its outer surface a thin film or layer 3, of a finely-divided, photoconductive inorganic pigment embedded in a matrix of a film-forming, insulating material. The combination of the cellulose film 1, and the paper coating film 2, is in effect a commercial coated paper of any of the various types sold under numerous different brand names by different manufacturers, except that the paper sheet 1 carries a hygroscopic salt.

Referring specifically to FIGURE 2, the numerals 4, -, 4 designate fused toner which has been deposited on the surface of the film 3 of the photoconductive pigment in the film-forming, insulating matrix in the electrophotographic reproduction process. The areas of the fused toner 4, -, 4 may form either a positive or negative image and in the case of a lithographic printing plate is ordinarily a positive image, since these are the hydrophobic areas of its surface which are receptive to lithographic printing ink. The areas 5, -, 5 are merely exposed areas of the surface of the film 3 in the case of copies not intended for use as a lithographic printing plate. In the case of the lithographic printing plate, these areas are specially treated to render them hydrophilic. This may be done, for example, by treating the areas with an acidified ferrocyanide solution.

The particular embodiment of our electrophotographic master illustrated by FIGURE 3 is provided with punched attachment edges for affixing it to the cylinder of a lithographic printing press. Both its length between the attachment ends and its width are predetermined to permit its use on the particular lithographic printing press upon which it is intended to be used. The cross-section of this electrophotographic master is illustrated by FIGURE 1.

In producing the sheet adapted for the electrophotographic reproduction of images, in accordance with this invention, we may, for example, impregnate a sheet of paper with an aqueous solution of one of the hygroscopic salts listed hereinbefore in Table I, in the course of the manufacture of the paper. We may, for example, deposit an amount of calcium chloride within the range of about 0.4%, to about 2.5%, by weight. This impregnated paper may then be coated with a casein-clay coating fol-

lowing the usual paper-mill coating techniques. A coating composition which we may use is illustrated by Example 1.

EXAMPLE 1.—PIGMENTED CASEIN COATING

	Parts by weight
Casein	15
Aqua ammonia (30%)	3
Water	82
Blanc fixe (dry)	75
Clay (dry)	25

As an alternative to the casein of Example 1, we may use as the film-forming material of the composition a converted starch or one of the butadiene-styrene latices. As an alternative to the mixture of blanc fixe and clay, we may use either alone, or we may use calcium carbonate, calcium sulphite, satin white, talc, or one of the titanium pigments.

As an alternative to the pigmented casein coating illustrated by Example 1, or one of the similar aqueous coating compositions mentioned above, we may apply a clear or pigmented lacquer coating as the film 2. Clear lacquer coatings which are suitable for this purpose are illustrated by Examples 2-4, inclusive, given by Table II.

TABLE II

Example Nos.....	2	3	4
Cellulose acetobutyrate.....wt. percent..	10	-----	-----
Polyvinyl butyral.....do.....	-----	10	-----
Ethyl cellulose.....do.....	-----	-----	10
Toluene.....do.....	62.5	25.0	62.5
Ethanol.....do.....	15	52.5	15
Butyl acetate.....do.....	14	14	14

As noted hereinbefore, the hygroscopic inorganic salt may be introduced into the paper-base by including it in the composition with which the paper is coated to form the film 2. In following this alternative, a hygroscopic salt which does not react with the other ingredients of the composition and which is soluble in the solvent of the composition must be used. These requirements impose some limitations on the hygroscopic salts which may be used. Thus, for example, calcium chloride is unsuitable for use with a casein coating composition, such as that illustrated by Example 1 since it causes the precipitation of the casein from the ammoniacal solution. Again, limitations are imposed on the use of this alternative when utilizing coating compositions which utilize organic solvents due to the insolubility of inorganic hygroscopic salts in the solvents.

Lithium chloride, zinc chloride and zinc nitrate are suitable hygroscopic salts for use on an aqueous casein solution such as that illustrated by Example 1. Thus, we may add from about 1.0%, by weight, to about 1.2%, by weight, of lithium chloride to the composition illustrated by Example 1, to secure the requisite conductivity in the paper base sheet which is coated with the composition. Again, we may add an amount of the less hygroscopic zinc nitrate within the range of about 2.0% to about 10%, by weight, to the composition illustrated by Example 1, to secure a suitable impregnation of the base sheet of paper.

The film 3 is then deposited on the film 2. We apply this film from a composition in which the film-forming material is dissolved in an organic solvent. We may use any one of a number of film-forming materials as the insulating matrix which retains the inorganic pigment on the surface of the intermediate coating 2, and forms the sensitive electrophotographic coating 3. Silicone resins, polyvinyl chloride resins, the polyethylenes, phenolic resins, polyester resins, methacrylate resins, polystyrene resins, styrenated alkyd resins, and vinyl acetate-vinyl chloride copolymer resins are suitable for this purpose.

The photoconductive, inorganic pigment which we use

in the film 3 may be, for example, zinc oxide or lead oxide. A satisfactory zinc oxide for our purpose is that sold under the trade name of "Florence Green Seal No. 8." This zinc oxide meets both ASTM specification D79-44 and Federal specification TT-Z301 and has the following analysis:

Insoluble in HCl.....	.03% maximum.
Loss at 110° C.....	.25% maximum.
Total sulfur as SO ₃	.04% maximum.
Lead oxide (PbO).....	.01% maximum.
Total zinc oxide as ZnO.....	99.5% minimum.

In this sensitive electrophotographic coating, we prefer to use about 1 part, by weight, of the insulating, film-forming material to an amount of the zinc oxide within the range of about 2.6 parts, by weight, to about 4.5 parts, by weight, and prefer to use about 1 part of the film-forming material to an amount of the zinc oxide within the range of about 2.8 parts, by weight, to about 4.0 parts, by weight.

The examples which follow specifically illustrate coating compositions which are suitable for the deposition of the electrophotographic coating 3 on the paper base coated with the film 2 in the production of the new products in accordance with this invention. It will be understood that the compositions of the films which are deposited by these various compositions are identical with the composition of the non-volatile components therein, i.e. all the ingredients except the volatile solvent or solvents in the composition.

EXAMPLE 5

	Parts by weight
Silicone resin solution (G.E.-SR-82).....	26
Zinc oxide (Florence Green Seal No. 8).....	39
Toluene	35
Total.....	100

The silicone resin solution used in this composition contained 60% solids, by weight, and 40%, by weight, of xylene. The solution had a viscosity within the range of about 5 to about 30 centipoises at 25° C. and was straw in color.

EXAMPLE 6

	Parts by weight
Copolymer of n-butyl methacrylate and iso-butyl methacrylate (Lucite 46).....	12.25
Zinc oxide (Florence Green Seal No. 8).....	43
Toluene	56.25
Total.....	111.5

The copolymer of n-butyl methacrylate and iso-butyl methacrylate used in this composition was prepared by the use of equal parts, by weight, of the two monomers and has a density of 1.05 and a refractive index at 25° C. of 1.4778.

EXAMPLE 7

	Parts by weight
Polymerized iso-butyl methacrylate (Lucite 45).....	12.25
Zinc oxide (Florence Green Seal No. 8).....	43
Toluene	56.25
Total.....	111.5

The polymerized iso-butyl methacrylate used in this composition had a density of 1.05, a refractive index of 1.477 and a dielectric constant of 2.5.

EXAMPLE 8

	Parts by weight
Styrene butadiene copolymer (Pliolite S5B).....	10
Zinc oxide (Florence Green Seal No. 8).....	34
Toluene	71.5
Total.....	111.5

The styrene-butadiene copolymer used in this composition was high in styrene, had a softening point of

50° C.±3° C. a solution viscosity within the range of about 160 to about 195 seconds as measured by a No. 4 Ford cup of a xylene solution containing 33½%, by weight, of the resin, a specific gravity of 1.05, a refractive index of 1.585, a specific surface resistivity of 10×10^{16} and a dielectric constant of 2.56 at 1000 cycles.

EXAMPLE 9

	Percent by weight
Styrenated alkyd copolymer solution (Cycopol S-101-1) -----	24.0
Zinc oxide (Florence Green Seal No. 8) -----	42.5
Xylene -----	33.5
Total -----	100.5

The styrenated alkyd copolymer resin solution used in this composition contained 50%±1%, by weight, of solids dissolved in petroleum spirits. The solution had a color of 5-8 (Gardner 1933) a viscosity at 25° C. of Z1-Z4 and weighed 7.6 pounds per gallon. The solid resin had an acid number of 3-8.

Images may be reproduced on both the electrophotographic master sheet and the electrophotographic master, in accordance with this invention in generally the same manner that images have been reproduced on the prior art paper-base electrophotographic sheets. The steps involved in such electrophotographic reproduction have been generally described hereinbefore. Furthermore, the equipment that has heretofore been used with the paper-base electrophotographic sheets is entirely suitable for the reproduction of images using our new products. Thus, neither new techniques nor new equipment are required for the use of these products. These are important advantages of these new products.

These products offer two additional advantages over the prior art paper-base electrophotographic sheets, from the standpoint of their processing to reproduce images. One of these advantages has already been noted hereinbefore. Unlike the prior art paper-base sheets, these new products require no concern as to the moisture content of the base sheet when the electrostatic image is being formed. The moisture content of the paper-base is controlled by the hygroscopic salt carried by the paper-base and the sheets require no conditioning to assure a satisfactory moisture content. This eliminates a troublesome factor which is inherently involved in the use of the prior art paper-base electrophotographic sheets.

Like the prior art paper-base electrophotographic sheets, our new products have unlimited shelf-life. This is a definite advantage over the prior art pre-sensitized paper and metal planographic printing plates, diazo reproduction paper and blue print paper. These new products have this advantage to a materially greater degree than the prior art paper-base electrophotographic sheets, since they present no moisture content problem.

The copies on both our new products and on the prior art paper-base electrophotographic sheets are as permanent as the color of the toner used in their production. A toner pigmented with, for example, carbon black, produces an image which is absolutely fast to light. The superiority of these products in this respect, over other types of reproduction papers is very definite.

As already noted hereinbefore, the prior art paper-base lithographic printing plates prepared by electrophotographic methods have the definite advantage of ease of preparation and they are entirely suitable for making short lithographic press runs, on, for example, the small lithographic presses of the office duplicating and equipment type. The lithographic printing plates in accordance with this invention, offer exactly the same advantages offered by the prior art printing plates made from electrophotographic masters. Those advantages are described hereinbefore, in connection with our new electrophotographic sheets. An outstanding advantage is

the ease with which they can be developed into a lithographic printing plate.

In the foregoing, details and specific illustrations of compositions suitable for use in the production of the electrophotographic sheets, the electrophotographic masters and the lithographic printing plates made therefrom, in accordance with this invention, have been given for the purpose of fully explaining the invention. However, it will be understood that many variations can be made in the details which have been given, without departing from the spirit of this invention or the scope of the following claims.

We claim:

1. A sheet adapted for the electrophotographic reproduction of images, which comprises a paper sheet which contains lithium chloride dispersed throughout its body structure, and which carries on one of its surfaces a pigmented film of an organic film-forming material which, in turn, carries as an outer surface an electrophotographic coating of photoconductive zinc oxide in a matrix of a film-forming, electrical insulating material which bonds the zinc oxide to the surface of the said sheet.

2. A sheet adapted for the electrophotographic reproduction of images, which comprises a paper sheet which contains calcium chloride dispersed throughout its body structure, which carries on one of its surfaces a pigmented film of an organic film-forming material which, in turn, carries on its outer surface an electrophotographic coating of photoconductive zinc oxide in a matrix of a film-forming, electrical insulating material which bonds the zinc oxide to the surface of the underlying film.

3. A sheet adapted for the electrophotographic reproduction of images, which comprises a paper sheet which contains a hygroscopic, inorganic salt dispersed throughout its body structure, which carries on one of its surfaces a pigmented film of an organic film-forming material which, in turn, carries on its outer surface an electrophotographic coating of photoconductive zinc oxide in a matrix of a styrenated alkyd copolymer resin which bonds the zinc oxide to the surface of the underlying film.

4. A sheet adapted for the electrophotographic reproduction of images, which comprises a paper sheet which contains lithium chloride in an amount within the range of about 0.2%, by weight, to about 1.3%, by weight, dispersed throughout its body structure, and which carries on one of its surfaces a pigmented film of an organic film-forming material which, in turn, carries as an outer surface an electrophotographic coating of photoconductive zinc oxide in a matrix of a film-forming electrical insulating material which bonds the zinc oxide to the surface of the said sheet.

5. A sheet adapted for the electrophotographic reproduction of images, which comprises a paper sheet which contains calcium chloride in an amount within the range of about 0.5%, by weight, to about 2.5%, by weight, dispersed throughout its body structure, which carries on one of its surfaces a pigmented film of an organic film-forming material which, in turn, carries on its outer surface an electrophotographic coating of zinc oxide in a matrix of a film-forming, electrical insulating material which bonds the zinc oxide to the surface of the underlying film.

6. A sheet adapted for the electrophotographic reproduction of images which comprises a paper sheet which has lithium chloride dispersed throughout its body structure, which carries on one of its surfaces a film of an organic, film-forming material having lithium chloride dispersed therein, which in turn, carries on its outer surface an electrophotographic coating comprising finely-divided photoconductive zinc oxide in a matrix of a film-forming, electrical insulating material which binds the zinc oxide to the surface of the underlying film.

7. A sheet adapted for the electrophotographic reproduction of images which comprises a paper sheet which has zinc chloride dispersed throughout its body structure,

11

which carries on one of its surfaces a film of an organic, film-forming material having zinc chloride dispersed therein which, in turn, carries on its outer surface an electrophotographic coating comprising finely-divided photoconductive zinc oxide in a matrix of a film-forming, electrical insulating material which binds the zinc oxide to the surface of the underlying film.

8. A sheet adapted for the electrophotographic reproduction of images which comprises a paper sheet which has zinc nitrate dispersed throughout its body structure, which carries on one of its surfaces a film of an organic, film-forming material having zinc nitrate dispersed therein, which in turn, carries on its outer surface an electrophotographic coating comprising finely-divided photoconductive zinc oxide in a matrix of a film-forming, electrical insulating material which binds the zinc oxide to the surface of the underlying film.

12

References Cited in the file of this patent

UNITED STATES PATENTS

2,297,691	Carlson	Apr. 4, 1939
2,287,348	Hayden	June 23, 1942
2,774,921	Walkup	Dec. 18, 1956
2,825,814	Walkup	Mar. 4, 1958

FOREIGN PATENTS

203,907	Australia	Nov. 1, 1956
---------	-----------	--------------

OTHER REFERENCES

- Young et al.: R.C.A. Review, December 1954, pp. 469-484. (Copy in Sci. Lib.)
 Sugarman: The American Pressman; November 1955, pp. 33-83. (Copy in Div. 60.)
 Metcalfe et al.: Journal of the Oil and Colour Chemists Association, vol. 39. No. 11 pp. 845-856 (November 1956). (Copy in Sci. Lib.)