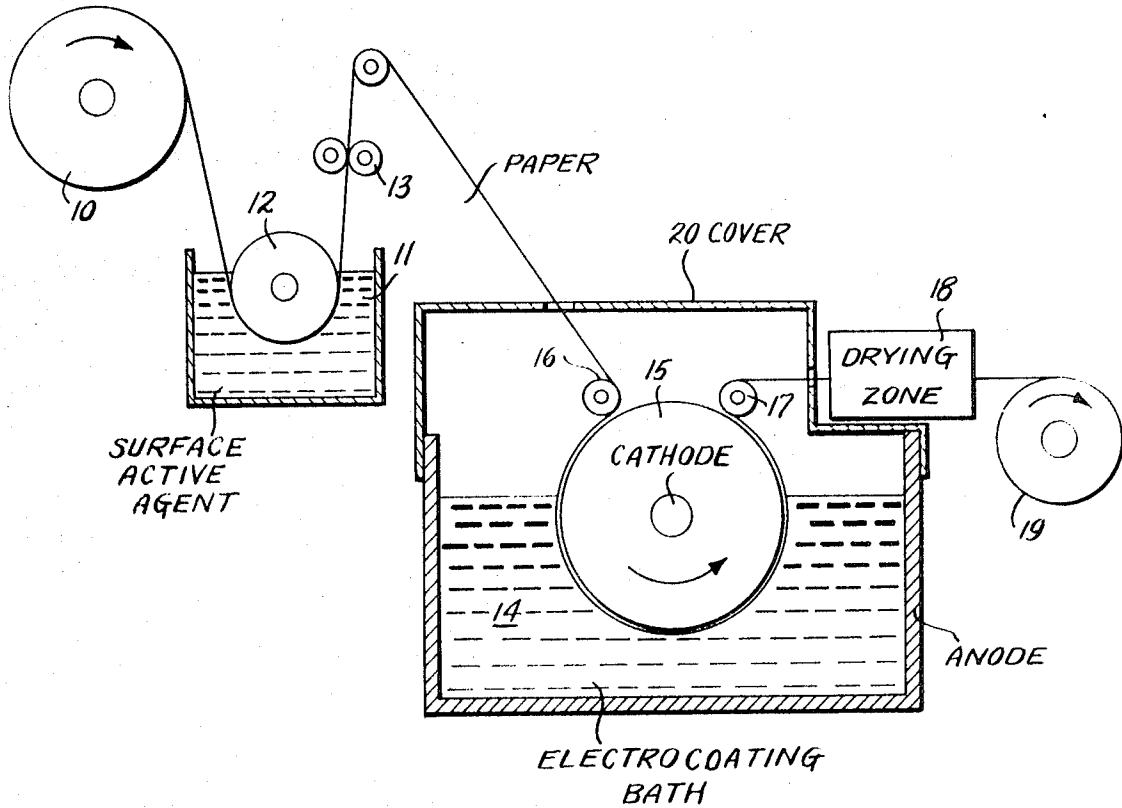


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PRODUCTION OF ELECTROPHOTOGRAPHIC PAPER
BY ELECTROPHORETIC DEPOSITION
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PRODUCTION OF ELECTROPHOTOGRAPHIC PAPER BY ELECTROPHORETIC DEPOSITION

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ABSTRACT OF THE DISCLOSURE

Electrophotographic paper is provided by electrophoretically depositing on paper zinc oxide and a resinous binder associated therewith from nonaqueous medium at the cathode of a unidirectional electrical system.

The present invention relates to the production of electrophotographic paper for use in electrostatic copying processes by the electrophoretic deposition of zinc oxide and a resinous binder associated therewith from nonaqueous medium on to the paper base immersed therein supported on the cathode of a unidirectional electrical system.

The production of zinc oxide-coated electrophotographic paper using zinc oxide-pigmented resin coatings is well known and the problems connected therewith are also well known.

Zinc oxide is heavy so that excessive coating material adds unnecessarily to the cost and weight of the paper. Moreover, a non-uniform deposit is detrimental since it causes the production of a background pattern when the paper is exposed and developed by deposition of toner particles as is well known in xerography. The normal coating techniques are inadequate because the surface of paper is rough and the surface volume of the paper is considerable and must be filled before a uniform surface can be provided. The coating used to fill this surface volume is not necessary to performance and only serves to produce a final coating which is unnecessarily heavy and non-uniform in thickness, being thicker wherever the coating fills a depression in the original surface.

The advantage of an electrophoretically deposited coating is its uniformity in thickness which is independent of any irregularity in the substrate which receives the coating. This permits a thinner, lighter and more uniform coating to be provided.

In accordance with the present invention, the paper is rendered conductive as by impregnation with a solution of a surface active agent, preferably a cationic surface active agent, and the conductive paper is advanced through a nonaqueous electrocoating bath while in the vicinity of the cathode and preferably in direct contact with the cathode of a unidirectional electrical system. In the invention, the electrocoating bath contains zinc oxide pigment dispersed in an organic solvent medium in which an oil-free binder resin (preferably an addition polymer) is present in large proportion with respect to the pigment. Since the paper is porous and conductive, the electrical system is able to effectively operate through the intervening paper to cause the zinc oxide pigment and the resin associated therewith in the electrocoating bath to be electrically propelled toward the cathode and to deposit on the surface of the paper providing a smooth and uniform coating which follows the surface configuration of the paper which is coated.

Cationic surface active agents are particularly preferred for rendering the paper conductive, but any conductive agent may be used including anionic and nonionic agents. While selection of surface active agent to provide the desired conductivity is a secondary feature of the invention, suitable anionic agents are illustrated by sulfates such as

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sodium lauryl sulfate and sulfonates such as sodium octylphenoxy polypropylene oxide sulfonate. Non-ionic agents are illustrated by octylphenoxy polyoxypropylene ethanol. Appropriate cationic surface active agents are illustrated by alkyl benzyl triethyl ammonium chloride. Numerous other surface active agents within the classes noted above are well known. With reference to the bath containing the surface active agent, a concentration of agent of from 0.1-5% is appropriate.

A feature of importance in the selection of the surface active agent is its relationship to the solvent medium used in the electrocoating bath. It is particularly preferred to employ a surface active agent which is essentially insoluble in the solvent medium of the bath. Thus, selecting a cationic surface active agent such as alkyl benzyl triethyl ammonium chloride which is poorly soluble in hydrocarbon solvents, this surface active agent can be applied from solution in a solvent medium comprising xylene enriched with isopropanol (typically 3-5%) in order to adequately dissolve the agent which is conveniently used in 1% concentration. On the other hand, and especially after the impregnated paper has been dried, the surface active agent is poorly soluble in the substantially pure aromatic hydrocarbon solvent medium of the electrocoating bath so that gross contamination of the electrocoating bath with surface active agent can be avoided or minimized. It is a feature of the invention to find that electrodeposition can be moved out away from the cathode and onto the surface of the paper without using a soluble antistatic agent.

Accordingly, it is preferred to employ an electrocoating bath which consists essentially of hydrocarbon solvent, either aromatic or aliphatic, and with the surface active agent being essentially insoluble in such medium, though soluble in stronger solvent systems which can be used for impregnation of the paper base.

While the paper can be rendered conductive and then dried, when it is used without drying, excess liquid is desirably expressed from the conductive paper before it is led into the electrocoating bath.

The invention will be described in greater detail with reference to the accompanying drawing in which the single figure is a diagrammatic sectional view depicting the process of the invention.

Referring more particularly to the drawing, ordinary paper is taken from a roll 10 and passed through a bath 11 containing surface active agent, the paper passing beneath the roller 12. The paper wet with nonaqueous medium containing the surface active agent is then passed through squeeze rolls 13 to express excess liquid. The conductive paper so provided is then passed to an electrocoating bath 14, the walls of which form the anode of a unidirectional electrical system. A metal roller 15 is positioned partially submerged within the bath 14, the roller 15 being connected as cathode. The conductive paper is passed through the bath 14 while held on the surface of roller 15 by means of rolls 16 and 17 to cause the electrodeposition of a photoconductive coating on the outer surface of the paper. The wet-coated paper is passed through a drying zone 18 and then wound on a wind-up roll 19.

The electrocoating bath in the invention is nonaqueous as previously indicated, and it is preferred that the liquid medium constituting the bulk of the bath be a hydrocarbon solvent which may be mineral spirits, naphtha, or an aromatic hydrocarbon such as toluene, xylene or a mixture of the foregoing. While hydrocarbon solvents are preferred, oxygen-containing solvents can also be used such as ketones like methyl ethyl ketone, or esters such as butyl acetate. Halogen-containing solvents such as trichloroethylene are also useful. The more active solvents, such

as the oxygen-containing solvents, are preferably used in small amount to supplement the hydrocarbon solvents. When the solvent is volatile or inflammable, the electrocoating bath 14 is covered with a cover 20 to reduce loss of material and to maintain the concentration of the solvent vapors in the air in the vicinity of the electrodes (where arcing may occur) above the upper limit of solvent-air mixtures which can burn.

The photoconductive material is zinc oxide, the merits of which are well recognized in the field. The zinc oxide is very finely divided, and can be generally defined as being of pigment grade. The use of zinc oxide in photoconductive coatings is well known and the same grades of material useful for this known purpose are useful herein.

In order to hold the deposited zinc oxide particles together, a resinous binder is used. The specific nature of the resinous binder is of some importance since it has been found that the presence of a small proportion of carboxyl group is highly beneficial in enhancing adhesion of the zinc oxide coating to the paper base. Also, the carboxyl-functional resins appear to wet the zinc oxide better which helps to cause the resin to migrate with the zinc oxide particles toward the cathode. However, resins devoid of functional groups are also useful.

It is desired to stress that the use of carboxyl functional resins in an electrocoating system in which the resin is to deposit at the cathode of the system is surprising since, in aqueous medium, acidic resins are well known to deposit at the anode. It would seem that in the nonaqueous system of the invention ionization of the carboxyl groups does not take place to any controlling extent so that the primary factors influencing resin movement is association with the dispersed zinc oxide particles which migrate to the cathode.

Broadly, resins having an acid number of from 0 to about 60 may be used, but it is preferred to employ resins of lower acid number, e.g., below 30. Acid numbers of from 6-30 are preferred, more preferably from 8 to 20.

Referring more particularly to the resins which may be utilized, the limiting factors are that the resin must possess significant solubility in the nonaqueous solvent medium which is used and be capable of wetting the zinc oxide in order to form a paste therewith. In order to illustrate resins devoid of functional groups which may be utilized in accordance with the invention, reference is made to a copolymer of styrene and butadiene having a molecular weight in the range of 400,000 to 3 million, preferably from 750,000 to 1.5 million and which contains styrene and butadiene in a weight ratio of 20/40. Up to about 8% by weight of fumaric acid may be included in the copolymer.

These resins are at least colloiddally soluble in aromatic hydrocarbon solvents such as xylene and toluene and preferably possess a glass transition temperature range of from -20°C . to -5°C . Glass transition temperature in the systems under consideration represents a meaningful factor since it is preferred that the resin which may exist in the solution in colloidal form be capable of flowing to bind the zinc oxide particles to the paper base even when no heat is used. On the other hand, heat can be used to dry the coated paper and this permits higher glass transition temperatures to be used.

The zinc oxide pigment is simply ground into the resin solution in order to form a paste in which resin is associated with the pigment for electrical transport therewith. While the pigment to binder ratio is subject to variation, it is preferred to provide an initial solvent-based paste containing zinc oxide and resinous binder in a weight ratio of from about 5:1 to 5:4, the paste being diluted with additional solvent to provide the dilution which is desired. The proportion of resin over that used in the initial paste is then increased and additional resin is added before, during or after solvent dilution. Thus, the final electrocoating bath will contain a pigment to binder ratio of from about 2:1 to 1:4 and, for best results, the bath will

contain a pigment to binder ratio of from about 1:1 to about 1:2. When the resin has an acid number of 6 or higher, it seems to become better associated with the zinc oxide and both deposition and adhesion are improved.

The concentration of the nonaqueous bath is of secondary consideration, the resin solids content being appropriately within the range of from 1-25% by weight, preferably in the range of from 5-15% by weight.

The resinous binder which is used is preferably an addition polymer, especial reference being made to acrylic copolymers illustrated by copolymers of ethyl acrylate and methyl methacrylate and preferably containing a preponderance of the acrylate component in order to minimize the glass transition temperature of the copolymer and these copolymers will desirably include a small proportion of unsaturated acid such as acrylic acid, methacrylic acid, crotonic acid or itaconic acid so as to provide the limited acid number referred to hereinbefore. On the other hand, functional groups may desirably be included in the copolymer, especial reference being made to the hydroxy group which may be incorporated by the presence of allyl alcohol, hydroxyethyl methacrylate or the like or which may be provided by reaction of monoepoxide such as propylene oxide with any excess acidity which may be present in the copolymer. Still other functional groups such as amine groups are desirably present, e.g., the copolymer may include an ethylenically unsaturated amine such as dimethyl amino ethyl methacrylate in an amount to provide from 2-25 equivalent percent of amine.

Polyvinyl chloride copolymers are also useful, especially those which include from 60-90% by weight of polyvinyl chloride, with the balance of the copolymer being ethylenically unsaturated material copolymerizable therewith and especially vinyl acetate or ethylene. These copolymers may include a small proportion of ethylenically unsaturated acid including acrylic acid or maleic acid and typically possess a molecular weight in the range of 100,000 to 700,000, e.g., 400,000.

The presence of hydroxy or amine functionality in the resin may contribute to the desirability of its selection and other aspects of resin selection may have significance, but oil-modified resins must be avoided since the oil component leads to discoloration which is inconsistent with the provision of useful coated paper.

The electrophotographic coatings of the invention preferably include dyes and sensitizers which enhance the sensitivity of the zinc oxide to become excited by the light exposure to which it is subjected and to enhance the capacity of the paper to respond to illumination in the visible range. Conventional agents of this type are known and these agents have been found to codeposit with the resin and binder. For best results, it is preferred to employ dye selection as noted below.

In the electrophoretically deposited coatings of the invention, it has been found that the phthalein dyes are particularly effective, reference being made to 4',5'-dichlorofluorescein and to 2',7'-dichlorofluorescein. A very small amount of methanol (1-2% of the weight of the paste) is helpful to disperse the dye in the paste.

The particular nature of the paper to be coated is of secondary consideration and the accompanying examples include the use of a commercially available conductive paper as well as ordinary bond writing paper and newsprint.

The nature of the supporting cathode is of secondary significance, a steel roller being illustrative. Similarly, the anode can be constituted by any metal, but it will be appreciated that the anode releases metal ions to the nonaqueous bath. Nonetheless, iron-containing metals have been used successfully, and the use of zinc is particularly contemplated.

It is contemplated that relatively high voltages of 1 to 20 kilovolts, preferably from 2-10 kilovolts will be

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particularly employed from which the desirability of closing the tank as previously discussed will be self-evident. In connection with the electrical current used, it will be understood that a unidirectional electrical current is contemplated, a term which is intended to include momentary reversals in current with the deposition of coating occurring while the current is in a single direction to deposit material at the cathode. Below 1 kilovolt, electrophoretic movement and deposition are unduly slow and, above 20 kilovolts, arcing is encountered and deposition is excessive.

The invention is illustrated in the examples which follow.

EXAMPLE 1

Paste composition

	Parts by wt.
Zinc oxide pigment -----	200
Styrene-butadiene resin (25% solids solution in toluene)—see Note 1 -----	160
Chlorinated paraffin (70% chlorine by weight) having a specific gravity of 1.65 and a Ball and Ring melting point of 100° C. -----	10
Methyl Green -----	.006
Acridine Orange -----	.006
3',3'',5',5''-tetrabromophenolsulfophthalein -----	.006

NOTE.—Copolymer of styrene and butadiene in a weight ratio of 20/40 having a molecular weight of about 1,000,000, Pliolite S-5B (Goodyear Rubber & Tire Co.) illustrates a commercially available resin useful in the above example in place of the copolymer noted.

The paste is formed by simply grinding the ingredients together to provide a uniform paste having a viscosity of 28 seconds measured in a No. 1 Zahn Cup.

Conductive paper of the type conventionally used in the production of electrophotographic paper is passed through an electrocoating bath on the surface of a metal roller cathode with the bath containing a mixture of 20 parts of the paste described above diluted with 80 parts of toluene and sufficient additional styrene-butadiene resin solution to provide a pigment to binder weight ratio of 2:1 and with speed regulated to cause the paper to be immersed in the bath for a period of from 1–5 seconds. Various voltages in the range of 1–10 kv. are used for deposition. The coated paper is then baked at 300° F. for a period of from 2–4 minutes.

The coatings are satisfactory, though the adhesion is not as good as might be desired and there is some cracking of the coating during the bake. On the other hand, the product is satisfactory and readable prints from a type-written original can be made by sending the finished paper through a Bruning 2000 copier which is a conventional dry copier utilizing visible light and a lens system exposure. Adhesion, evenness of deposition and the tendency of the coating to crack are all improved by increasing the proportion of resin in the mixture which is easily done by simply adding resin solution to the diluted paste.

EXAMPLE 2

Example 1 is repeated to provide a comparable product possessing improved adhesion by increasing the proportion of resin. This is done by adding additional styrene-butadiene resin to the paste prior to dilution with toluene (3 parts of additional resin solution being added to 20 parts of the paste).

EXAMPLE 3

Examples 1 and 2 are repeated utilizing, in place of the 160 parts of styrene-butadiene resin, an acrylic copolymer containing ethyl acrylate and methyl methacrylate in proportions providing a solution copolymer having a glass transition temperature of -10° C. together with a small proportion of acrylic acid providing an acid number in the range of 13–17. The resin is provided in 25% resin solids xylene solution. Examples 1 and 2 are also altered in this example by using ordinary bond writing paper and newsprint handled in the manner

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shown in the drawing. More particularly, these non-conductive papers are passed beneath roller 12 through a bath of toluene containing by weight 4% of isopropanol and 1% of nonyl benzyl triethyl ammonium chloride.

The impregnated paper is then passed through press rolls 13 before being passed through the electrocoating bath.

The results in the present example are comparable to those reported in Examples 1 and 2, but the acidic resin exhibits a superior capacity to bind the zinc oxide particles to one another and to the base so that better adhesion is obtained at any given ratio of pigment to binder.

The zinc oxide pigment used in the foregoing examples is made using a French furnace in which high purity electrolytic zinc is melted and vaporized, and the vapors are burned to form zinc oxide particles having an average specific surface diameter in the range of from 0.136 to 0.408 micron.

The invention is defined in the claims which follow.

I claim:

1. A method for the production of electrophotographic paper comprising passing a conductive paper through a nonaqueous electrocoating bath having a solvent portion constituted essentially by a hydrocarbon solvent medium, with said paper being rendered conductive by the presence therein of a surface active agent which is substantially insoluble in said hydrocarbon solvent medium, said conductive paper being interposed between the cathode and the anode of a unidirectional electrical system having a voltage of at least about 1,000 volts, said nonaqueous bath containing photoconductive zinc oxide pigment dispersed therein and an oil-free resinous binder therefor, said resinous binder being associated with said pigment in a pigment to binder ratio of from 2:1 to 1:4 for codeposition at the cathode.

2. A method as recited in claim 1 in which the weight ratio of pigment to resinous binder in said bath is from about 1:1 to about 1:2.

3. A method as recited in claim 1 in which said resinous binder is an addition polymer.

4. A method as recited in claim 1 in which said resinous binder is an addition polymer containing carboxyl functionality providing an acid number of from 6–30.

5. A method as recited in claim 1 in which said electrocoating bath further includes a phthalein dye.

6. A method as recited in claim 5 in which said dye is 4',5'-dichlorofluorescein.

7. A method as recited in claim 5 in which said dye is 2',7'-dichlorofluorescein.

8. A method as recited in claim 1 in which said nonaqueous bath includes zinc oxide and resinous binder dispersed in the hydrocarbon solvent.

9. A method as recited in claim 1 in which said resinous binder is an acrylic copolymer.

10. A method as recited in claim 1 in which said resinous binder is a copolymer of styrene and butadiene.

11. A method as recited in claim 1 in which said conductive paper is supported on said cathode.

12. A method as recited in claim 1 in which said unidirectional electrical system is operated at a voltage in the range of from 1–20 kilovolts.

13. A method as recited in claim 12 in which said bath is employed in a closed chamber.

14. A method as recited in claim 1 in which said conductive paper is rendered conductive by the presence therein of cationic surface active agent.

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