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PROCESS FOR THE MANUFACTURE OF AN ELECTROPHOTOGRAPHIC MATERIAL

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6 Claims

ABSTRACT OF THE DISCLOSURE

The present process makes it possible to manufacture permanently moisture-insensitive electrophotographic material by coating the material with a resin layer containing a photoconductor, the novel feature consisting in first surrounding the photoconductor with a thin continuous layer of a resin having high electric resistance and being permeable to light. The photoconductor so pretreated is dispersed with a resin acting as binder in a medium that does not dissolve the resin layer on the photoconductor, and then the preparation is applied to a support.

It is known that electrophotographic layers can be manufactured by dispersing an inorganic or organic photoconductor (that is to say a compound becoming an electric conductor under the influence of light), such as zinc oxide, in a resin capable of forming a connecting layer that does not conduct electricity. Such a layer, applied to a support, can be given a negative charge in the dark, for example by a corona discharge. When this layer is exposed to light under a master, the exposed areas are discharged, whereupon the unexposed areas can be rendered visible by being sprinkled with an insulating powder that can be positively charged because the powder particles are attracted in the areas carrying a negative charge and an image results which can be fixed in a variety of ways, for example by melting the powder or spraying with a lacquer.

According to the most commonly employed method for the manufacture of electrophotographic layers, a hydrophobic resin is used that is dissolved in an organic solvent. The photoconductor is dispersed in this binder, a support e.g. paper or film, is coated with the mixture and the solvent is evaporated. This procedure furnishes an insulating layer that is insensitive to moisture. This property is absolutely necessary to ensure that the electric properties of the layer are not impaired, independent of the moisture content of the surroundings.

While it would be desirable to be able to use hydrophilic binders of the usual composition, they do not give satisfactory results. Thus it is known to dispense with organic solvents, using binders that contain acid groups and volatile bases which, after having been applied to the support, are expelled by heating. This does furnish a water-insoluble layer but it is still very sensitive to moisture. If it is attempted to push the reaction of the binder containing acid groups with the volatile base further by intensifying the heating, elimination of water and anhydride formation occurs, and the layer becomes at first, as desired, insensitive to moisture. The elimination of water is, however, an at least partially reversible reaction and after some time the layer reabsorbs so much water from the air that it loses its favourable properties.

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The aforementioned disadvantages of the known methods are avoided in the instant process. The latter makes it possible to manufacture permanently moisture-insensitive material by coating the material with a resin layer containing a photoconductor and fixing the resin layer, the novel feature consisting in first surrounding the photoconductor with a thin continuous layer of a resin having high electric resistance, and then making a preparation from the photoconductor so pretreated and a resin acting as binder in a medium that does not dissolve the resin layer on the photoconductor, and then applying the preparation to the support.

In the performance of the present process the usual bases or supports, e.g. films or preferably paper, may be used.

In the present process, the photoconductor is surrounded, that is to say the individual particles of the substance used as photoconductor are enveloped, with a very thin continuous layer of a resin having a high electric resistance, preferably a hydrophobic resin. To the hydrophobic resins belong those which are insoluble in water. In the form of a thin layer, in the presence of moisture, such a resin should have a high specific electric resistance, advantageously exceeding 10^{13} ohm-cm./cm.². On the other hand, these resins should be soluble in organic solvents. Furthermore, they must be capable of forming a thin film on the particles of the photoconductor. Examples of suitable relevant products are the polymers of styrene, vinyl acetate and vinyl chloride, with which, if desired, a small proportion of a carboxylic acid, such as acrylic or maleic acid, may have been copolymerized. Such polymers can be dissolved e.g. in acetone. Further film-forming substances are silicone resins, which are soluble in toluene.

The photoconductor pre-treated in this manner is made up in a medium that does not dissolve the resin coating on the photoconductor particles, together with a hydrophobic resin that acts as binder, into an aqueous preparation. For this purpose there are advantageously used less hydrophobic through to distinctly hydrophilic resins that contain groups imparting solubility in water, preferably carboxylic acid groups. Insofar as their degree of polymerization and their content of solubilizing groups are concerned, these polymers should be of a nature such that they are soluble in water at least in the form of their alkali metal or ammonium salts. In general, this is the case when the copolymer, in the form of the free acid, has an acid number from 80 to 400 (acid number indicates, as is usual the mgs. of KOH needed to neutralize 1 g. of copolymer).

Customarily such copolymers are manufactured by polymerizing a polymerizable carboxylic acid with at least one polymerizable monomer that is free from carboxylic acid groups. As such monomers there are suitable the known, ethylenically unsaturated compounds such as acrylic acid esters, vinyl esters of lower carboxylic acids, e.g. vinyl acetate, and vinyl chloride or styrene. Suitable polymerizable carboxylic acids are crotonic, methacrylic, chloracrylic, acrylic and maleic acid. Particularly good results are obtained with copolymers from vinyl acetate and maleic acid. There may be specially mentioned copolymers of this kind having a molecular weight of about 40,000, in which the molecular ratio maleic acid:vinyl acetate is such that the copolymer is soluble in an alkaline medium, that is to say at least 1:4. Such products are very easy to swell in water and form with alkali metal hydroxides, ammonia or readily volatile amines salts that are readily soluble.

Particularly useful photoconductors for use in the present process are inorganic photoconductors such as the oxides of antimony, aluminium, bismuth, cadmium, mercury, molybdenum and lead. Preferred use is made of zinc oxide; for the manufacture of high-grade layers a zinc oxide of maximum purity is needed, advantageously the product prepared by the so-called French method, that is to say by the air oxidation of zinc vapours. The photoconductor must always be sufficiently finely divided, having a particle size which is preferably below 1μ .

If desired, further substances may be incorporated with the layer. Inter alia, the following elements or their compounds may be added in an amount of 0.1% to 5%, referred to the weight of the photoconductor: Boron, thallium, lithium, lead, cobalt and/or silver. These substances can be incorporated with zinc oxide in the usual manner by migration at 400 to 600° C., or they may be added to the mixture in the form of salt solutions. Such additives may produce valuable effects. Inter alia, the speed of the photoconductor layer can be raised, the charging rate accelerated, the distribution of the charge and with it the image definition improved and/or the contrast effect can be controlled.

When a water-soluble resin is used as binder, there may be added to the preparation substances which on being heated render the resin water-insoluble. As substances of this kind there may be mentioned compounds of hexavalent chromium such as ammonium bichromate and non-volatile amines containing at least two reactive amino groups. Such additives come into consideration above all when the hydrophilic resin is a salt from a polymer containing acid groups imparting solubility in water and a volatile nitrogen base.

The proportions of the various substances to be used in the present process may vary within relatively wide limits. Of the preferably hydrophobic resin to be applied in a thin coating to the photoconductor a very small amount will suffice, and the resin is advantageously applied in the form of a strongly dilute solution in an organic solvent. At any rate the chosen amount of this resin should be such that the photoconductor retains its property of being a readily flowing powder and does not turn tacky. The optimal proportion of hydrophobic resin is easy to determine by preliminary experiments and is in general about 0.2% of the weight of the photoconductor.

Of the resin acting as binder there are used for example 5 to 20%, referred to the photoconductor. The amount of water for the aqueous preparation is advantageously chosen so that, on the one hand, the substances to be dissolved in water, e.g. a water-soluble resin, pass readily and completely into solution and, on the other hand, the resulting mixture has a consistency adequate for coating the support. It may be, for example, 1 to 10 times the amount of, preferably water-soluble, resin acting as binder.

In other respects it is advantageous to perform the process in the following manner: The photoconductor is introduced into a solution of a hydrophobic resin in a suitable organic solvent, the excess liquor is removed, e.g. by filtration and/or centrifugation so that the photoconductor once more forms a dry powder, from the photoconductor thus pretreated and a binder resin an aqueous preparation is made which is then applied to the support and dried on it. This procedure is substantially simpler than the known method according to which the whole of the binder resin is dissolved in an organic solvent and the dispersion of the photoconductor obtained with this solution is spread over the support. For the performance of the present process a relatively small amount of solvent is required which is much easier to recover because this operation can be performed in apparatus that are easy to close. There is a much greater choice of solvent available because its properties have ceased completely to affect the coating on the support.

By varying the ratio between photoconductor and copolymer, for example within the limits indicated above,

the contrastiness of the images produced on the material of this invention can be controlled. Contrastiness can also be intensified or weakened by varying the exposure time.

In general, it is advantageous to coat the support on both sides. In this manner the mechanical properties of the material compared with unilaterally coated material can be significantly improved, above all the curling tendency can be reduced. In addition bilateral coating furnishes for a lower total layer thickness better, that is to say faster electrophotographic material. The total layer thickness should, however, be at least 15μ both with unilaterally and bilaterally coated material. On the other hand, the total layer thickness should in general not exceed 40μ . The temperature at which the material must be heated to form the insoluble polyamide is advantageously within the range from 100 to 120° C., and the time for which the material is to be maintained at this temperature ranges from 1 to 30 minutes.

Images can be produced in known manner on the electrophotographic material manufactured by the present invention. As usual, the material is given a negative charge by corona discharges and then exposed in contact under a master or in an enlarging apparatus, whereupon the image is rendered visible and fixed, for example as indicated above.

The image can be rendered visible or developed for example with a coloured powder capable of being given a positive or negative charge and a vehicle. When in the development a magnet brush or a non-conductive liquid is used, iron filings constitute a useful vehicle.

Provided the coloured powder has a suitable melting point, ranging for instance from 60 to 120° C., it can be fixed on the support by a simple heating step.

Very numerous kinds of resin are available for making meltable developer powders. Particularly good results are obtained with polyvinyl acetate. It is advantageous to use a polyvinyl acetate melting between 60 and 90° C. The polyvinyl acetate is easy to dye a variety of tints. This makes it possible to produce very dark shades without the aid of pigments such as lampblack, and the electrophotographic images produced in this manner do not tend to give off the dyestuff and prove particularly fast to abrasion. Furthermore, the colored powder can be freely chosen, irrespective of whether a positively or negatively charged developer is required, because in this case a material having the desired charge can be incorporated. Finally, the resins are substantially colorless and are suitable for producing transparent shades, which is absolutely necessary for the development in various colors.

Even when the binder resin (which may even be water-soluble) used for the manufacture of the electrophotographic layer according to this invention has not been made water-insensitive separately, a material is obtained that is suitable for the production of electrophotographic images irrespective of the degree of moisture in the ambient air. The distribution of the electric charge is very even, and, above all, the reproduction of large areas of very dense colours is very good.

Furthermore, the present process makes it possible to produce electrophotographic layers of considerably differing contrasts. More especially, very flat gradations can be achieved, so that half-tone images can be produced. However, this does not preclude the possibility of sensitizing the layer, e.g. by means of suitable dyestuffs. This is particularly important because in the past half-tone images could be obtained electrophotographically only with the use of reticulated screens. By the present process the contrastiness of the sensitive layer can be substantially varied by changing the electric properties of the hydrophobic resin and of the resin acting as binder. Photosensitive layers of minimum contrastiness are obtained when the electric conductivity of the binder resin is 10 to 100 times that of the hydrophobic resin used for enveloping the photoconductor particles. The sensitizers may be added e.g. during the treatment of the photoconductor with the

hydrophobic resin in the organic solvent or subsequently in an aqueous medium.

Finally, the present process offers the advantage that a very wide variety of supports may be used. More especially, plain papers may be used that have not been especially manufactured for the present process, nor need they have been specially prepared for it.

Unless otherwise indicated, parts and percentages in the following examples are by weight.

Example 1

0.25 part of a copolymer from vinyl chloride, vinyl acetate and a small proportion of maleic acid (e.g. the product marketed under the trade name Hostalit) is dissolved in 100 parts by volume of acetone. This solution is mixed with 100 parts of zinc oxide obtained by oxidizing zinc vapours, and the mixture is stirred for 30 minutes, then filtered and the residue is dried. The zinc oxide pre-treated in this manner is then mixed with a solution obtained from 10 parts of a commercial copolymer from vinyl acetate and maleic acid in the ratio of 2.4:1 (e.g. the product marketed by Imperial Chemical Industries Limited under the trademark Nitromul) by neutralization with sodium hydroxide in 150 parts of water. Paper is coated with this preparation so that the content of zinc oxide amounts to 20 g. per square metre. The water-soluble resin contained in the layer remains completely water-soluble even after it has been dried. An image can be produced on this material by a negative charge under a device for corona discharges of 10 kilovolts, exposure under a master and development in the dark with a usual electrostatic powder. An image can be so produced even when the relative atmospheric humidity is very high, e.g. above 80%.

Example 2

A 0.1% solution of a silicone resin ("Resin 6602," makers Société des Usines Chimiques Rhone-Poulenc) in toluene is diluted with acetone. 100 parts of this mixture are mixed with 100 parts of zinc oxide. The solvents are evaporated and the zinc oxide pretreated in this manner is then further processed as described in Example 1.

Example 3

The procedure is as described in Example 1, except that the copolymer from vinyl acetate and maleic acid in the ratio of 2.4:1 is replaced by the ammonium salt of the copolymer prepared from styrene and acrylic acid in the ratio of 3:2. The layer is dried without being heated, during which a certain amount of ammonia escapes; it is insoluble in water but very sensitive to moisture, and its gradation is equivalent to a medium strong contrastiness.

Example 4

The binder used is a copolymer prepared from vinyl acetate and acrylic acid (Résine X 209A, makers Cie. Rousselot) in the form of its water-soluble ammonium salt. The substance used for enveloping the zinc oxide particles is a silicone resin (Resin SI 129 G, 5155, makers Societe Industrielle de Silicone S.A.). Otherwise, the procedure of Example 1 is adopted, to furnish an electrophotographic layer which is very easy to charge and on which sharply defined images can be produced.

Example 5

The vinylacetate-acrylic acid copolymer mentioned in Example 4, in the form of the free acid, is stirred with ethanol. The zinc oxide treated with silicone resin as described in Example 4 is dispersed in this mixture, the ratio of zinc oxide:binder resin being 85:15. The desired viscosity is adjusted by adding further ethanol, and a layer of 20 μ thickness is produced on paper.

Example 6

A mixture of 25 ml. of N-aqueous ethylamine solution and 10 g. of a copolymer from vinyl acetate and crotonic

acid in the ratio of 3:1, molecular weight 30,000 to 40,000, is dissolved in water. 90 grams of zinc oxide, which have previously been stirred for ½ hour in an 0.5% solution of polyvinyl butyral, then filtered and dried, are then dispersed in the solution. The further processing is performed as described in Example 3.

What is claimed is:

1. A process for the manufacture of an electrophotographic material by coating a support with a resin layer containing zinc oxide as a photoconductor and fixing said resin layer which process comprises adding the zinc oxide to a solution in an organic solvent of a hydrophobic and water-insoluble resin having a high electric resistance of a member selected from the group consisting of a vinyl chloride-vinyl acetate, copolymer, polyvinyl butyral and a silicone resin, removing the excess liquid, thereby surrounding the zinc oxide with a thin continuous layer of said resin, and then making an aqueous preparation suitable for coating the support from the zinc oxide thus pretreated and a water-soluble copolymer containing carboxylic acid groups and acting as a binder in a medium wherein the resin layer on the zinc oxide is insoluble, applying the aqueous preparation to a film or paper support and drying the aqueous coating.

2. A process for the manufacture of an electrophotographic material by coating a support with a resin layer containing zinc oxide as a photoconductor and fixing said resin layer which process comprises adding the zinc oxide to a solution of a hydrophobic and water-insoluble silicone resin having a high electric resistance in an organic solvent, removing the excess liquid, thereby surrounding the zinc oxide with a thin continuous layer of said resin, and then making an aqueous preparation suitable for coating the support from the zinc oxide thus pretreated and a water-soluble copolymer containing carboxylic acid groups and acting as a binder in a medium wherein the resin layer on the zinc oxide is insoluble, applying the aqueous preparation to a film or paper support and drying the aqueous coating.

3. A process for the manufacture of an electrophotographic material by coating a support with a resin layer containing zinc oxide as a photoconductor and fixing said resin layer which process comprises adding the zinc oxide to a solution in acetone of a hydrophobic and water-insoluble copolymer having a high electric resistance of vinyl chloride, vinyl acetate and a minor proportion of maleic acid, removing the excess liquid, thereby surrounding the zinc oxide with a thin continuous layer of said copolymer, and then making an aqueous preparation suitable for coating the support from the zinc oxide thus pretreated and an aqueous solution of the sodium salt of a copolymer from vinyl acetate and maleic acid, applying the aqueous preparation to a paper support and drying the aqueous coating.

4. A process for the manufacture of an electrophotographic material by coating a support with a resin layer containing zinc oxide as a photoconductor and fixing said resin layer which process comprises adding the zinc oxide to a solution of a hydrophobic and water-insoluble silicone resin having a high electric resistance in toluene and acetone, removing the excess liquid, thereby surrounding the photoconductor with a thin continuous layer of said resin and then making an aqueous preparation suitable for coating the support from the zinc oxide thus pretreated and an aqueous solution of the sodium salt of a copolymer from vinyl acetate and maleic acid, applying the aqueous preparation to a paper support and drying the aqueous coating.

5. A process for the manufacture of an electrophotographic material by coating a support with a resin layer containing a zinc oxide as a photoconductor and fixing said resin layer which process comprises adding the zinc oxide to a solution in acetone of a hydrophobic and water-insoluble copolymer having a high electric resistance of vinyl chloride, vinyl acetate and a minor proportion of maleic acid, removing the excess liquid, there-

by surrounding the zinc oxide with a thin continuous layer of said copolymer, and then making an aqueous preparation suitable for coating the support from the zinc oxide thus pretreated and an aqueous solution of the ammonium salt of a copolymer from styrene and acrylic acid, applying the aqueous preparation to a paper support and drying the aqueous coating.

6. A process for the manufacture of an electrophotographic material by coating a support with a resin layer containing zinc oxide as a photoconductor and fixing said resin layer which process comprises adding the zinc oxide to a solution of a hydrophobic and water-insoluble silicone resin having a high electrical resistance in an organic solvent, removing the excess liquid, thereby surrounding the zinc oxide with a thin continuous layer of said resin, and then making an aqueous preparation suitable for coating the support from the zinc oxide thus pretreated and an aqueous solution of the ammonium salt of a copolymer from vinyl acetate and acrylic acid, applying the preparation to a paper support and drying the aqueous coating.

References Cited

UNITED STATES PATENTS

2,717,246	9/1955	Kienle	117—100	X
2,875,054	2/1959	Griggs et al.	117—34	
2,993,787	7/1961	Sugarman	96—1.8	
3,121,006	2/1964	Middleton et al.	96—1.5	
3,128,204	4/1964	Schaum et al.	117—34	X
3,139,354	6/1964	Wolff	117—100	X
3,155,504	11/1964	Damm et al.	96—1.7	
3,160,503	12/1964	Cady	117—34	X
3,224,993	12/1965	Wynne	117—100	X
3,245,786	4/1966	Cassiers et al.	96—1.8	
3,330,693	7/1967	Rumberger	117—100	X

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